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Hemilabile Phosphine Ligands in Molybdenum and Tungsten Octahedral Environments

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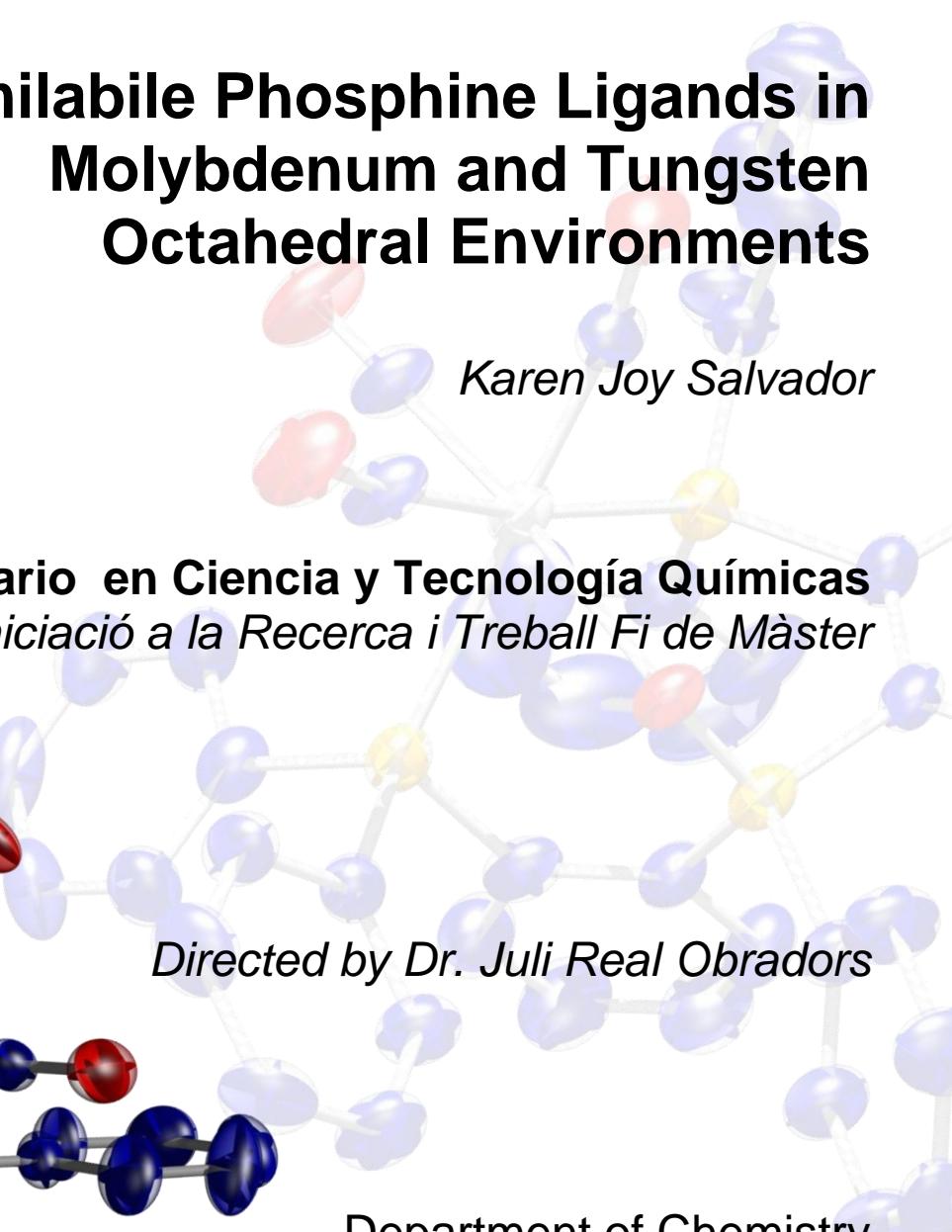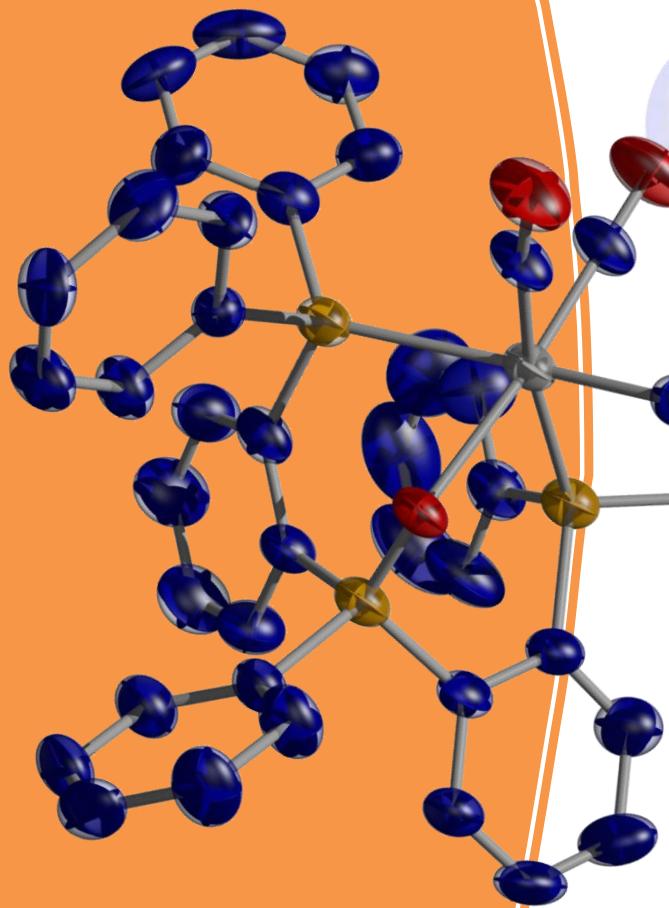
Memòria presentada per superar el mòdul Laboratori d'Iniciació a la Recerca corresponent al Màster Universitari Ciència i Tecnologia Quimiques

Karen Joy Salvador

Vist i plau

Dr. Juli Real i Obradors
Bellaterra, 30/07/2010

To the people who have put their hands on this work
and to the people who shared their time and believed in me…

Juli, Joan Carles, Nacho, Dani, Ori,
Laia, Joan, Fran, Jordi, Adu,
Nanay, Tatay, Manong, Ading, Anti, Pinsan.

Thank you…*Salamat…*

This one is for you all…

ABSTRACT

The synthesis of three bidentate, hemilabile phosphine ligands, newly synthesized in the research group (**TPOdiphos**, **DPPrPOdiphos** and **SODPdiphos**), has been up-scaled and optimized. The ligand substitution reaction on $Mo(CO)_6$ and $W(CO)_6$ has been studied and the corresponding complexes *fac*-[M**TPOdiphos**$(CO)_3$], *fac*-[M**DPPrPOdiphos**$(CO)_3$], and *fac*-[M**SODPdiphos**$(CO)_3$], (M= Mo, W) have been isolated in good yields and characterized by NMR, IR and HR MS. In the case of *fac*-[Mo**TPOdiphos**$(CO)_3$] the XRD crystal structure was resolved. The complexes were found to be octahedral, neutral molecules, with the metal in the zero oxidation state and the ligand adopting a *facial* P,P,O-coordination. The hard ligand atom (oxygen) is expected to exhibit special features the future applications of these novel ligands.

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1   INTRODUCTION

For the past decade, high attention has been given to phosphine chemistry as shown by an extensive number of studies conducted to synthesize new ligands and to study their properties and applications.[1,2,3,4] From time to time, new phosphines are announced and the regularity of reports including combinatorial synthetic procedures, reaffirm the current intense interest in phosphine science. A "renaissance" of activity is underway as scientists seek not only to find new ligands and improve those existing ones but the process of ligand design itself. But what makes these phosphine ligands so attractive?

To begin with, thousands of P-ligands have been prepared and tested in various selective reactions,[5,6,7] Secondly, one of the key aspects is the great potential for both electronic and steric modification of these ligands. One can easily change the properties of a phosphine by changing the substituents attached to the phosphorous. Another key advantage is the facile characterization by ^{31}P NMR.

And among these phosphine ligands, lies a group of phosphines with both soft and hard nucleophilic centers within the molecule. These ligands would bind well enough but would readily dissociate the "hard" ligand component, thus generating a vacant site for substrate binding. They are called *hemilabile* phosphines. The first hemilabile ligands emerged in 1970s.[8]

In this work, 3 new bidentate, hemilabile phosphine ligands developed by our group such as TPOdiphos, DPPrPOdiphos and SODPdiphos were studied and their syntheses optimized. These ligands bear the same skeleton structure as shown below. They differ depending on which electron withdrawing groups (i.e., PO and SO_2) bridge the two phosphine bearing aryls and if these aryls bear any other substituent as in **L3** which bears methyl groups at the para− position.

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[1] Chengye, Y., Weizhen, Y., Chengming, Z., Yongzheng, H. *Phosphorus Chem.* **1981**: 615.

[2] Delacroix, O and Gaumont, A. C. *Curr. Org. Chem.*, **2005**, *9*: 1851.

[3] Harris, J. R., Haynes II, M.T, Thomas, A. M., Woerpel, K. A. *J. Org. Chem.* DOI: 10.1021/jo1008367. Publication Date (Web): July 6, 2010

[4] Honaker, M., Hovland, J. and Salvatore, R. N. *Curr. Org. Chem.* **2007**, *4*: 31.

[5] Sun, J. and Fu, G. *J. Am. Chem. Soc.* **2010**, *132*: 4568.

[6] Chung, Y. K. and Fu, G. *Angew. Chem. Int. Ed. Engl.* **2009**; *48*: 2225.

[7] Vallcorba V., O.; Tesis Doctoral, **2010**.

[8] (a) Bader, A. and Lindner, E. *Coord. Chem. Rev.* **1991**, *108*: 27. (b) Slone, C. S., Weinberger, D. A., Mirkin, C. A. *The Transition Metal Coordination Chemistry of Hemilabile Ligands. In Progres in Inorganic Chemistry*; Karlin, K. D., Ed. Wiley: New York, **1999**, 48: 233. (c) Braunstein, P. and Naud, F. *Angew. Chem., Int. Ed.* **2001**, 40, 680. (d) Bassetti, M. *Eur. J. Inorg. Chem.* **2006**, 4473.
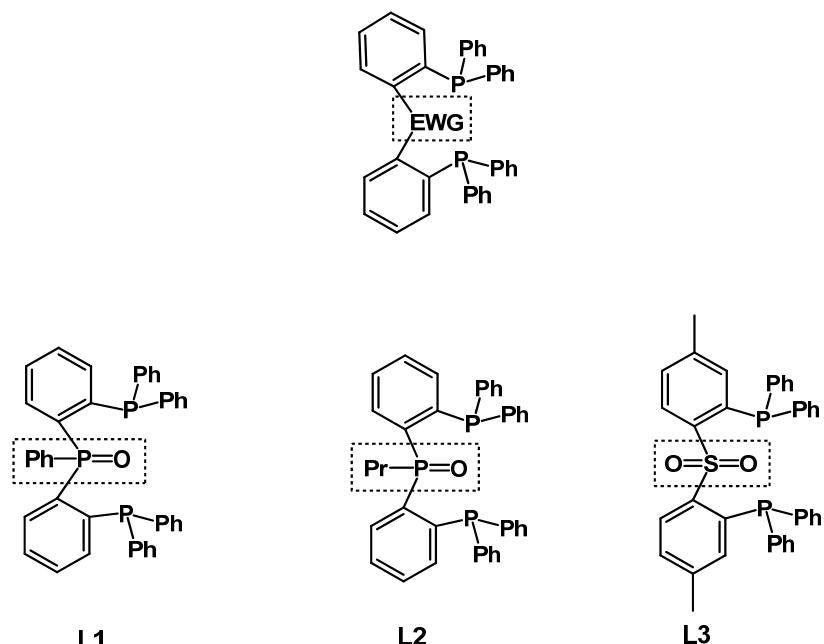
Figure 1.1. Ligands developed by the group and are used in the current study.

The advantage of these bidentate ligands is it has a better effect in stabilizing a complex than monodentate ligands. Moreover, the presence of E=O oxygen bearing moieties may give rise to a weaker and labile metal-oxygen (E=O–M) bond and a phosphorus atom closely coordinated to the central atom.

These types of compounds hold a promising future to a wide variety of reactions especially those catalyzed by transition metals.[9,10] Complexes containing hemilabile ligands have been winning lots of attention and has been applied to homogeneous catalysis and in the synthesis of complex organic molecules. [11,12] More recently, they have been found as potential candidates for the reversible binding of analytes to the transition metal center. These are hybrid ligands of the general formula P−E=O where the two groups, P (phosphorus) and E=O, exhibit different donor properties toward the metal center (Figure 1.2). And due to their dynamic chelating capability, they have found a good application in chemical sensing.[13]

[9] Grushin, V. *Organometallics*, **2001**, *20*: 3950.
[10] Grushin, V. *J. Am. Chem. Soc.*, **1999**, *121*:5831.
[11] Rothenberg, G. Catalysis. Concepts and Green Applications. Wiley. **2008**.
[12] Hegedus, L. *Transition metals in the synthesis of complex organic molecules*. Univ. Science Books, **1994**.
[13] Angell, S., Rogers, C., Zhang, Y., Wolf, M. and Jones Jr., W. *Coord. Chem. Rev.* **2006**, *250*: 1829.
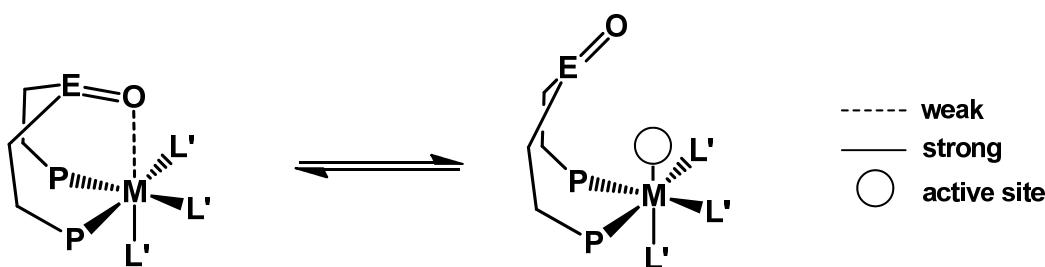
Figure 2.1. Figure showing the dynamic chelating ability of hemilabile ligands.

There are a number of labile groups reported in the literature, and in general, oxygen-based substituents, such as ethers, esters, and phosphine oxides, are the most labile.[8(a,b)] Another interesting application taking advantage of this feature is additive oxidation which may have various applications in the field of catalysis and organic synthesis.[14]

More and more applications are discovered for these types of compounds and more and more studies are conducted to get even more results. This work has been done as a contribution to the study of metal/ligand systems relevant to homogeneous catalysis. Specifically this study concentrates to the synthetic methodology and some modifications for obtaining hemilabile, bidentate phosphine ligands bridged by electron withdrawing groups, to obtain quantitative amounts and to study its complexing behavior with molybdenum(0) and tungsten(0).

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[14] McDonough, J., Weir, J., Sukcharoenphon, K., Hoff, C., Kryatova, O., Rybak-Akimova, E., Scott, B., Kubas, G., Mendiratta, A. and Cummins, C. *J. Am. Chem. Soc.*, **2006**, *128*: 31, 10295.

2 OBJECTIVES

This work has been done as a contribution to the study of metal/ligand systems relevant to homogeneous catalysis. The first objective of this work has been the optimization of the synthesis of three new hemilabile, bidentate phosphine ligands developed by our research group: **L1**, **L2** and **L3**.
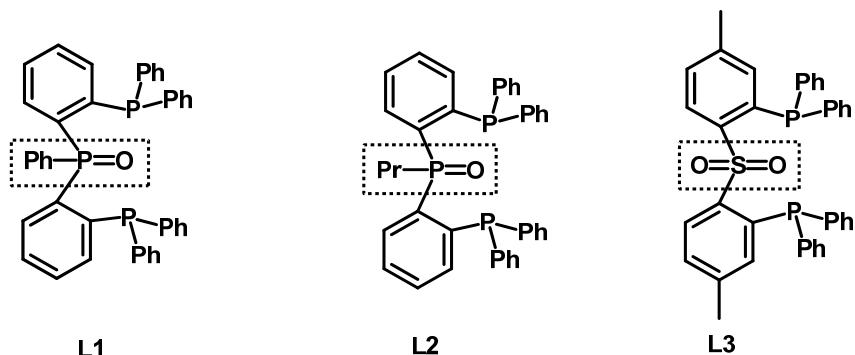
Figure 2.1 Ligands **L1**, **L2** and **L3**.

These ligands bear a similar skeleton structure but differ on the central electron withdrawing group. Ph−P=O, Pr-P=O and O=S=O groups bridge the two phosphine bearing aryls or "wings" and define a very large P,P-bite angle. This part of the study was aimed to synthesize and purify these three ligands easily and in "*large amounts*", in the laboratory scale. For these ligands, the starting materials are cheap and readily available from commercial sources.

The second objective has been to asses the coordination character of ligands **L1**, **L2** and **L3** with group 6 metals (Mo and W) that typically prefer octahedral structures. Preliminary results in our group have shown that these ligands coordinate to square planar metal ions (Pd^{II} and Pt^{II}, Figure 2.2) in a cis-P,P mode, but with the oxygen atoms strongly oriented towards the metal. This has suggested that with the earlier, more electropositive, transition metals fac-P,P,O (facial octahedral) coordination compounds could be obtained. However, it is impossible to predict if **L1**, **L2** or **L3** will act as bidentate cis-P,P or tridentate fac-P,P,O ligands (Figure 2.2).

cis-P,P sq. planar   cis-P,P oct.   fac-P,P,O oct.
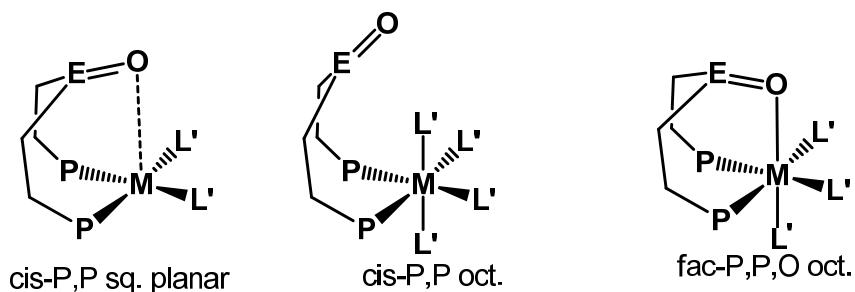
Figure 2.2 Coordination modes of **L1**-**L3** with square planar and octahedral centers.

3 RESULTS AND DISCUSSIONS

3.1. Synthesis and Characterization of the Ligands L1, L2 and L3

For the synthesis of the ligands, two routes have been developed (Scheme 3.1): **Route 1** includes a two-step synthesis where the "wings" of the ligand must be prepared first and later on attached to a bridging group which bears the electron withdrawing group (EWG) R−P=O or O=S=O. On the other hand, **Route 2** is a simple, one-step reaction wherein the ligand skeleton is directly lithiated and reacted with chlorodiphenylphosphine to form the desired ligand.
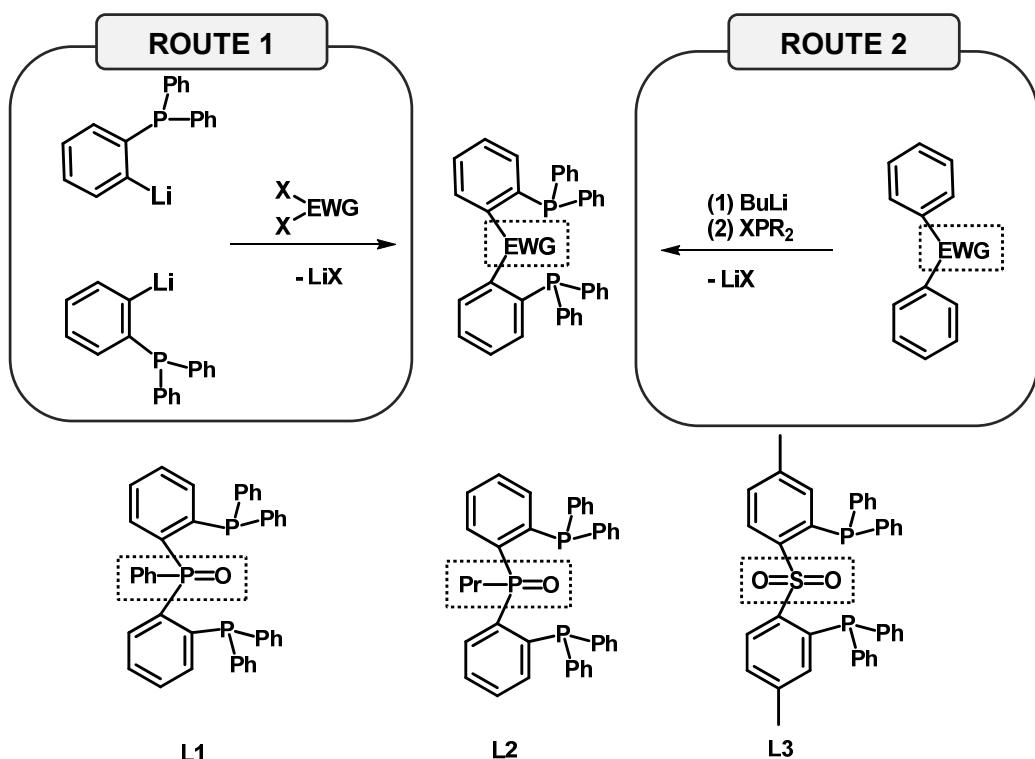
Scheme 3.1. New hemilabile diphosphine ligands bridged by electronegative groups.

Ligands **L1** and **L2** were synthesized using **Route 1** and ligand **L3** using **Route 2** (Scheme 3.1). The synthesis and characterization of these ligands will be discussed in this section.

Route 1 involves the prior synthesis of the aryl peripheries. For **L1** and **L2** o-bromodiphenylphosphine is a common intermediate that has to be prepared and then lithiated and reacted with the core group bearing the electronegative moiety. The essential part of the synthesis is the lithiation step. During the addition of the reactants, temperatures were kept low to avoid possible formation of byproducts.
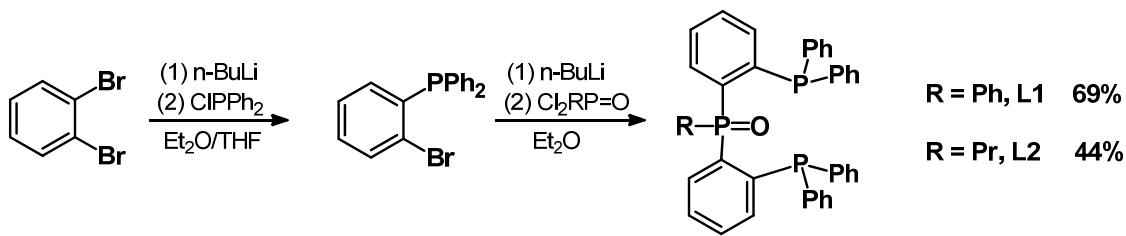
Scheme 3.2. Reactions for the synthesis of ligands **L1** and **L2**.

(1) n-BuLi
(2) ClPPh$_2$
Et$_2$O/THF

(1) n-BuLi
(2) Cl$_2$RP=O
Et$_2$O

R = Ph, L1   69%

R = Pr, L2   44%

In the lithiation of 1,2-dibromobenzene (Scheme 3.3), an excess of n-BuLi could cause lithium exchange of both bromo substituents and would lower the yield of the o-bromodiphenylphosphine, and give rise to the possible formation of 1,2-bis(diphenylphosphino)benzene at the end of the procedure. Therefore, the addition of n-BuLi was done via syringe with 2% mmols less than the stoichiometric equivalent of 1,2-dibromobenzene. It was added slowly allowing the n-BuLi to react first so as to ensure complete mono-lithiation (Scheme 3.2). Successively, PCl(Ph)$_2$ was added via slow addition using syringe.
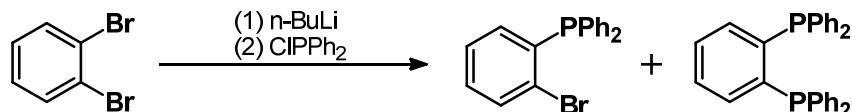
(1) n-BuLi
(2) ClPPh$_2$

Scheme 3.3. Possible products given by the addition of excess BuLi.

In second step, o-bromodiphenylphosphine was reacted with an excess amount of n-BuLi and then with 0.5 equivalents of P(O)Cl$_2$Ph for **L1** or P(O)Cl$_2$Pr for **L2** (Scheme 3.2). This step presents a problem that can be solved by using carefully dried, distilled and degassed solvents. Dichlorophosphine oxide reactants are prone to hydrolysis (Scheme 3.4) and may produce other potentially hazardous decomposition products. Therefore, the step was strictly done under the hood and in minimum moisture conditions to avoid accident and to achieve maximum yield of the desired phosphine ligand.

2 H$_2$O   2 HCl
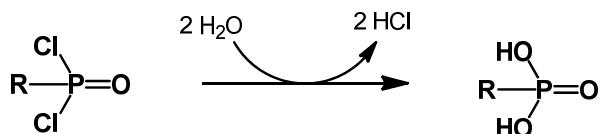
Scheme 3.4. Hydrolysis of dichlorophosphine oxide derivatives.

Taking this into consideration, **Route 1**, however presents a greater advantage through the possibility of modification of the central group substituent, **R** and further modifications on the aryl substituents of the ligand. In this case, **R = Ph** for **L1** and **n-Pr** for **L2**. Through this, **Route 1** allows easy electronic and steric modifications. It is also suggested that any dichlorophosphine oxide derivative (i.e., R= alkyl, aryl, etc.) should yield

the corresponding ligand using this synthetic route under proper reaction conditions. The lower reaction yield was observed with the synthesis of **L2** (44%) which may be attributed to the high reactivity of dichloropropylphosphine oxide.

The ligands were characterized through ^{31}P, ^{1}H NMR, and other techniques, but ^{31}P was most useful. The phosphines were designed to display a unique set of NMR signals. Where **L1** and **L2** should display a triplet and doublet signal signifying the success of the synthesis. The spectrum of **L1** shows peaks at δ_P −11.86, d, and δ_{PO} 34.15, t with J_{PP}= 19 Hz (Figure 3.5). Some peak broadening was observed in the spectrum but the peaks integrate to a ratio of 1:2 which pertains to the one $Ar_3P=O$ and two PAr_3.
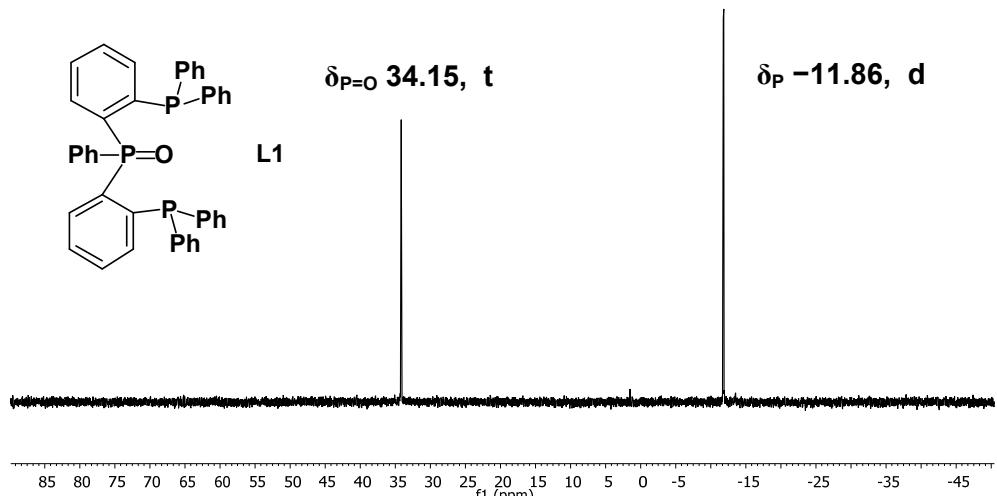
Figure 3.5. $^{31}P\{^{1}H\}$ NMR showing the triplet-doublet pattern of **L1**.

L1 was oxidized with H_2O_2 for referencing purposes (Figure 3.6). The spectrum shows peaks for **L1O₂** at the usual $P^V=O$ "oxidized P range". We see that the spectrum has preserved the same triplet (δ_P 35.13) and doublet (δ_P 32.38) pattern, with J_{PP}= 8Hz. The triplet was displaced only a few ppm but the oxidized Ps were displaced 44 ppm. The shifts were in congruence with the literature (t, δ 36.78 and d, 33.65).[1] Peaks are sharp and well defined and integrate to a ratio of 1:2.

[1] Miyata, K., Hasegawa, Y., Kuramochi, Y., Nakagawa, T., Yokoo, T. and Kawai, T. *Eur. J. Inorg. Chem.* **2009**, 4777–4785
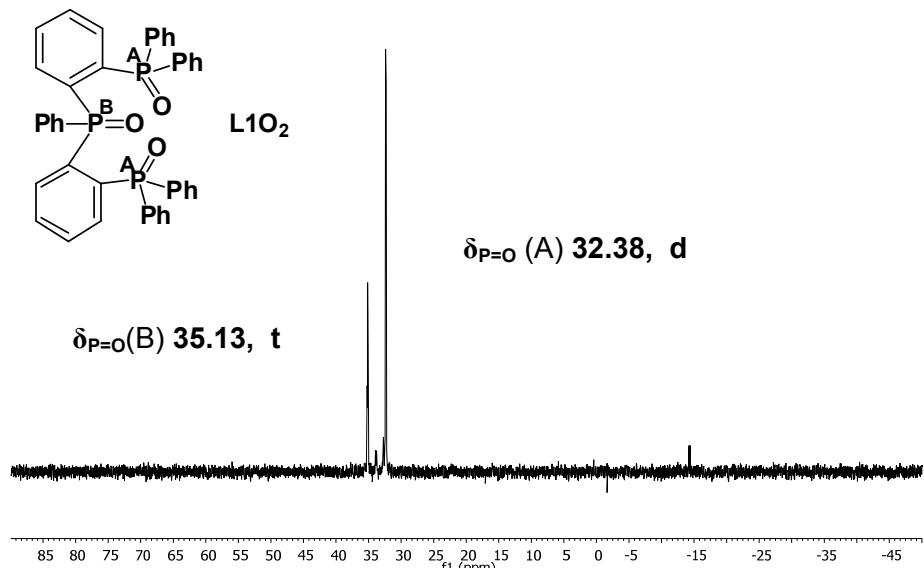
Figure 3.6. $^{31}P\{^1H\}$ NMR showing the triplet-doublet pattern of **L1O$_2$**.

L2, bearing almost the same structure but only differs with the phosphine oxide substituent, shows the same triplet-doublet pattern and at a very slightly different shift. The ^{31}P NMR peaks of the free ligand were observed at δ_P −14.88, d, and $\delta_{P=O}$ 34.48, t.

Route 2 is a direct lithiation and substitution reaction, a one-pot reaction. Triphenyphosphine oxide could not be lithiated directly, consequently, this route could not be used for ligands such as **L1** or **L2** (Scheme 3.7).
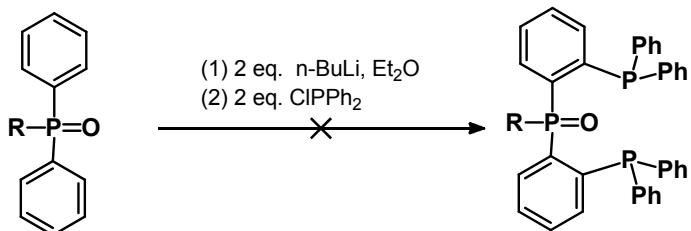
Scheme 3.7. Scheme showing the reaction of RPh$_2$P=O with BuLi and ClPPh$_2$

However, preliminary work in our group has shown that aryl sulfones can be lithiated.[2] The availability of p-tolyl sulfone and its property to favor direct dilithiation in the ortho positions selectively was taken into advantage. Hence, **L3** was synthesized using this route.

n-BuLi was added to the reaction solution in a slow manner and allowing it to react at a time. The amount of n-BuLi added is important to obtain the desired ligand. That is, both mono− and di− lithiation are possible by controlling the amount of the reagent. However in this case, we opted to add 2 eqs. of n-BuLi to lithiate both ortho positions of the two "wings". Ortho− lithiation is favored due to the presence of two oxygens of the sulfone group. These

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[2] Tello, I., Tesis Doctoral, **2010**

oxygens produce an inductive effect and cause the stabilization of lithiation at the otho-position (Scheme 3.8).
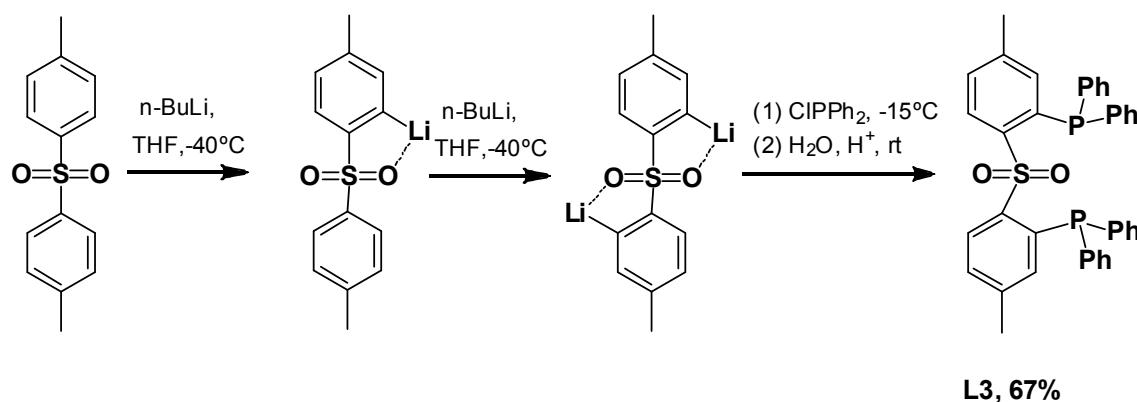
Scheme 3.8. Reaction route for **L3** synthesis.

The easy control of the synthetic route at low temperatures makes the synthesis of **L3** the easiest among the three ligands. After a fast purification through flash chromatography, a singlet peak during the $^{31}P\{^1H\}$ NMR analysis of the ligand was observed at δ −13.98. To further characterize and reference the ligand, it was oxidized with H_2O_2. The oxidized ligand shows a single peak at δ 33.46 (Figure 3.9).
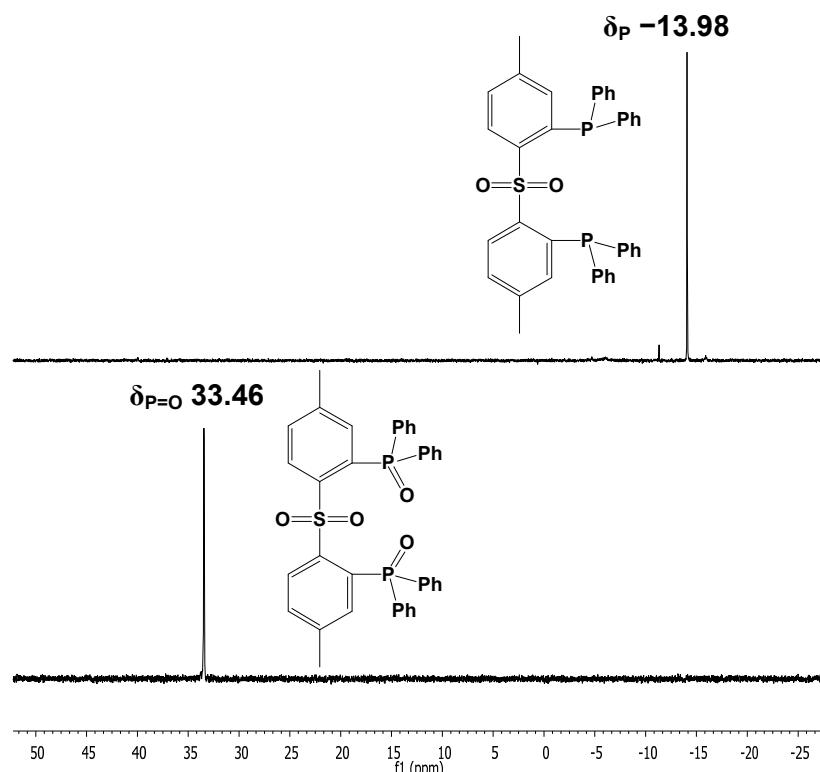
Figure 3.9. $^{31}P\{^1H\}$ NMR comparison of **L3** and its oxidized analogue.

The IR spectra of the ligands **L1**, **L2**, **L3** and **oxidized L3** was also obtained and the data gathered are shown on the table below.

Table 3.10. Characteristic IR stretching data [cm^{-1}] for the E=O double bonds in sulfone and phosphine oxide compunds.

Ligands	P=O stretching	SO$_2$ stretching	
		Symmetric	Assymetric
L1, TPOdiphos	1198		
L2, DPPrPOdiphos	1173		
L3, SODPdiphos		1148	1300
L3O$_2$, (**L3**-P,P-oxide)	1176	1117	1380
Ph$_2$SO$_2$[a]		1156	1310
Ph$_3$PO[a]	1180		

[a] I. Tello, Tesis Doctoral, 2010.

3.2. Synthesis and Characterization of Mo(0) and W(0) Complexes of L1-L3

In the current study, reactions involving the successful compexation of molybdenum carbonyl fragments with the ligand were accomplished by refluxing a 1:1 stoichiometric mixtures of Mo(CO)$_6$ and **L1**-**L3**, using toluene as the solvent (Scheme 3.11). Given these conditions, complexes **C1**, **C2** and **C3** were produced from the reactions. On the other hand, attempted reactions performed at room temperature or by refluxing using low boiling point solvents such as CH$_2$Cl$_2$ proved to be unsuccessful. No change in the physical aspects of the reaction solutions were observed after >6 hours of refluxing or by continuous agitation for >72 hours, respectively.
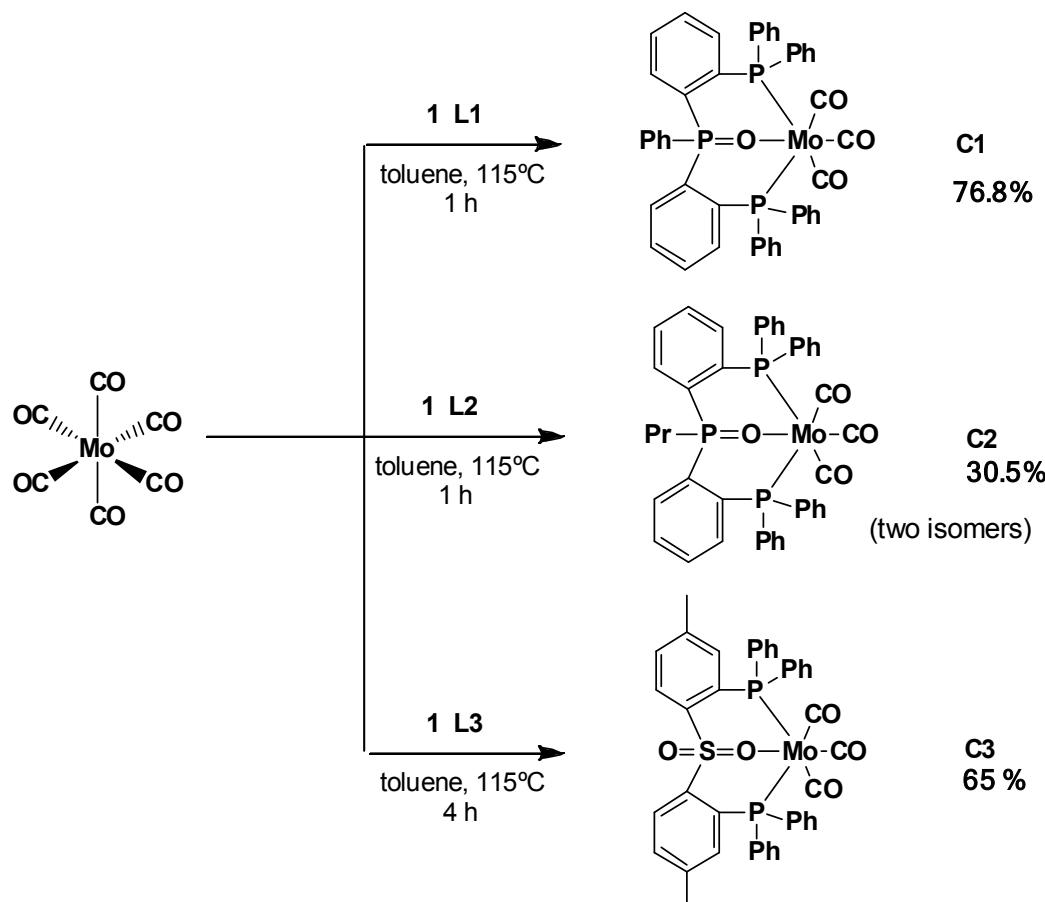
Scheme 3.11. Reaction scheme employed to synthesize molybdenum carbonyl complexes of **L1**, **L2** and **L3**.

Variable completion time for the reactions was observed with molybdenum complexes, from 1 to 4 hours reaction time. The NMR of **C1** shows peaks at $\delta_{P=O}$ 37.27, t, and δ_{PO-Mo} 30.49, d. A considerable shift of the signal pertaining to the coordinated phosphine group (Figure 3.12) was observed. In the case of **C2**, a mixture of two molybdenum containing products was obtained after an hour of reaction (Figure 3.13). Interestingly the signals of the phosphine-phosphorus (P-Mo) are very close in both the major and the minor products, but the signal of the phosphine oxide-phosphorus are shifted: this will be interpreted as the minor product being cis-P,P-[Mo(**L2**)(CO)$_4$], a complex in which

the P=O oxygen remains uncoordinated. The NMR of **C3**, however, shows a single peak at δ_P 31.12. The formation of **C3** with respect to time is shown in Figure 3.14.

$\delta_{P=O}$ **37.27, t** δ_{PMo} **30.49, d**

δ_P **−11.86, d**

$\delta_{P=O}$ **34.15, t**
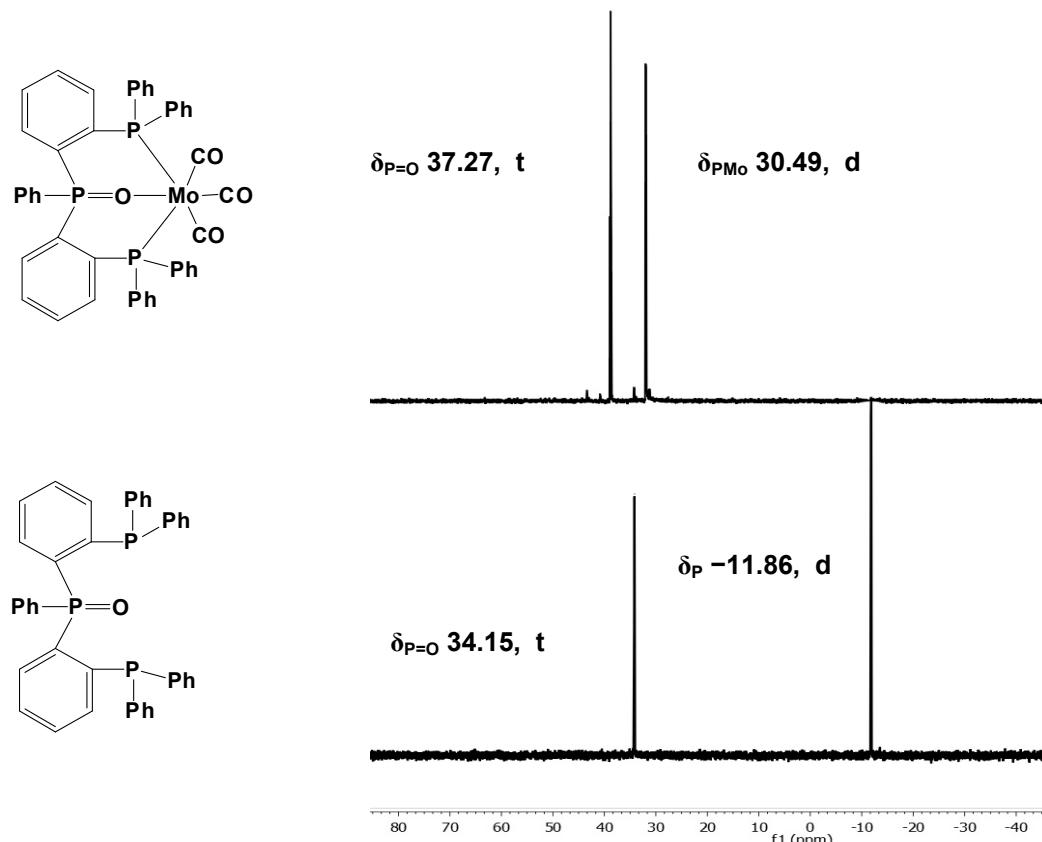
Figure 3.12. $^{31}P\{^{1}H\}$ signal displacement upon complexation (t= 1h) of **L1** with [Mo(CO)$_6$]

$\delta_{P=O}$ **44.20, t**
major

δ_P **29.74, t**
major

$\delta_{P=O}$ **45.59, t**
minor

δ_P **29.81, d**
minor
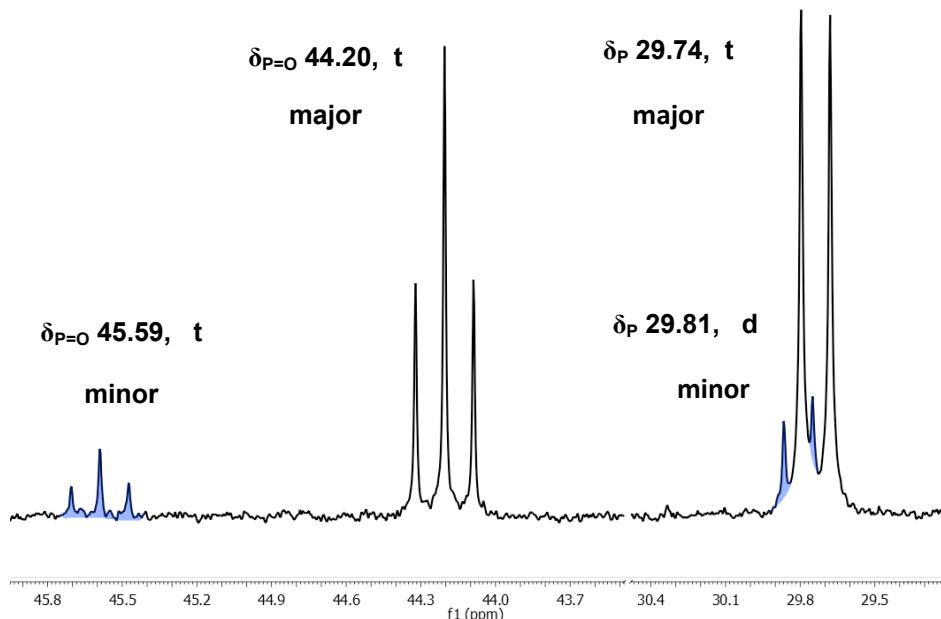
Figure 3.13. $^{31}P\{^{1}H\}$ NMR of reaction mixture of [Mo(CO)$_6$] and **L2** showing the major and minor products
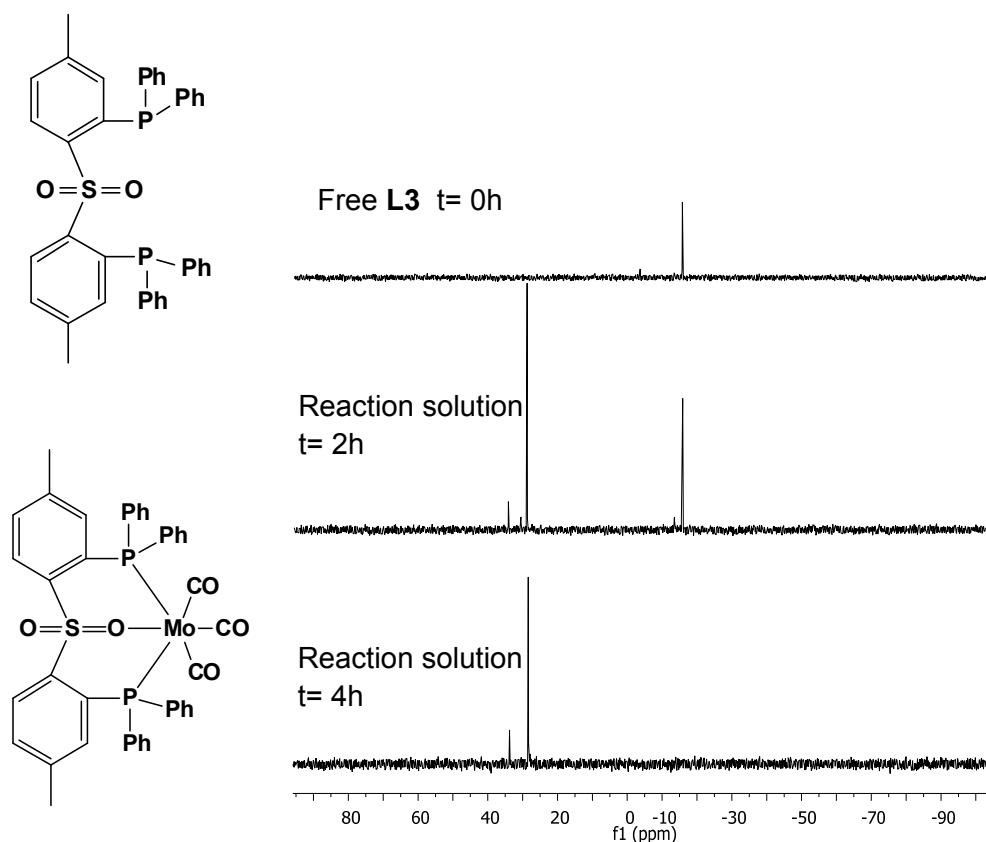
Figure 3.14. $^{31}P\{^1H\}$ showing the formation of [Mo(SODPdiphos)(CO)$_3$] with time.

Tungsten complexes were harder to obtain owing to the fact that W(CO)$_6$ is more kinetically inert than Mo(CO)$_6$. **C4** and **C5** were generally formed, after four hours of reflux, regardless of the solvent used (Scheme 3.15). Higher temperatures were employed to allow complexation of **L1** and **L3** with W(CO)$_6$.
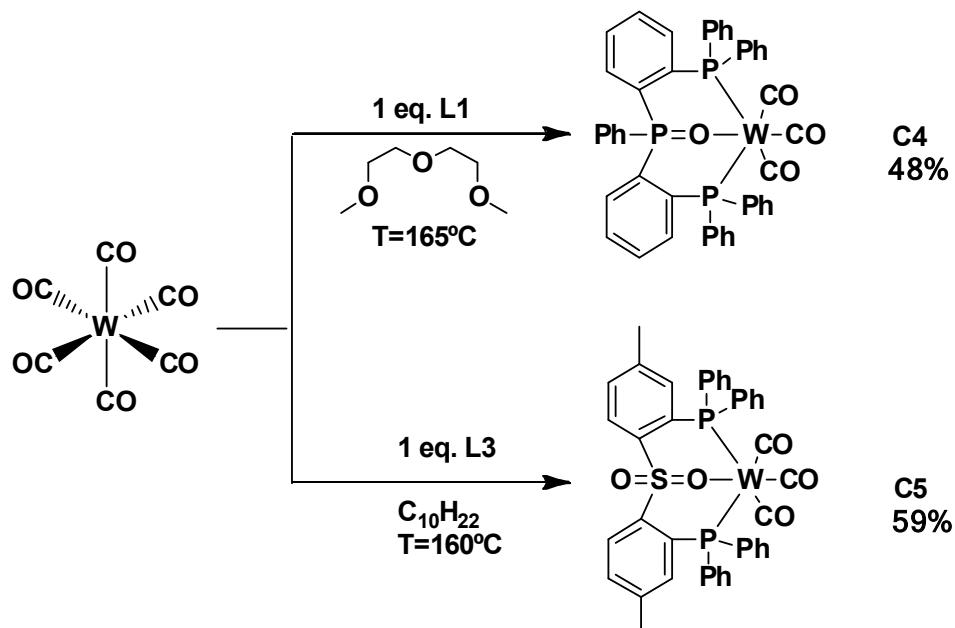
Scheme 3.15. Reactions of ligands with octahedral, d^6 W(0).

Reaction progress was monitored by performing ^{31}P NMR tests of homogeneous samples taken from the reaction mixtures at 2 and 4 hours reaction times.
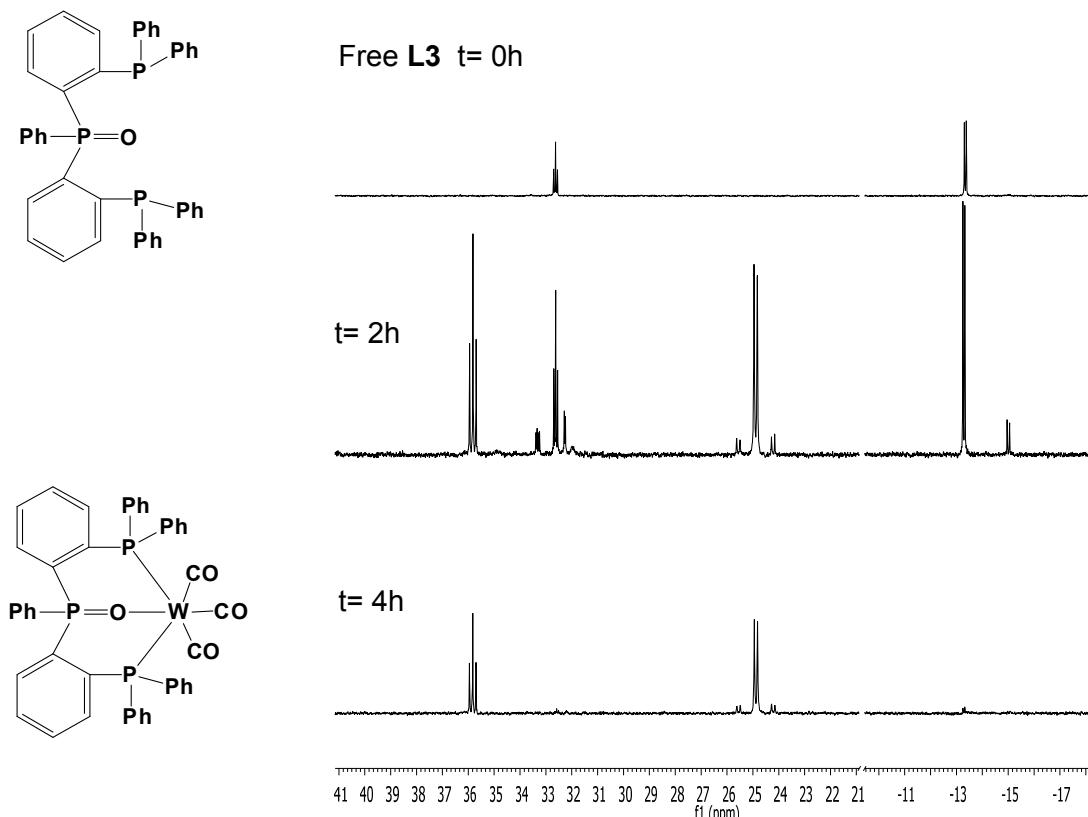
Figure 3.16. ^{31}P{^{1}H} showing the formation of [W(TPOdiphos)(CO)$_3$] with time.

NMR peaks corresponding to the P directly coordinated with W were observed at δ_P 25.58, s, for **C4** and at δ_P 22.83, s, for **C5**. The spin active ^{183}W (I=1/2, abundance 14%) gives rise to satellites by coupling to phosphorus in the ^{31}P{^{1}H} spectra, for **C4** ^{1}**J$_{P-W}$** = 217 Hz and for **C5** ^{1}**J$_{P-W}$** =233 Hz. Both conforming to the values found in previous studies.[3,4]

The complexes displayed varying solubilities in various halogenated solvents (i.e, CHCl$_3$ and CH$_2$Cl$_2$) − **C2**, **C3** and **C5** being the more soluble products and **C1** and **C4** as the complexes with the lower solubility. A property that can be attributed to the difference in the core group and the substituent groups attached to the central phosphine oxide. **C1** and **C4** are only slightly soluble in CH$_2$Cl$_2$ and in CHCl$_3$. Complexes **C2**, **C3** and **C5** are more soluble in both solvents.

[3] Martínez Cuevas, F. *Treball de Recerca; Laboratori d´Iniciació a la Recerca, Máster en Ciencia y Tecnología Químicas,* **2007**
[4] Craig Taylor, R., Keiter, R., and Cary, L. W. *Inorg. Chem.,* **1974**, 1928−1932

IR study of ligands L1, L2 and L3 and their Mo(0) and W(0) complexes

IR spectroscopy is a classical tool for the characterization of organic and inorganic molecules that has IR active groups such as CO, SO_2 and PO. The analysis of spectra of the complexes allowed us to obtain additional information on the coordinating property of the central oxygen. Generally, a coordination of the O in SO_2 or PO would cause a decrease in the frequency of the vibration between the phosphorous and oxygen. Hence, a displacement of spectral band pertaining to these groups suggests a change in the environment of the bonds involved, thus a possible coordination. Furthermore, the number of expected CO stretches in an IR spectrum depends on the number of IR active groups present and the orientation of the coordinating ligand.

All molybdenum (**C1**, **C2** and **C3**) and tungsten complexes (**C4** and **C5**) each showed three new intense peaks between 1775 cm^{-1} to 1920 cm^{-1} which pertain to the terminal CO groups. Also, spectral data for the complexes were compared to the IR spectra of their corresponding free ligands. Aside from the appearance of the 3 CO bands, a noticeable decrease in the frequency of the PO band of **C1**, from 1198 cm^{-1} to 1154 cm^{-1} (Figure 3.17), may suggest metal−O coordination. The absence of the characteristic weak peak at ν ~2000 cm^{-1} also suggests the absence of trans− COs in the molecule. With regards to the case of **C2**, which is a mixture of two products, we also observed three intense CO peaks between the ranges 1775 cm^{-1} to 1920 cm^{-1}. And at the PO region, there is a noticeable displacement from 1173 cm^{-1} to 1150 cm^{-1} while the other peak positions remain unchanged. **C4** also shows a decrease in the PO vibration frequency from 1198 cm^{-1} to 1151 cm^{-1}, almost the same decrease as in **C1**.
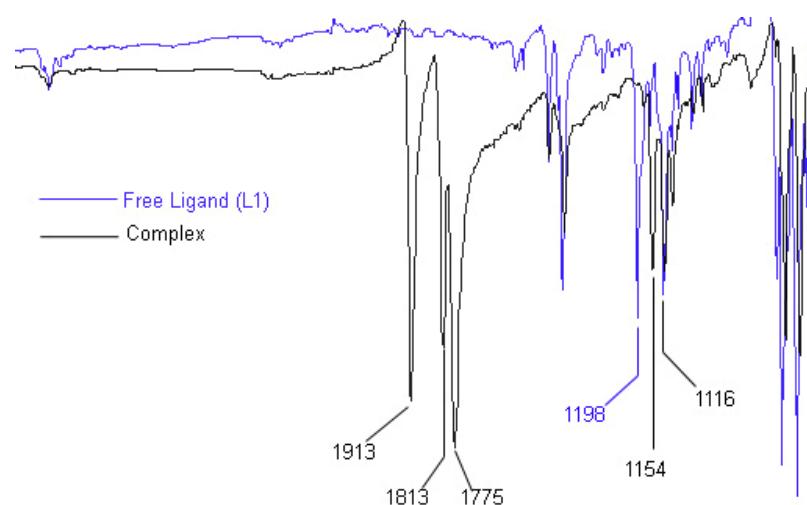
Figure 3.17. IR Spectral overlay of **C1** and **L1** showing the $M(CO)_3$ characteristic pattern and the ν(P=O) peak displacement (values in cm^{-1}).

With the complexes bearing **L3**, **C3** and **C5**, we also observed the same CO stretches and the same displacement but for the SO_2 group. For **C3** and **C5**, the SO_2 asymmetric stretch was retained at ~1300 cm^{-1}. On the other hand, the symmetric stretches were displaced from 1148 cm^{-1} to 1134 cm^{-1} and 1148 cm^{-1} to 1129 cm^{-1} for **C3** and **C5**, respectively. Table 3.18 shows a summary of the characteristic E=O peaks of the complexes compared to that of their corresponding ligands.

Table 3.18. Characteristic IR stretching data [cm^{-1}] for the E=O double bonds for the free ligands and their Mo(0) and W(0) octahedral complexes.

Ligands/Complexes	P=O stretching	SO_2 stretching	
		Symmetric	Assymetric
L1, TPOdiphos	1198		
L2, DPPrPOdiphos	1173		
L3, SODPdiphos		1148	1300
C1, [Mo(CO)$_3$(TPOdiphos)]	1154*		
C2, [Mo(CO)$_3$(DPPrPOdiphos)]	1150*		
C3, [Mo(CO)$_3$(SODPdiphos)]		1134*	1300
C4, [W(CO)$_3$(TPOdiphos)]	1150*		
C5, [W(CO)$_3$(SODPdiphos)]		1129*	1297

*displaced peaks

HRMS of C1, C3, C4 and C5

The conclusions formulated from the IR data were further supported by the determination of the exact masses of the complexes. The found and calculated exact mass envelopes for **C1**, **C3**, **C4** and **C5** were in congruence with the proposed composition, including the number of COs in the complexes (n=3). For all complexes, the data is presented in the annex. In the case of **C1**, the spectra are shown below (Figure 3.19).
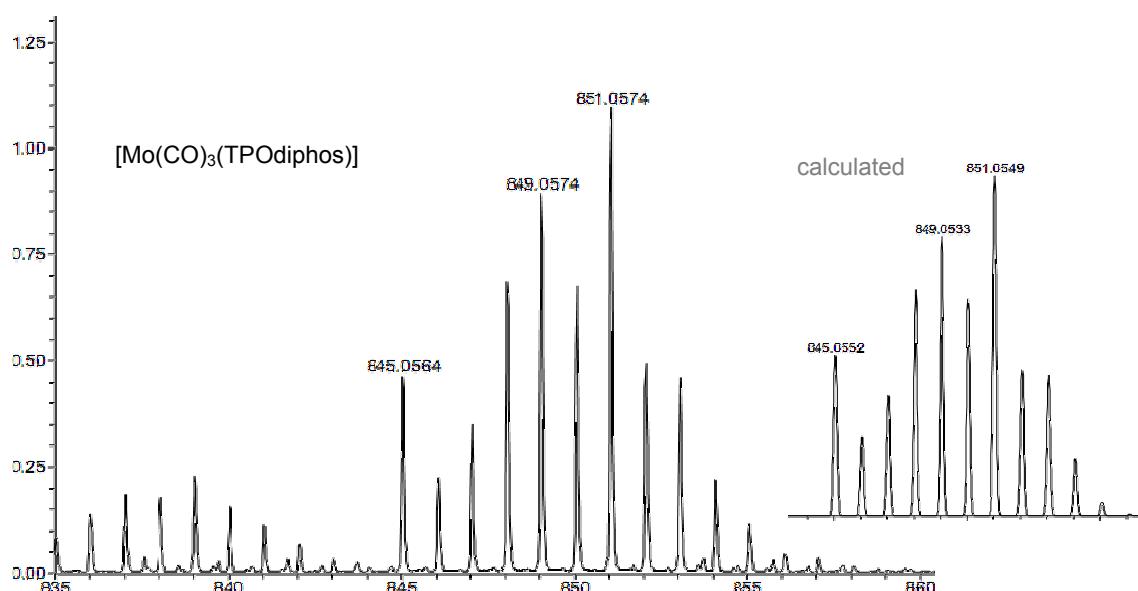
Figure 3.19. Experimental and calculated HRMS of **C1**

The simulated isotopic pattern for **C1**, **C3**, **C4** and **C5** calculated for complexes match the experimental data and were within the margin of 3% deviation. This strengthens the pre-conclusions that the ligands were able to complex the O in the E=O group to the metal center Mo and W.

Crystal Structure of *fac*-[Mo(TPOdiphos)(CO)$_3$]

Crystals of *fac*-[Mo(TPOdiphos)(CO)$_3$] were obtained by the slow diffusion of diethyl ether to a saturated solution of the complex in CH_2Cl_2. To be able to confidently conclude what configuration the complex bears, an XRD study was undertaken. This section of the study is focused with the discussion of crystallographic data and its implications. A complete CIF file can be found in the Annex. Table 3.20 contains the relevant crystal and refinement data. Table 3.21 collects selected distances and Table 3.22 selected angles. Figure 3.23 shows an ORTEP plot of the molecule.

Table 3.20. Crystal data and structure for *fac*-[Mo(TPOdiphos)(CO)$_3$]

Empirical Formula	$C_{45}H_{35}MoO_4P_3$
Formula weight	828.58
Crystal System	Monoclinic
Space group	P2$_1$/a
Unit cell dimensions [Å]	a = 19.7966(14) α = 90º b = 9.8803(7) β = 95.880(2)º c = 39.196(3) γ = 90º
Formula Units per cell	8
Crystal size [mm]	0.18 x 0.13 x 0.12
Crystal color	Transparent orange
Cell volume, Å^3	7626.257(6)
Density, ρ_{calc} (g/cm^3)	1.44
Measurement temperature (K)	295(2)
Wavelength MoKα, λ [Å]	0.71073
Absorption coefficient, μ, cm^{-1}	0.514
R factor (all)	0.2143
R Factor (gt)	0.0795
wR Factor (ref)	0.219
wR Factor (gt)	0.16
Goodness of Fit	0.867

The unit cell contains two chemically equivalent but crystallographically different molecules of *fac*-[Mo(TPOdiphos)(CO)$_3$], labeled type 1 and type 2 in the tables. The coordination of molybdenum is octahedral, albeit distorted by the fact that the ligand atoms are of a very different nature. The bond lengths of Mo to P have a median value of 2.56 Å. The Mo-P distances are somewhat long owing to the fact that they are trans to the CO ligands which form a very strong bond to molybdenum(0), an electron rich d^6 metal. This is in agreement to the short Mo-CO distance in the facial Mo(CO)$_3$ group.

It is interesting to see how the oxygen of the phosphine oxide part of L1 has displaced CO in the coordination sphere of the soft, electron rich molybdenum(0). The bond lengths between Mo and O have a median value of 2.26 Å. This value is considerably longer than

that reported for most oxo-molybdenum complexes.[5] This implies a role on the hemilability of this part of the ligand. It is suggested that this bond between Mo and O will be the first to break and will be able to generate an active site during catalysis. Another interesting feature of the complex is the relationship between the CO bond lengths that are trans to the P,P,O coordination. The CO bonds trans− to the Ps has an average distance of 1.16 Å and the CO bonds trans− to the E=O group has an average value of 1.18 Å.

Table 3.21. Selected distances [Å]

	MoL1 (type 1)[1]	MoL1 (type 2)[2]
Mo_1-P_1 (Mo_2-P_4)	2.567(2)	2.560(2)
Mo_1-P_3 (Mo_2-P_6)	2.568(2)	2.548(2)
Mo_1-O_1 (Mo_2-O_2)	2.263(4)	2.266(5)
Mo_1-C_{11} (Mo_2-C_{26})	1.922(8)	1.925(9)
Mo_1-C_{12} (Mo_2-C_{22})	1.902(8)	1.899(8)
Mo_1-C_{13} (Mo_2-C_{24})	1.936(8)	1.951(8)
P_2-O_1 (P_5-O_2)	1.501(5)	1.493(5)
$C_{11}-O_{11}$ ($C_{26}-O_{26}$)	1.174(8)	1.179(9)
$C_{12}-O_{12}$ ($C_{22}-O_{22}$)	1.183(8)	1.176(8)
$C_{13}-O_{13}$ ($C_{24}-O_{24}$)	1.155(8)	1.154(8)

Table 3.22. Selected angles [deg]

	MoL1 (struct. 1)[1]		MoL1 (struct. 2)[2]
$C_{12}-Mo_1-C_{11}$	86.6(3)	$C_{22}-Mo_2-C_{26}$	82.0(3)
$C_{12}-Mo_1-C_{13}$	86.5(3)	$C_{22}-Mo_2-C_{24}$	84.7(3)
$C_{12}-Mo_1-P_1$	100.0(3)	$C_{22}-Mo_2-P_6$	90.2(3)
$O_1-Mo_1-P_1$	73.90(13)	$O_2-Mo_2-P_6$	86.03(13)
$O_1-Mo_1-C_{11}$	99.9(2)	$O_2-Mo_2-C_{26}$	102.1(3)
$O_1-Mo_1-P_3$	85.82(12)	$O_2-Mo_2-P_4$	72.24(12)
$C_{11}-Mo_1-P_3$	90.4(2)	$C_{26}-Mo_2-P_4$	90.3(2)
$C_{12}-Mo_1-P_3$	92.6(2)	$C_{22}-Mo_2-P_4$	104.8(2)
$P_1-Mo_1-P_3$	98.05(7)	$P_6-Mo_2-P_4$	97.97(6)
$O_1-Mo_1-C_{13}$	96.1(2)	$O_2-Mo_2-C_{24}$	96.9(3)
$C_{11}-Mo_1-C_{13}$	80.7(3)	$C_{26}-Mo_2-C_{24}$	84.7(3)
$P_1-Mo_1-C_{13}$	90.9(3)	$P_6-Mo_2-C_{24}$	88.3(2)
$Mo_1-C_{11}-O_{11}$	170.7(7)	$Mo_2-C_{26}-O_{26}$	169.7(7)
$Mo_1-C_{12}-O_{12}$	178.3(7)	$Mo_2-C_{22}-O_{22}$	176.2(7)
$Mo_1-C_{13}-O_{13}$	172.2(7)	$Mo_2-C_{24}-O_{24}$	174.7(8)
$C_{11}-Mo_1-P_1$	169.0(2)	$C_{26}-Mo_2-P_6$	169.8(2)
$O_1-Mo_1-C_{12}$	173.4(3)	$O_2-Mo_2-C_{22}$	174.8(3)
$P_3-Mo_1-C_{13}$	171.1(3)	$P_4-Mo_2-C_{24}$	166.9(2)
$P_2-O_1-Mo_1$	124.8(3)	$P_5-O_2-Mo_2$	125.2(3)

The P-Mo-P bond angle measures an average of 98º while the equatorial C-Mo-C bond angles measures a little acute: 80.7(3)º for molecule 1 and 84.7(3)º for molecule 2. It was also evident that the axial bonds were oriented towards the E=O group, the trans C-Mo-O angle measures an average value of 174º. Distortions of the equatorial CO bonds were supposed to have been affected by the bulky diphenyl substituent of the phosphine groups. The ORTEP plots of the complexes are shown below. Hydrogen atoms were removed to simplify the structure.

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[5] Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, Wiley, 5th Ed
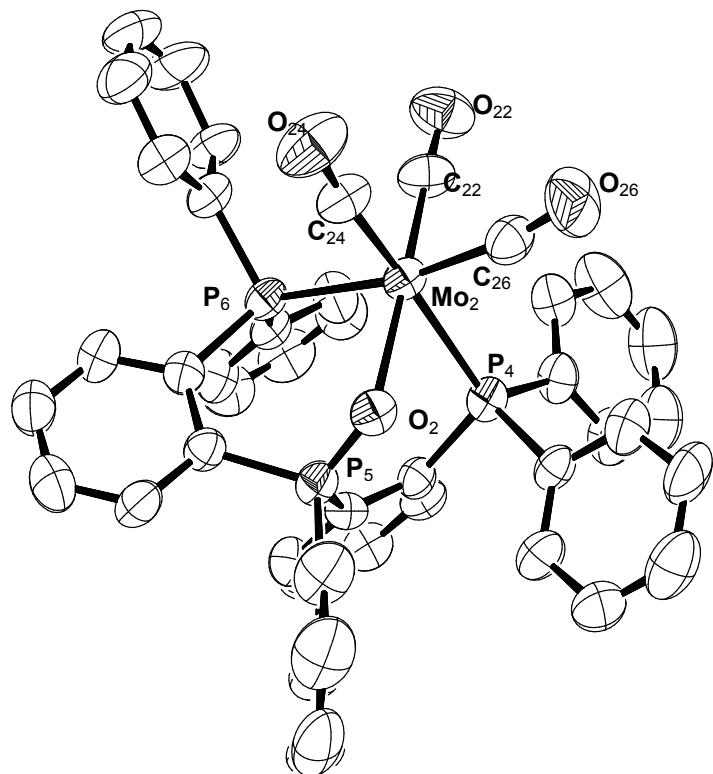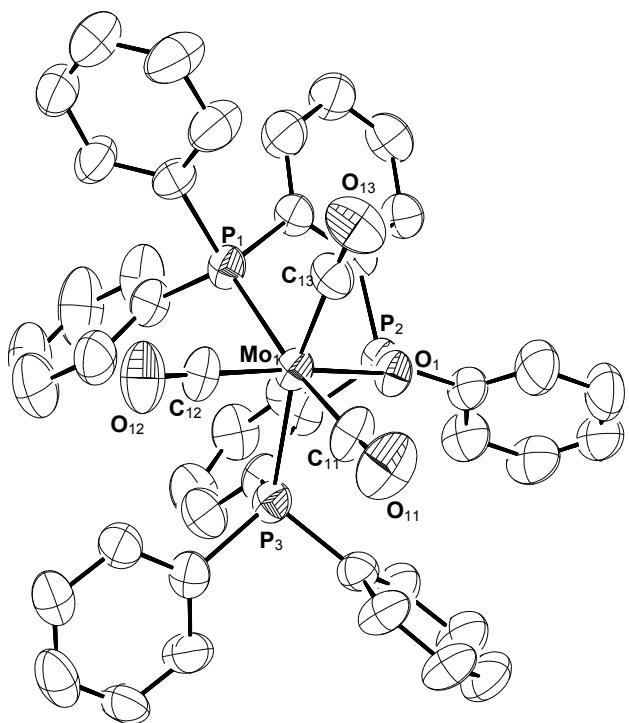
Figure 3.23. ORTEP visualizations of the molecules 1 and 2 of *fac*-[Mo(TPOdiphos)(CO)₃]

4 EXPERIMENTAL

4.1. General Procedures and Characterization of Products

All routinary synthetic procedures including reaction handling and the handling and purification of solvents were done under inert atmosphere (i.e., N_2/vacuum). Solvents employed for air sensitive steps were generally dried, distilled over the necessary reagents and degassed prior to use. Toluene, THF, hexane and ethyl ether were distilled over sodium and benzophenone; CH_2Cl_2 was distilled over CaH_2. All other reagents were of commercial sources or prepared according to established methods and checked spectroscopically whenever necessary.

4.1.1. NMR and IR Spectroscopy

Reaction progress was monitored through ^1H and $^{31}P\{^1H\}$ NMR. Final reaction products were characterized employing spectroscopic techniques: ^1H and $^{31}P\{^1H\}$ NMR. The chemical shifts are reported in the δ scale. ^1H are referenced to TMS and ^{31}P spectra are referenced by using a capillary tube containing 85% H_3PO_4 as external standard. The NMR spectra were recorded at 250MHz and 400MHz using Bruker DPX250-Auto and AV400, respectively, at the *Servei de Ressonància Magnètica Nuclear* (SeRMN), UAB. Characterization of the ligands and the coordination complexes through IR spectroscopy was carried out on a Bruker TENSOR27^{TM} infrared spectroscope employing ATR mode at the *Servei de Analisis Química* (SAQ), UAB.

4.1.2. High Resolution Mass Spectroscopy – Electrospray Ionization (HRMS-ESI[+])

High resolution determination of the masses was performed at the SAQ, UAB using a micrOTOF-Q mass spectroscope equipped with electrospray ionizer (ESI[+]) in positive ion mode. The determinations were performed by Dr. Mª Jesús Ibarz Esteva.

4.1.3. X-Ray Diffraction Analysis

Crystals grown by solvent diffusion were found appropriate for crystal structure determination. They were mounted on a MicroMount^{TM} and were analyzed at room temperature on a Bruker SMART APEX by X-Ray Diffraction spectroscopy (XRD) at the *Servei de Difracció de RX* de la UAB.

4.2 Synthesis of Ligands

4.2.1. Synthesis of 2-bromophenyldiphenylphosphine (L0)

This ligand was synthesized by slightly modifying the procedure developed at our group by I. Tello, which in turn, was obtained from the literature.[1]
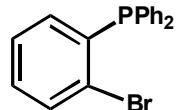
In a side arm flask charged with 1,2-dibromobenzene (FluoroChem, 96%, 51 mmol, 12.03 g) dissolved in dry, degassed 50:50 ether/THF mixed solvent (100 ml), n-BuLi (Aldrich, 2.5 M in hexanes, 20 mL, 50 mmol) was added drop wise at −120ºC (85:10:5, ether:acetone:pentane/liquid N_2 slush bath). The reaction was stirred for an hour at −120ºC. Maintaining the same condition, chlorodiphenylphosphine (Aldrich, 96%, 51 mmol, 11.4 g) was added slowly via syringe and was allowed to react for an hour. The temperature was slowly increased to −80ºC (acetone/liquid N_2) and a degassed aqueous solution of NH_4Cl was added (5 g in 50 ml H_2O). The organic and aqueous layers were separated and the aqueous layer was discarded. The organic layer was washed with degassed water (10 mL x 3). The solution was filtered through anhydrous $MgSO_4$ and the solvent was evaporated to dryness under reduced pressure. The product was obtained as a white solid that was further purified by flash chromatography over silica gel using CH_2Cl_2 as eluent. Yield: 17 g, 96%.

$^{31}P\{^1H\}$ **NMR** (162 MHz, CDCl$_3$, 298 K) δ −4.47 (s, PAr$_3$).

^{1}**H NMR** (250 MHz, CDCl$_3$, 298 K) δ 6.75-6.83 (m, 1H), 7.16-7.45 (m, 12H), 7.62 (m, 1H).

4.2.2. Synthesis of bis{2-(diphenylphosphino)phenyl}(phenyl)phosphine oxide TPOdiphos, (L1)

This ligand was prepared according to the experience of our group, and its synthesis optimized.

A side-arm flask was charged with **L0** (C$_{18}$H$_{14}$BrP, 14.27 g, 41.8 mmol) dissolved in degassed, dry ether (120 mL). The solution was cooled down to −80ºC (acetone/liquid N_2 slush bath) and n-BuLi was added drop wise (Aldrich, 2.5 M in hexanes, 16.8 mL, 42 mmol). The mixture was stirred for 1 hr at −80ºC and 3 more h at rt. The temperature was again decreased to −80ºC and dichlorophenylphosphine oxide (Aldrich, 98%, 4.10 g, 20.92 mmol) was slowly added via syringe. The reaction was gradually warmed up to room temperature and was stirred for 24 hours. The solvent was removed through cannula

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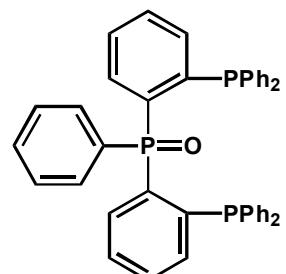
[1] (a) Luo, X., Zhang, H., Duan, H., Liu, Q., Zhu, L., Zhang, T. and Lei, A. *Org. Lett.*, **2007**, *9*, 4571. (b) Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315.

filtration at −80ºC and the white product was washed with ether (20 mL x 3) and degassed water (50 mL). Dry methanol (60 ml) was then added and it was refluxed for 2 hours. The solvent was again removed through cannula filtration and the residue was washed with ether (50 mL) and dried under reduced pressure to obtain a white solid product. Yield: 18.8 g, 69%.

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) δ 33.29 (t, Ar$_3$P=O, J_{PP} = 12.0 Hz), −12.68 (d, Ar$_3$P, J_{PP} = 12.0 Hz).

^{1}H NMR (250 MHz, CDCl$_3$, 298 K): δ 6.78-6.83 (m, 1 H), 7.21-7.40 (m, 12 H), 7.60-7.66 (m, 1 H).

IR [cm^{-1}] (ν P=O, strong) 1198.

4.2.3. Synthesis of bis(2-(diphenylphosphino)phenyl)(propyl)phosphine oxide (L2),

This ligand was prepared according to the experience of our group, and its synthesis optimized.

In a Schlenk flask charged with of **L0** (15.20 g, 44.55 mmol) dissolved in 100 mL of degassed dry ether, an excess amount of n-BuLi (Aldrich, 2.5 M in hexanes, 17.80 mL, 44.55 mmol) was added dropwise at –80ºC. The solution was allowed to react for an hour at this temperature and for three more hours at room temperature. The formation of white precipitate was observed as the reaction goes. The temperature was again lowered to –80ºC and dichloropropylphosphine oxide (Alfa Aesar, 98%, 3.60 g, 22.27 mmol) was added drop by drop. The solution was gradually warmed and allowed to react at room temperature for 24 hours. The suspension was brought to reflux temperature and was refluxed for 6 hours. The solvent was entirely removed and the white precipitate was washed with degassed water (50 ml) and ether (3 x 20 ml). All the solvent was removed and the white product was allowed to dry under reduced pressure. Yield: 6 g, 44%.

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) δ 34.48 (t, J_{PP}= 20 Hz, 1 P=O), −14.88 (d, J_{PP}= 20 Hz, 2 PAr$_3$).

IR [cm^{-1}] (ν P=O, strong) 1173.
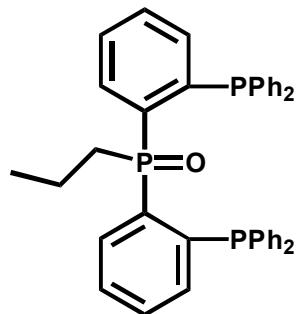
4.2.4. Synthesis of (sulfonylbis(3-methyl-6,1-phenylene))bis(diphenylphosphine) SODPdiphos (L3)

This ligand was prepared according to the experience of our group, and its synthesis optimized.

p-Tolyl sulfone (Acros, 6.15 g, 25 mmol) was dissolved in dry, degassed THF (100 ml) in a 250 ml side arm flask. The solution was cooled down to −41ºC (CH$_3$CN/liquid N$_2$) and n-BuLi (2.5 M in hexane, Aldrich, 22.5 ml, 55 mmol) was added drop wise. The mixture was stirred at −41ºC for an hour and two more hours at −15ºC (ethylene glycol/liquid N$_2$ slush bath). A solution of chlorodiphenylphosphine (Aldrich, 10.75 ml, 58.75 mmol) in dry THF (25 ml) was added slowly. The solvent was evaporated and the resulting white residue was treated with degassed HCl (1% aq soln) and was extracted with CH$_2$Cl$_2$ (3 x 30 ml). The aqueous layer was discarded and the organic layer was filtered through Na$_2$SO$_4$ and the resulting solution was dried under reduced pressure to yield a yellowish to yellow-green oil that was purified by flash chromatography over silica gel with dry CH$_2$Cl$_2$ and washing with ether. The solution was dried under reduced pressure producing a white solid product. Yield: 10 g, 67%.
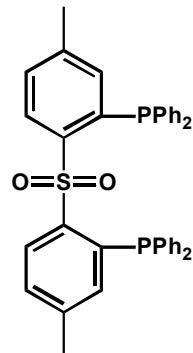
^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K) δ −13.98 (s, PAr$_3$).

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 8.60–8.39 (m, 1H), 7.27–7.11 (m, 7H), 7.02–6.86 (m, 4H), 6.79 (s, 1H), 2.16 (s, 3H).

IR [cm^{-1}] 3051, 1583, 1477, 1433, 1378, 1300 (ν SO$_2$ asymm stretch), 1148 (ν SO$_2$ symm stretch), 1114, 1091, 821, 742, 721, 692, 673, 629.

4.2.5. Synthesis of (sulfonylbis(3-methyl-6,1-phenylene))bis(diphenyl phosphine oxide)

In an open 50 ml round bottom flask charged with **L3** (500 mg, 814 mmol), glacial acetic acid (2.5 ml, Panreac) and acetone (3 ml) were added. The suspension was stirred and cooled down to 0ºC and H$_2$O$_2$ (35%, J.T. Baker, 0.5 ml) was added. The suspension was left to react for 20 minutes at 0ºC and the suspension was heated until all the acetone was evaporated. The suspended solids were dissolved and the solution became transparent as it was heated. The solution was cooled down to room temperature. Cold H$_2$O (20 ml) was added to precipitate the product. The white insoluble product was filtered off using a glass sintered filter and was washed with water (15 ml) and ether (3 x 10 ml). The white product was dried under reduced pressure. Yield: 169 mg, 32%.
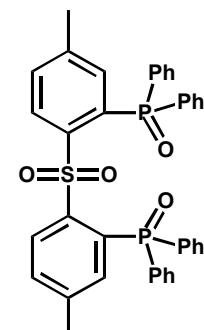
^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) δ 33.46 (s, PAr$_3$).

IR [cm^{-1}] 3061, 1436, 1326, 1176 (ν P=O), 1158, 1380 (ν SO$_2$ asymm stretch), 1117 (ν SO$_2$ symm stretch), 1102, 874, 833, 753, 723, 704, 692, 671, 625.

4.3. Synthesis of Metal Complexes

4.3.1. Synthesis of *fac*-[Mo(TPOdiphos)(CO)$_3$]

A side arm flask was charged with Mo(CO)$_6$ (Strem, 98%, 204 mg, 0.77 mmol) and with a suspension of **L1** (500 mg, 0.77 mmol) in dry, degassed toluene (30 ml). The solution was refluxed for an hour and the formation of an orange, transparent solution was observed as the reaction proceeds. After 1 hr at reflux temperature, the solvent was evaporated at rt under reduced pressure and the remaining residue was dissolved in CH$_2$Cl$_2$. Cold, dry ether was added to cause the formation of the product as a precipitate. The yellow−orange solid product was filtered, washed with dry ether (3 x 5 ml) and dried under reduced pressure. Yield: 491 mg, 76.8%.
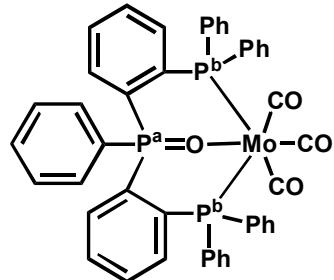
^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) δ 37.24 (t, J_{PP} = 19.6 Hz, P$_a$), 30.44 (d, J_{PP}= 19.4 Hz, 2P$_b$).

IR [cm^{-1}] 1913, 1813, 1775, 1479, 1433, 1154 (ν P=O), 1116, 1093, 737, 690, 661

HRMS ESI$^+$ Experimental m/z, Int. % (calculated m/z, Int. % for C$_{45}$H$_{33}$O$_4$P$_3$Mo, M+Na$^+$): 851.0574, 100 (851.0549, 100); 849.0574, 81.7 (849.0533, 82.1); 850.0592, 61.8 (850.0546, 63.8); 845.0564, 42.5 (845.0552, 47.4)

XRD The crystals grown by the diffusion of diethyl ether into a saturated solution of the complex in CH$_2$Cl$_2$ were found to be suitable for X-Ray diffraction. The data was successfully gathered and the structure of the crystal was resolved.

4.3.2. Synthesis of [W(TPOdiphos)(CO)$_3$]

A flask was charged with W(CO)$_6$ (275 mg, 0.79 mmol) and with a solution of **L1** (500 mg, 0.77 mmol) in annhydrous diglyme (MeOCH$_2$CH$_2$OCH$_2$CH$_2$OMe, Aldrich, 30 ml). The solution was refluxed at 165ºC for four hours. The formation of a deep red solution and a brown precipitate was observed as the reaction proceeds. The solvent was removed and the *terra cotta* colored product was washed
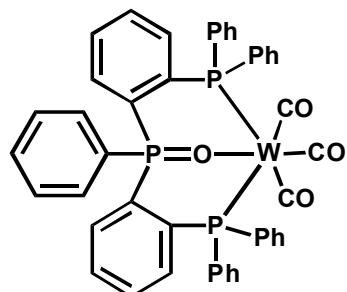
with hexane (10 ml) and ether (3 x 20 ml). The product was purified by repeated crystallization by dissolving the product in CH_2Cl_2 and adding cold, dry ether to precipitate the solid. The product was filtered and dried under reduced pressure. Yield: 341 mg, 48%

^{1}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) δ 36.46 (t), 25.51 (d with ^{183}W sat., $^1J_{PW}$ = 217 Hz).

IR [cm^{-1}] 1905, 1805, 1770, 1480, 1433, 1150 (ν P=O−W), 1117, 1092, 816, 738, 690.

HRMS ESI$^+$ Experimental m/z, Int. % (calculated m/z, Int. % for $C_{45}H_{33}O_4P_3W$, M+Na$^+$): 937.1011, 100 (937.1001, 100); 939.1047 (939.1028, 79.7); 936.1010, 70.9 (936.0987, 66.7); 935.0988, 67.4 (935.0966, 64.6)

4.3.3. Reaction of Mo(CO)$_6$ with L2

A flask was charged with Mo(CO)$_6$ (Strem, 98%, 214 mg, 827 mmol) and with **L2** (500 mg, 816 mmol) in dry, degassed toluene (30 ml). The solution was refluxed at 110ºC for an hour and the formation of a transparent, yellow solution was observed as the reaction proceeds. All the solvent was removed under reduced pressure. The yellow residue was re-dissolved in dry CH_2Cl_2 and the product was precipitated with cold, dry, ether. The yellow impure product was washed with ether (3 x 20 ml), filtered and dried under reduced pressure. Yield: 198 mg, 30.5%
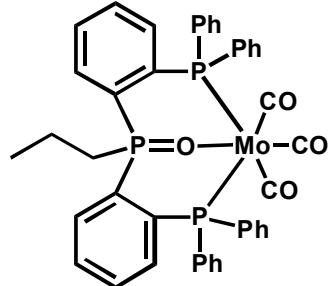
^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) Major Product (ca. 90%) δ 44.20 (t, J_{PP}= 19 Hz), 29.74 (d, J_{PP}= 19 Hz). Minor Product (ca. 10%) δ 45.59 (t, J_{PP} = 18 Hz), 29.81 (d, J_{PP}= 18 Hz).

IR [cm^{-1}] 1909, 1804, 1776, 1479, 1433, 1151 (ν P=O), 1120, 744, 691

4.3.4. Synthesis of [Mo(SODPdiphos)(CO)$_3$]

A flask was charged with Mo(CO)$_6$ (53.4 mg, 0.202 mmol) and with a solution of **L3** (120 mg, 0.202 mmol) in dry, degassed toluene (30 ml). The solution was refluxed at 120ºC for four hours. The formation of a yellow, transparent solution was observed. Eventually, a yellow precipitate was formed as the reaction proceeds. The solvent was removed and the solid was washed with cold, dry ether (3 x 5 ml). The product was purified by repeated recrystallizations by dissolving the product in CH_2Cl_2 (5 ml) and by adding cold dry, degassed ether (30 ml). The precipitated product was filtered and was dried under reduced pressure. Yield: 97 mg, 65 %
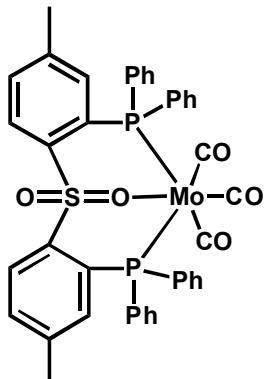
^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$) δ 31.12 (s, PAr$_3$).

IR [cm^{-1}] 1920, 1830, 1778, 1584, 1480, 1434, 1300 (v SO$_2$ asymm stretch), 1134 (v SO$_2$ stretch), 1090, 830, 748, 696, 669.

HRMS ESI$^+$ Experimental m/z, Int. % (calculated m/z, Int. % for C$_{41}$H$_{32}$O$_5$SP$_2$Mo, M+Na$^+$): 819.0376, 100 (819.0400, 100); 817.034, 81.0 (817.0387, 80.2); 813.0381, 49.0 (813.0406, 46.6); 821.0396, 47.7 (821.0413, 43.8).

4.3.5. Synthesis of [W(SODPdiphos)(CO)]$_3$

A flask was charged with W(CO)$_6$ (275 mg, 0.781 mmol) and with a solution of **L3** (500mg, 0.774 mmol) in degassed decane (30 ml). The solution was refluxed at 160ºC for a total of four hours. The formation of a yellow, transparent solution was observed. Eventually, the formation of a yellow precipitate was observed as the reaction proceeds. The solvent was removed and the product was washed with cold, ether (3 x 5 ml). The yellow product was purified by repeated recrystallizations in CH$_2$Cl$_2$ and the addition of dry ether. Yield: 412 mg, 59%
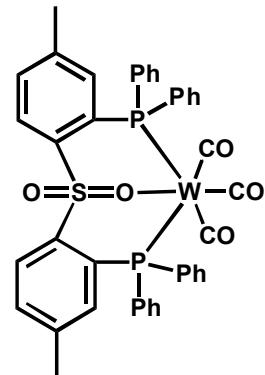
^{31}P{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K) δ 22.83 (s with ^{183}W sat., $^1J_{PW}$ =233 Hz).

IR [cm^{-1}] 1905, 1805, 1770, 1572, 1481, 1434, 1297 (v SO$_2$ asymm stretch), 1130 (v SO$_2$ stretch), 1092, 1027, 831, 749, 695, 670, 639.

HRMS ESI$^+$ Experimental m/z, Int. % (calculated m/z, Int. % for C$_{41}$H$_{32}$O$_5$SP$_2$W, M+Na$^+$): 905.0840, 100.0 (905.0852, 100.0); 907.0863, 77.2 (907.0881, 82.3); 904.0825, 61.5 (904.0841, 63.9).

ANNEX

2-BrPhPPh2
Espectre 31P amb desacoblament de 1H

-4.47

90　80　70　60　50　40　30　20　10　0　-10　-20　-30　-40　-50　-60　-70　-80　-90　-100
f1 (ppm)
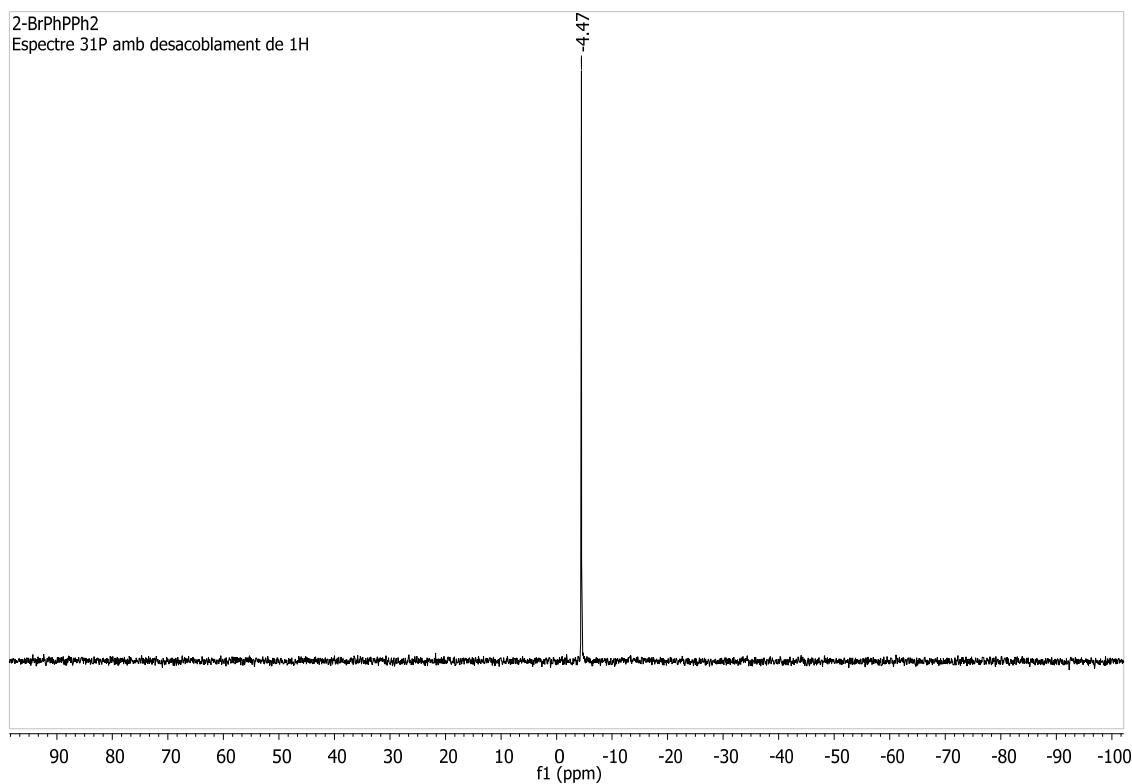
Annex 1.1. $^{31}P\{^{1}H\}$ NMR of 2-bromophenyldiphenylphosphine ($C_{18}H_{14}PBr$), **L0**

2-BrPhPPh2
Espectre 1H 250 MHz

10.5　10.0　9.5　9.0　8.5　8.0　7.5　7.0　6.5　6.0　5.5　5.0　4.5　4.0　3.5　3.0　2.5　2.0　1.5　1.0　0.5
f1 (ppm)
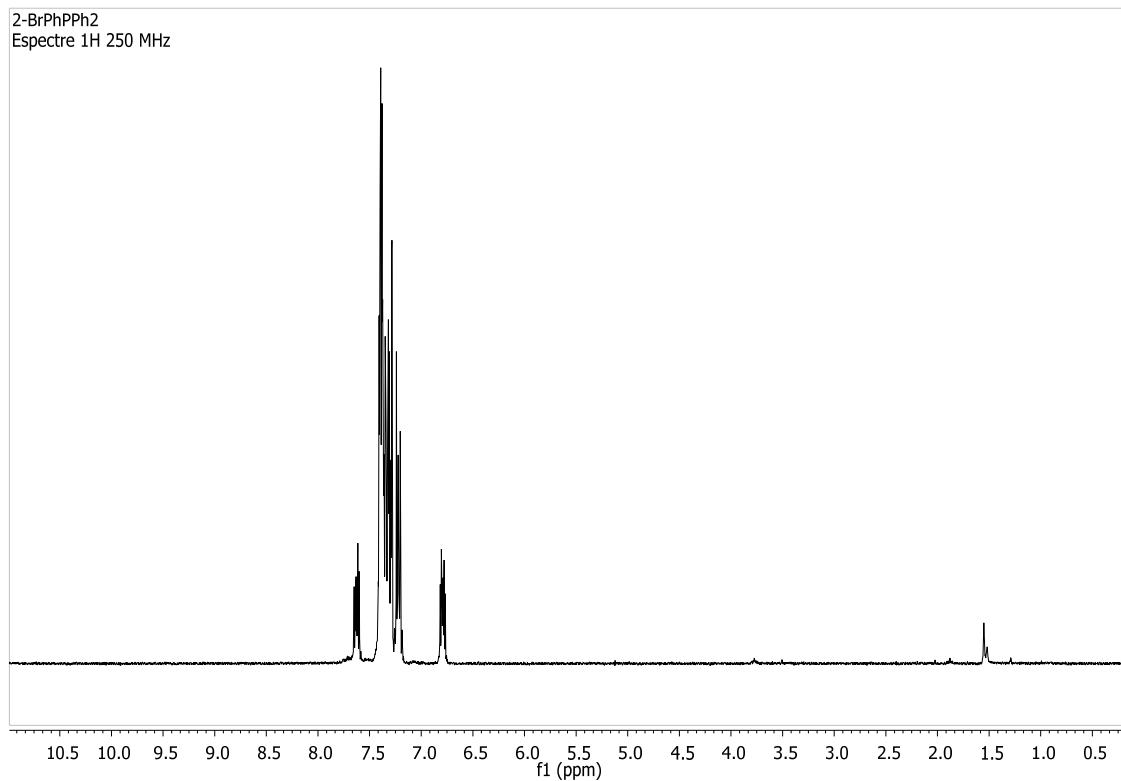
Annex 1.2. ^{1}H NMR of 2-bromophenyldiphenylphosphine ($C_{18}H_{14}PBr$), **L0**
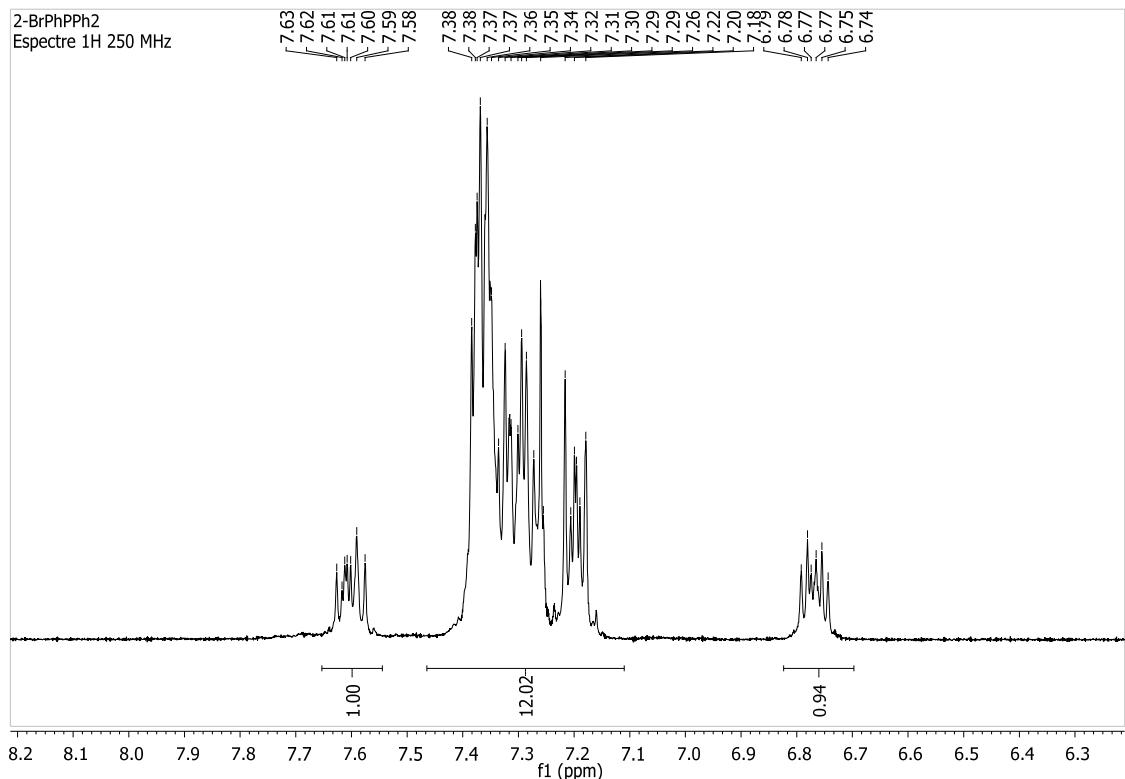
Annex 1.3. Amplification of the ^{1}H NMR of 2-bromophenyldiphenyl phosphine ($C_{18}H_{14}PBr$), **L0**
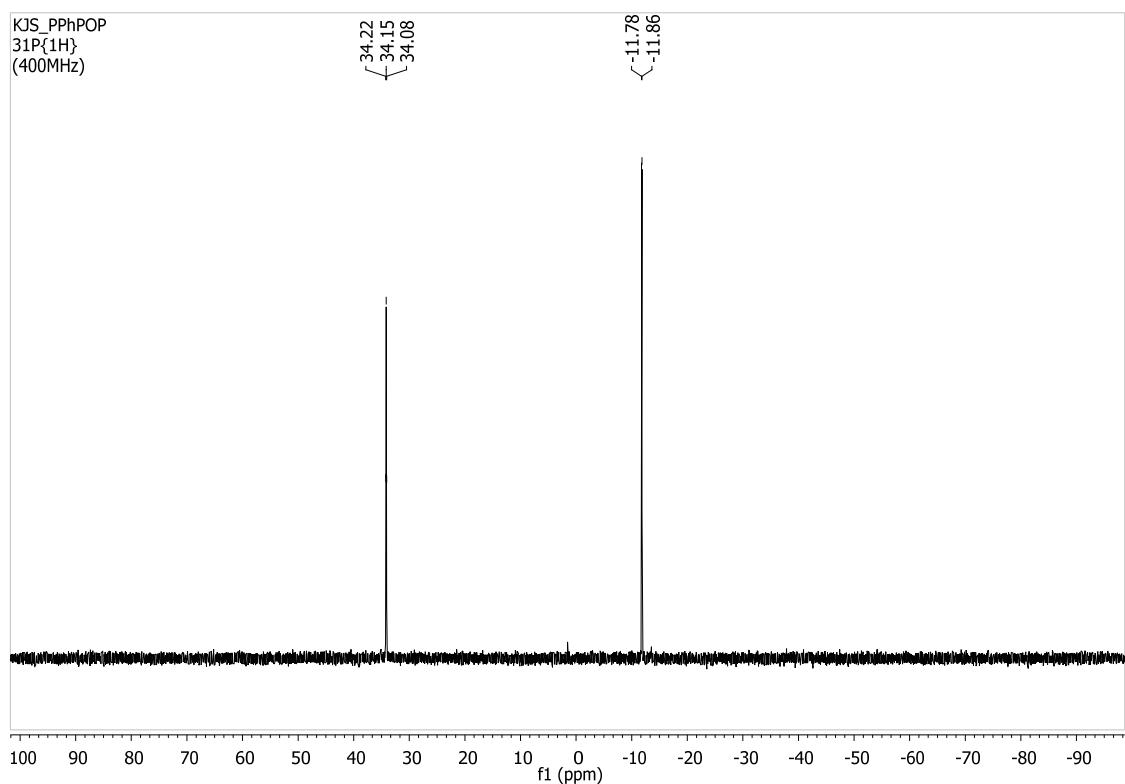
Annex 1.4. $^{31}P\{^1H\}$ NMR of bis(2-(diphenylphosphino)phenyl)(phenyl)phosphine oxide (TPOdiphos), **L1**

KJS_PPhPOP
31P{1H}
(400MHz)

32.70
32.63
32.55

-13.31
-13.38

Name	Displacement	Range	Class	J's
1 A (d)	-13.34	-13.23...-13.46	d	11.98
2 B (t)	32.63	32.78 .. 32.49	t	11.98, 11.98

34.0 33.6 33.2 32.8 32.4 32.0 31.6 -12.0 -12.4 -12.8 -13.2 -13.6 -14.0 -14.4
f1 (ppm)
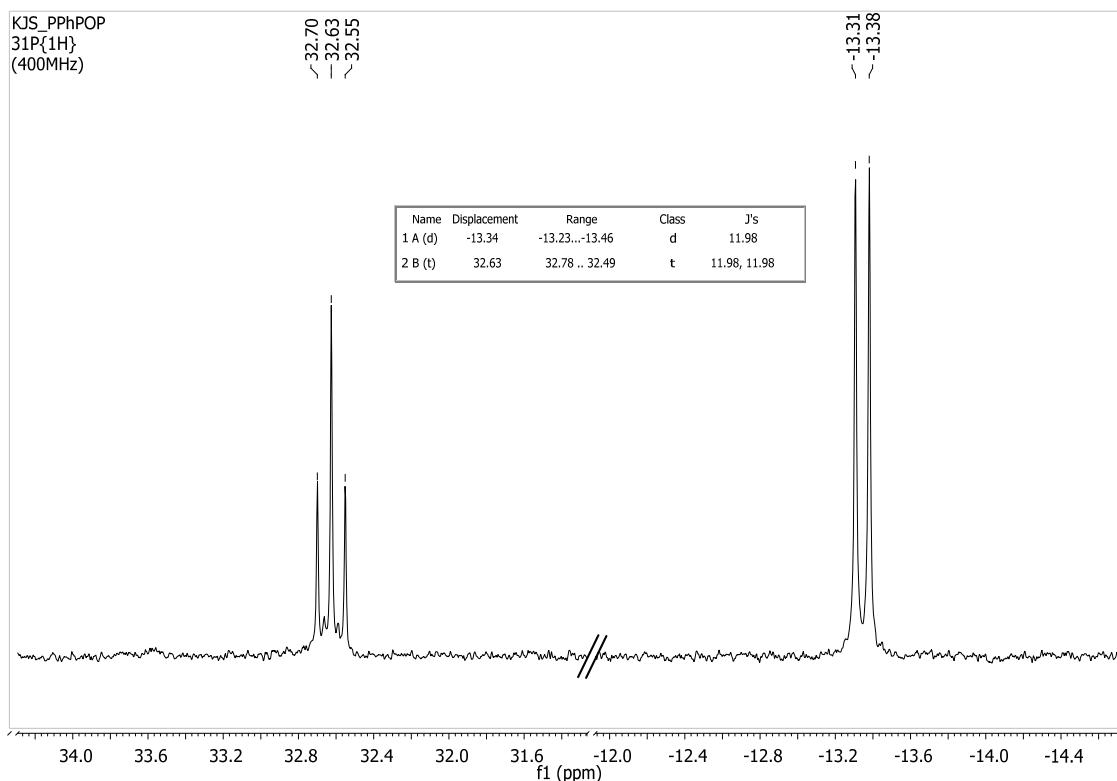
Annex 1.5. Amplification of the ^{31}P{^{1}H} NMR of bis(2-diphenylphosphino)phenyl)(phenyl)phosphine oxide (TPOdiphos), **L1**

KJS_PPhPOP
1H (400 MHz)

7.69
7.68
7.67
7.66
7.65
7.64
7.59
7.58
7.57
7.56
7.55
7.54
7.53
7.41
7.39
7.38
7.33
7.33
7.32
7.31
7.30
7.29
7.27
7.26 Chloroform-d
7.23
7.23
7.22
7.21
7.20
7.19
7.18
7.16
7.11
7.10
7.09
7.08
7.08
7.06
7.06

8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
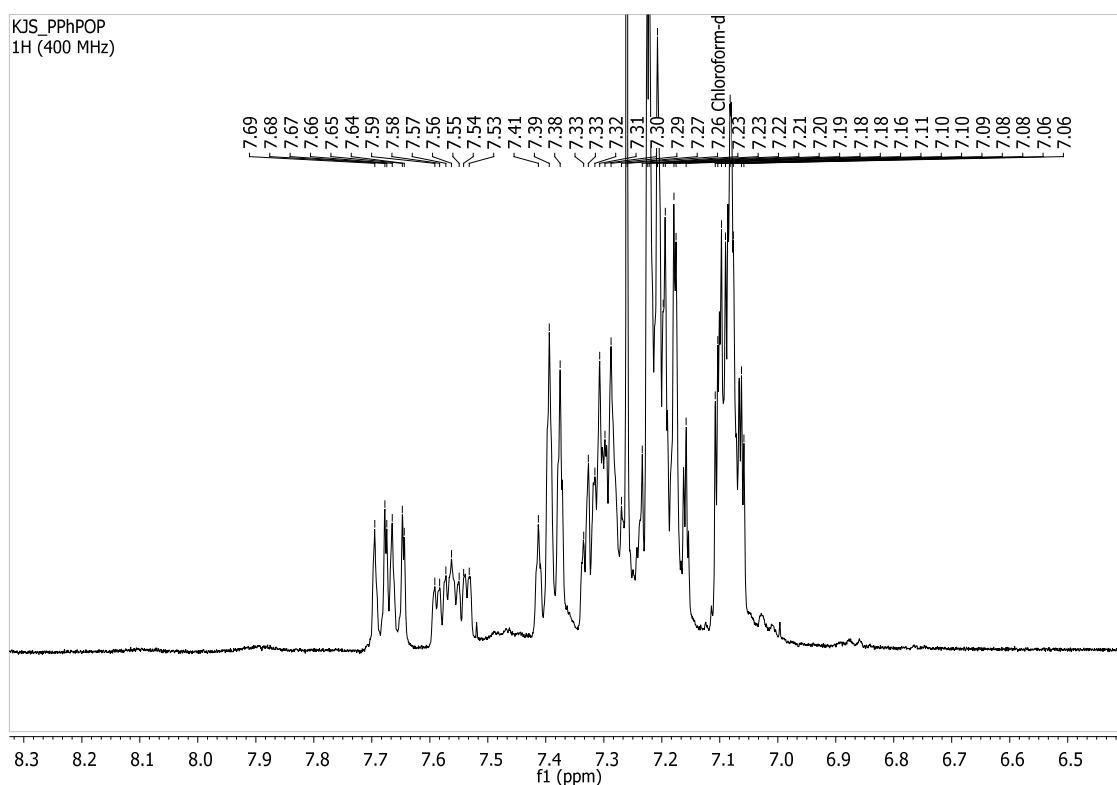
Annex 1.9. ^{1}H NMR of bis(2-diphenylphosphino)phenyl)(phenyl)phosphine oxide (TPOdiphos), **L1**
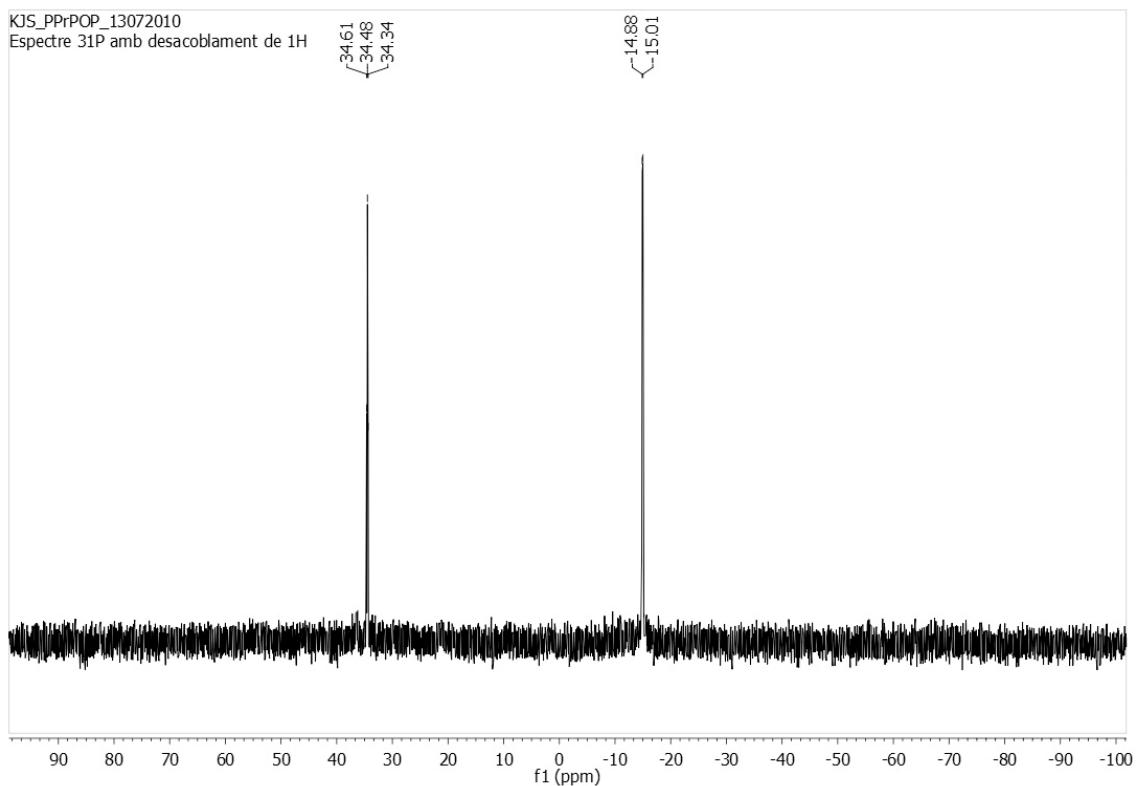
KJS_PPrPOP_13072010
Espectre 31P amb desacoblament de 1H

34.61
34.48
34.34

14.88
15.01

Annex 1.8. ^{31}P{^{1}H} NMR of bis(2-(diphenylphosphino)phenyl) (propyl)phosphine oxide (DPPrOdiphos), **L2**

KJS_PPrPOP_13072010
Espectre 31P amb desacoblament de 1H

34.61
34.48
34.34

14.88
15.01
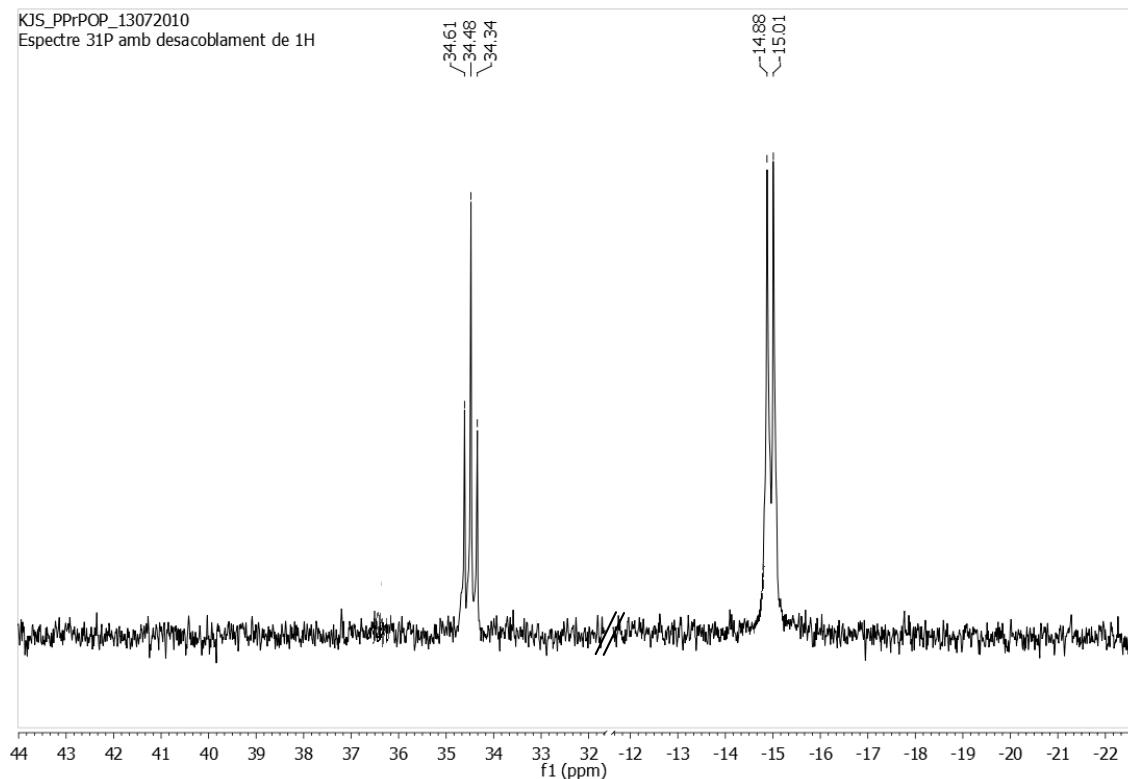
Annex 1.9. Amplification of the ^{31}P{^{1}H} NMR of bis(2-diphenylphosphino)phenyl) (propyl)phosphine oxide (DPPrOdiphos), **L2**

—14.08

100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Annex 1.10. ^{31}P{^{1}H} NMR of (sulfonylbis (3-methyl-6,1-phenylene)) bis(diphenyl phosphine) (SODPdiphos), **L3**

Karen_Ligand 3 (400 Hz, 298K, CDCl3)
1H (400 MHz)

7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.11
7.11
7.09
6.93
6.93
6.91
6.89
6.71

8.46
8.46
8.45
8.44
8.43

1.9

16.2
8.3
2.5

6.0

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)
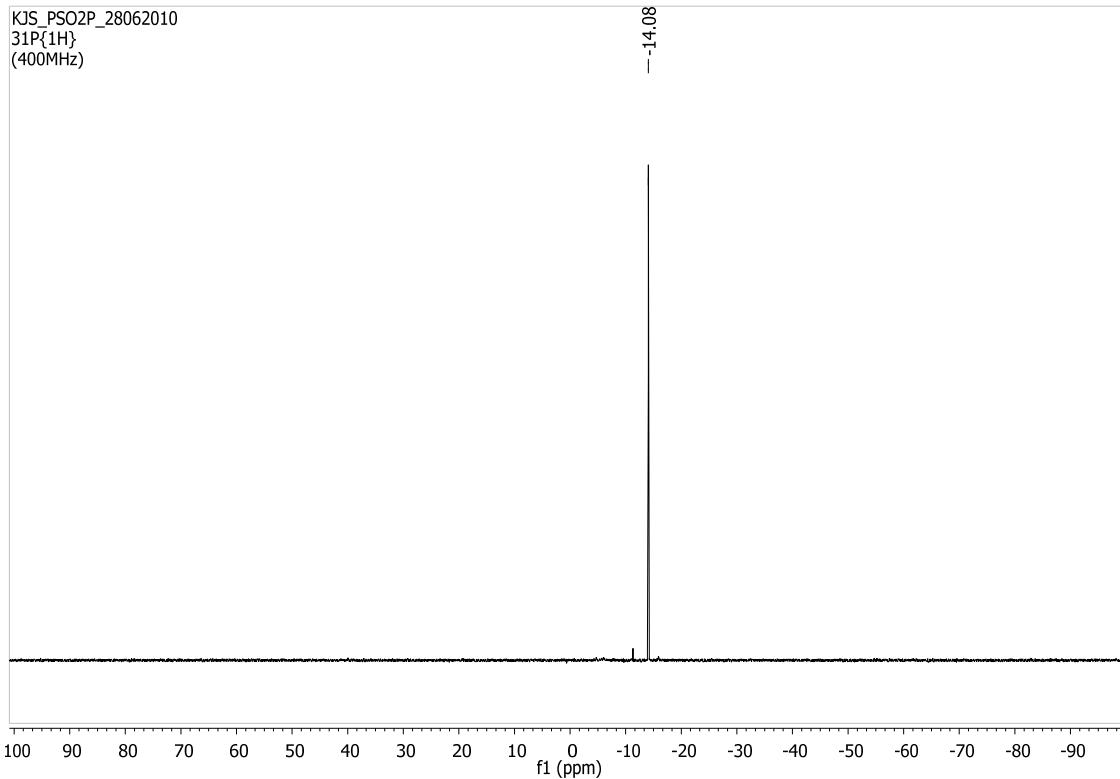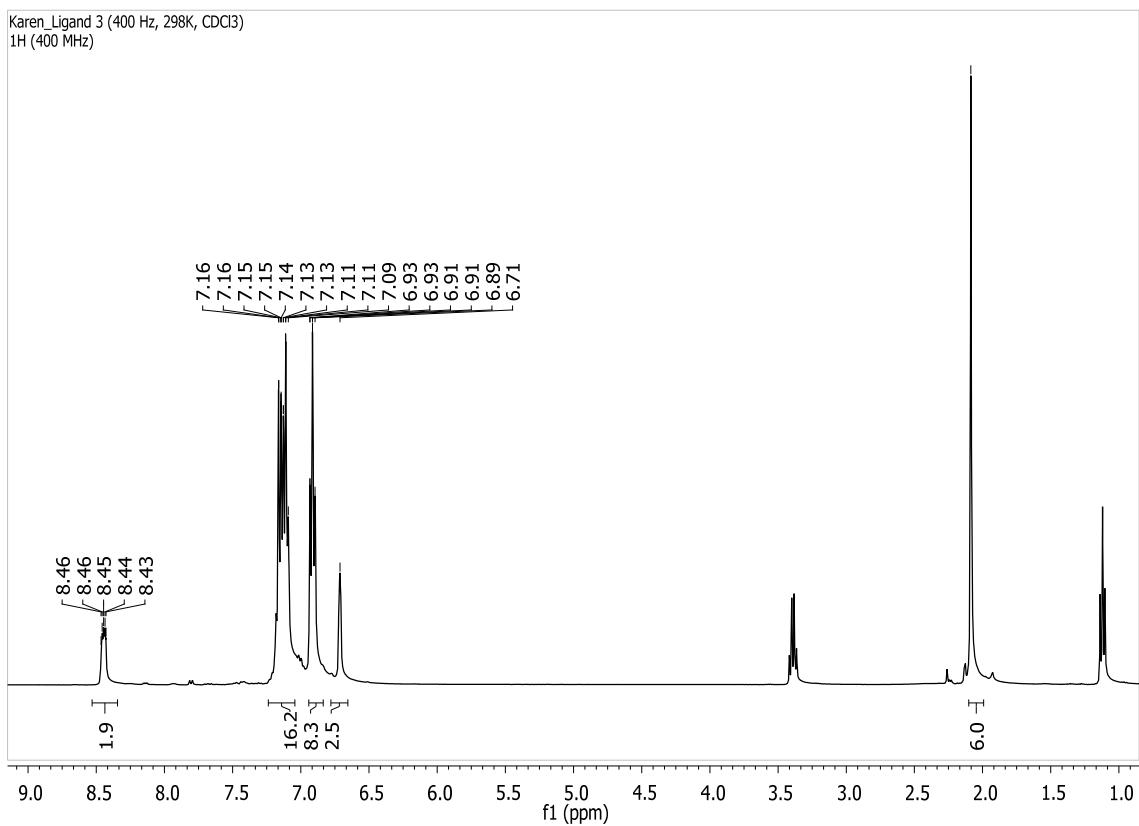
Annex 1.11. ^{1}H NMR of (sulfonylbis (3-methyl-6,1-phenylene)) bis(diphenyl phosphine) (SODPdiphos), **L3**

KJS_PPSO2Poxidized ligand_29062010
31P{1H}
(400MHz)

33.46

100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)
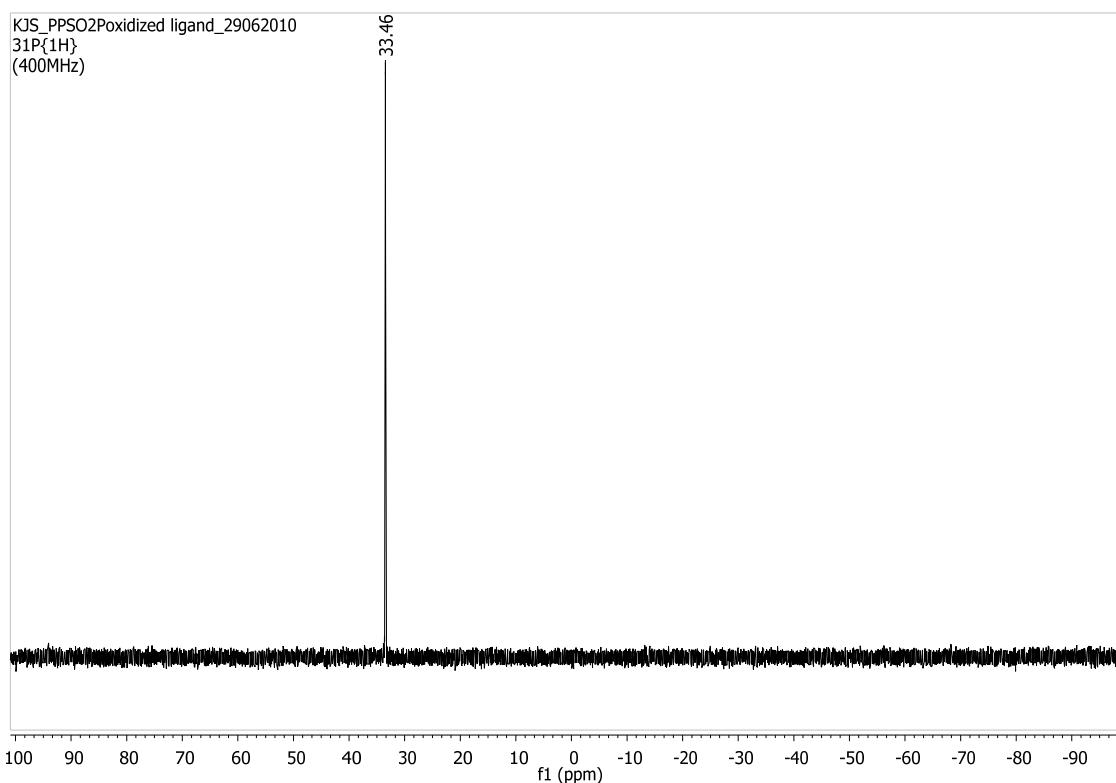
Annex 1.12. $^{31}P\{^1H\}$ NMR of (sulfonylbis(3-methyl-6,1-phenylene))bis(diphenyl phosphine oxide) (SODPdiphos oxide)

K Complex Mo(PPhPOP), CDCl3, 298K, 400Hz
31P{1H}
(400MHz)

37.37
37.25
37.12
30.50
30.38

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25 -35 -45
f1 (ppm)
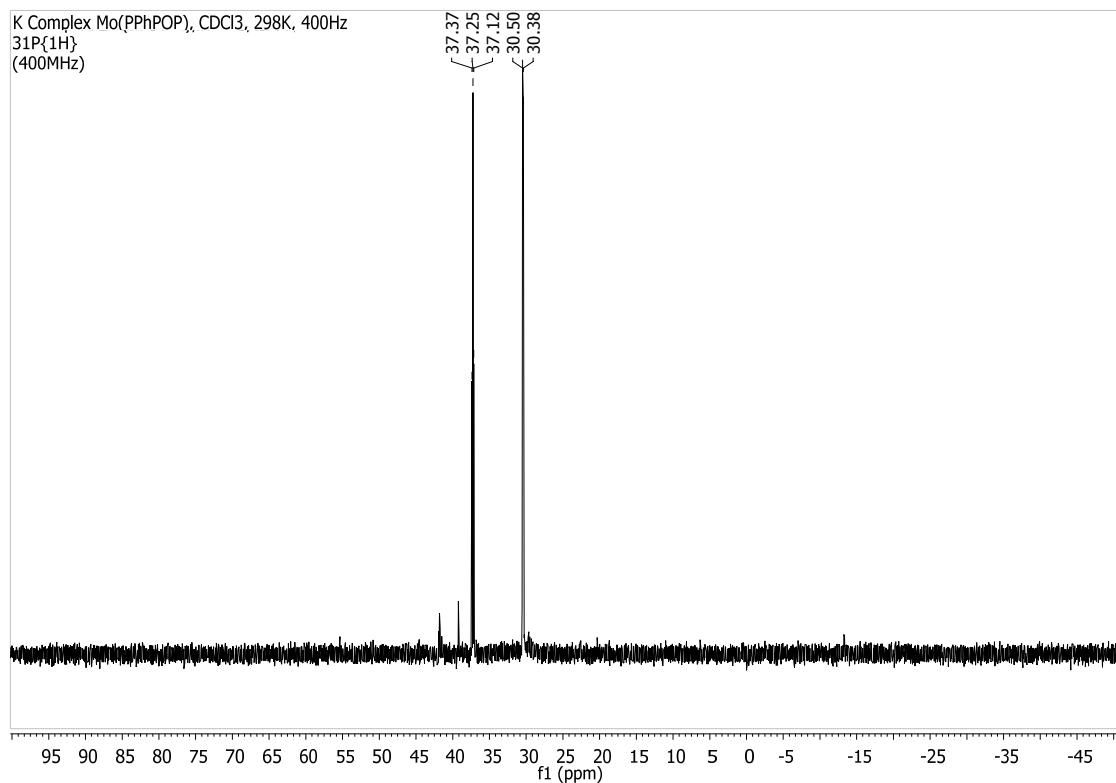
Annex 1.13. $^{31}P\{^1H\}$ NMR of [Mo(TPOdiphos)(CO)$_3$]

K Complex Mo(PPhPOP), CDCl3, 298K, 400Hz
31P{1H}
(400MHz)

37.37
37.25
37.12

30.50
30.38
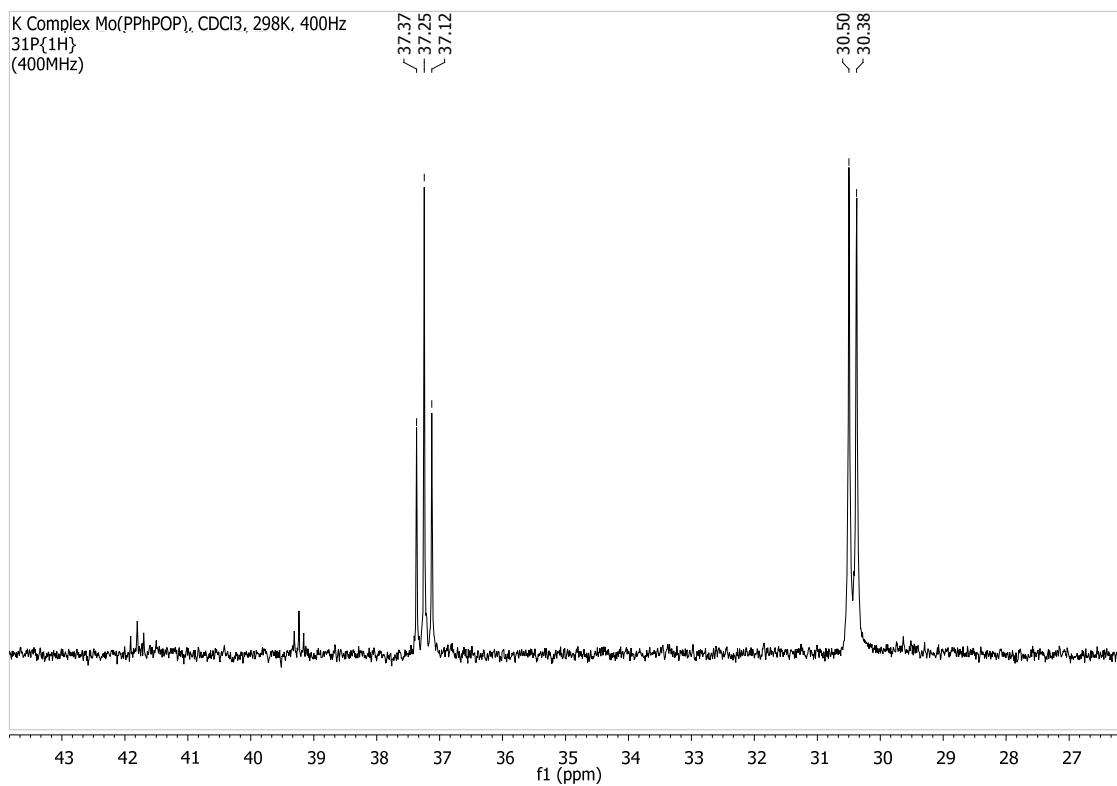
Annex 1.14. Amplification of the $^{31}P\{^1H\}$ NMR of [Mo(TPOdiphos)(CO)$_3$]

KJS_WPPhPOP_09072010
31P{1H}
(400MHz)

36.58
36.46
36.33
26.25
26.11
25.58
25.45
24.91
24.78
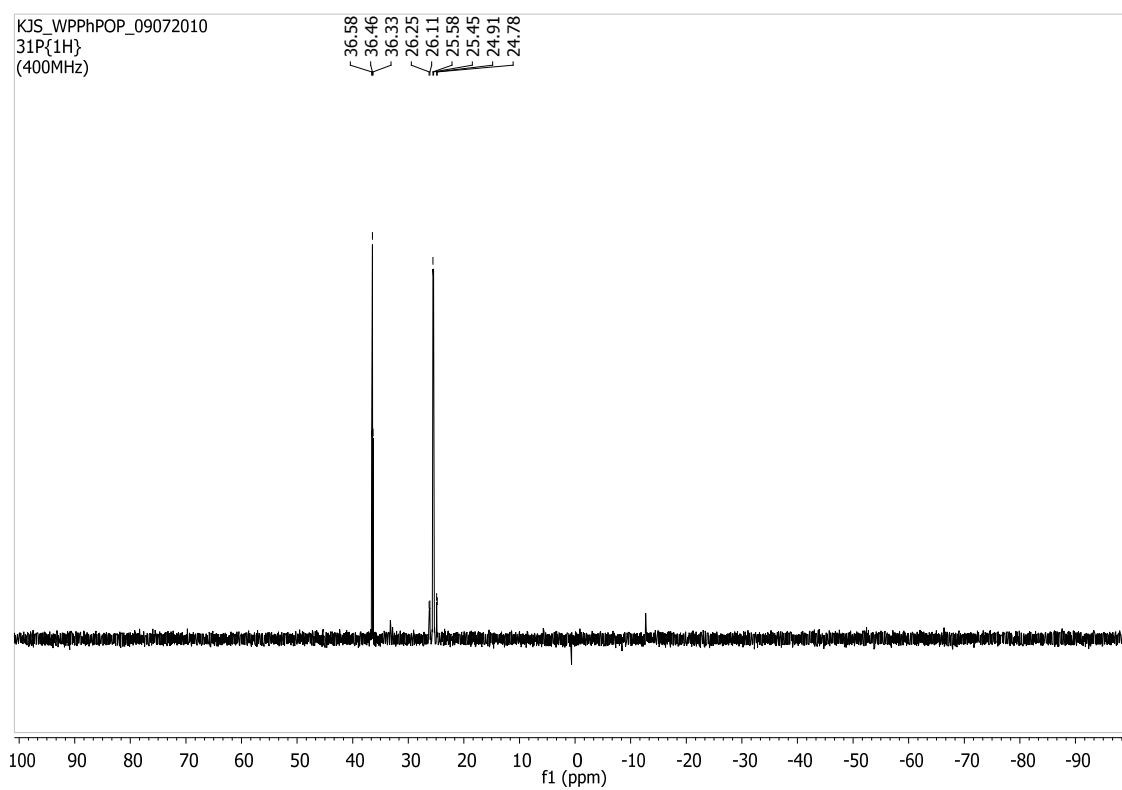
Annex 1.15. $^{31}P\{^1H\}$ NMR of [W(TPOdiphos)(CO)$_3$]
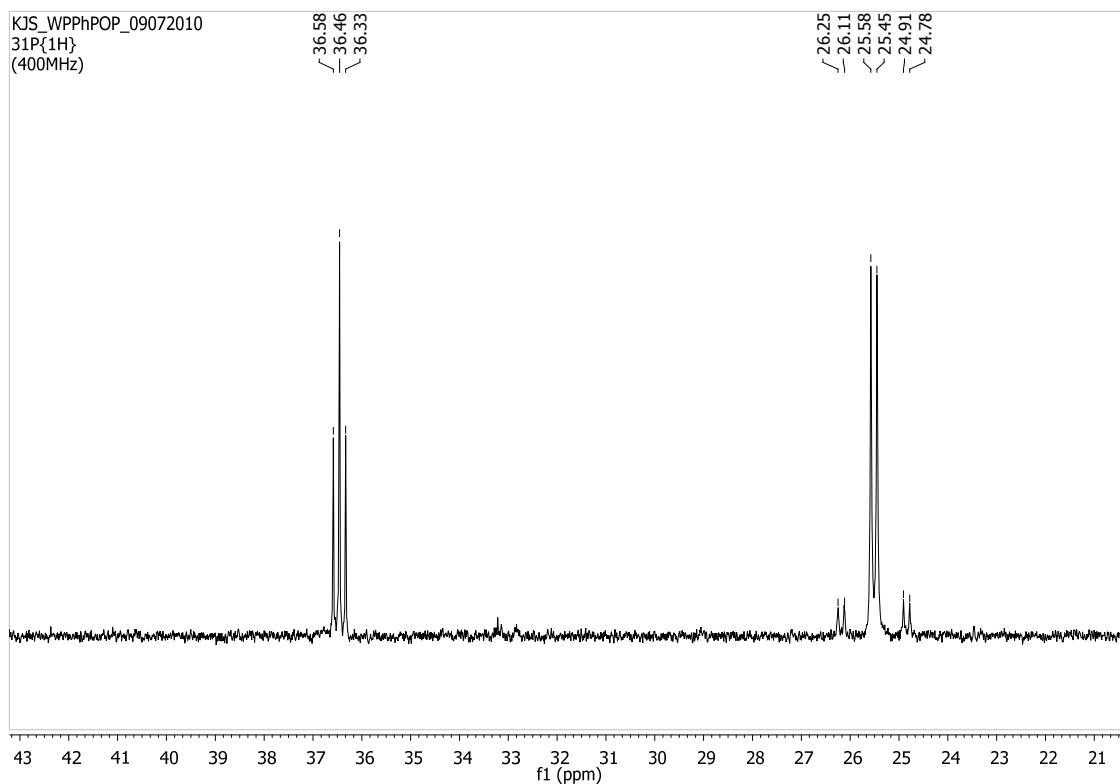
Annex 1.16. Amplification of the $^{31}P\{^1H\}$ NMR of [W(TPOdiphos)(CO)$_3$]
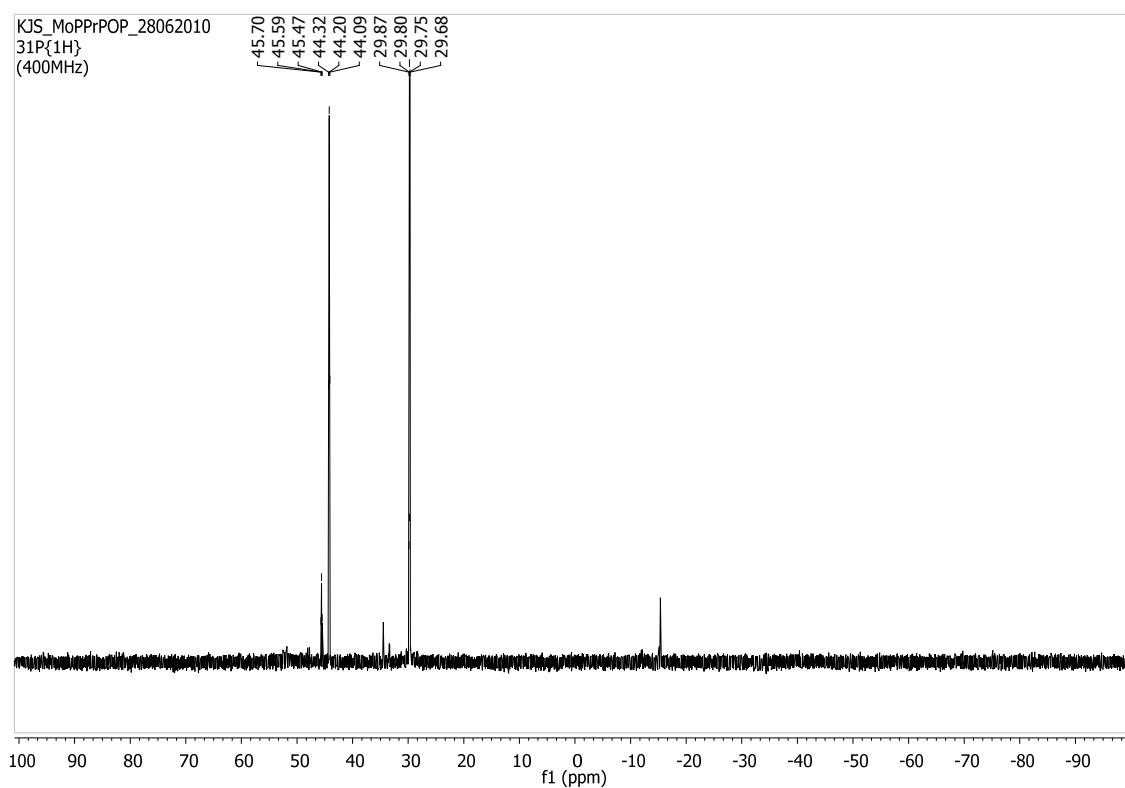
Annex 1.17. $^{31}P\{^1H\}$ NMR of the reaction mixture of [Mo(CO)$_6$] and **L2**
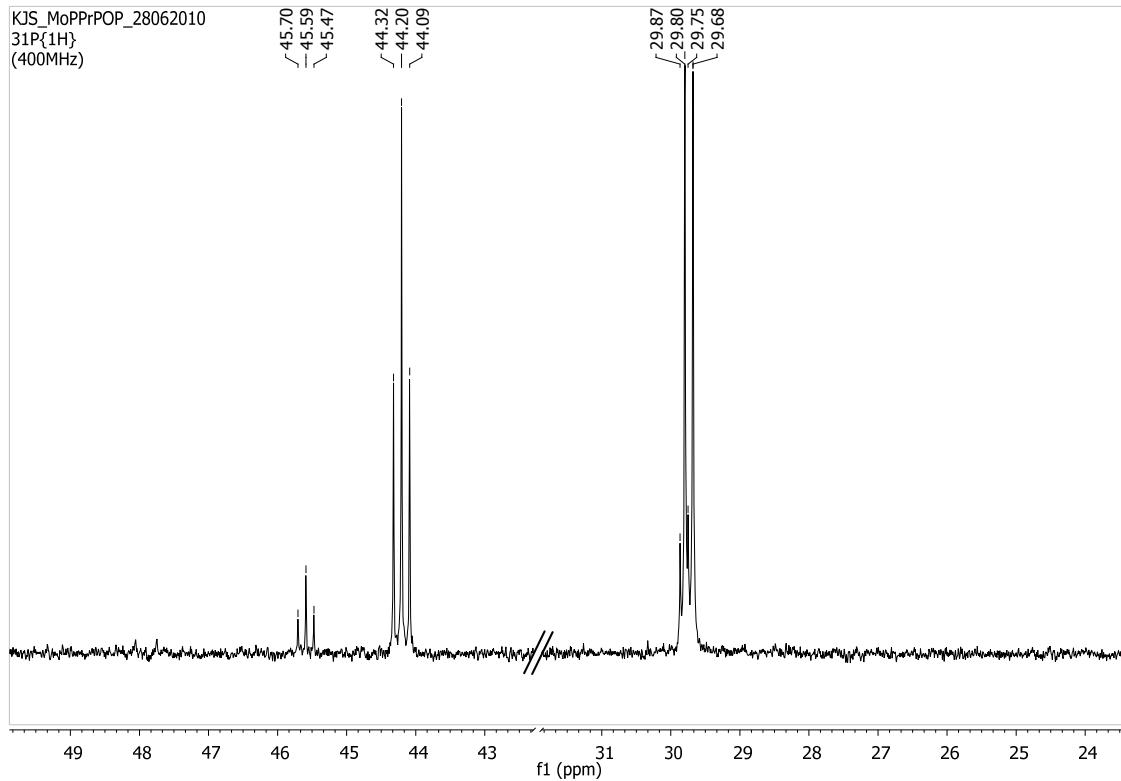
Annex 1.18. Amplification of the $^{31}P\{^{1}H\}$ NMR of the reaction mixture of [Mo(CO)$_6$] and **L2**
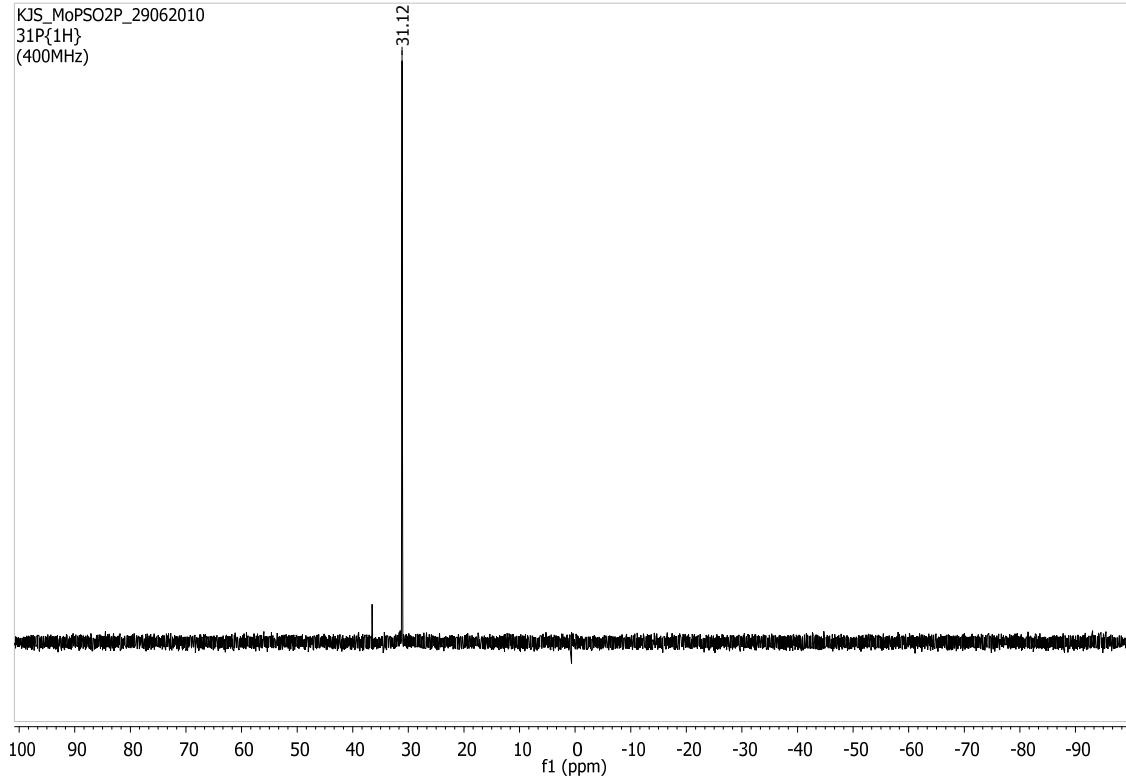
Annex 1.21. ^{31}P Spectrum of [Mo(SODPdiphos)(CO)$_3$]

KJS_WPSO2P_13072010
Espectre 31P amb desacoblament de 1H

23.98
22.83
21.67
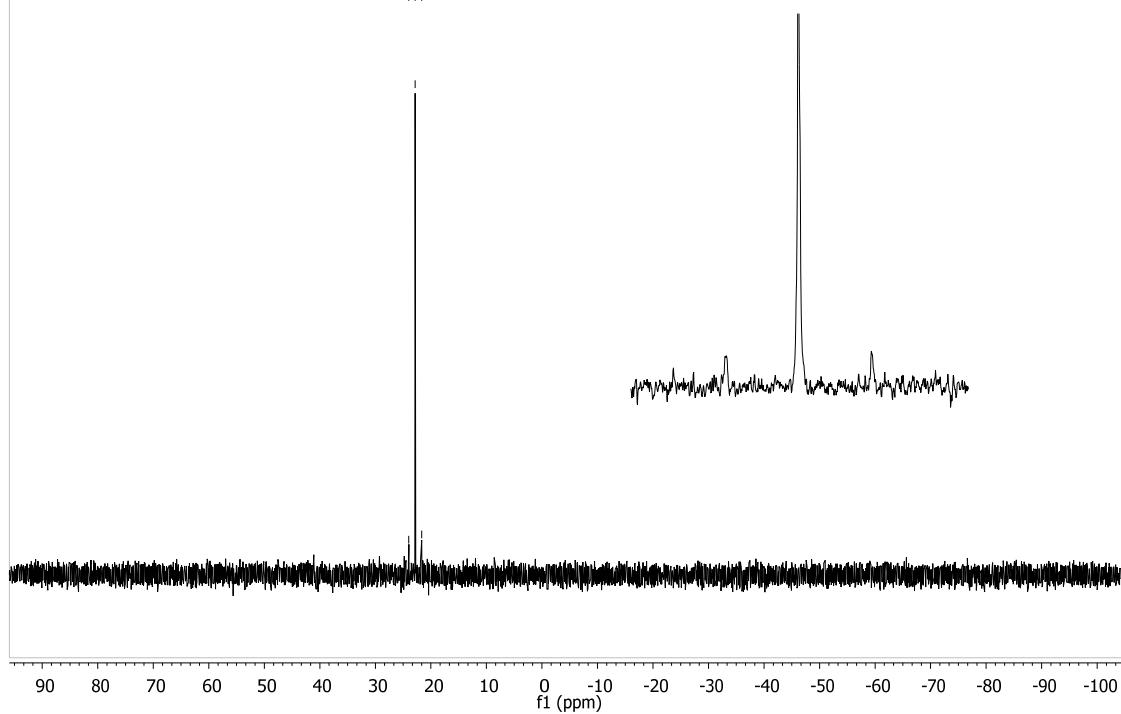
Annex 1.22. $^{31}P\{^1H\}$ NMR of [W(SODPdiphos)(CO)$_3$]

ANNEX II. IR Spectra
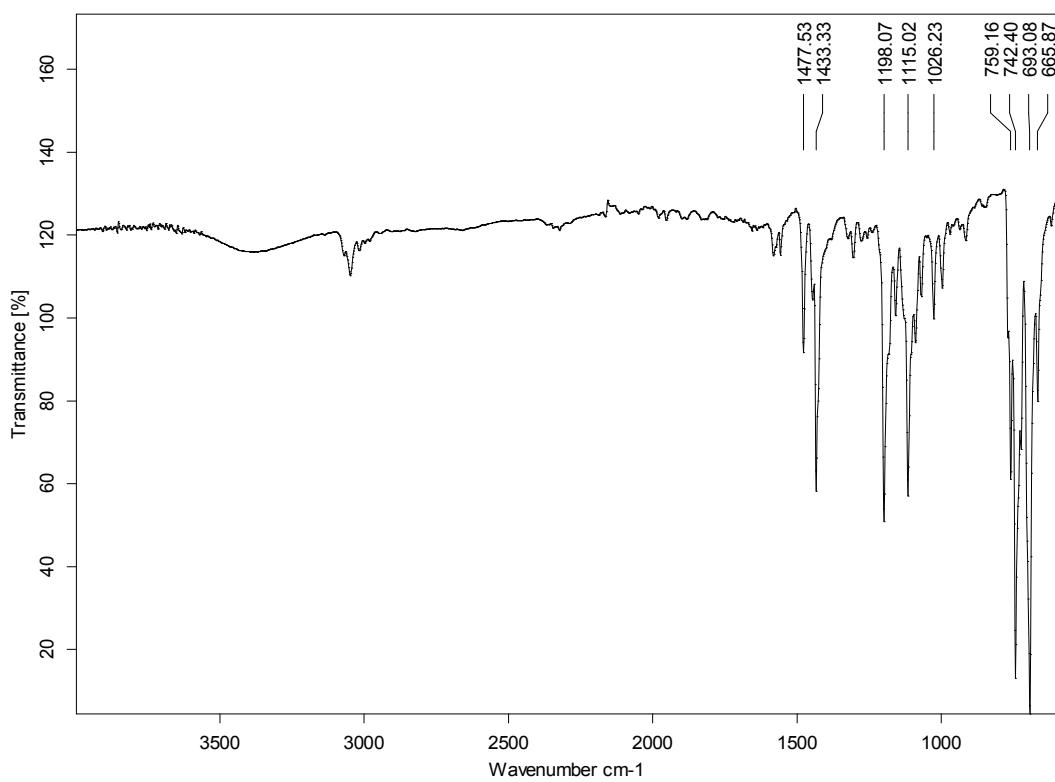
Annex 2.1. IR spectrum of TPOdiphos, **L1**
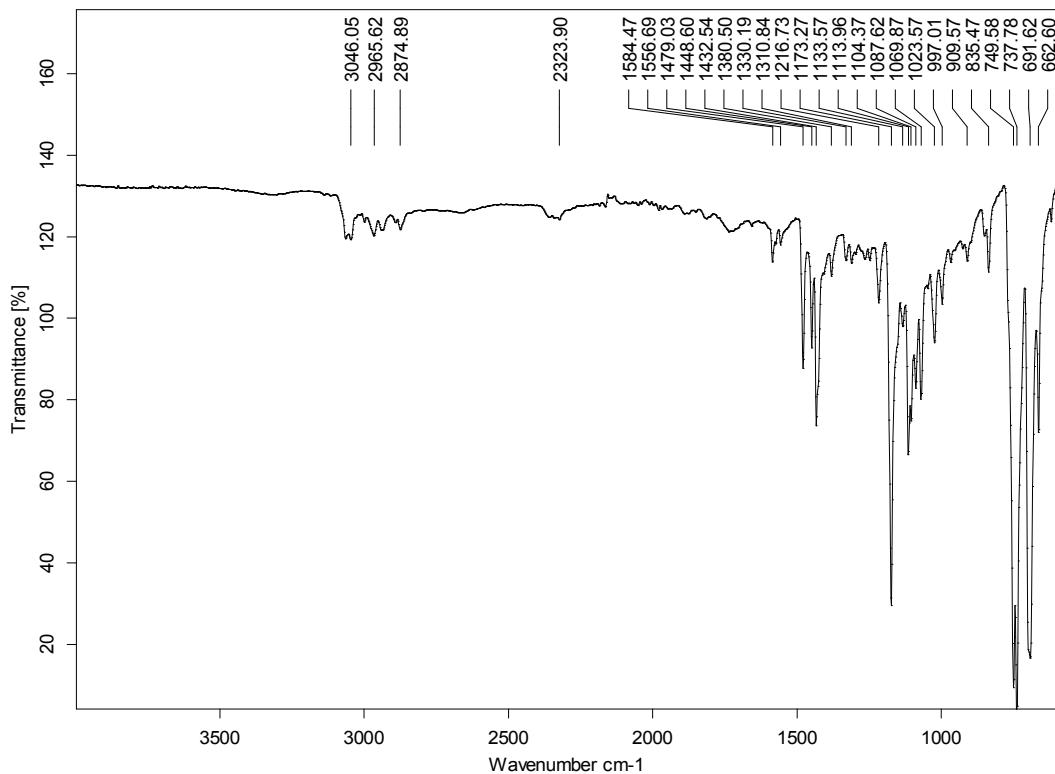
Annex 2.2. IR spectrum of DPPrPOdiphos, **L2**
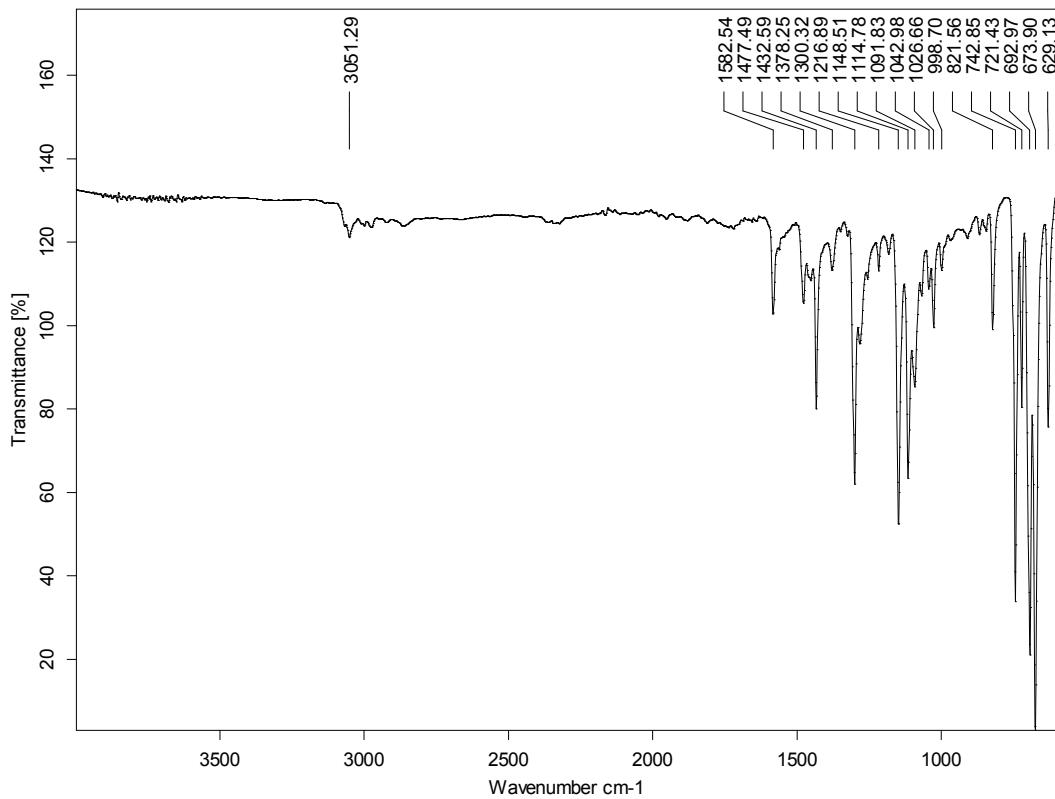
Annex 2.3. IR spectrum of SODPdiphos, **L3**
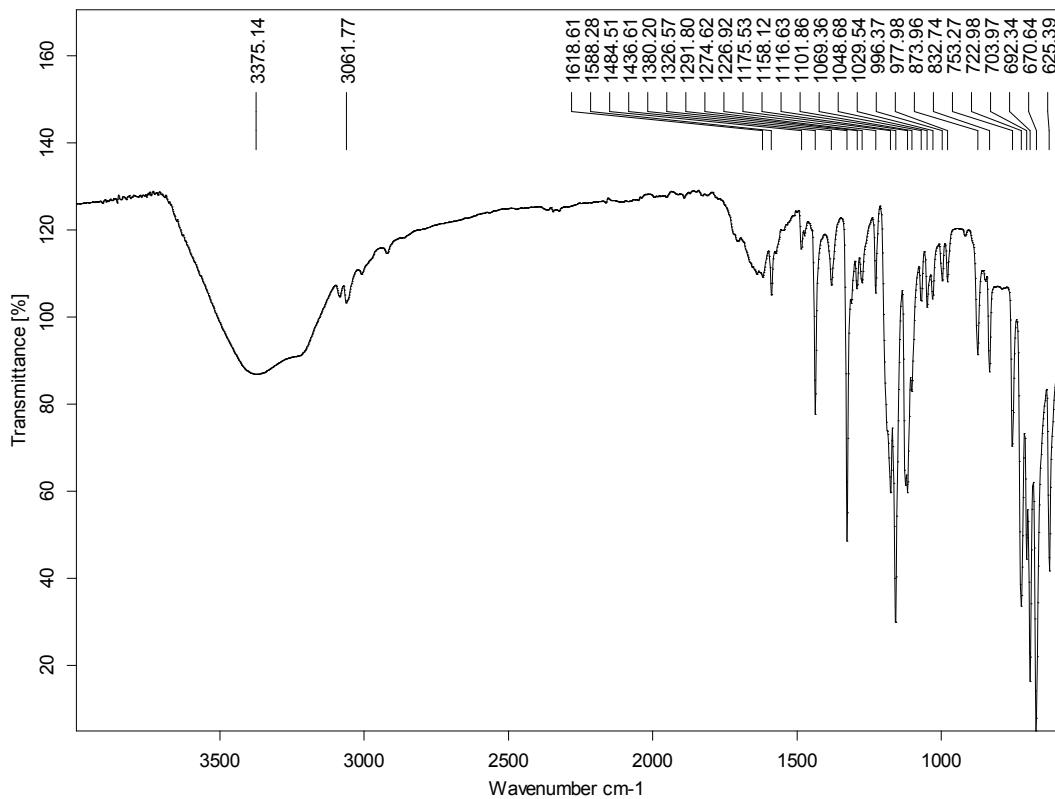
Annex 2.4. IR spectrum of SODPdiphos oxide, **L3O₂**
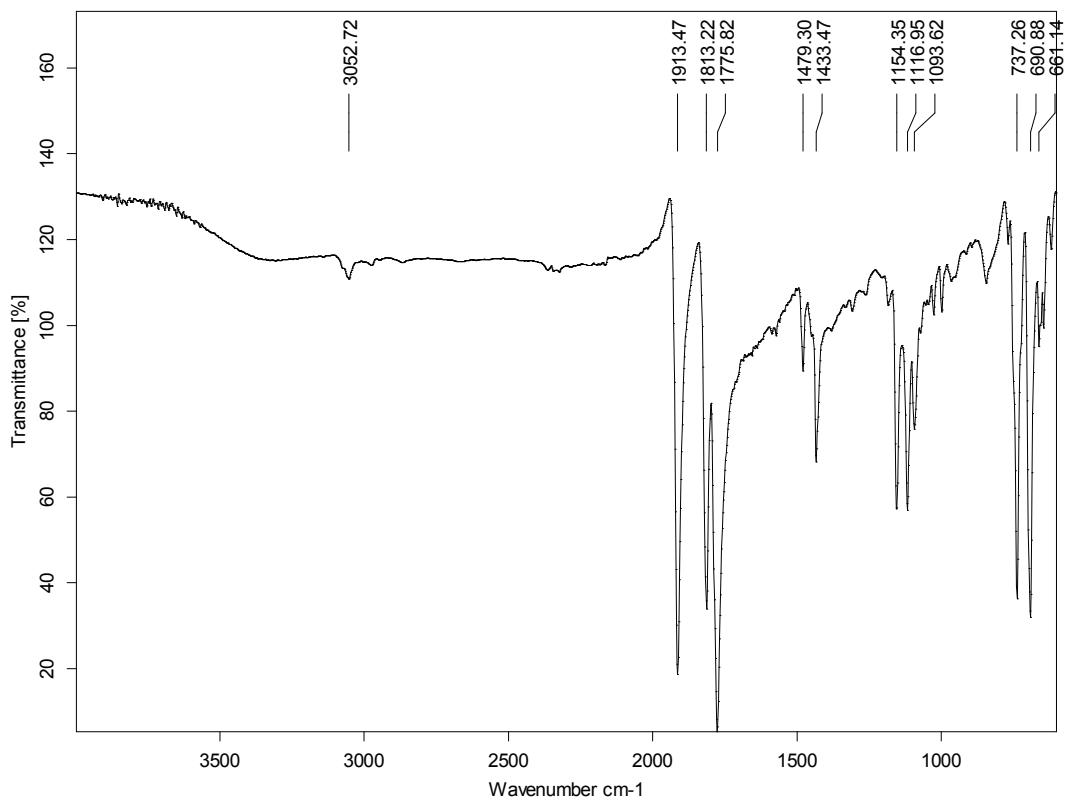
Annex 2.5. IR spectrum of [Mo(TPOdiphos)(CO)$_3$]
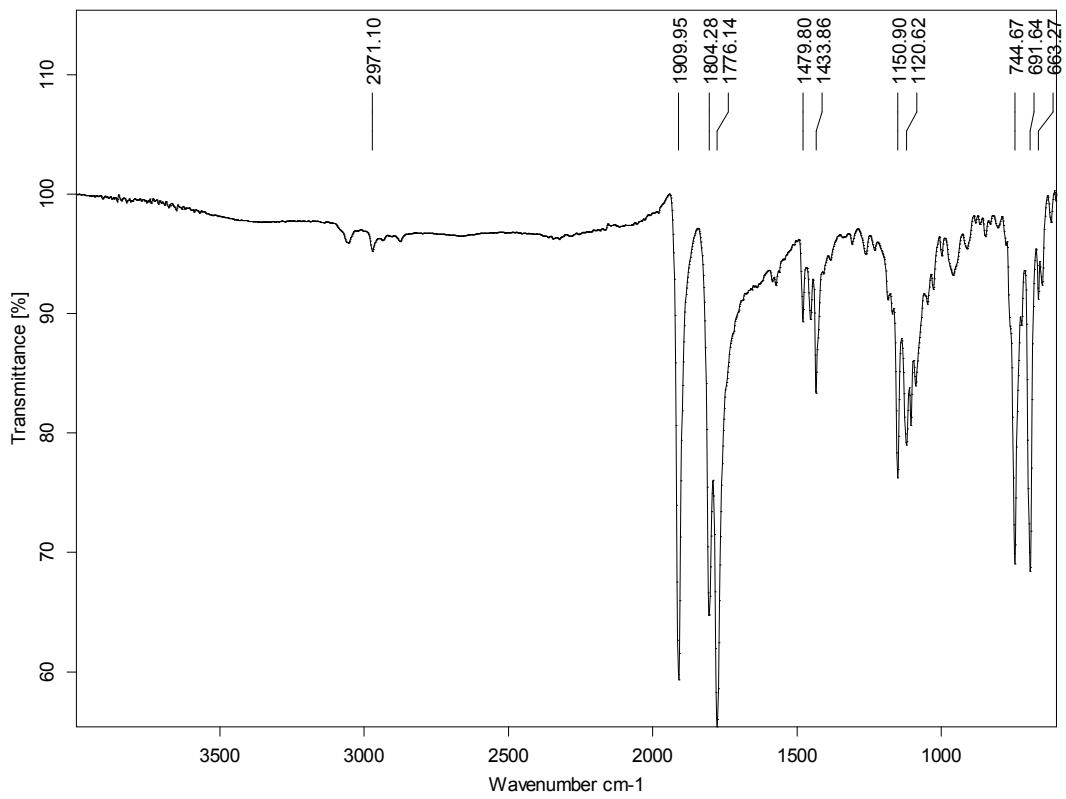
Annex 2.5. IR spectrum of [Mo(DPPrPOdiphos)(CO)$_3$]
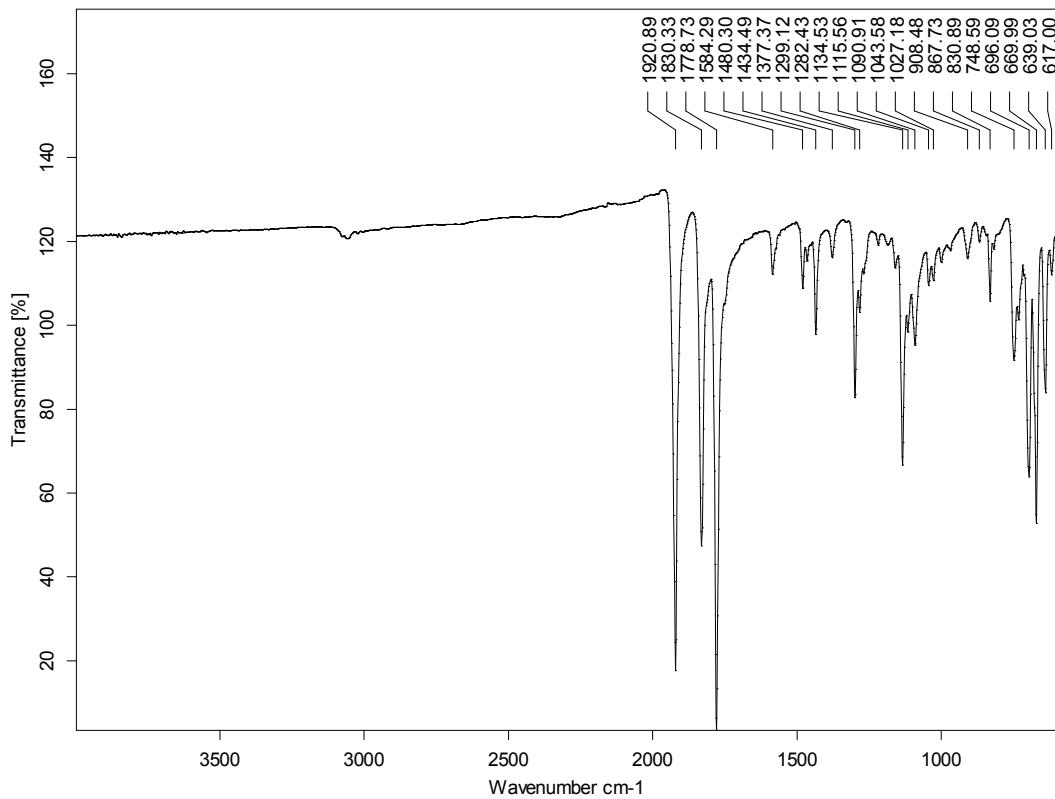
Annex 2.6. IR spectrum of [Mo(SODPdiphos)(CO)$_3$]
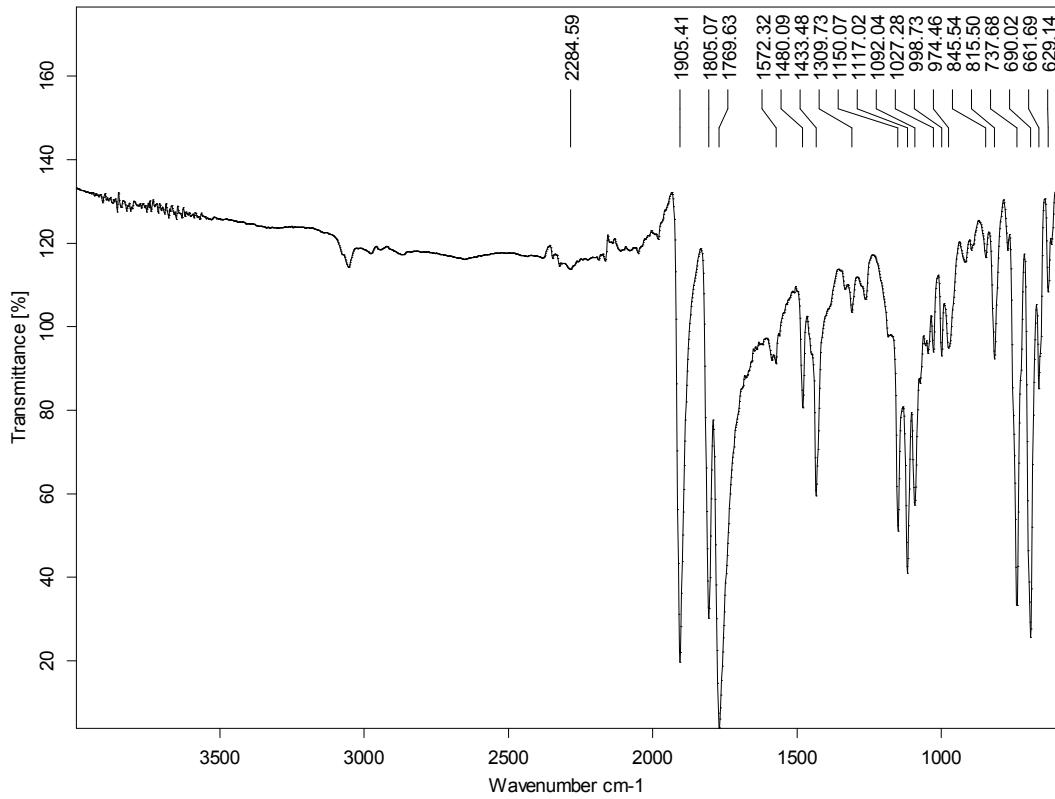
Annex 2.7. IR spectrum of [W(TPOdiphos)(CO)$_3$]
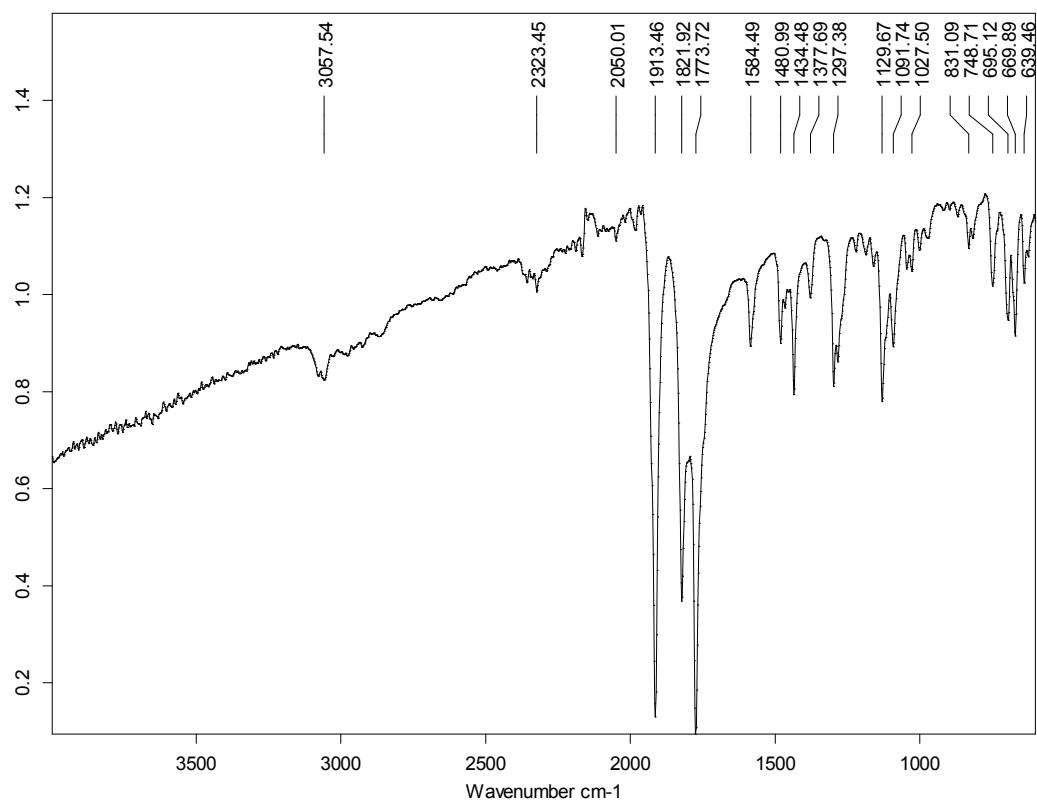
Annex 2.7. IR spectrum of [W(SODPdiphos)(CO)$_3$]

ANNEX III. HRMS-ESI[+] Spectra

Annex 3.1. Experimental and Calculated High Resolution Mass Spectra of *fac*-[Mo(TPOdiphos)(CO)$_3$]

3.1.a. Experimental

3.1.b. Calculated
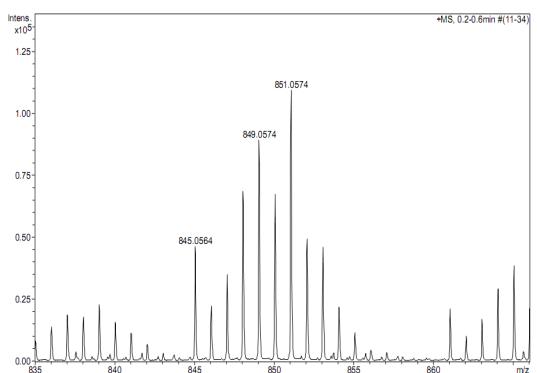
#	m/z	I	I %
1	845.0564	46462	42.5
2	846.0614	22635	20.7
3	847.0565	35123	32.1
4	848.0577	68706	62.8
5	849.0574	89421	81.7
6	850.0592	67647	61.8
7	851.0574	109446	100.0
8	852.0631	49566	45.3
9	853.0600	46202	42.2
10	854.0659	22158	20.2
11	855.0609	11689	10.7
12	856.0692	4110	3.8
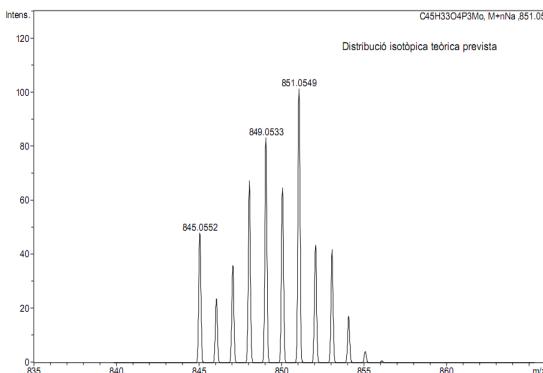
#	m/z	I	I %
1	845.0552	47	47.4
2	846.0586	23	23.3
3	847.0536	36	35.5
4	848.0543	66	66.4
5	849.0533	82	82.1
6	850.0546	64	63.8
7	851.0549	100	100.0
8	852.0572	43	43.1
9	853.0560	41	41.4
10	854.0592	17	17.0
11	855.0626	4	4.1
12	856.0659	1	0.7

Annex 3.2. Experimental and Calculated High Resolution Mass Spectra of [W(TPOdiphos)(CO)$_3$]

3.2.a. Experimental
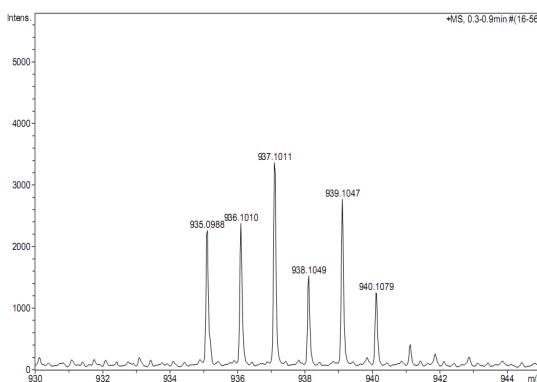
3.2.b. Calculated

#	m/z	I	I %
1	935.0988	2269	67.4
2	936.1010	2384	70.9
3	937.1011	3365	100.0
4	938.1049	1528	45.4
5	939.1047	2775	82.5
6	940.1079	1264	37.6
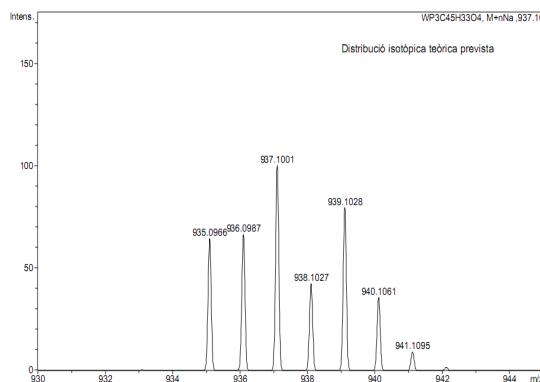
#	m/z	I	I %
1	935.0966	65	64.6
2	936.0987	67	66.7
3	937.1001	100	100.0
4	938.1027	43	42.6
5	939.1028	80	79.7
6	940.1061	36	35.9

Annex 3.3. Experimental and Calculated High Resolution Mass Spectra of [Mo(SODPdiphos)(CO)$_3$]

3.5.a. Experimental
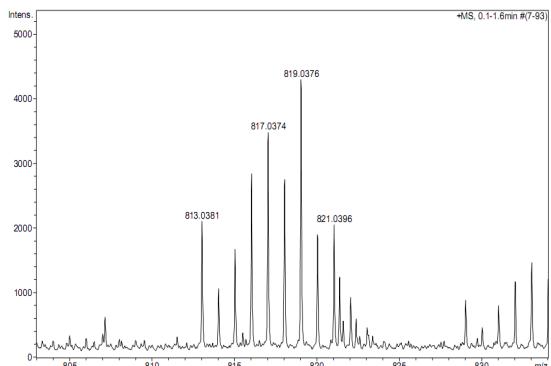
#	m/z	I	I %
1	813.0381	2108	49.0
2	814.0419	1069	24.8
3	815.0382	1679	39.0
4	816.0385	2845	66.1
5	817.0374	3486	81.0
6	818.0380	2756	64.1
7	819.0376	4302	100.0
8	820.0398	1907	44.3
9	821.0396	2054	47.7
10	821.3751	1250	29.1
11	822.0458	935	21.7
12	822.3789	601	14.0

3.5.b. Calculated
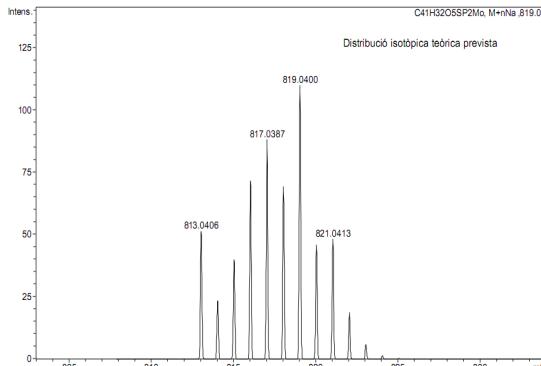
#	m/z	I	I %
1	813.0406	47	46.6
2	814.0440	21	21.3
3	815.0389	36	36.4
4	816.0397	65	65.2
5	817.0387	80	80.2
6	818.0399	63	63.0
7	819.0400	100	100.0
8	820.0426	42	41.9
9	821.0413	44	43.8
10	822.0446	17	17.1
11	823.0479	5	5.4
12	824.0404	1	1.3

Annex 3.4. Experimental and Calculated High Resolution Mass Spectra of [W(SODPdiphos)(CO)$_3$]

3.6.a. Experimental
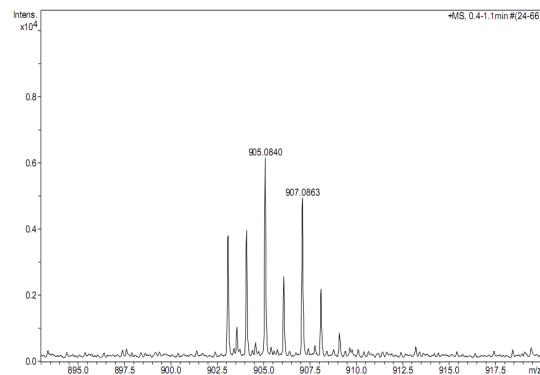
#	m/z	I	I %
1	903.0808	3614	58.7
2	904.0825	3785	61.5
3	905.0840	6158	100.0
4	906.0858	2372	38.5
5	907.0863	4753	77.2
6	908.0886	2000	32.5
7	909.0919	669	10.9

3.6.b. Calculated
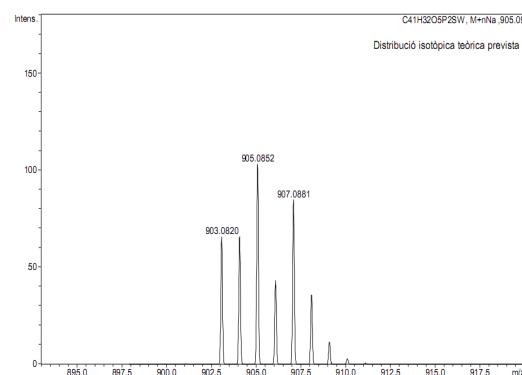
#	m/z	I	I %
1	903.0820	64	64.1
2	904.0841	64	63.9
3	905.0852	100	100.0
4	906.0881	42	41.9
5	907.0881	82	82.3
6	908.0915	35	34.7
7	909.0948	11	11.4

(1)

(2)
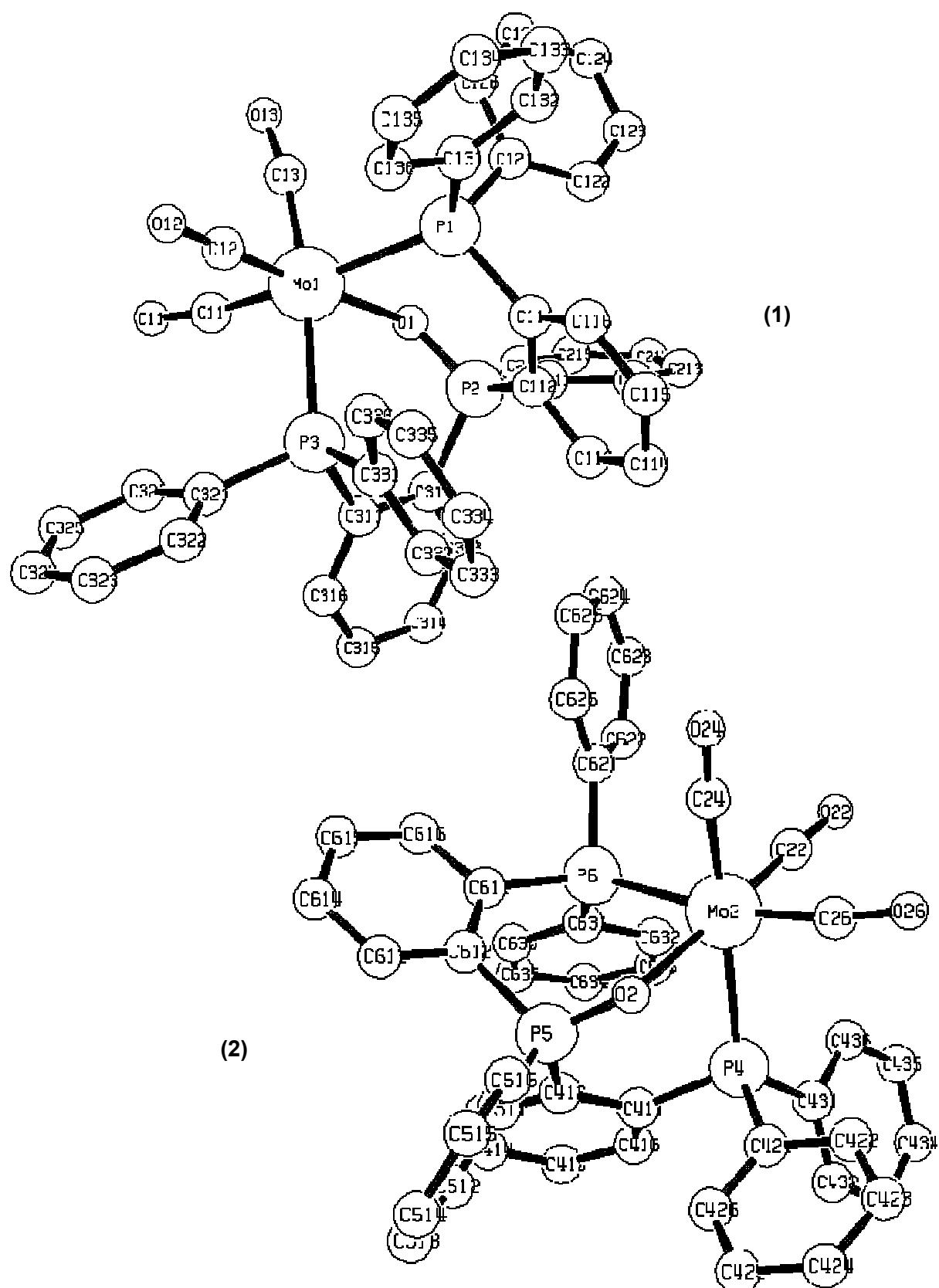
```
#\#CIF_1.1
```

```
#   CIF produced by WinGX routine CIF_UPDATE
#   Created on 2007-07-14 at 12:51:17
#   Using CIFtbx version 2.6.2 16 Jun 1998

#   Dictionary name : cif_core.dic
#   Dictionary vers : 2.3
#   Request file    : c:\wingx\files\archive.dat
#   CIF files read  : kml1 struct


data_kml1

_audit_creation_date                    2007-07-14T12:51:17-00:00
_audit_creation_method                  'WinGX routine CIF_UPDATE'
_audit_conform_dict_name                cif_core.dic
_audit_conform_dict_version             2.3
_audit_conform_dict_location            ftp://ftp.iucr.org/pub/cif_core.dic
_publ_requested_category                FM


#----------------------------------------------------------------------------#
#                        CHEMICAL INFORMATION                                #
#----------------------------------------------------------------------------#

_chemical_name_systematic
;
 ?
;
_chemical_formula_moiety                'C45 H35 Mo1 O4 P3'
_chemical_formula_sum                   'C45 H35 Mo O4 P3'
_chemical_formula_weight                828.58
_chemical_compound_source               'synthesis as described'


#----------------------------------------------------------------------------#
#                        UNIT CELL INFORMATION                               #
#----------------------------------------------------------------------------#

_symmetry_cell_setting                  monoclinic
_symmetry_space_group_name_H-M          'P 21/a'
_symmetry_space_group_name_Hall         '-P 2yab'
_symmetry_Int_Tables_number             14
loop_
    _symmetry_equiv_pos_as_xyz
'x, y, z'
'-x+1/2, y+1/2, -z'
'-x, -y, -z'
'x-1/2, -y-1/2, z'

_cell_length_a                          19.7966(14)
_cell_length_b                          9.8803(7)
_cell_length_c                          39.196(3)
_cell_angle_alpha                       90
_cell_angle_beta                        95.880(2)
_cell_angle_gamma                       90
_cell_volume                            7626.3(10)
_cell_formula_units_Z                   8
_cell_measurement_temperature           293(2)
_cell_measurement_reflns_used           0
_cell_measurement_theta_min             0
_cell_measurement_theta_max             0
_cell_measurement_wavelength            0.71073


#----------------------------------------------------------------------------#
#                        CRYSTAL INFORMATION                                 #
#----------------------------------------------------------------------------#

_exptl_crystal_description              prism
```

```
_exptl_crystal_colour                  orange
_exptl_crystal_size_max                0.18
_exptl_crystal_size_mid                0.13
_exptl_crystal_size_min                0.12
_exptl_crystal_density_diffrn          1.443
_exptl_crystal_density_method          'not measured'
_exptl_crystal_F_000                   3392
_exptl_special_details
;
 ?
;


#----------------------------------------------------------------------------#
#                     ABSORPTION CORRECTION                                   #
#----------------------------------------------------------------------------#

_exptl_absorpt_coefficient_mu          0.514
_exptl_absorpt_correction_type         none


#----------------------------------------------------------------------------#
#                        DATA COLLECTION                                      #
#----------------------------------------------------------------------------#

_diffrn_ambient_temperature            293(2)
_diffrn_radiation_wavelength           0.71073
_diffrn_radiation_type                 MoK\a
_diffrn_radiation_monochromator        graphite
_diffrn_radiation_probe                x-ray
_diffrn_reflns_av_R_equivalents        0.1414
_diffrn_reflns_av_unetI/netI           0.2194
_diffrn_reflns_number                  51199
_diffrn_reflns_limit_h_min             -26
_diffrn_reflns_limit_h_max             24
_diffrn_reflns_limit_k_min             -13
_diffrn_reflns_limit_k_max             13
_diffrn_reflns_limit_l_min             -53
_diffrn_reflns_limit_l_max             46
_diffrn_reflns_theta_min               1.57
_diffrn_reflns_theta_max               29.11
_diffrn_reflns_theta_full              29.11
_diffrn_measured_fraction_theta_full
                                       0.91
_diffrn_measured_fraction_theta_max
                                       0.91
_reflns_number_total                   18654
_reflns_number_gt                      7583
_reflns_threshold_expression           >2sigma(I)


#----------------------------------------------------------------------------#
#                     COMPUTER PROGRAMS USED                                  #
#----------------------------------------------------------------------------#

_computing_structure_solution          'SHELXS-86 (Sheldrick, 1986)'
_computing_structure_refinement        'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics          'Ortep-3 for Windows (Farrugia, 1997)'
_computing_publication_material        'WinGX publication routines (Farrugia,
1999)'


#----------------------------------------------------------------------------#
#                     REFINEMENT INFORMATION                                  #
#----------------------------------------------------------------------------#

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
```

```
   not relevant to the choice of reflections for refinement.  R-factors based
   on F^2^ are statistically about twice as large as those based on F, and R-
   factors based on ALL data will be even larger.
;
_refine_ls_structure_factor_coef        Fsqd
_refine_ls_matrix_type                   full
_refine_ls_weighting_scheme              calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.0854P)^2^+7.9807P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary             direct
_atom_sites_solution_secondary           difmap
_atom_sites_solution_hydrogens           geom
_refine_ls_hydrogen_treatment            mixed
_refine_ls_extinction_method             none
_refine_ls_number_reflns                 18654
_refine_ls_number_parameters             955
_refine_ls_number_restraints             0
_refine_ls_R_factor_all                  0.2143
_refine_ls_R_factor_gt                   0.0795
_refine_ls_wR_factor_ref                 0.219
_refine_ls_wR_factor_gt                  0.16
_refine_ls_goodness_of_fit_ref           0.867
_refine_ls_restrained_S_all              0.867
_refine_ls_shift/su_max                  0.059
_refine_ls_shift/su_mean                 0.004
_refine_diff_density_max                 0.877
_refine_diff_density_min                 -1.355
_refine_diff_density_rms                 0.096


#----------------------------------------------------------------------------#
#                 ATOMIC TYPES, COORDINATES AND THERMAL PARAMETERS          #
#----------------------------------------------------------------------------#

loop_
    _atom_type_symbol
    _atom_type_description
    _atom_type_scat_dispersion_real
    _atom_type_scat_dispersion_imag
    _atom_type_scat_source
C C 0.0033 0.0016 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
H H 0 0 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
Mo Mo -1.6832 0.6857 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
O O 0.0106 0.006 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
P P 0.1023 0.0942 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'


loop_
    _atom_site_label
    _atom_site_type_symbol
    _atom_site_fract_x
    _atom_site_fract_y
    _atom_site_fract_z
    _atom_site_U_iso_or_equiv
    _atom_site_adp_type
    _atom_site_occupancy
    _atom_site_symmetry_multiplicity
    _atom_site_calc_flag
    _atom_site_refinement_flags
    _atom_site_disorder_assembly
    _atom_site_disorder_group




Mo1 Mo 0.10065(3)   0.27287(6)  0.119198(16) 0.04196(19) Uani 1 1 d . . .
Mo2 Mo 0.28649(3)   0.54472(6)  0.379096(16) 0.04184(18) Uani 1 1 d . . .
P1  P  0.20852(11)  0.22043(19) 0.09046(5)   0.0464(5)   Uani 1 1 d . . .
P2  P  0.10340(11) -0.04805(18) 0.09148(5)   0.0469(5)   Uani 1 1 d . . .
P3  P  0.11836(11)  0.10075(19) 0.16839(5)   0.0463(5)   Uani 1 1 d . . .
P4  P  0.32092(10) 0.36346(18) 0.33753(5)   0.0440(5)   Uani 1 1 d . . .
```

```
P5  P   0.43965(11) 0.60605(18) 0.35273(5)  0.0436(5)      Uani 1 1 d . . .
P6  P   0.38369(10) 0.51090(18) 0.42619(5)  0.0429(5)      Uani 1 1 d . . .
O1  O   0.0754(2)   0.0917(4)   0.08490(11) 0.0448(12)     Uani 1 1 d . . .
O2  O   0.3654(2)   0.6365(4)   0.34803(12) 0.0466(12)     Uani 1 1 d . . .
C11 C   0.0118(4)   0.3147(7)   0.1319(2)   0.051(2)       Uani 1 1 d . . .
C12 C   0.1326(4)   0.4192(7)   0.14803(19) 0.052(2)       Uani 1 1 d . . .
C13 C   0.0738(4)   0.4085(7)   0.08481(19) 0.055(2)       Uani 1 1 d . . .
C22 C   0.2262(4)   0.4553(8)   0.4064(2)   0.058(2)       Uani 1 1 d . . .
C24 C   0.2633(4)   0.7108(8)   0.40216(19) 0.053(2)       Uani 1 1 d . . .
C26 C   0.2035(5)   0.5767(8)   0.3501(2)   0.056(2)       Uani 1 1 d . . .
O11 O  -0.0411(3)   0.3577(6)   0.13774(17) 0.0789(19)     Uani 1 1 d . . .
O12 O   0.1513(3)   0.5124(6)   0.16544(16) 0.0826(19)     Uani 1 1 d . . .
O13 O   0.0528(4)   0.4946(6)   0.06683(16) 0.090(2)       Uani 1 1 d . . .
O22 O   0.1859(3)   0.4037(6)   0.42223(17) 0.0845(19)     Uani 1 1 d . . .
O24 O   0.2443(4)   0.8069(6)   0.41497(16) 0.089(2)       Uani 1 1 d . . .
O26 O   0.1479(3)   0.5931(7)   0.33686(18) 0.094(2)       Uani 1 1 d . . .
C111 C  0.2394(4)   0.0477(7)   0.10005(18) 0.0489(19)     Uani 1 1 d . . .
C112 C  0.1927(4)  -0.0602(7)   0.10213(18) 0.0449(18)     Uani 1 1 d . . .
C113 C  0.2175(5)  -0.1874(8)   0.1125(2)   0.060(2)       Uani 1 1 d . . .
H113 H  0.1868     -0.2577      0.1143      0.072          Uiso 1 1 calc R . .
C114 C  0.2850(5)  -0.2124(9)   0.1199(2)   0.076(3)       Uani 1 1 d . . .
H114 H  0.3005     -0.2982      0.1266      0.091          Uiso 1 1 calc R . .
C115 C  0.3304(5)  -0.1062(9)   0.1173(3)   0.079(3)       Uani 1 1 d . . .
H115 H  0.3768     -0.1217      0.1219      0.095          Uiso 1 1 calc R . .
C116 C  0.3077(5)   0.0205(8)   0.1082(2)   0.067(2)       Uani 1 1 d . . .
H116 H  0.339       0.0903      0.1073      0.081          Uiso 1 1 calc R . .
C121 C  0.1953(4)   0.2169(7)   0.04343(19) 0.0485(19)     Uani 1 1 d . . .
C122 C  0.2039(4)   0.1025(8)   0.0242(2)   0.063(2)       Uani 1 1 d . . .
H122 H  0.2182      0.0224      0.0351      0.076          Uiso 1 1 calc R . .
C123 C  0.1915(5)   0.1061(10) -0.0111(2)   0.078(3)       Uani 1 1 d . . .
H123 H  0.1953      0.0264     -0.0234      0.094          Uiso 1 1 calc R . .
C124 C  0.1741(5)   0.2213(10) -0.0284(2)   0.078(3)       Uani 1 1 d . . .
H124 H  0.1669      0.2224     -0.0522      0.094          Uiso 1 1 calc R . .
C125 C  0.1675(5)   0.3363(10) -0.0096(2)   0.077(3)       Uani 1 1 d . . .
H125 H  0.156       0.4173     -0.0208      0.093          Uiso 1 1 calc R . .
C126 C  0.1774(5)   0.3343(8)   0.0257(2)   0.063(2)       Uani 1 1 d . . .
H126 H  0.1719      0.4138      0.0379      0.076          Uiso 1 1 calc R . .
C131 C  0.2864(4)   0.3216(7)   0.0982(2)   0.052(2)       Uani 1 1 d . . .
C132 C  0.3367(5)   0.3223(8)   0.0758(2)   0.067(2)       Uani 1 1 d . . .
H132 H  0.3296      0.2751      0.0553      0.081          Uiso 1 1 calc R . .
C133 C  0.3954(5)   0.3900(9)   0.0833(3)   0.073(3)       Uani 1 1 d . . .
H133 H  0.428       0.3905      0.0678      0.087          Uiso 1 1 calc R . .
C134 C  0.4071(5)   0.4580(8)   0.1138(3)   0.078(3)       Uani 1 1 d . . .
H134 H  0.4478      0.5041      0.1191      0.094          Uiso 1 1 calc R . .
C135 C  0.3589(4)   0.4583(8)   0.1365(2)   0.066(2)       Uani 1 1 d . . .
H135 H  0.3674      0.5033      0.1574      0.079          Uiso 1 1 calc R . .
C136 C  0.2975(4)   0.3919(7)   0.1287(2)   0.059(2)       Uani 1 1 d . . .
H136 H  0.2642      0.3947      0.1438      0.07           Uiso 1 1 calc R . .
C211 C  0.0824(4)  -0.1488(7)   0.05348(19) 0.051(2)       Uani 1 1 d . . .
C212 C  0.1300(5)  -0.2288(8)   0.0391(2)   0.070(3)       Uani 1 1 d . . .
H212 H  0.1739     -0.237       0.0499      0.084          Uiso 1 1 calc R . .
C213 C  0.1114(6)  -0.2957(9)   0.0088(2)   0.079(3)       Uani 1 1 d . . .
H213 H  0.1431     -0.3495     -0.0007      0.094          Uiso 1 1 calc R . .
C214 C  0.0485(6)  -0.2850(10) -0.0073(2)   0.081(3)       Uani 1 1 d . . .
H214 H  0.0367     -0.3325     -0.0275      0.097          Uiso 1 1 calc R . .
C215 C  0.0020(5)  -0.2044(10)  0.0060(2)   0.083(3)       Uani 1 1 d . . .
H215 H -0.0414     -0.1959     -0.0053      0.1            Uiso 1 1 calc R . .
C216 C  0.0195(5)  -0.1347(9)   0.0365(2)   0.077(3)       Uani 1 1 d . . .
H216 H -0.0121     -0.0782      0.0453      0.092          Uiso 1 1 calc R . .
C311 C  0.0732(4)  -0.0604(7)   0.16044(19) 0.0467(18)     Uani 1 1 d . . .
C312 C  0.0696(4)  -0.1245(6)   0.12786(19) 0.0451(18)     Uani 1 1 d . . .
C313 C  0.0368(4)  -0.2497(7)   0.1235(2)   0.056(2)       Uani 1 1 d . . .
H313 H  0.0351     -0.2933      0.1024      0.067          Uiso 1 1 calc R . .
C314 C  0.0073(4)  -0.3089(8)   0.1496(2)   0.066(2)       Uani 1 1 d . . .
H314 H -0.0139     -0.3926      0.1463      0.079          Uiso 1 1 calc R . .
C315 C  0.0087(5)  -0.2459(8)   0.1806(2)   0.073(3)       Uani 1 1 d . . .
H315 H -0.0127     -0.2854      0.1982      0.088          Uiso 1 1 calc R . .
C316 C  0.0418(5)  -0.1237(8)   0.1860(2)   0.068(2)       Uani 1 1 d . . .
```

```
H316  H 0.0429    -0.0828    0.2074       0.081        Uiso 1 1 calc R . .
C321  C 0.0872(4) 0.1565(7)  0.20876(19)  0.0480(19)   Uani 1 1 d . . .
C322  C 0.1271(5) 0.1562(8)  0.2397(2)    0.063(2)     Uani 1 1 d . . .
H322  H 0.1719    0.1268     0.2407       0.076        Uiso 1 1 calc R . .
C323  C 0.1007(5) 0.1998(9)  0.2696(2)    0.074(3)     Uani 1 1 d . . .
H323  H 0.1284    0.1981     0.2902       0.089        Uiso 1 1 calc R . .
C324  C 0.0368(5) 0.2439(9)  0.2692(2)    0.071(3)     Uani 1 1 d . . .
H324  H 0.02      0.2739     0.2892       0.085        Uiso 1 1 calc R . .
C325  C -0.0029(5) 0.2436(10) 0.2389(2)   0.087(3)     Uani 1 1 d . . .
H325  H -0.0474   0.2746     0.2383       0.105        Uiso 1 1 calc R . .
C326  C 0.0205(5) 0.1987(10) 0.2086(2)    0.080(3)     Uani 1 1 d . . .
H326  H -0.0085   0.197      0.1884       0.096        Uiso 1 1 calc R . .
C331  C 0.2040(4) 0.0460(8)  0.18462(19)  0.054(2)     Uani 1 1 d . . .
C332  C 0.2212(5) -0.0841(8) 0.1951(2)    0.078(3)     Uani 1 1 d . . .
H332  H 0.1891    -0.1531    0.1935       0.093        Uiso 1 1 calc R . .
C333  C 0.2888(7) -0.1091(12) 0.2081(3)   0.109(4)     Uani 1 1 d . . .
H333  H 0.3012    -0.1961    0.2153       0.13         Uiso 1 1 calc R . .
C334  C 0.3362(6) -0.0112(15) 0.2104(3)   0.107(4)     Uani 1 1 d . . .
H334  H 0.3806    -0.0312    0.2189       0.129        Uiso 1 1 calc R . .
C335  C 0.3192(6) 0.1161(14) 0.2004(3)    0.103(4)     Uani 1 1 d . . .
H335  H 0.3516    0.1845     0.2023       0.124        Uiso 1 1 calc R . .
C336  C 0.2542(5) 0.1433(10) 0.1876(2)    0.074(3)     Uani 1 1 d . . .
H336  H 0.2431    0.2311     0.1805       0.089        Uiso 1 1 calc R . .
C411  C 0.4117(4) 0.3239(7)  0.34541(17)  0.0415(17)   Uani 1 1 d . . .
C412  C 0.4605(4) 0.4269(7)  0.35244(18)  0.0420(17)   Uani 1 1 d . . .
C413  C 0.5280(4) 0.3959(8)  0.36220(19)  0.055(2)     Uani 1 1 d . . .
H413  H 0.5596    0.4653     0.3663       0.066        Uiso 1 1 calc R . .
C414  C 0.5488(4) 0.2621(8)  0.3658(2)    0.059(2)     Uani 1 1 d . . .
H414  H 0.594     0.2415     0.3728       0.071        Uiso 1 1 calc R . .
C415  C 0.5024(5) 0.1609(8)  0.3592(2)    0.061(2)     Uani 1 1 d . . .
H415  H 0.5163    0.0711     0.3613       0.074        Uiso 1 1 calc R . .
C416  C 0.4351(4) 0.1904(7)  0.34929(19)  0.053(2)     Uani 1 1 d . . .
H416  H 0.4044    0.1196     0.3451       0.063        Uiso 1 1 calc R . .
C421  C 0.3123(4) 0.4221(7)  0.29300(17)  0.0436(18)   Uani 1 1 d . . .
C422  C 0.2471(5) 0.4414(8)  0.2776(2)    0.065(2)     Uani 1 1 d . . .
H422  H 0.2108    0.4237     0.2903       0.078        Uiso 1 1 calc R . .
C423  C 0.2337(5) 0.4860(10) 0.2442(2)    0.078(3)     Uani 1 1 d . . .
H423  H 0.1893    0.4977     0.2344       0.093        Uiso 1 1 calc R . .
C424  C 0.2874(6) 0.5127(9)  0.2257(2)    0.082(3)     Uani 1 1 d . . .
H424  H 0.2792    0.5418     0.2031       0.099        Uiso 1 1 calc R . .
C425  C 0.3523(5) 0.4971(10) 0.2400(2)    0.076(3)     Uani 1 1 d . . .
H425  H 0.3885    0.5168     0.2275       0.092        Uiso 1 1 calc R . .
C426  C 0.3643(5) 0.4505(8)  0.27416(19)  0.064(2)     Uani 1 1 d . . .
H426  H 0.4087    0.4392     0.2839       0.077        Uiso 1 1 calc R . .
C431  C 0.2820(4) 0.1969(7)  0.3324(2)    0.053(2)     Uani 1 1 d . . .
C432  C 0.2900(5) 0.1137(8)  0.3052(2)    0.070(3)     Uani 1 1 d . . .
H432  H 0.3158    0.1434     0.2882       0.084        Uiso 1 1 calc R . .
C433  C 0.2609(5) -0.0118(9) 0.3024(3)    0.084(3)     Uani 1 1 d . . .
H433  H 0.2658    -0.0652    0.2832       0.101        Uiso 1 1 calc R . .
C434  C 0.2246(6) -0.0588(10) 0.3279(3)   0.095(4)     Uani 1 1 d . . .
H434  H 0.2065    -0.1457    0.3265       0.114        Uiso 1 1 calc R . .
C435  C 0.2149(5) 0.0206(10) 0.3552(3)    0.093(3)     Uani 1 1 d . . .
H435  H 0.189     -0.0109    0.3721       0.112        Uiso 1 1 calc R . .
C436  C 0.2442(4) 0.1519(8)  0.3581(2)    0.060(2)     Uani 1 1 d . . .
H436  H 0.2382    0.2067     0.3768       0.072        Uiso 1 1 calc R . .
C511  C 0.4788(4) 0.6902(7)  0.31890(18)  0.049(2)     Uani 1 1 d . . .
C512  C 0.5331(5) 0.6427(9)  0.3034(2)    0.071(3)     Uani 1 1 d . . .
H512  H 0.551     0.5579     0.3093       0.085        Uiso 1 1 calc R . .
C513  C 0.5618(5) 0.7191(11) 0.2790(2)    0.082(3)     Uani 1 1 d . . .
H513  H 0.5986    0.6862     0.2687       0.099        Uiso 1 1 calc R . .
C514  C 0.5350(7) 0.8441(12) 0.2704(2)    0.091(4)     Uani 1 1 d . . .
H514  H 0.5545    0.8963     0.2543       0.11         Uiso 1 1 calc R . .
C515  C 0.4805(6) 0.8931(10) 0.2850(3)    0.091(3)     Uani 1 1 d . . .
H515  H 0.4625    0.9773     0.2785       0.109        Uiso 1 1 calc R . .
C516  C 0.4522(5) 0.8164(8)  0.3095(2)    0.075(3)     Uani 1 1 d . . .
H516  H 0.4152    0.8496     0.3197       0.09         Uiso 1 1 calc R . .
C611  C 0.4600(4) 0.6176(7)  0.42485(18)  0.0428(17)   Uani 1 1 d . . .
C612  C 0.4817(4) 0.6622(7)  0.39362(18)  0.0440(18)   Uani 1 1 d . . .
```

```
C613  C 0.5368(4) 0.7490(8)   0.3937(2)    0.056(2)      Uani 1 1 d . . .
H613  H 0.5499    0.7806       0.373        0.068         Uiso 1 1 calc R . .
C614  C 0.5724(4) 0.7890(8)   0.4239(2)    0.068(2)      Uani 1 1 d . . .
H614  H 0.6099    0.8456       0.4237       0.082         Uiso 1 1 calc R . .
C615  C 0.5522(4) 0.7446(8)   0.4546(2)    0.063(2)      Uani 1 1 d . . .
H615  H 0.5754    0.7728       0.4752       0.076         Uiso 1 1 calc R . .
C616  C 0.4976(4) 0.6584(8)   0.4548(2)    0.056(2)      Uani 1 1 d . . .
H616  H 0.4857    0.6265       0.4756       0.068         Uiso 1 1 calc R . .
C621  C 0.3557(4) 0.5591(7)   0.46772(18)  0.0474(19)    Uani 1 1 d . . .
C622  C 0.3359(4) 0.4643(9)   0.4903(2)    0.066(2)      Uani 1 1 d . . .
H622  H 0.3399    0.3728       0.4853       0.079         Uiso 1 1 calc R . .
C623  C 0.3101(6) 0.5028(12)  0.5206(2)    0.092(3)      Uani 1 1 d . . .
H623  H 0.2961    0.4371       0.5354       0.111         Uiso 1 1 calc R . .
C624  C 0.3054(5) 0.6338(12)  0.5286(2)    0.083(3)      Uani 1 1 d . . .
H624  H 0.2894    0.6589       0.5492       0.1           Uiso 1 1 calc R . .
C625  C 0.3240(5) 0.7308(10)  0.5066(2)    0.075(3)      Uani 1 1 d . . .
H625  H 0.3202    0.8219       0.512        0.091         Uiso 1 1 calc R . .
C626  C 0.3483(4) 0.6944(8)   0.4764(2)    0.062(2)      Uani 1 1 d . . .
H626  H 0.3601    0.7613       0.4614       0.074         Uiso 1 1 calc R . .
C631  C 0.4172(4) 0.3410(7)   0.43526(17)  0.0437(18)    Uani 1 1 d . . .
C632  C 0.3703(4) 0.2357(7)   0.4306(2)    0.059(2)      Uani 1 1 d . . .
H632  H 0.3256    0.2547       0.4224       0.071         Uiso 1 1 calc R . .
C633  C 0.3893(5) 0.1040(8)   0.4380(2)    0.074(3)      Uani 1 1 d . . .
H633  H 0.3575    0.0345       0.4348       0.088         Uiso 1 1 calc R . .
C634  C 0.4546(6) 0.0762(9)   0.4500(2)    0.078(3)      Uani 1 1 d . . .
H634  H 0.467     -0.012       0.4561       0.094         Uiso 1 1 calc R . .
C635  C 0.5019(5) 0.1753(10)  0.4530(2)    0.078(3)      Uani 1 1 d . . .
H635  H 0.5471    0.1542       0.4597       0.093         Uiso 1 1 calc R . .
C636  C 0.4831(5) 0.3084(8)   0.4463(2)    0.061(2)      Uani 1 1 d . . .
H636  H 0.5156    0.3765       0.4492       0.074         Uiso 1 1 calc R . .

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    _atom_site_aniso_U_11
    _atom_site_aniso_U_22
    _atom_site_aniso_U_33
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    _atom_site_aniso_U_13
    _atom_site_aniso_U_12
Mo1 0.0541(4)  0.0320(3)  0.0394(4)  -0.0021(3)  0.0030(3)   0.0009(3)
Mo2 0.0501(4)  0.0382(3)  0.0374(4)   0.0044(3)  0.0053(3)   0.0057(3)
P1  0.0568(13) 0.0380(10) 0.0442(11) -0.0044(9)  0.0044(10) -0.0038(10)
P2  0.0577(13) 0.0335(10) 0.0490(12) -0.0073(9)  0.0034(10) -0.0004(10)
P3  0.0562(13) 0.0379(10) 0.0436(11) -0.0008(9) -0.0004(10) -0.0014(10)
P4  0.0535(13) 0.0372(10) 0.0408(11)  0.0023(8)  0.0028(9)   0.0001(9)
P5  0.0542(13) 0.0383(10) 0.0386(11)  0.0025(8)  0.0058(9)  -0.0028(10)
P6  0.0554(13) 0.0386(10) 0.0349(10)  0.0028(8)  0.0060(9)   0.0024(9)
O1  0.058(3)   0.032(2)   0.043(3)   -0.007(2)  -0.001(2)    0.003(2)
O2  0.053(3)   0.044(3)   0.043(3)    0.007(2)   0.005(2)    0.005(2)
C11 0.047(5)   0.043(4)   0.062(5)   -0.008(4)   0.006(4)   -0.002(4)
C12 0.066(6)   0.043(4)   0.045(5)   -0.006(4)  -0.011(4)    0.008(4)
C13 0.082(6)   0.038(4)   0.044(5)    0.002(4)  -0.005(4)    0.017(4)
C22 0.072(6)   0.056(5)   0.051(5)    0.024(4)   0.024(4)    0.006(5)
C24 0.069(6)   0.050(5)   0.041(4)    0.010(4)   0.005(4)    0.029(4)
C26 0.064(6)   0.058(5)   0.047(5)    0.000(4)   0.004(4)    0.012(4)
O11 0.061(4)   0.061(4)   0.116(5)    0.003(4)   0.016(4)    0.007(3)
O12 0.096(5)   0.060(4)   0.086(5)   -0.024(3)  -0.022(4)    0.005(4)
O13 0.132(6)   0.058(4)   0.078(4)    0.011(3)   0.000(4)    0.021(4)
O22 0.075(5)   0.095(5)   0.087(5)    0.031(4)   0.027(4)    0.005(4)
O24 0.132(6)   0.063(4)   0.074(4)   -0.001(3)   0.016(4)    0.042(4)
O26 0.070(5)   0.108(5)   0.097(5)    0.004(4)  -0.023(4)    0.027(4)
C111 0.065(6)  0.043(4)   0.037(4)   -0.006(3)  -0.001(4)    0.006(4)
C112 0.055(5)  0.032(4)   0.048(4)   -0.002(3)   0.002(4)    0.002(4)
C113 0.068(6)  0.042(4)   0.069(6)    0.004(4)   0.000(5)    0.000(4)
C114 0.073(7)  0.062(6)   0.090(7)    0.001(5)  -0.004(6)    0.015(6)
C115 0.066(7)  0.064(6)   0.106(8)    0.000(6)  -0.004(6)    0.013(5)
C116 0.063(6)  0.053(5)   0.085(7)   -0.004(5)   0.003(5)   -0.003(5)
C121 0.056(5)  0.044(4)   0.047(4)   -0.003(4)   0.011(4)   -0.008(4)
```

```
C122 0.081(6)   0.057(5)   0.051(5)  -0.013(4)   0.010(5)   0.001(5)
C123 0.119(9)   0.062(6)   0.056(6)  -0.018(5)   0.016(6)  -0.006(6)
C124 0.099(8)   0.093(7)   0.045(5)  -0.013(5)   0.020(5)   0.000(6)
C125 0.102(8)   0.080(6)   0.051(6)   0.023(5)   0.015(5)   0.001(6)
C126 0.097(7)   0.048(5)   0.046(5)   0.002(4)   0.020(5)  -0.002(5)
C131 0.060(5)   0.042(4)   0.054(5)   0.000(4)  -0.001(4)  -0.001(4)
C132 0.083(7)   0.065(5)   0.059(6)  -0.001(4)   0.025(5)  -0.014(5)
C133 0.064(6)   0.072(6)   0.084(7)   0.016(5)   0.015(5)  -0.025(5)
C134 0.075(7)   0.053(5)   0.099(8)   0.018(5)  -0.022(6)  -0.023(5)
C135 0.059(6)   0.058(5)   0.077(6)   0.001(5)  -0.010(5)  -0.005(5)
C136 0.066(6)   0.050(5)   0.059(5)   0.003(4)   0.004(4)  -0.011(4)
C211 0.062(6)   0.043(4)   0.048(5)  -0.010(4)   0.008(4)  -0.003(4)
C212 0.086(7)   0.055(5)   0.070(6)  -0.014(5)   0.013(5)   0.000(5)
C213 0.110(9)   0.062(6)   0.068(7)  -0.026(5)   0.031(6)  -0.007(6)
C214 0.106(9)   0.081(7)   0.058(6)  -0.028(5)   0.019(6)  -0.041(7)
C215 0.074(7)   0.105(8)   0.068(7)  -0.030(6)  -0.008(5)  -0.008(6)
C216 0.081(7)   0.082(6)   0.067(6)  -0.028(5)   0.003(5)  -0.002(6)
C311 0.056(5)   0.034(4)   0.050(5)   0.001(3)   0.003(4)  -0.005(4)
C312 0.049(5)   0.029(4)   0.057(5)  -0.001(3)   0.004(4)   0.003(3)
C313 0.066(6)   0.038(4)   0.063(5)  -0.008(4)   0.009(5)  -0.009(4)
C314 0.072(6)   0.035(4)   0.090(7)   0.001(5)   0.006(5)  -0.014(4)
C315 0.095(8)   0.061(6)   0.063(6)   0.012(5)   0.005(5)  -0.029(5)
C316 0.082(7)   0.060(5)   0.061(6)  -0.002(4)   0.007(5)  -0.012(5)
C321 0.058(5)   0.046(4)   0.042(4)  -0.003(3)   0.013(4)   0.007(4)
C322 0.067(6)   0.081(6)   0.042(5)  -0.010(4)   0.005(4)   0.007(5)
C323 0.084(7)   0.086(7)   0.050(6)   0.001(5)  -0.003(5)  -0.013(6)
C324 0.094(8)   0.067(6)   0.053(6)  -0.001(4)   0.008(5)   0.018(5)
C325 0.085(8)   0.123(9)   0.058(6)   0.017(6)   0.021(6)   0.041(7)
C326 0.091(8)   0.097(7)   0.053(6)   0.006(5)   0.013(5)   0.012(6)
C331 0.061(5)   0.049(4)   0.049(5)  -0.002(4)  -0.001(4)   0.007(4)
C332 0.096(8)   0.047(5)   0.084(7)  -0.011(5)  -0.021(6)   0.018(5)
C333 0.117(10)  0.083(8)   0.114(9)  -0.025(7)  -0.046(8)   0.038(8)
C334 0.067(8)   0.138(11)  0.108(9)  -0.034(9)  -0.032(7)   0.037(8)
C335 0.066(8)   0.131(11)  0.106(9)  -0.002(8)  -0.022(6)  -0.003(8)
C336 0.073(7)   0.080(6)   0.066(6)   0.012(5)  -0.014(5)  -0.004(6)
C411 0.046(5)   0.041(4)   0.036(4)   0.000(3)   0.001(3)   0.005(4)
C412 0.041(4)   0.044(4)   0.042(4)   0.005(3)   0.010(3)   0.005(3)
C413 0.058(6)   0.051(5)   0.054(5)  -0.003(4)   0.000(4)   0.000(4)
C414 0.054(5)   0.062(5)   0.063(6)   0.003(4)   0.010(4)   0.014(5)
C415 0.076(7)   0.048(5)   0.061(5)   0.006(4)   0.010(5)   0.014(5)
C416 0.067(6)   0.044(4)   0.049(5)  -0.001(4)   0.014(4)   0.005(4)
C421 0.061(5)   0.037(4)   0.033(4)   0.002(3)   0.005(4)  -0.005(4)
C422 0.072(6)   0.072(6)   0.049(5)  -0.003(4)  -0.005(5)   0.001(5)
C423 0.094(8)   0.098(7)   0.037(5)   0.004(5)  -0.010(5)   0.009(6)
C424 0.124(10)  0.073(6)   0.047(6)   0.012(5)  -0.004(7)  -0.007(7)
C425 0.080(7)   0.101(7)   0.050(6)   0.008(5)   0.016(5)  -0.017(6)
C426 0.073(6)   0.081(6)   0.038(5)   0.007(4)   0.006(4)   0.000(5)
C431 0.065(6)   0.039(4)   0.053(5)   0.001(4)  -0.001(4)  -0.008(4)
C432 0.086(7)   0.048(5)   0.074(6)  -0.004(5)  -0.001(5)  -0.007(5)
C433 0.100(8)   0.058(6)   0.089(8)  -0.002(5)  -0.015(7)  -0.009(6)
C434 0.115(10)  0.047(6)   0.116(10)  0.004(6)  -0.023(8)  -0.025(6)
C435 0.083(8)   0.069(7)   0.125(10)  0.035(7)  -0.004(7)  -0.016(6)
C436 0.061(6)   0.052(5)   0.065(6)   0.011(4)  -0.004(5)  -0.006(4)
C511 0.066(6)   0.049(4)   0.034(4)   0.001(3)   0.015(4)  -0.010(4)
C512 0.093(7)   0.068(6)   0.054(5)   0.003(5)   0.016(5)  -0.004(5)
C513 0.097(8)   0.095(7)   0.059(6)  -0.009(6)   0.031(6)  -0.026(7)
C514 0.130(11)  0.100(9)   0.043(6)   0.009(6)   0.003(6)  -0.055(8)
C515 0.133(11)  0.070(6)   0.070(7)   0.018(6)   0.007(7)  -0.025(7)
C516 0.105(8)   0.055(5)   0.065(6)   0.010(5)   0.011(6)  -0.008(5)
C611 0.044(4)   0.040(4)   0.045(4)  -0.001(3)   0.003(4)   0.004(3)
C612 0.052(5)   0.041(4)   0.039(4)   0.001(3)   0.007(4)  -0.005(4)
C613 0.069(6)   0.060(5)   0.042(5)  -0.007(4)   0.010(4)  -0.001(4)
C614 0.058(6)   0.064(5)   0.081(7)  -0.006(5)  -0.001(5)  -0.013(5)
C615 0.057(6)   0.063(6)   0.067(6)  -0.012(5)  -0.006(5)   0.003(5)
C616 0.071(6)   0.052(5)   0.045(5)  -0.003(4)  -0.002(4)  -0.001(4)
C621 0.061(5)   0.043(4)   0.038(4)   0.002(3)   0.004(4)   0.011(4)
C622 0.089(7)   0.068(5)   0.045(5)   0.000(4)   0.025(5)  -0.001(5)
C623 0.125(10)  0.104(8)   0.056(6)   0.005(6)   0.049(6)  -0.006(7)
```

```
C624 0.096(8) 0.106(8) 0.053(6) -0.011(6)  0.035(6) -0.001(7)
C625 0.086(7) 0.073(6) 0.069(6) -0.020(5)  0.014(6)  0.013(5)
C626 0.074(6) 0.057(5) 0.055(5)  0.000(4)  0.012(5)  0.006(5)
C631 0.056(5) 0.040(4) 0.035(4)  0.006(3)  0.004(4)  0.005(4)
C632 0.059(6) 0.041(4) 0.074(6)  0.004(4) -0.002(5)  0.003(4)
C633 0.090(8) 0.043(5) 0.088(7)  0.006(5)  0.009(6)  0.002(5)
C634 0.107(9) 0.047(5) 0.082(7)  0.010(5)  0.017(6)  0.019(6)
C635 0.077(7) 0.071(6) 0.084(7)  0.013(5)  0.003(6)  0.026(6)
C636 0.074(6) 0.054(5) 0.054(5)  0.003(4) -0.007(5)  0.006(5)
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#----------------------------------------------------------------------------#
#                          MOLECULAR GEOMETRY                                 #
#----------------------------------------------------------------------------#
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```
_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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    _geom_bond_site_symmetry_2
    _geom_bond_publ_flag

Mo1 C12      1.902(8) . ?
Mo1 C11      1.922(8) . ?
Mo1 C13      1.936(8) . ?
Mo1 O1       2.263(4) . ?
Mo1 P1       2.567(2) . ?
Mo1 P3       2.568(2) . ?
Mo2 C22      1.899(8) . ?
Mo2 C26      1.925(9) . ?
Mo2 C24      1.951(8) . ?
Mo2 O2       2.266(5) . ?
Mo2 P6       2.548(2) . ?
Mo2 P4       2.560(2) . ?
P1 C121      1.836(8) . ?
P1 C111      1.838(7) . ?
P1 C131      1.836(8) . ?
P2 O1        1.501(5) . ?
P2 C112      1.779(8) . ?
P2 C312      1.802(7) . ?
P2 C211      1.804(7) . ?
P3 C331      1.830(8) . ?
P3 C321      1.841(7) . ?
P3 C311      1.836(7) . ?
P4 C431      1.819(7) . ?
P4 C411      1.833(7) . ?
P4 C421      1.830(7) . ?
P5 O2        1.493(5) . ?
P5 C511      1.806(7) . ?
P5 C612      1.815(7) . ?
P5 C412      1.818(7) . ?
P6 C631      1.827(7) . ?
P6 C621      1.836(7) . ?
P6 C611      1.847(7) . ?
C11 O11      1.174(8) . ?
C12 O12      1.183(8) . ?
C13 O13      1.155(8) . ?
C22 O22      1.176(8) . ?
C24 O24      1.154(8) . ?
C26 O26      1.179(9) . ?
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C111 C116    1.385(11) . ?
C111 C112    1.418(10) . ?
C112 C113    1.394(10) . ?
C113 C114    1.362(11) . ?
C114 C115    1.391(12) . ?
C115 C116    1.366(11) . ?
C121 C122    1.378(10) . ?
C121 C126    1.379(10) . ?
C122 C123    1.381(11) . ?
C123 C124    1.352(12) . ?
C124 C125    1.369(12) . ?
C125 C126    1.378(11) . ?
C131 C136    1.381(10) . ?
C131 C132    1.392(11) . ?
C132 C133    1.348(11) . ?
C133 C134    1.370(12) . ?
C134 C135    1.371(12) . ?
C135 C136    1.388(11) . ?
C211 C216    1.356(11) . ?
C211 C212    1.392(11) . ?
C212 C213    1.377(11) . ?
C213 C214    1.340(13) . ?
C214 C215    1.360(13) . ?
C215 C216    1.394(11) . ?
C311 C316    1.382(10) . ?
C311 C312    1.421(10) . ?
C312 C313    1.400(9) . ?
C313 C314    1.362(11) . ?
C314 C315    1.362(11) . ?
C315 C316    1.379(11) . ?
C321 C326    1.384(11) . ?
C321 C322    1.378(10) . ?
C322 C323    1.398(11) . ?
C323 C324    1.337(12) . ?
C324 C325    1.358(12) . ?
C325 C326    1.388(12) . ?
C331 C336    1.379(11) . ?
C331 C332    1.381(10) . ?
C332 C333    1.404(13) . ?
C333 C334    1.343(15) . ?
C334 C335    1.350(15) . ?
C335 C336    1.360(13) . ?
C411 C416    1.402(9) . ?
C411 C412    1.411(9) . ?
C412 C413    1.387(10) . ?
C413 C414    1.388(10) . ?
C414 C415    1.365(11) . ?
C415 C416    1.379(11) . ?
C421 C426    1.356(10) . ?
C421 C422    1.379(10) . ?
C422 C423    1.383(11) . ?
C423 C424    1.371(13) . ?
C424 C425    1.357(12) . ?
C425 C426    1.412(11) . ?
C431 C432    1.368(10) . ?
C431 C436    1.387(11) . ?
C432 C433    1.367(11) . ?
C433 C434    1.372(14) . ?
C434 C435    1.357(14) . ?
C435 C436    1.421(12) . ?
C511 C512    1.371(11) . ?
C511 C516    1.388(11) . ?
C512 C513    1.383(12) . ?
C513 C514    1.372(14) . ?
C514 C515    1.360(14) . ?
C515 C516    1.387(12) . ?
C611 C616    1.383(10) . ?
C611 C612    1.409(9) . ?
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C612 C613    1.389(10) . ?
C613 C614    1.371(11) . ?
C614 C615    1.378(11) . ?
C615 C616    1.376(11) . ?
C621 C622    1.373(10) . ?
C621 C626    1.390(10) . ?
C622 C623    1.394(11) . ?
C623 C624    1.337(13) . ?
C624 C625    1.367(12) . ?
C625 C626    1.370(11) . ?
C631 C636    1.369(10) . ?
C631 C632    1.394(10) . ?
C632 C633    1.377(10) . ?
C633 C634    1.359(12) . ?
C634 C635    1.351(12) . ?
C635 C636    1.385(11) . ?


loop_
    _geom_angle_atom_site_label_1
    _geom_angle_atom_site_label_2
    _geom_angle_atom_site_label_3
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    _geom_angle_site_symmetry_1
    _geom_angle_site_symmetry_3
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C12 Mo1 C11       86.6(3) . . ?
C12 Mo1 C13       86.5(3) . . ?
C11 Mo1 C13       80.7(3) . . ?
C12 Mo1 O1        173.4(3) . . ?
C11 Mo1 O1        99.9(2) . . ?
C13 Mo1 O1        96.1(2) . . ?
C12 Mo1 P1        100.0(3) . . ?
C11 Mo1 P1        169.0(2) . . ?
C13 Mo1 P1        90.9(3) . . ?
O1  Mo1 P1        73.90(13) . . ?
C12 Mo1 P3        92.6(2) . . ?
C11 Mo1 P3        90.4(2) . . ?
C13 Mo1 P3        171.1(3) . . ?
O1  Mo1 P3        85.82(12) . . ?
P1  Mo1 P3        98.05(7) . . ?
C22 Mo2 C26       82.0(3) . . ?
C22 Mo2 C24       86.5(3) . . ?
C26 Mo2 C24       84.7(3) . . ?
C22 Mo2 O2        174.8(3) . . ?
C26 Mo2 O2        102.1(3) . . ?
C24 Mo2 O2        96.9(3) . . ?
C22 Mo2 P6        90.2(3) . . ?
C26 Mo2 P6        169.8(2) . . ?
C24 Mo2 P6        88.3(2) . . ?
O2  Mo2 P6        86.03(13) . . ?
C22 Mo2 P4        104.8(2) . . ?
C26 Mo2 P4        90.3(2) . . ?
C24 Mo2 P4        166.9(2) . . ?
O2  Mo2 P4        72.24(12) . . ?
P6  Mo2 P4        97.97(6) . . ?
C121 P1 C111      101.4(3) . . ?
C121 P1 C131      101.9(3) . . ?
C111 P1 C131      102.5(4) . . ?
C121 P1 Mo1       113.9(3) . . ?
C111 P1 Mo1       111.8(3) . . ?
C131 P1 Mo1       122.7(3) . . ?
O1 P2 C112        116.3(3) . . ?
O1 P2 C312        111.2(3) . . ?
C112 P2 C312      103.1(3) . . ?
O1 P2 C211        108.4(3) . . ?
C112 P2 C211      107.2(4) . . ?
C312 P2 C211      110.4(3) . . ?
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C331 P3  C321       99.8(4) . . ?
C331 P3  C311       102.7(3) . . ?
C321 P3  C311       101.9(3) . . ?
C331 P3  Mo1        120.5(3) . . ?
C321 P3  Mo1        114.5(2) . . ?
C311 P3  Mo1        114.8(2) . . ?
C431 P4  C411       102.9(3) . . ?
C431 P4  C421       100.6(3) . . ?
C411 P4  C421       102.8(3) . . ?
C431 P4  Mo2        124.5(3) . . ?
C411 P4  Mo2        111.2(2) . . ?
C421 P4  Mo2        112.4(2) . . ?
O2   P5  C511       107.9(3) . . ?
O2   P5  C612       113.8(3) . . ?
C511 P5  C612       108.4(3) . . ?
O2   P5  C412       114.6(3) . . ?
C511 P5  C412       109.2(3) . . ?
C612 P5  C412       102.7(3) . . ?
C631 P6  C621       101.7(3) . . ?
C631 P6  C611       104.4(3) . . ?
C621 P6  C611       101.5(3) . . ?
C631 P6  Mo2        119.6(2) . . ?
C621 P6  Mo2        109.5(3) . . ?
C611 P6  Mo2        117.6(2) . . ?
P2   O1  Mo1        124.8(3) . . ?
P5   O2  Mo2        125.2(3) . . ?
O11  C11 Mo1        170.7(7) . . ?
O12  C12 Mo1        178.3(7) . . ?
O13  C13 Mo1        172.2(7) . . ?
O22  C22 Mo2        176.2(7) . . ?
O24  C24 Mo2        174.7(8) . . ?
O26  C26 Mo2        169.7(7) . . ?
C116 C111 C112      117.9(7) . . ?
C116 C111 P1        121.6(6) . . ?
C112 C111 P1        120.3(6) . . ?
C113 C112 C111      118.9(7) . . ?
C113 C112 P2        116.2(6) . . ?
C111 C112 P2        125.0(5) . . ?
C114 C113 C112      122.3(8) . . ?
C113 C114 C115      118.3(8) . . ?
C116 C115 C114      120.9(9) . . ?
C115 C116 C111      121.7(8) . . ?
C122 C121 C126      117.1(7) . . ?
C122 C121 P1        123.4(6) . . ?
C126 C121 P1        119.5(6) . . ?
C121 C122 C123      120.5(8) . . ?
C124 C123 C122      122.4(8) . . ?
C123 C124 C125      117.5(8) . . ?
C124 C125 C126      121.2(9) . . ?
C121 C126 C125      121.3(8) . . ?
C136 C131 C132      118.7(8) . . ?
C136 C131 P1        118.2(6) . . ?
C132 C131 P1        122.8(6) . . ?
C133 C132 C131      121.5(8) . . ?
C132 C133 C134      119.9(9) . . ?
C135 C134 C133      120.0(9) . . ?
C134 C135 C136      120.6(9) . . ?
C131 C136 C135      119.2(8) . . ?
C216 C211 C212      119.0(8) . . ?
C216 C211 P2        118.0(6) . . ?
C212 C211 P2        122.6(7) . . ?
C213 C212 C211      119.3(9) . . ?
C214 C213 C212      121.4(9) . . ?
C213 C214 C215      119.9(9) . . ?
C214 C215 C216      120.0(9) . . ?
C211 C216 C215      120.3(9) . . ?
C316 C311 C312      117.7(7) . . ?
C316 C311 P3        121.1(6) . . ?
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C312 C311 P3        121.2(6) . . ?
C313 C312 C311      119.0(7) . . ?
C313 C312 P2        118.6(6) . . ?
C311 C312 P2        122.4(5) . . ?
C314 C313 C312      121.1(8) . . ?
C313 C314 C315      120.2(7) . . ?
C314 C315 C316      120.1(8) . . ?
C311 C316 C315      121.9(8) . . ?
C326 C321 C322      117.7(8) . . ?
C326 C321 P3        119.4(6) . . ?
C322 C321 P3        122.9(6) . . ?
C321 C322 C323      120.4(8) . . ?
C324 C323 C322      121.8(9) . . ?
C323 C324 C325      118.0(9) . . ?
C324 C325 C326      122.4(10) . . ?
C321 C326 C325      119.6(9) . . ?
C336 C331 C332      118.1(8) . . ?
C336 C331 P3        117.2(6) . . ?
C332 C331 P3        124.8(7) . . ?
C331 C332 C333      117.9(10) . . ?
C334 C333 C332      122.0(10) . . ?
C333 C334 C335      120.0(11) . . ?
C334 C335 C336      119.3(11) . . ?
C335 C336 C331      122.7(10) . . ?
C416 C411 C412      116.4(7) . . ?
C416 C411 P4        121.8(6) . . ?
C412 C411 P4        121.3(5) . . ?
C413 C412 C411      121.1(6) . . ?
C413 C412 P5        115.2(6) . . ?
C411 C412 P5        123.5(5) . . ?
C412 C413 C414      120.4(8) . . ?
C415 C414 C413      119.5(8) . . ?
C414 C415 C416      120.7(8) . . ?
C415 C416 C411      121.9(8) . . ?
C426 C421 C422      117.5(7) . . ?
C426 C421 P4        125.6(6) . . ?
C422 C421 P4        116.8(6) . . ?
C421 C422 C423      122.5(9) . . ?
C424 C423 C422      118.6(9) . . ?
C425 C424 C423      120.8(9) . . ?
C424 C425 C426      119.2(9) . . ?
C421 C426 C425      121.4(8) . . ?
C432 C431 C436      119.1(7) . . ?
C432 C431 P4        123.3(7) . . ?
C436 C431 P4        117.6(6) . . ?
C433 C432 C431      121.8(9) . . ?
C432 C433 C434      119.7(10) . . ?
C435 C434 C433      120.5(9) . . ?
C434 C435 C436      119.9(10) . . ?
C431 C436 C435      118.9(9) . . ?
C512 C511 C516      118.9(8) . . ?
C512 C511 P5        125.6(6) . . ?
C516 C511 P5        115.4(6) . . ?
C511 C512 C513      121.0(9) . . ?
C514 C513 C512      119.1(10) . . ?
C515 C514 C513      121.3(10) . . ?
C514 C515 C516      119.4(10) . . ?
C515 C516 C511      120.4(10) . . ?
C616 C611 C612      117.4(7) . . ?
C616 C611 P6        120.9(6) . . ?
C612 C611 P6        121.7(5) . . ?
C613 C612 C611      120.0(7) . . ?
C613 C612 P5        118.8(6) . . ?
C611 C612 P5        121.3(6) . . ?
C614 C613 C612      121.0(8) . . ?
C613 C614 C615      119.5(8) . . ?
C614 C615 C616      119.9(8) . . ?
C611 C616 C615      122.2(8) . . ?
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C622 C621 C626      117.0(7) . . ?
C622 C621 P6        121.8(6) . . ?
C626 C621 P6        121.0(6) . . ?
C621 C622 C623      121.1(8) . . ?
C624 C623 C622      120.3(9) . . ?
C623 C624 C625      120.0(9) . . ?
C624 C625 C626      120.2(9) . . ?
C625 C626 C621      121.2(8) . . ?
C636 C631 C632      117.8(7) . . ?
C636 C631 P6        126.4(6) . . ?
C632 C631 P6        115.9(6) . . ?
C633 C632 C631      120.9(8) . . ?
C634 C633 C632      119.5(9) . . ?
C635 C634 C633      120.7(9) . . ?
C634 C635 C636      120.0(9) . . ?
C631 C636 C635      120.9(9) . . ?
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