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Diels-Alder reactions of phosphaalkene and phosphadiene complexes

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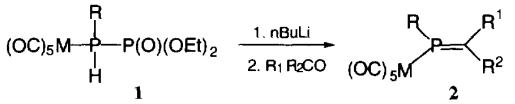
Summary – Electron-rich dienes are well suited to cycloaddition reactions with unstable phosphaalkene-$Mo(CO)_5$ complexes. The chemical properties of the resulting adducts have been examined briefly. (1-Phospha-1,3-diene)$Mo(CO)_5$ complexes are generated transiently from the corresponding 1,2-dihydrophosphetes and reacted with various dienophiles in Diels-Alder-like reactions. The above cycloadditions offer a general approach to dihydro- or tetrahydrophosphinines which are intermediates in the synthesis of new phosphinine derivatives.

phosphaalkene complexes / 1-phospha-1,3-diene complexes / [4+2] cycloaddition / 1,2-dihydrophosphete / phosphinine

Recent studies of transient phosphaalkene- and 1-phospha-1,3-diene-$W(CO)_5$ complexes have highlighted their reactivity as dienophiles and dienes in Diels-Alder-like reactions [1, 2]. The present work shows the scope and limitations of such cycloaddition reactions and represents a further development of these studies.

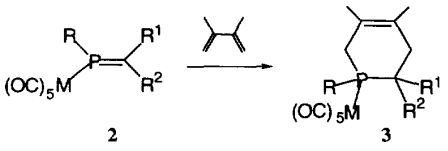
We have demonstrated previously that various phosphaalkene-$M(CO)_5$ complexes may be easily prepared by a "phospha-Wittig" reaction [3] of the phosphorylphosphane complexes **1** with a range of carbonyl derivatives (eq 1).



1 **2** (1)

Depending upon their substitution pattern, the products are either stable compounds or reactive transients. These unstable species can be trapped *in situ* by a number of reagents. We note particularly their reactivity towards an excess of 2,3-dimethyl-1,3-butadiene, which gives the corresponding [4+2] cycloadducts **3** (eq 2) [1].

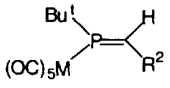
Most of these cycloaddition reactions have been performed using *P*-phenyl-substituted phosphaalkene complexes. Our attempts to apply such Diels-Alder reactions to *P-tertio*-butyl-substituted phosphaalkene complexes (**2a** : M = W, R = *t*Bu, R^1 = H, R^2 = *i*Pr and **2b** : M = Mo, R = *t*Bu, R^1 = H, R^2 = 2-pyridyl) were



2 **3** (2)

unsuccessful, owing to poor reactivity of the diene at low temperatures. Cyclopentadiene proved to be a more efficient trapping reagent for hindered phosphaalkene complexes [4], but this range of dienes was clearly too restricted to be synthetically useful. Thus, we tested more electron-rich open chain dienes as cycloaddition reagents for phosphaalkene complexes and carried out a preliminary study of the resulting adducts. Electron-rich dienes have been extensively used as cycloaddition reagents for free phosphaalkenes [5].

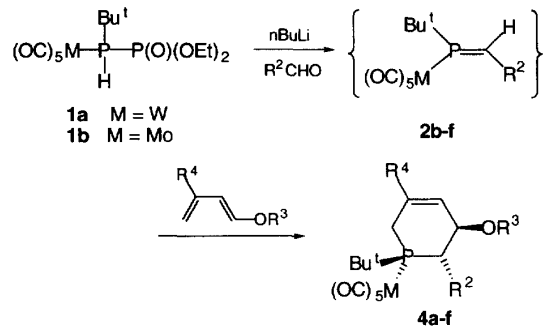
Phosphaalkenes **2b-f** were chosen as representative substrates.



2b M = Mo, R^2 = 2-pyridyl
2c M = W, R^2 = 2-pyridyl
2d M = Mo, R^2 = 6-methyl-2-pyridyl
2e M = Mo, R^2 = 2-thienyl
2f M = Mo, R^2 = 2-furyl

* Correspondence and reprints

Complexes **2b** and **2c** were formed by reaction of 2-pyridinecarboxaldehyde with **1b** and **1a**, respectively. Complexes **2d**, **2e** and **2f** were generated in an analogous fashion from **1b** and 6-methyl-2-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde and 2-furancarboxaldehyde respectively. The phosphaalkene complexes **2b-f** were reacted *in situ* with excess diene, as shown in eq 3 and table I.



(3)

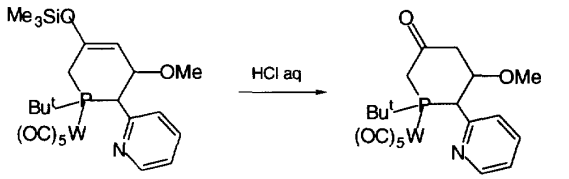
Table I. [4+2] Cycloaddition reactions between phosphaalkene-M(CO)$_5$ complexes and dienes.

Starting compound, phosphaalkene	Diene	Product	R^2	Yield
1b, **2b**	OMe	**4a**		63%
2b	Me$_3$SiO, OMe	**4b**		69%
2d	OSiMe$_3$	**4c**		40%
1a, **2c**	Me$_3$SiO, OMe	**4d**		60%
1b, **2e**		**4e**		50%
2f		**4f**		-

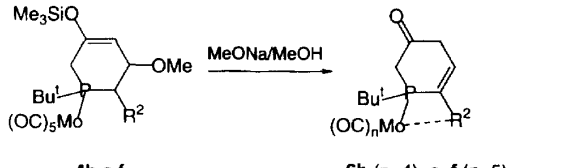
1-Methoxy-1,3-butadiene, 1-(trimethylsilyloxy)-1,3-butadiene and Danishefsky's diene were efficient trapping reagents for phosphaalkene complexes **4a-f**. Such electron-rich dienes operate at very low temperatures (−78 to 25°C), and are ideally suited to cycloaddition reactions with unstable species.

In each reaction in table I, the final product **4** is obtained as a single isomer, which reflects the excellent stereocontrol in both the synthesis of the intermediate phosphaalkene (*E* isomer) and the cycloaddition reaction. The observed regiochemistry is consistent with a cycloaddition reaction under electronic control, governed by the strong electronic polarization of the phosphaalkenes ($P^{\delta+}C^{\delta-}$) and the dienes involved. The stereochemistries of complexes **4**, (eq 3) were established by ^{1}H NMR spectroscopy.

The chemical properties of the new phosphorus heterocycles **4a-f** have been examined briefly. As expected, compounds **4b-f** are acid- and base-sensitive : hydrolysis of **4d** with aqueous HCl affords the corresponding keto-derivative **5**, while methanolysis of complexes **4b**, **4e-f** yields the unsaturated ketones **6**.

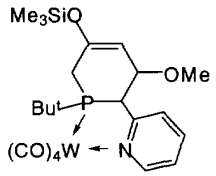


(4)



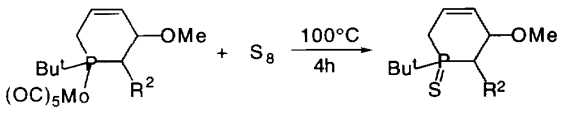
(5)

The pyridyl-substituted phosphorus heterocycles are P,N bidentate ligands whose chelating properties have been demonstrated as follows. Methanolysis of the molybdenum complex **4b** at room temperature directly affords the P-N chelated complex **6b** by displacement of a CO ligand (see eq 5). Heating of the W(CO)$_5$ complex **4d** at about 80°C affords the corresponding W(CO)$_4$ chelated complex **7a**.



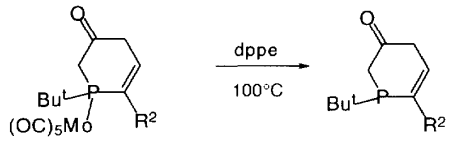
7a

The various heterocyclic ligands described above are easily removed from the corresponding molybdenum complexes either by reaction with sulfur (eq 6) or through a ligand displacement reaction. Bis(diphenylphosphino)ethane (dppe) proved highly efficient for this purpose [6], as shown in eq 7.



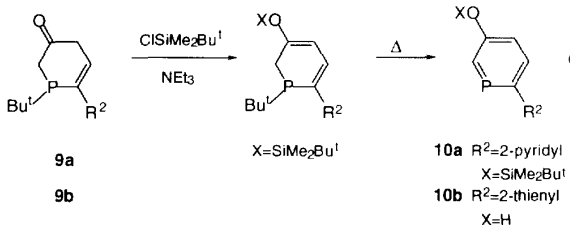
(6)

To illustrate the synthetic potential of the cycloaddition reactions between phosphaalkenes and dienes shown in eq 3, we tested the conversion of **9a** and **9b** into phosphinine derivatives. G. Märkl *et al* have previously reported that tetrahydrophosphininones, which



(7)

are analogues of **9**, are suitable precursors for various phosphinine derivatives [7]. Accordingly, we were able to convert compounds **9a** and **9b** into phosphinines by enolization of the carbonyl function and subsequent thermolysis (eq 8).



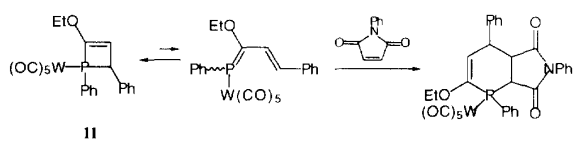
(8)

Compound **10a** is a new representative of the very restricted series of 2-pyridylphosphinines [8] whose chemistry is poorly developed.

The reaction sequence described here (eq 3-8) should afford a general access to a wide variety of new, functionalized phosphinines. The large number of aldehydes available for the "phospha-Wittig" conversion into phosphaalkene complexes makes this a rather versatile route. Considering the trapping reaction with electron-rich dienes, a number of strategies for the conversion of phosphaalkene complexes analogous to **4** into phosphinines may be envisaged, of which only one has been tested here. Whilst it is synthetically rather cumbersome, this approach could be applied to target species which are otherwise inaccessible.

The [4+2] Diels-Alder cycloaddition reaction of 1-phospha-1,3-diene complexes and dienophiles has been even less extensively investigated than the cycloadditions between dienes and phosphaalkene complexes. Previous work [2] has shown that a (1-phospha-1,3-butadiene)$W(CO)_5$ complex, transiently generated by a concerted ring-opening reaction of the corresponding 1,2-dihydrophosphete complex **11**, may be trapped *in situ* by dienophiles such as *N*-phenylmaleimide (eq 9), benzaldehyde and dimethyl acetylenedicarboxylate.

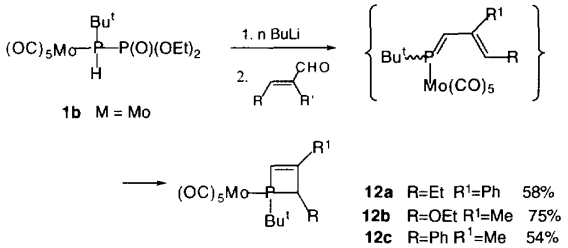
To expand the potential of this rather useful reaction, we prepared some new 1,2-dihydrophosphete complexes



(9)

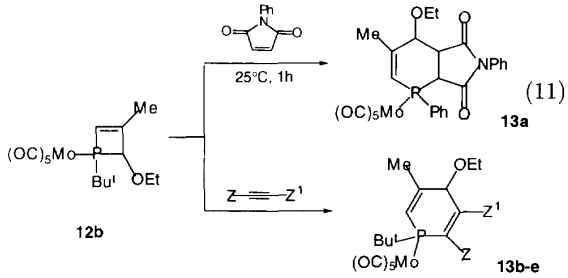
by reaction of the "phospha-Wittig" reagent **1b** with α,β-unsaturated aldehydes [9].

When 2-phenyl-2-pentenal, 3-ethoxy-2-methyl-2-propenal or 2-methyl-3-phenyl-2-propenal react with **1b**, the intermediate 1-phospha-1,3-butadienes cyclize spontaneously to afford the four-membered rings **12a-c**.



(10)

The final products were characterized as mixtures of two isomers. Complexes **12a-c** have been tested in cycloaddition reactions with *N*-phenylmaleimide. The reactivity of the dihydrophosphetes appears to be highly dependent upon their substitution pattern. In the case of complexes **12a** and **12c**, no reaction is observed up to about 110°C, at which temperature an unexploitable decomposition occurs. On the other hand, complex **12b** reacts quantitatively with *N*-phenylmaleimide at room temperature (eq 11) within 1 h. This result shows that **12b** equilibrates with its 1-phosphabutadiene isomer even under ambient conditions.



(11)

(12)

Table II. [4+2] Cycloaddition reactions of **12b** with alkynes.

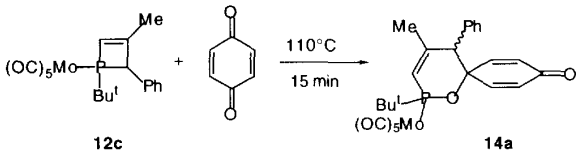
Entry	Z—≡—Z¹	Conditions	Product	Yield
1	MeO_2C—C≡C—CO_2Me	40°C, 4 h	**13b**	60%
2	EtO_2C—C≡C—Ph	80°C, 24 h	**13c**	45%
3	H—C≡C—Ph	75°C, 2 h	**13d**	36%
4	H—C≡C—	70°C, 1 h	**13e**	30%

In order to exploit its high reactivity, complex **12b** was also used as a diene precursor in the reaction with the various alkynes reported in table II. As expected, the electron-rich 4-ethoxy-substituted diene is an excellent cycloaddition reagent. Even poorly activated alkynes (entries 3 and 4) react under mild conditions. This reactivity is considerably higher than for the

2-ethoxy-substituted species derived from **11**, which only reacts with *N*-phenylmaleimide at 120°C [2]. In the case of unsymmetrical alkynes, the reaction with **12b** is regioselective. Steric rather than electronic factors seem to control this selectivity, as shown in entries 2, 3 and 4. We did not observe any correlation between the regiochemistry of the final products and the polarization of the alkyne used. Therefore, from the reactions above, we can draw no conclusions on the effect of the ethoxy substituent on the polarization of the phosphadiene moiety.

The inertness of the electron-poorer 1,2-dihydrophosphete molybdenum complexes **12a** and **12c** toward *N*-phenylmaleimide up to 110°C poses questions concerning the 1,2-dihydrophosphete/1-phospha-1,3-diene equilibrium in these complexes. Is it ineffective, or is the reactivity of the diene inadequate? The second hypothesis is supported by the experiments reported below.

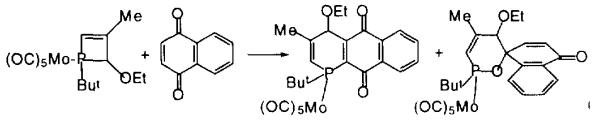
Reaction of **12c** with benzoquinone (eq 13) led to the spirocyclic derivative **14a** as a mixture of two isomers. This very rapid cycloaddition showed that the equilibrium between the 1,2-dihydrophosphete and the open diene is quite effective, at least around 110°C.



12c **14a**

(13)

The analogous reaction of complex **12b** with naphthoquinone at 55°C led to a mixture of three products as a result of cycloadditions at either the carbon-carbon double bond or the carbonyl function (eq 14).



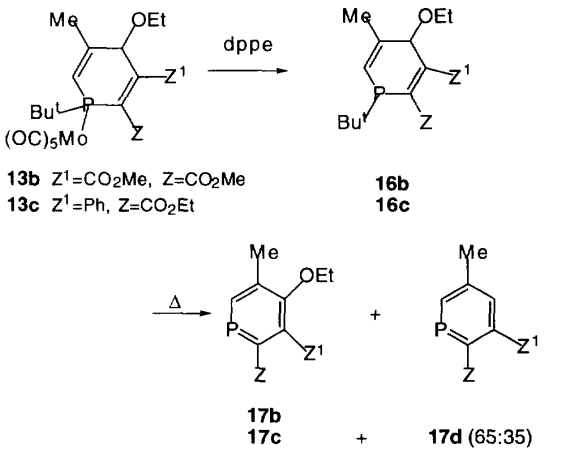
12b **15** **14b, c**

(14)

In the final part of this work we intend to show that the cycloaddition reaction between 1-phosphabutadienes and alkynes provides an alternative approach to phosphinine derivatives to the best known [4+2] cycloadditions between phosphaalkenes and dienes. This is demonstrated for the 1,4-dihydrophosphinine complexes **13b** and **13c**. Decomplexation of these phosphorus heterocycles by a ligand exchange reaction, followed by thermolysis afforded the target phosphinines (eq 15).

From a preparative standpoint, the second reaction is of little value, as a mixture of two phosphinines **17c** and **17d** is obtained through elimination of the H and OEt groups, respectively. On the other hand, the first example in eq 15 affords exclusively the 4-ethoxy-substituted phosphinine **17b**.

These preliminary results demonstrate that phosphinines may be obtained through a synthetic strategy



13b Z^1=CO_2Me, Z=CO_2Me **16b**
13c Z^1=Ph, Z=CO_2Et **16c**

17b
17c + **17d** (65:35)

(15)

based upon cycloadditions between 1-phospha-1,3-diene complexes and alkynes. The corresponding reactions of uncomplexed 1-phospha-1,3-dienes towards alkynes, and the ring opening of uncomplexed phosphetenes to 1-phospha-1,3-dienes are not well understood at present [10]. The next step of this work will be a comparative study of the behavior of complexed and free 1,2-dihydrophosphetes with respect to ring opening and Diels-Alder reactions.

Experimental section

All reactions were carried out under argon in dry solvents. Silica gel was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct inlet method. Elemental analyses were performed by the Service d'analyse du CNRS, Gif-sur-Yvette, France.

[*tert*-Butyl(diethoxyphosphoryl)phosphine] $W(CO)_5$ and $Mo(CO)_5$ complexes (**1a** and **1b**) were prepared according to published procedures [11]. 1-Methoxy-1,3-butadiene, 1-(trimethylsilyloxy)-1,3-butadiene and Danishefsky's diene were purchased from Aldrich-Chimie.

Cycloaddition of unstable phosphaalkene complexes with dienes. General Procedure

A solution of complex **1a** (or **1b**) (2 mmol) in THF was cooled to −78°C. *n*BuLi (1.4 mL, 1.6 M solution in hexane) was then added. After a few minutes an excess diene (4 mmol) and the suitable aldehyde (2.2 mmol) were added successively. The reaction mixture was allowed to warm to 0°C and hydrolyzed. After extraction with ether and drying over $MgSO_4$, the final product was purified by crystallization from ether/hexane mixtures.

4a : two compounds in a 90:10 ratio were observed in the reaction mixture by ^{31}P NMR. The major product was recovered in 63% yield after crystallization.

^{31}P NMR (THF) δ 37.4.

^{1}H NMR (C_6D_6) δ 0.66 (d, $^3J_{H-P}$ = 13.6 Hz, CMe_3), 1.89 (*ABX*, $^2J_{AB}$ = 16.0 Hz, $^2J_{H-P}$ = 7.0 Hz, 1H, CH_2), 2.16 (m, *AB*, 1H, CH_2), 2.84 (s, OCH_3), 3.34 (dd, $^2J_{H-P}$ = 13.5 Hz, $^3J_{H-H}$ = 10.0 Hz, PCH), 4.64 (d, $^3J_{H-H}$ = 10.0 Hz, *CH*OMe), 5.5-5.7 (m, 1H, =CH),

5.8-5.9 (m, 1H, =CH), 6.56 (1H, Py), 6.8-7.0 (2H, Py), 8.4 (d, $^3J_{H-H}$ = 4.3 Hz, 1H, Py).

^{13}C NMR (C_6D_6) δ 25.50 (d, $^1J_{C-P}$ = 16.1 Hz, PCH_2), 26.50 (d, $^2J_{C-P}$ = 5.0 Hz, CMe_3), 32.58 (d, $^1J_{C-P}$ = 13.1 Hz, $PCMe_3$), 47.78 (d, $^1J_{C-P}$ = 10.6 Hz, PCH), 57.25 (s, OMe), 81.08 (d, $^2J_{C-P}$ = 9.1 Hz, *C*HOMe), 122.1, 124.03, 125.48 (d, J_{C-P} = 2.5 Hz), 130.70 (d, J_{C-P} = 5.0 Hz), 135.82, 149.25, 158.35 (C), 207.15 (d, $^2J_{C-P}$ = 8.6 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 473 (M-CO, 13), 445 (M-2CO, 19), 417 (M-3CO, 26), 389 (M-4CO, 39), 205 (M-Mo(CO)$_5$-C_4H_{10}, 100).

IR (decalin) ν (CO) 1 940 cm^{-1}.

Anal calc for $C_{20}H_{22}O_6N$ Mo P : C, 48.11; H, 4.44; N, 2.81. Found : C, 48.06; H, 4.37; N, 2.93.

Minor product : ^{31}P NMR (THF) δ 33.6 ppm. Given that the 1-methoxy-1,3-butadiene used in this reaction is a mixture of isomers, the minor product should be a stereomer of **4a**.

4b : A single isomer of **4b** was observed in the reaction mixture. **4b** was recovered in 69% yield after crystallization.

^{31}P NMR (C_6D_6) δ 34.4.

^{1}H NMR (C_6D_6) δ 0.26 (s, $SiMe_3$), 0.69 (d, $^3J_{H-P}$ = 13.8 Hz, CMe_3), 2.29 (*AB*, $^2J_{AB}$ = 16.1 Hz, 1H, PCH_2), 2.7 (m, A*B*, 1H, PCH_2), 2.90 (s, OMe), 3.37 (dd, $^2J_{H-P}$ = 13.8 Hz, PCH), 4.83 (m, $^3J_{H-H}$ = 9.5 Hz, J_{H-H} = 2.3 Hz, *CH*OMe), 5.29 (broad, 1H, =CH), 6.6 (m, 1H), 6.9-7.0 (m, 2H), 8.45 (d, $^3J_{H-H}$ = 4.7 Hz, 1H).

^{13}C NMR (C_6D_6) δ −0.19 (s, $SiMe_3$), 26.39 (d, $^2J_{C-P}$ = 5.5 Hz, C*Me*$_3$), 31.24 (d, $^1J_{C-P}$ = 16.1 Hz, PCH_2), 32.40 (d, $^1J_{C-P}$ = 12.6 Hz, $PCMe_3$), 47.79 (d, $^1J_{C-P}$ = 11.1 Hz, PCH), 56.24 (s, OMe), 81.05 (d, $^2J_{C-P}$ = 11.6 Hz, *C*HOMe), 105.93 (s, =CH), 122.14, 125.54, 135.92, 148.92 (C), 149.32, 158.34 (C), 206.89 (d, $^1J_{C-P}$ = 8.6 Hz, *cis* CO), 210.17 (d, $^2J_{C-P}$ = 24.1 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (rel intensity) 561 (M-CO, 10), 533 (M-2CO, 17), 505 (M-3CO, 23), 262 ($C_{13}H_{17}NOPSi$, 100).

IR (decalin) ν (CO) 1 940, 2 030 cm^{-1}.

Anal calc for $C_{23}H_{30}O_7NP$ Mo Si : C, 47.02; H, 5.15; N, 2.38. Found : C, 47.07; H, 5.26; N, 2.66.

4c : A single isomer was obtained after crystallization, in 40% yield.

^{31}P NMR ($CDCl_3$) δ 37.1.

^{1}H NMR ($CDCl_3$) δ −0.23 (s, $OSiMe_3$), 0.98 (d, $^3J_{H-P}$ = 13.6 Hz, CMe_3), 2.24 (m, *AB*, 1H, CH_2), 2.56 (s, CH_3), 2.7-2.9 (m, A*B*, 1H, CH_2), 3.45 (dd, $^2J_{H-P}$ = 13.5 Hz, $^3J_{H-H}$ = 9.5 Hz, PCH), 4.98 (broad d, $CHOSiMe_3$), 5.7-6.0 (m, 2H, CH=CH), 7.01 (d, $^3J_{H-H}$ = 7.6 Hz, 2H), 7.46 (t, 1H).

^{13}C NMR ($CDCl_3$) δ −0.43 ($OSiMe_3$), 24.01 (CH_3), 25.66 (d, $^1J_{C-P}$ = 16.8 Hz, PCH_2), 26.98 (d, $^2J_{C-P}$ = 5.1 Hz, C*Me*$_3$), 33.41 (d, $^1J_{C-P}$ = 13.4 Hz, *C*Me$_3$), 49.28 (d, $^1J_{C-P}$ = 9.7 Hz, PCH), 72.65 (d, $^2J_{C-P}$ = 9.8 Hz, *C*H-OTMS), 121.84, 123.13, 123.33, 133.77 (d, $^2J_{C-P}$ = 4.7 Hz), 136.1, 157.15 (C), 158.76 (C), 206.78 (d, $^2J_{C-P}$ = 8.3 Hz, *cis* CO) ppm.

4d : A single isomer of **4d** was obtained in 60% yield, as a colorless solid : mp 141°C.

^{31}P NMR (C_6D_6) δ 18.8 ($^1J_{P-W}$ = 249 Hz).

^{1}H NMR (C_6D_6) δ 0.26 (s, $SiMe_3$), 0.69 (d, $^3J_{H-P}$ = 14.1 Hz, CMe_3), 2.40 (*AB*, $^2J_{A-B}$ = 16.1 Hz, 1H, PCH_2), 2.9 (m, A*B*, 1H, PCH_2), 2.90 (s, OMe), 4.15 (dd, $^2J_{H-P}$ = 13.3 Hz, $^3J_{H-H}$ = 9.5 Hz, PCH), 4.83 (m, $^3J_{H-H}$ = 9.4 Hz, J_{H-H} = 2.2 Hz, *CH*OMe), 5.29 (br, 1H, =CH), 6.6 (m, 1H), 6.9-7.0 (m, 2H), 8.45 (d, $^3J_{H-H}$ = 4.6 Hz, 1H).

^{13}C NMR (C_6D_6) δ 0.18 ($SiMe_3$), 26.44 (d, $^2J_{C-P}$ = 4.5 Hz, C*Me*$_3$), 32.1 (d, $^1J_{C-P}$ = 20.6 Hz, PCH_2), 33.3 (d, $^1J_{C-P}$ = 17.1 Hz, P*C*Me), 47.7 (d, $^1J_{C-P}$ = 14.6 Hz, PCH), 56.31 (s, OMe), 81.14 (d, $^2J_{C-P}$ = 10.1 Hz, *C*HOMe), 105.70 (s, =CH), 122.21, 125.68, 135.97, 148.82 (C), 149.40, 158.01 (C), 198.12 (d, $^2J_{C-P}$ = 6.5 Hz, *cis* CO) ppm.

Mass spectrum (^{184}W) *m/e* (rel intensity) 647 (M-CO, 21), 619 (M-2CO, 60), 563 (M-4CO, 25), 479 (M-5CO-C_4H_9, 100).

IR (decalin) ν (CO) 1 930 (vs), 1 940 (sh), 2 065 (m) cm^{-1}.

Anal calc for $C_{23}H_{30}NO_7$ P SiW : C, 40.90; H, 4.48. Found : C, 40.86; H, 4.29.

4e : A single isomer was obtained in 50% yield after crystallization.

^{31}P NMR ($CDCl_3$) δ 37.62.

^{1}H NMR ($CDCl_3$) δ 0.29 (s, $OSiMe_3$), 1.09 (d, $^3J_{H-P}$ = 13.9 Hz, CMe_3), 2.29 (*AB*, $^2J_{AB}$ = 16.2 Hz, 1H, PCH_2), 2.94 (m, 1H, PCH_2), 3.16 (s, OMe), 3.70 (dd, $^2J_{H-P}$ = 13.8 Hz, $^3J_{H-H}$ = 9.5 Hz, PCH), 4.39 (m, $^3J_{H-H}$ = 9.6 Hz, J_{H-H} = 2.6 Hz, *CH*OMe), 5.10 (1H, =CH), 7.0 (m, 1H), 7.15 (m, 1H), 7.25 (m, 1H).

^{13}C NMR ($CDCl_3$) δ 0.17 (s, $SiMe_3$), 26.64 (d, $^2J_{C-P}$ = 4.5 Hz, C*Me*$_3$), 31.43 (d, $^1J_{C-P}$ = 15.7 Hz, PCH_2), 33.26 (d, $^1J_{C-P}$ = 12.9 Hz, *C*Me$_3$), 43.92 (d, $^1J_{C-P}$ = 9.7 Hz, PCH), 56.84 (s, OMe), 82.19 (d, $^2J_{C-P}$ = 13.6 Hz, *C*HOMe), 105.84 (s, =CH), ... 206.03 (d, $^2J_{C-P}$ = 8.5 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 566 (M-CO, 11), 510 (M-3CO, 68), 482 (M-4CO, 26), 454 (M-5CO, 19), 356 (M-5CO-Mo, 100).

4f was obtained by reaction of **1b** with 2-furancarboxaldehyde in the presence of 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene. It was characterized only by ^{31}P NMR in the reaction mixture and hydrolyzed directly to the corresponding phosphininone **6f**, as shown below.

4f : ^{31}P NMR (THF) δ 35.8 ppm.

Hydrolysis and methanolysis reactions of complexes **4**

a) Addition of HCl_{aq} (3 N solution) to a solution of complex **4d** (2.0 g, 3.0 mmol) in THF and stirring at room temperature for 6 h afforded quantitatively complex **5**, which was recrystallized from a CH_2Cl_2/hexane mixture. **5** : colorless solid, mp 163°C (dec).

^{31}P NMR (THF) δ 24.2 ($^1J_{P-W}$ = 249 Hz).

^{1}H NMR (C_6D_6) δ 0.78 (d, $^3J_{H-P}$ = 15.0 Hz, CMe_3) 2.14 (dd, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 9.9 Hz, 1H, *CH*$_2$CHOMe), 2.71 (*AB*, $^2J_{A-B}$ = 11.4 Hz, 1H, PCH_2), 2.71 (s, OMe), 2.90 (A*B*, $^2J_{A-B}$ = 11.4, $^2J_{H-P}$ = 11.4 Hz, 1H, PCH_2), 3.05 (dd, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 4.4 Hz, 1H, *CH*$_2$CHOMe), 3.49 (dd, $^2J_{H-P}$ = 12.2 Hz, $^3J_{H-H}$ = 9.6 Hz, PCH), 4.17 (m, 1H, *CH*OMe), 6.59 (t, 1H), 6.83 (d, 1H), 7.01 (m, 1H), 8.38 (d, $^3J_{H-H}$ = 4.3 Hz, 1H).

^{13}C NMR (C_6D_6) δ 26.46 (d, $^2J_{C-P}$ = 5.0 Hz, C*Me*$_3$), 34.11 (d, $^1J_{C-P}$ = 15.1 Hz, *C*Me$_3$), 43.11 (d, $^1J_{C-P}$ = 8.1 Hz, P*C*H$_2$CO), 47.39 (s, CO*C*H$_2$CH), 49.82 (d, $^1J_{C-P}$ = 11.6 Hz, PCH), 57.38 (s, OMe), 79.24 (d, $^2J_{C-P}$ = 7.5 Hz, *C*HOMe), 122.46, 125.26, 136.20, 149.51, 157.52 (C), 197.35 (d, $^2J_{C-P}$ = 7.05 Hz, *cis* CO), 199.44 (s, CH$_2$*C*OCH$_2$) ppm.

Mass spectrum (^{184}W) *m/e* (relative intensity) 575 (M-CO, 23), 547 (M-2CO, 43), 406 (M-5CO-C_4H_9, 100).

Anal calc for $C_{20}H_{22}NO_7PW$: C, 39.82; H, 3.68. Found : C, 39.57; H, 3.69.

b) An excess of MeONa (2 mmol in MeOH) was added to solutions of complexes **4b,e,f** (1 mmol) in ether at 0°C. After stirring for 2 h at room temperature the reaction mixture was hydrolyzed at 0°C with aqueous HCl. The final product was purified by column chromatography on silica gel.

6b was obtained from **4b** in 90% yield after chromatography with hexane/ether (60:40) as eluent. **6b** : yellow solid; mp 170°C (dec).

^{31}P NMR ($CDCl_3$) δ 28.4 ppm.

^1H NMR (C_6D_6) δ 0.71 (d, $^3J_{H-P}$ = 15.0 Hz, CMe_3), 2.4 (*AB*, $^2J_{AB}$ = 23 Hz, $^2J_{H-P}$ = 4.7 Hz, 1H, PCH_2), 2.6 (m, A*B*, 1H, PCH_2), 2.9 (2H, CO CH_2), 5.52 (dt, $^3J_{H-P}$ = 15.6 Hz, $^3J_{H-H}$ = 4.1 Hz, PC=CH), 6.01 (m, 1H), 6.32 (d, $^3J_{H-H}$ = 7.7 Hz, 1H), 6.65 (m, 1H), 8.50 (d, $^3J_{H-H}$ = 4.9 Hz, 1H).

^{13}C NMR ($CDCl_3$) δ 26.24 (d, $^2J_{C-P}$ = 7.0 Hz, C*Me*$_3$), 34.38 (d, $^1J_{C-P}$ = 11.6 Hz, *C*Me_3), 38.48 (d, $^1J_{C-P}$ = 9.1 Hz, PCH_2), 41.61 (s, CO*C*H_2), 121.14 (C=*C*H), 122.90, 135.33 (*C*), 135.82, 138.40, 155.24, 161.29 (d, $^2J_{C-P}$ = 21.1 Hz, N*C*), 201.41 (d, $^2J_{C-P}$ = 8.6 Hz, PCH_2*C*OCH_2), 208.19 (d, $^2J_{C-P}$ = 7.5 Hz, CO), 210.08 (d, $^2J_{C-P}$ = 9.1 Hz, CO), 215.69 (d, $^2J_{C-P}$ = 33.2 Hz, CO), 220.96 (d, $^2J_{C-P}$ = 7.5 Hz, CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (rel intensity) 457 (M, 11), 345 (M-4CO, 23), 190 (M-Mo(CO)$_4$-C_4H_9, 100).

6e was obtained from **4e** in 45% yield after chromatography. Yellow oil.

^{31}P NMR ($CDCl_3$) δ 50.9.

^1H NMR ($CDCl_3$) δ 1.15 (d, $^3J_{H-P}$ = 15.3 Hz, CMe_3), 3.07 (*AB*, $^2J_{A-B}$ = 12.9 Hz, $^2J_{H-P}$ = 2.4 Hz, 1H, PCH_2), 3.2 (m, 2H), 3.34 (A*B*, $^2J_{A-B}$ = 12.9 Hz, $^2J_{H-P}$ = 4.1 Hz, 1H, PCH_2), 6.50 (dt, $^3J_{H-P}$ = 20.3 Hz, $^3J_{H-H}$ = 3 Hz, =CH), 6.93 (m, 1H), 7.05 (m, 1H), 7.20 (m, 1H).

^{13}C NMR ($CDCl_3$) δ 27.57 (d, $^2J_{C-P}$ = 6.4 Hz, C*Me*$_3$), 34.98 (d, $^1J_{C-P}$ = 11.2 Hz, *C*Me_3), 42.81 (s, CO*C*H_2), 43.23 (d, $^1J_{C-P}$ = 7.4 Hz, PCH_2), 125.88, 127.23, 127.7, 130.29 (d, J_{C-P} = 19.1 Hz, *C*), 139.19, 141.70 (d, J_{C-P} = 18.1 Hz, *C*), 200.75 (C=O), 205.39 (d, $^2J_{C-P}$ = 7.9 Hz, *cis* CO), 209.34 (d, $^2J_{C-P}$ = 24.6 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (rel intensity) 490 (M, 15), 462 (M-CO, 26), 434 (M-2CO, 11), 406 (M-3CO, 92), 378 (M-4CO, 38), 350 (M-5CO, 74), 252 (M-5CO-Mo, 100).

6f was obtained by hydrolysis of the crude **4f**. Yield 40% from **1b**. Colorless oil.

^{31}P NMR ($CDCl_3$) δ 48.2.

^1H NMR ($CDCl_3$) δ 1.12 (d, $^3J_{H-P}$ = 15.5 Hz, CMe_3), 3.05 (*AB*, $^2J_{A-B}$ = 12.9 Hz, $^2J_{H-P}$ = 3.0 Hz, 1H, PCH_2), 3.2 (m, 2H, $COCH_2$), 3.30 (A*B*, $^2J_{A-B}$ = 12.9 Hz, $^2J_{H-P}$ = 3.8 Hz, 1H, PCH_2), 6.35 (s, 2H), 6.58 (dt, $^3J_{H-P}$ = 20.3 Hz, $^3J_{H-H}$ = 4.3 Hz, =CH), 7.3 (s, 1H).

^{13}C NMR ($CDCl_3$) δ 27.26 (d, $^2J_{C-P}$ = 6.9 Hz, C*Me*$_3$), 34.67 (d, $^1J_{C-P}$ = 12.1 Hz, *C*Me_3), 42.49 (s, CO*C*H_2), 42.92 (d, $^1J_{C-P}$ = 7.9 Hz, PCH_2), 108.51 (d, $^2J_{C-P}$ = 3.8 Hz, C=*C*H), 111.59, 126.91 (d, $^1J_{C-P}$ = 20.2 Hz, P-*C*=), 135.66, 142.21, 152.89 (d, $^2J_{C-P}$ = 14.4 Hz, *C*), 200.67 (d, $^2J_{C-P}$ = 5.6 Hz, C=O), 205.37 (d, $^2J_{C-P}$ = 8.6 Hz, *cis* CO), 209.72 (d, $^2J_{C-P}$ = 25.2 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 474 (M, 9), 446 (M-CO, 21), 418 (M-2CO, 26), 390 (M-3CO, 26), 362 (M-4CO, 23), 334 (M-5CO, 57), 236 (M-5CO-Mo, 68), 180 (236-C_4H_8, 100).

Synthesis of the P,N chelated complex **7a**

Complex **4d** was heated in toluene at 80°C for 8 h to afford quantitatively the chelated complex **7a** : yellow solid.

^{31}P NMR (C_6D_6) δ 41.0 ($^1J_{P-W}$ = 242 Hz).

^1H NMR (C_6D_6) δ 0.15 (s, Si Me_3), 0.81 (d, $^3J_{H-P}$ = 14.6 Hz, CMe_3), 2.60 (*AB*, $^2J_{A-B}$ = 16.6 Hz, $^2J_{H-P}$ = 8.0 Hz, 1H, PCH_2), 2.76 (s, OMe), 3.1-3.3 (m, 2H), 4.0 (m, 1H, *CH*OMe), 5.18 (br, 1H, =CH), 5.93 (m, 1H), 6.70 (m, 1H), 6.95 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 8.85 (d, $^3J_{H-H}$ = 5.6 Hz, 1H).

^{13}C NMR (C_6D_6) δ 0.02 ($SiMe_3$), 25.17 (d, $^2J_{C-P}$ = 6.0 Hz, C*Me*$_3$), 29.73 (d, $^1J_{C-P}$ = 17.1 Hz, PCH_2), 32.0 (d, $^1J_{C-P}$ = 19.1 Hz, *C*Me_3), 52.80 (d, $^1J_{C-P}$ = 17.1 Hz, PCH), 57.54 (s, OMe), 78.51 (d, $^2J_{C-P}$ = 4.2 Hz, *C*HOMe), 107.78 (=CH), 122.79, 136.70, 149.03 (d, J_{C-P} = 7.0 Hz), 156.21, 164.16 (d, J_{C-P} = 12.1 Hz, C), 205.72 (d, $^2J_{C-P}$ = 5.5 Hz, *cis* CO), 206.9 (d, $^2J_{C-P}$ = 7.6 Hz, *cis* CO), 210.45 (d, $^2J_{C-P}$ = 32.4 Hz, *trans* CO), 211.32 (d, $^2J_{C-P}$ = 4.5 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 647 (M, 20), 619 (M-CO, 32), 476 (100).

Decomplexation procedures

a) With S_8 : Complex **4a** (0.75 g, 1.5 mmol) was reacted with excess S_8 (0.23 g) in toluene at 100°C for 4 h. After evaporation of the solvent, the final product was purified by column chromatography with hexane/ether 60:40 as eluent. The sulfide **8** was obtained in 67% yield as a colorless solid, mp 170°C.

^{31}P NMR ($CDCl_3$) δ 57.5.

^1H NMR (C_6D_6) δ 0.84 (d, $^3J_{H-P}$ = 16.2 Hz, CMe_3), 1.9-2.1 (m, 1H, PCH_2), 2.2-2.4 (m, 1H, PCH_2), 2.93 (s, OMe), 4.06 (dd, $^2J_{H-P}$ = 11.1 Hz, $^3J_{H-H}$ = 7.8 Hz, PCH), 4.9 (m, *CH*OMe), 5.3-5.5 (m, 1H, HC=), 5.84 (A*B*, J_{AB} = 10.1 Hz, =CH), 6.6 (m, 1H, py), 7.1 (m, 1H, py), 8.07 (d, 1H, py), 8.32 (d, 1H, py).

^{13}C NMR ($CDCl_3$) δ 24.17 (C*Me*$_3$), 27.35 (d, $^1J_{C-P}$ = 46.8 Hz, PCH_2), 34.94 (d, $^1J_{C-P}$ = 46.8 Hz, *C*Me_3), 47.18 (d, $^1J_{C-P}$ = 35.2 Hz, PCH), 55.76 (OMe), 78.96 (*C*HOMe), 121.33 (d, J_{C-P} = 6.0 Hz, =CH), 123.06 (d, J_{C-P} = 27.2 Hz, =CH), 130.55 (d, J_{C-P} = 5.5 Hz), 136.01, 149.03, 155.02 (C(py)) ppm.

Mass spectrum *m/e* (relative intensity) 295 (M, 27), 175 (66), 160 (M-*t*Bu-Py, 100).

b) With dppe : complex **6b** (0.60 g, 1.3 mmol) and dppe (0.52 g, 1.3 mmol) were heated at 100°C for 3 h in toluene (5 mL). Hexane was added to the cooled reaction mixture in order to precipitate the $(CO)_4$Mo(dppe) complex. After filtration and evaporation of the solvent, the phosphine **9a** was obtained in 44% yield by crystallization from hexane at −20°C.

1-*t*-Butyl-6-(2-pyridyl)-1,2-dihydro-3(4*H*)-phosphininone **9a** : pale yellow solid.

^{31}P NMR (C_6D_6) δ −1.6.

^1H NMR (C_6D_6) δ 0.97 (d, $^3J_{H-P}$ = 12.1 Hz, CMe_3), 2.38 (*AB*, J_{AB} = 13.8 Hz, J = 4.5 Hz, 1H, CH_2), 2.6-2.9 (m, 3H, CH_2), 6.6 (m, 1H), 6.9-7.1 (m, 2H), 7.60 (m, 1H), 8.45 (d, $^3J_{H-H}$ = 3.8 Hz) ppm.

^{13}C NMR (C_6D_6) δ 28.48 (d, $^2J_{C-P}$ = 13.6 Hz, C*Me*$_3$), 31.65 (d, $^1J_{C-P}$ = 19.1 Hz, *C*Me_3), 34.59 (d, $^1J_{C-P}$ = 23.1 Hz, PCH_2), 42.45 (CO*C*H_2), 121.60 (d, $^2J_{C-P}$ = 14.6 Hz, =CH), 121.86, 135.83, 138.61 (d, J_{C-P} = 5.0 Hz), 149.68 (unsaturated C are not detected), 203.70 (*C*O).

Mass spectrum m/e (relative intensity) 247 (M, 26), 190 (M-tBu, 100).

Anal calc for $C_{14}H_{18}NOP$: C, 68.00; H, 7.34. Found : C, 67.71; H, 7.33.

1-t-Butyl-6-(2-thienyl)-1,2-dihydro-3(4H)-phosphininone **9b** : The same decomplexation procedure as for **9a**, starting from complex **6e** led to **9b** in 70% yield after chromatography. Yellow oil.

^{31}P NMR ($CDCl_3$) δ 3.8.

^{1}H NMR ($CDCl_3$) δ 0.99 (d, $^3J_{H-P}$ = 12.6 Hz, CMe_3), 2.79 (AB, $^2J_{A-B}$ = 13.8 Hz, $^2J_{H-P}$ = 7.4 Hz, 1H, PCH_2), 2.91 (AB, $^2J_{A-B}$ = 13.8 Hz, $^2J_{H-P}$ = 3.8 Hz, 1H, PCH_2), 3.01 (AB, $^2J_{A-B}$ = 22.2 Hz, $^3J_{H-H}$ = 4.0 Hz, 1H, CH_2), 3.24 (AB, $^2J_{A-B}$ = 22.2 Hz, $^3J_{H-H}$ = 4.4 Hz, $^4J_{H-P}$ = 2.1 Hz, 1H, CH_2), 6.58 (dt, $^3J_{H-P}$ = 5.7 Hz, $^3J_{H-H}$ = 4.3 Hz, P-C=CH), 7.0 (m, 1H), 7.2 (m, 2H).

^{13}C NMR ($CDCl_3$) δ 28.34 (d, $^2J_{C-P}$ = 13.3 Hz, CMe_3), 31.80 (d, $^1J_{C-P}$ = 18.6 Hz, CMe_3), 34.93 (d, $^1J_{C-P}$ = 23.9 Hz, PCH_2), 42.43 (s, $COCH_2$), 125.0, 125.2, 127.6, 129.94 (d, J_{C-P} = 20.0 Hz, C), 131.98, 146.72 (d, J_{C-P} = 32.7 Hz, C), 205.13 (C=O) ppm.

Mass spectrum m/e (relative intensity) 252 (M, 21), 196 (M-C_4H_8, 47), 57 (C_4H_9, 100).

Synthesis of phosphinines **10a** *and* **10b**

t-Butyldimethylchlorosilane (0.19 g, 1.3 mmol) was added to a solution of **9a** (0.30 g, 1.2 mmol) and triethylamine (0.33 mL, 2.4 mmol) in THF, at room temperature. After 20 min, the ^{31}P NMR spectrum of the reaction mixture showed quantitative formation of the silylated enol ether : δ −36.3 ppm. Ether was added and the ammonium salt was separated by filtration. The solution was evaporated to dryness and thermolyzed at 250°C for about 15 min in a Kugelrohr oven. The crude product was distilled at 250°C/3 mm Hg. Phosphinine **10a** was obtained in 79% yield (with respect to **9a**) as a colorless oil.

3-(t-Butyldimethylsilyloxy)-6-(2-pyridyl)phosphinine **10a** :

^{31}P NMR (ether) δ 209.

^{1}H NMR (C_6D_6) δ 0.10 (s, 6H, $SiMe_2$), 0.97 (s, 9H, $SiCMe_3$), 6.71 (broad t, J = 6.0 Hz), 7.03 (dt, J_{H-P} = 9.3 Hz, J = 2.6 Hz), 7.17 (t, J = 6.1 Hz), 7.82 (broad d, J = 7.4 Hz), 8.07 (dd, J_{H-P} = 37.3 Hz, J_{H-H} = 2.4 Hz), 8.57 (d, J = 4.0 Hz), 8.79 (dd, J_{H-P} = 9.2 Hz, J = 5.17 Hz).

^{13}C NMR (C_6D_6) δ −4.38 ($SiMe_2$), 18.35 ($SiCMe_3$), 25.77 ($SiCMe_3$), 120.30 (d, J_{C-P} = 16.6 Hz), 122.01, 124.13 (d, J_{C-P} = 14.1 Hz), 136.47, 136.84 (d, J_{C-P} = 14.1 Hz), 141.28 (d, J_{C-P} = 51.8 Hz), 149.92, 159.1 (d, J_{C-P} = 25.7 Hz), 159.70 (d, J_{C-P} = 16.1 Hz) 161.20 (d, J_{C-P} = 46.8 Hz) ppm.

Mass spectrum m/e (relative intensity) 303 (M, 32), 246 (M-tBu, 100).

6-(2-Thienyl)-3-phosphininol **10b** was prepared through an analogous procedure and purified by column chromatography with hexane/ether 80:20 as eluent : colorless oil.

Yield 15%.

^{31}P NMR ($CDCl_3$) δ 202.6.

^{1}H NMR ($CDCl_3$) δ 6.9-7.1 (m, 2H), 7.2-7.4 (m, 2H), 7.91 (dd, $^2J_{H-P}$ = 33.1 Hz, J_{H-H} = 2.6 Hz), 8.0 (m, 1H) ppm.

Mass spectrum m/e 194 (M, 100).

Synthesis of the (1,2-dihydrophosphete)Mo(CO)$_5$ complexes, **12**. *General Procedure*

A solution of complex **1b** (1.0 g, 2.2 mmol) in THF was cooled to −78°C, nBuLi (1.5 mL, 1.6 M solution in hexane) was then added. After a few minutes, an excess (3 mmol) of the suitable aldehyde (2-phenyl-2-pentenal, 3-ethoxy-2-methyl-2-propenal or 2-methyl-3-phenyl-2-propenal) was added. The reaction mixture was then allowed to warm to room temperature. After hydrolysis, evaporation of the solvent and extraction with ether, the final product was purified by chromatography with hexane/ether (99:1) as eluent.

12a : was obtained in 58% yield, as a mixture of two isomers (75:25 ratio).

Minor isomer : ^{31}P NMR (C_6D_6) δ 99.4 ppm.

The major isomer was obtained in pure form after crystallization from hexane :

^{31}P NMR (C_6D_6) δ 78.6.

^{1}H NMR (C_6D_6) δ 1.11 (t, $^3J_{H-H}$ = 7.2 Hz, CH_2CH_3), 1.30 (d, $^3J_{H-P}$ = 14.8 Hz, CMe_3), 1.6-1.8 (m, 1H, CH_2), 1.9-2.3 (m, 1H, CH_2), 3.1 (m, 1H, PCH), 6.57 (dd, $^2J_{H-P}$ = 22.4 Hz, $^4J_{H-H}$ = 1.2 Hz, =CH), 7.4 (m, Ph).

^{13}C NMR ($CDCl_3$) δ 14.96 (d, $^3J_{C-P}$ = 3.1 Hz, CH_2CH_3), 22.6 (s, CH_2), 27.18 (d, $^2J_{C-P}$ = 6.7 Hz, CMe_3), 34.45 (d, $^1J_{C-P}$ = 4.5 Hz, CMe_3), 43.28 (d, $^1J_{C-P}$ = 27.5 Hz, PCH), 126.76, 127.22 (d, $^1J_{C-P}$ = 32.3 Hz, =CH), 129.3, 130.1, 134.34 (d, J_{C-P} = 15.2 Hz), 155.61 (d, J_{C-P} = 5.3 Hz), 206.68 (d, $^2J_{C-P}$ = 8.8 Hz, *cis* CO), 210.66 (d, $^2J_{C-P}$ = 23.7 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) m/e (relative intensity) 470 (M, 9), 386 (M-3CO, 62), 358 (M-4CO, 36), 330 (M-5CO, 100).

Anal calc for $C_{20}H_{21}O_5PMo$: C, 51.30; H, 4.52. Found : C, 51.67; H, 4.72.

12b was obtained in 75% yield, as a mixture of two isomers in a 88:12 ratio.

Minor isomer : ^{31}P NMR (C_6D_6) δ 107.5 ppm.

Major isomer : ^{31}P NMR (C_6D_6) δ 83.1 ppm.

^{1}H NMR ($CDCl_3$) δ 1.20 (d, $^3J_{H-P}$ = 14.2 Hz, CMe_3), 1.34 (t, $^3J_{H-H}$ = 6.8 Hz, CH_2CH_3), 1.90 (s, Me), 3.4-3.8 (m, 2H, OCH_2CH_3), 4.25 (d, $^2J_{H-P}$ = 4.4 Hz, $CHOEt$), 6.18 (d, $^2J_{H-P}$ = 25.1 Hz, =CH).

^{13}C NMR ($CDCl_3$) δ 14.93 (s, CH_2CH_3), 16.65 (d, $^3J_{C-P}$ = 13.8 Hz, =C-CH_3), 26.20 (d, $^2J_{C-P}$ = 6.74 Hz, CMe_3), 32.93 (s, CMe_3), 67.42 (s, OCH_2), 77.47 (d, $^1J_{C-P}$ = 67.5 Hz, PCH-O), 128.52 (d, $^1J_{C-P}$ = 31.7 Hz, =CH), 154.95 (s, =C), 206.71 (d, $^2J_{C-P}$ = 8.9 Hz, *cis* CO), 210.51 (d, $^2J_{C-P}$ = 25.1 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) m/e (relative intensity) 424 (M, 19), 368 (M-2CO, 38), 224 (100).

12c : was obtained in 54% yield, as a mixture of two isomers in 75:25 ratio.

Minor isomer : ^{31}P NMR (ether) δ 112.5 ppm.

Major isomer : ^{31}P NMR (ether) δ 94.2 ppm.

^{1}H NMR (C_6D_6) δ 0.98 (d, $^3J_{H-P}$ = 14.4 Hz, CMe_3), 1.44 (s, CH_3), 3.52 (d, $^2J_{H-P}$ = 8.0 Hz, CH-Ph), 5.65 (d, $^2J_{H-P}$ = 16.6 Hz, =CH), 6.9-7.2 (m, Ph) ppm.

Mass spectrum (^{98}Mo) m/e (relative intensity) 456 (M, 28), 372 (M-3CO, 53), 256 (100).

Anal calc for $C_{19}H_{19}O_5P$ Mo : C, 50.24; H, 4.22; Found : C, 51.18; H, 4.15.

Cycloaddition reactions of complex **12b**

• *With N-phenylmaleimide*

A solution of complex **12b** (1.5 g, 3.6 mmol) and N-phenylmaleimide (0.62 g, 3.6 mmol) in THF was stirred at room temperature for 1 h. After evaporation of the solvent, the

final product was purified by column chromatography with hexane/ether (60:40) as eluent. **13a** was obtained as a mixture of two isomers in 85:15 ratio (80% yield).

Minor isomer : ^{31}P NMR (ether) δ 35.6 ppm.

Major isomer : ^{31}P NMR (ether) δ 33.5.

^{1}H NMR ($CDCl_3$) δ 1.13 (t, $^{3}J_{H-H}$ = 6.9 Hz, CH_2CH_3), 1.44 (d, $^{3}J_{H-P}$ = 16.7 Hz, CMe_3), 2.19 (s, =C-CH_3), 3.5 (m, 2H), 3.6-3.7 (m, 1H, OCH_2), 4.09 (dd, $^{3}J_{H-P}$ = 9.1 Hz, $^{2}J_{H-P}$ = 5.3 Hz, PCH), 4.26 (d, $^{3}J_{H-H}$ = 3.6 Hz, *CH*OEt), 5.97 (d, $^{2}J_{H-P}$ = 32.4 Hz, =CH), 7.2-7.5 (m, Ph).

^{13}C NMR ($CDCl_3$) δ 15.81 (CH_2CH_3), 27.8 (d, $^{3}J_{C-P}$ = 8.8 Hz, =C-*C*H_3), 28.51 (d, $^{2}J_{C-P}$ = 7.9 Hz, C*Me*$_3$), 36.75 (d, $^{1}J_{C-P}$ = 10.8 Hz, *C*Me_3), 43.48 (d, J_{C-P} = 6.8 Hz, *C*HCO-), 48.90 (d, J_{C-P} = 5.0 Hz, *C*HCO-), 67.08 (s, O*C*H_2CH_3), 73.93 (d, $^{3}J_{C-P}$ = 8.2 Hz, *C*HOEt), 121.51 (d, $^{1}J_{C-P}$ = 24.6 Hz, =CH), 127.06, 129.35, 129.80, 132.33 (*C*-N), 147.38 (d, $^{2}J_{C-P}$ = 6.0 Hz, =*C*-Me), 173.38 (d, J_{C-P} = 7.3 Hz, *C*O-N), 175.24 (d, J_{C-P} = 2.2 Hz, *C*O-N), 206.50 (d, $^{2}J_{C-P}$ = 8.4 Hz, *cis* CO), 210.64 (d, $^{2}J_{C-P}$ = 23.4 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 597 (M, 6), 541 (M-2CO, 28), 513 (M-3CO, 45), 485 (M-4CO, 36), 457 (M-5CO, 100).

- *With dimethyl 2-butynedioate*

A solution of complex **12b** (1.5 g, 3.6 mmol) and dimethyl 2-butynedioate (0.9 g, 7.2 mmol) in toluene (2 mL) was heated at 40°C for 4 h. The final product was purified by column chromatography with hexane/ether (90:10) as eluent. Yield : 60% after crystallization from ether/hexane. A single isomer is observed after purification.

13b : colorless solid, mp 92°C.

^{31}P NMR (ether) δ 18.8.

^{1}H NMR ($CDCl_3$) δ 1.16 (t, $^{3}J_{H-H}$ = 6.8 Hz, CH_2CH_3), 1.32 (d, $^{3}J_{H-P}$ = 16.0 Hz, CMe_3), 2.08 (s, =C-CH_3), 3.3-3.6 (m, 2H, O*C*H_2CH_3), 3.80 (s, CO_2Me), 3.83 (d, J_{H-P} = 0.6 Hz, CO_2Me), 5.01 (s, *CH*OEt), 6.00 (d, $^{2}J_{H-P}$ = 31.3 Hz, =CH).

^{13}C NMR ($CDCl_3$) δ 16.21 (CH_2CH_3), 23.86 (d, $^{3}J_{C-P}$ = 8.3 Hz, =C-CH_3), 28.17 (d, $^{2}J_{C-P}$ = 7.2 Hz, C*Me*$_3$), 37.07 (d, $^{1}J_{C-P}$ = 14.8 Hz, *C*Me_3), 53.45 (OMe), 53.71 (OMe), 64.59 (O*C*H_2CH_3), 74.05 (d, $^{3}J_{C-P}$ = 4.8 Hz, *C*HOEt), 120.43 (d, $^{1}J_{C-P}$ = 32.2 Hz, =CH), 133.93 (d, $^{1}J_{C-P}$ = 14.4 Hz, P*C*-CO_2), 143.55 (d, $^{2}J_{C-P}$ = 9.9 Hz, P-C=*C*), 143.70 (d, $^{2}J_{C-P}$ = 5.6 Hz, P-C=*C*), 167.50 (d, $^{2}J_{C-P}$ = 26.2 Hz, P-C-*C*O_2), 163.58 (-*C*O_2-), 205.83 (d, $^{2}J_{C-P}$ = 8.7 Hz, *cis* CO), 210.23 (d, $^{2}J_{C-P}$ = 23.0 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 538 (M-CO, 15), 482 (M-3CO, 21), 397 (M-4CO-*t*Bu, 42), 324 (100).

Anal calc for $C_{21}H_{25}O_{10}PMo$: C, 44.70; H, 4.47; Found : C, 44.60; H, 4.35.

- *With ethyl 3-phenyl-2-propynoate*

A solution of complex **12b** (1.5 g, 3.6 mmol) and ethyl 3-phenyl-2-propynoate (2.3 mL, 14 mmol) in a small amount of toluene (1 mL) was heated at 80°C for 24 h. The final product was purified by column chromatography with hexane/ether (90:10) as eluent. Yield : 45%. A single isomer is obtained after purification.

13c : colorless solid; mp 110°C.

^{31}P NMR (ether) δ 17.6 ppm.

^{1}H NMR ($CDCl_3$) δ 0.73 (t, $^{3}J_{H-H}$ = 7.1 Hz, CH_2CH_3), 0.92 (t, $^{3}J_{H-H}$ = 6.9 Hz, CH_2CH_3), 1.34 (d, $^{3}J_{H-H}$ = 15.6 Hz, CMe_3), 2.11 (s, =C-CH_3), 3.05 (m, 1H, OCH_2), 3.37 (m, 1H, OCH_2), 3.7-3.9 (m, 2H, OCH_2), 4.72 (s, 1H, *CH*OEt), 6.07 (d, $^{2}J_{H-P}$ = 30.5 Hz, =CH), 7.1-7.4 (m, Ph).

^{13}C NMR ($CDCl_3$) δ 13.72 (CH_2CH_3), 15.84 (CH_2CH_3), 24.18 (d, $^{3}J_{C-P}$ = 8.4 Hz, =C-*C*H_3), 27.83 (d, $^{2}J_{C-P}$ = 7.1 Hz, C*Me*$_3$), 36.01 (d, $^{1}J_{C-P}$ = 15.4 Hz, *C*Me_3), 62.15 (O*C*H_2CH_3), 65.15 (O*C*H_2CH_3), 77.06 (*C*HOEt), 120.26 (d, $^{1}J_{C-P}$ = 32.4 Hz, =CH), 129.60 (d, $^{2}J_{C-P}$ = 18.2 Hz, P-*C*-CO_2-), 140.13 (C(Ph)), 144.88 (d, $^{2}J_{C-P}$ = 4.6 Hz, PC=*C*), 150.03 (P-C=*C*), 168.54 (d, $^{2}J_{C-P}$ = 17.9 Hz, P-C-*C*O_2), 206.36 (d, $^{2}J_{C-P}$ = 8.6 Hz, *cis* CO), 210.83 (d, $^{2}J_{C-P}$ = 22.8 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 570 (M-CO, 13), 542 (M-2CO, 21), 514 (M-3CO, 26), 429 (M-4CO-*t*Bu, 100).

Anal calc for $C_{26}H_{29}O_8PMo$: C, 52.36; H, 4.90. Found : C, 52.21; H, 4.83.

- *With phenylacetylene*

A solution of complex **12b** (1.5 g, 3.6 mmol) and phenylacetylene (1.58 mL, 14.4 mmol) in a small amount of toluene (1 mL) was heated at 75°C for 2 h. The final product was purified by column chromatography with hexane/ether (95:5) as eluent and crystallization from hexane/ether mixtures. Yield : 36%.

^{31}P NMR (ether) δ 11.1 ppm.

^{1}H NMR ($CDCl_3$) δ 0.89 (t, $^{3}J_{H-H}$ = 6.9 Hz, CH_2CH_3), 1.28 (d, $^{3}J_{H-P}$ = 15.4 Hz, CMe_3), 2.18 (s, =C-CH_3), 3.12 (q, O*C*H_2CH_3), 5.18 (s, *CH*OEt), 6.13 (broad d, $^{2}J_{H-P}$ = 26.3 Hz, =CH), 6.37 (broad d, $^{2}J_{H-P}$ = 25.9 Hz, =CH), 7.3-7.5 (m, Ph).

^{13}C NMR (C_6D_6) δ 15.37 (CH_2CH_3), 23.70 (d, $^{3}J_{C-P}$ = 8.1 Hz, =C-*C*H_3), 26.54 (d, $^{2}J_{C-P}$ = 6.0 Hz, C*Me*$_3$), 33.13 (d, $^{1}J_{C-P}$ = 19.3 Hz, *C*Me_3), 61.46 (O*C*H_2CH_3), 73.91 (d, $^{3}J_{C-P}$ = 6.5 Hz, *C*HOEt), 118.66 (d, $^{1}J_{C-P}$ = 33.4 Hz, P-CH=), 121.40 (d, $^{1}J_{C-P}$ = 30.6 Hz, P-*C*H=), 141.36 (C(Ph)), 146.72 (P-C=*C*), 147.89 (P-C=*C*), 206.52 (d, $^{2}J_{C-P}$ = 8.0 Hz, *cis* CO), 210.8 (d, $^{2}J_{C-P}$ = 22.8 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 526 (M, 26), 414 (M-4CO, 100), 386 (M-5CO, 47).

Anal calc for $C_{23}H_{25}O_6PMo$: C, 52.68; H, 4.81. Found : C, 52.88; H, 4.74.

- *With 2-ethynylpyridine*

A solution of complex **12b** (1.5 g, 3.6 mmol) and ethynylpyridine (0.73 mL, 7.2 mmol) in toluene (4 mL) was heated at 70°C for 1 h. The final product was purified by chromatography with hexane/ether (70:30) as eluent. Yield : 30%. **13e** : colorless solid; mp 105°C.

^{31}P NMR (ether) δ 13.7.

^{1}H NMR ($CDCl_3$) δ 0.91 (t, $^{3}J_{H-H}$ = 6.9 Hz, CH_2CH_3), 1.30 (d, $^{3}J_{H-P}$ = 15.5 Hz, C*Me*$_3$), 2.15 (s, =C-CH_3), 3.1-3.2 (m, 2H, O*C*H_2CH_3), 5.42 (s, 1H, *CH*OEt), 6.13 (broad d, $^{2}J_{H-P}$ = 27.9 Hz, =CH), 7.15 (dm, $^{2}J_{H-P}$ = 26.4 Hz, *H*C=C-Py), 7.2-7.3 (m, 1H), 7.59 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 7.7 (m, 1H), 8.66 (d, $^{3}J_{H-H}$ = 4.0 Hz, 1H).

^{13}C NMR ($CDCl_3$) δ 15.39 (CH_2CH_3), 23.92 (d, $^{3}J_{C-P}$ = 8.5 Hz, =C-*C*H_3), 26.83 (d, $^{2}J_{C-P}$ = 6.2 Hz, C*Me*$_3$), 33.57 (d, $^{1}J_{C-P}$ = 19.7 Hz, *C*Me_3), 59.8 (O*C*H_2CH_3), 72.15 (d, $^{3}J_{C-P}$ = 6.3 Hz, *C*HOEt), 118.88 (d, $^{1}J_{C-P}$ = 33.5 Hz, P-*C*H=CMe), 121.41, 123.15, 124.16 (d, $^{1}J_{C-P}$ = 30.6 Hz, P-*C*H=CPy), 136.45, 145.59 (d, $^{3}J_{C-P}$ = 2.6 Hz, C(Py)), 146.00 (d, $^{2}J_{C-P}$ = 3.9 Hz, P-C=*C*Me), 149.23, 155.93 (d, $^{2}J_{C-P}$ = 8.9 Hz, P-C=*C*-Py), 205.90 (d, $^{2}J_{C-P}$ = 9.0 Hz, *cis* CO), 210.45 (d, $^{2}J_{C-P}$ = 21.1 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 527 (M, 19), 471 (M-2CO, 20), 443 (M-3CO, 28), 415 (M-4CO, 43), 387 (M-4CO, 53), 329 (M-4CO-*t*BuH, 100).

Anal calc for $C_{22}H_{24}O_6$ NPMo : C, 50.30; H, 4.60. Found : C, 50.71; H, 4.88.

Cycloaddition reaction of complex **12c** *with benzoquinone*

A solution of **12c** (0.23 g, 0.5 mmol) and 1,4-benzoquinone (0.21 g, 2 mmol) in xylene was heated at 110°C for 20 min. After evaporation the final product was purified by column chromatography. The excess benzoquinone was eluted with hexane/ether 90:10; complex **14a** was recovered then with hexane/ether 80:20 as eluent, as a mixture of two isomers in a 70:30 ratio. Yield : 50%. Colorless solid.

^{31}P NMR (C_6D_6) δ 166.0 (minor isomer), 144.4 (major isomer).

^{1}H NMR (C_6D_6) δ 0.97 (d, $^3J_{H-P}$ = 15.8 Hz, CMe_3), 1.45 (broad s, CH_3), 4.06 (broad s, C*H* Ph), 5.68 (d, $^3J_{H-H}$ = 10.1 Hz, =CH-CO), 5.98 (d, $^3J_{H-H}$ = 10.8 Hz, =CH CO), 6.01 (d, $^2J_{H-P}$ = 29.1 Hz, P-CH=), 6.44 (dd, $^3J_{H-H}$ = 10.3 Hz, $^4J_{H-H}$ = 3.1 Hz), 6.59 (dd, $^3J_{H-H}$ = 10.7 Hz, $^4J_{H-H}$ = 3.0 Hz), 6.7-7.0 (m, 5H, Ph).

^{13}C NMR (C_6D_6) δ 25.35 (d, $^2J_{C-P}$ = 7.5 Hz, C*Me*$_3$), 25.78 (d, $^3J_{C-P}$ = 8.4 Hz, C-*C*H$_3$), 37.87 (d, $^1J_{C-P}$ = 13.0 Hz, *C*Me$_3$), 55.14 (d, $^3J_{C-P}$ = 9.3 Hz, *C*H-Ph), 74.64 (d, $^2J_{C-P}$ = 9.6 Hz, P-O-*C*), 123.49 (d, $^1J_{C-P}$ = 18.6 Hz, P-CH=), 128.3, 129.1, 130.0, 130.4, 134.9 (*C*(Ph)), 144.2, 147.3, 147.4, 147.8, 183.94 (s, C=O), 206.50 (d, $^2J_{C-P}$ = 10.0 Hz, *cis* CO), 210.0 (d, $^2J_{C-P}$ = 26.2 Hz, *trans* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 564 (M, 26), 508 (M-2CO, 28), 480 (M-3CO, 21), 452 (M-4CO, 15), 424 (M-5CO, 36), 379 (100).

Cycloaddition reaction of complex **12b** *with 1,4-naphthoquinone*

A solution of complex **12b** (0.27 g, 0.64 mmol) and naphthoquinone (0.12 g, 0.77 mmol) in benzene was heated at 55°C for 1.5 h, to afford a mixture of three products, according to ^{31}P NMR analysis of the reaction mixture. After evaporation of the solvent, the three components of the mixture were separated by chromatography on a silica-gel column. Complex **15** was eluted first with an hexane/ether 90:10 mixture : violet solid.

^{31}P NMR (C_6D_6) δ 10.2.

^{1}H NMR (C_6D_6) δ 0.95 (t, $^3J_{H-H}$ = 7.0 Hz, CH_2CH_3), 1.18 (d, $^3J_{H-P}$ = 15.9 Hz, CMe_3), 1.71 (s, =C-Me), 3.56 (m, 1H, OCH_2CH_3), 3.98 (m, 1H, OCH_2CH_3), 4.81 (s, C*H*-OEt), 5.76 (d, $^2J_{H-P}$ = 31.4 Hz, P-CH=), 6.9 (m, 2H), 7.92 (m, 2H).

^{13}C NMR (C_6D_6) δ 15.92 (s, OCH_2CH_3), 24.06 (d, $^3J_{C-P}$ = 8.3 Hz, =C-CH_3), 28.46 (d, $^2J_{C-P}$ = 6.3 Hz, C*Me*$_3$), 35.94 (d, $^1J_{C-P}$ = 15.2 Hz, *C*Me$_3$), 69.85 (s, OCH_2CH_3), 70.72 (s, *C*HOEt), 120.85 (d, $^1J_{C-P}$ = 32.5 Hz, P-CH=), 126.70, 126.97, 129.4, 131.95, 134.14, 134.22, 142.76 (d, $^1J_{C-P}$ = 6.0 Hz), 147.8 (d, $^2J_{C-P}$ = 3 Hz), 182.90 (s, C=O), 185.88 (d, $^2J_{C-P}$ = 12.6 Hz, C=O), 206.23 (d, $^2J_{C-P}$ = 8.2 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 552 (M-CO, 38), 524 (M-2CO, 53), 496 (M-3CO, 32), 440 (M-5CO, 55), 382 (M-5CO-*t*BuH, 100).

Complex **14b** was eluted then with hexane/ether 85:15 and crystallized from pentane. Colorless solid.

^{31}P NMR (C_6D_6) δ 148.4.

^{1}H NMR ($CDCl_3$) δ 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, OCH_2CH_3), 1.33 (d, $^3J_{H-P}$ = 16.1 Hz, CMe_3), 2.07 ($^4J_{H-H}$ = 1.1 Hz, =C-CH_3), 2.4 (m, 1H, OCH_2CH_3), 3.0 (m, 1H, OCH_2CH_3), 3.19 (broad s, 1H, C*H*OEt), 6.00 (dd, $^2J_{H-P}$ = 36.6 Hz, $^4J_{H-H}$ = 1.4 Hz, P-CH=), 6.48 (*AB*, $^3J_{A-B}$ = 10.7 Hz, =CH-CO), 7.56 (td, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.65 (td, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.70 (A*B*, $^3J_{A-B}$ = 10.7 Hz, C*H*=CH-CO), 7.92 (dd, 1H), 8.12 (dd, 1H).

^{13}C NMR ($CDCl_3$) δ 14.95 (s, CH_2CH_3), 25.74 (d, $^3J_{C-P}$ = 7.8 Hz, =C-*C*H$_3$), 26.16 (d, $^2J_{C-P}$ = 7.6 Hz, C*Me*$_3$), 39.61 (d, $^1J_{C-P}$ = 17.6 Hz, CMe_3), 69.79 (s, OCH_2CH_3), 78.14 (P-O-C), 82.33 (d, $^2J_{C-P}$ = 7.2 Hz, *C*HOEt), 121.87 (d, $^1J_{C-P}$ = 17.4 Hz, P-CH=), 126.44, 128.87, 129.27, 129.42, 130.30 (*C*), 132.21, 141.55 (*C*-Me), 145.86 (*C*H=CH-CO), 146.54 (*C*=C-CO), 183.51 (s, C=O), 206.07 (d, $^2J_{C-P}$ = 9.4 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 582 (M, 19), 498 (M-3CO, 21), 470 (M-4CO, 34), 442 (M-5CO, 100).

Complex **14c** was eluted with hexane/ether 85:15 and crystallized from pentane. Colorless solid.

^{31}P NMR ($CDCl_3$) δ 152.4.

^{1}H NMR ($CDCl_3$) δ 0.72 (t, $^3J_{H-H}$ = 6.9 Hz, OCH_2CH_3), 1.28 (d, $^3J_{H-P}$ = 15.7 Hz, CMe_3), 2.09 (broad s, =C-CH_3), 2.60 (m, 1H, OCH_2CH_3), 3.18 (m, 1H, OCH_2CH_3), 4.44 (s, *CH*OEt), 6.31 (broad d, $^2J_{H-P}$ = 26.9 Hz, P-CH=), 6.48 (*AB*, $^3J_{A-B}$ = 10.5 Hz, =CH-CO), 6.89 (A*B*, *H*C=CH-CO), 7.51 (td, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.1 Hz), 7.70 (td, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.4 Hz), 8.12 (dd, 1H), 8.16 (dd, 1H).

^{13}C NMR ($CDCl_3$) δ 14.77 (s, OCH_2CH_3), 22.20 (d, $^3J_{C-P}$ = 8.7 Hz, =C-*C*H$_3$), 25.68 (d, $^2J_{C-P}$ = 8.2 Hz, C*Me*$_3$), 38.02 (d, $^1J_{C-P}$ = 12.2 Hz, *C*Me$_3$), 69.55 (OCH_2CH_3), 76.13 (P-O-C), 82.50 (d, $^3J_{C-P}$ = 9.6 Hz, *CH*OEt), 121.20 ($^1J_{C-P}$ = 17.4 Hz, P-CH=), 126.37, 127.55, 128.75, 131.12, 131.96 (*C*), 132.72, 143.28 (d, $^2J_{C-P}$ = 6.4 Hz, CH=*C*-Me), 144.9 (H*C*=CH-CO), 150.92 (*C*=C-CO), 183.87 (s, C=O), 206.26 (d, $^2J_{C-P}$ = 9.9 Hz, *cis* CO) ppm.

Mass spectrum (^{98}Mo) *m/e* (relative intensity) 582 (M, 2), 442 (M-5CO, 13), 344 (M-Mo(CO)$_5$, 100).

Decomplexation of the 1,4-dihydrophosphinines from their Mo(CO)$_5$ complexes **13b** *and* **13c**, *and thermolysis to* **17**

The decomplexation reaction was performed by heating **13b** (or **13c**) with one equivalent of dppe in toluene at 95°C for 4 h. The (dppe) Mo(CO)$_4$ complex was separated by addition of hexane, cooling at 0°C and filtration. The solution containing the crude dihydrophosphinine **16b** (^{31}P NMR (toluene) δ −25.4 and −41.5 ppm) (or **16c**) was evaporated and **16b** (or **16c**) was thermolyzed, without further purification, at 200°C for 2 h. The final product was purified by chromatography with hexane/ether 70:30 (or 95:5) as eluent.

Dimethyl 4-ethoxy-5-methyl-2,3-phosphininedicarboxylate **17b** : yield 25% from **13b**; orange solid.

^{31}P NMR ($CDCl_3$) δ 200.57.

^{1}H NMR ($CDCl_3$) δ 1.39 (t, $^3J_{H-H}$ = 7.0 Hz, OCH_2CH_3), 2.49 (t, $^4J_{H-H}$ = $^4J_{H-P}$ = 0.52 Hz, CH_3), 3.92 (s, CO_2CH_3), 3.97 (q, $^3J_{H-H}$ = 7.0 Hz, OCH_2CH_3), 3.98 (s, CO_2CH_3), 8.62 (d, $^2J_{H-P}$ = 38.9 Hz, CH).

^{13}C NMR ($CDCl_3$) δ 16.09 (s, OCH_2CH_3), 20.18 (d, $^3J_{C-P}$ = 2.6 Hz, CH_3), 53.42 (CO_2CH_3), 71.31 (d, J_{C-P} = 2.4 Hz, OCH_2CH_3), 139.78 (d, $^3J_{C-P}$ = 15.4 Hz, *C*OEt), 143.85 (d, $^2J_{C-P}$ = 13.5 Hz,

C-Me), 152.79 (d, $^1J_{C-P}$ = 56.8 Hz, *C*-CO_2Me), 157.05 (d, $^2J_{C-P}$ = 16.2 Hz, *C*-CO_2Me), 158.13 (d, $^1J_{C-P}$ = 51.2 Hz, CH), 167.44 (d, $^2J_{C-P}$ = 23.2 Hz, *C*O_2Me), 169.04 (s, *C*O_2Me) ppm.

Mass spectrum *m/e* (relative intensity) 270 (M, 34), 239 (M-OMe, 30), 210 (100), 178 (95).

Anal calc for $C_{12}H_{15}O_5$ P : C, 53.34; H, 5.59. Found : C, 53.3; H, 5.57.

A 65:35 mixture of two phosphinines **17c** and **17d** was obtained from **13c**, in 30% yield.

^{31}P NMR (ether) δ 214.4 (minor isomer), 184.8 (major isomer).

Major isomer : ^{1}H NMR ($CDCl_3$) δ 0.93 (t, $^3J_{H-H}$ = 6.9 Hz, CH_2CH_3), 0.95 (t, $^3J_{H-H}$ = 7.2 Hz, CH_2CH_3), 2.51 (d, $^3J_{H-P}$ = 1.3 Hz, C-CH_3), 3.44 (q, $^3J_{H-H}$ = 6.9 Hz, OCH_2CH_3), 3.99 (q, $^3J_{H-H}$ = 7.2 Hz, OCH_2CH_3), 7.4 (m, Ph), 8.56 (d, $^2J_{H-P}$ = 38.9 Hz, CH) ppm.

Mass spectrum *m/e* (relative intensity) 302 (M, 40), 77 (100).

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