2-Phosphanylphosphinines as Bridging Ligands for Dinuclear Transition Metal Carbonyls

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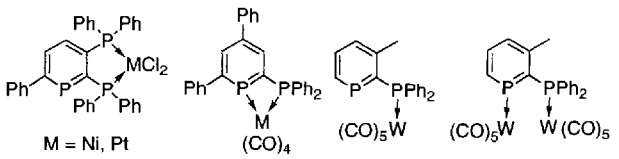
The 2-phosphanyl-4,5-dimethylphosphinines **1**–**5** are powerful bridging ligands able to stabilize metal–metal single and triple bonds between low-valent transition metal centres. Their reaction with $Mn_2(CO)_{10}$ in refluxing xylene yields the corresponding $Mn_2(CO)_8$ complexes **6** and **7**. Reaction with $[Fe_2Cp_2(CO)_4]$ under UV irradiation similarly yields the Fe–Fe-bridged $Fe_2Cp_2(CO)_2$ complexes **8** and **9**. An additional observation is that the 2-phosphininyl-3,4-dimethylphosphaferrocene **10** is formed upon reaction of the 2-phospholylphosphinine **5** with $[Fe_2Cp_2(CO)_4]$ at high temperature under CO pressure. A clean addition occurs at the Mo≡Mo triple bond of $[Mo_2Cp_2(CO)_4]$ to give the Mo–Mo single-bonded complexes **11**–**15**. The thermolysis of these complexes succeeds when the phosphanyl group is a phosphonite $P(OEt)_2$ (**13**) or $P(OAr)_2$ (**14**), affording cleanly the $Mo_2Cp_2(CO)_2$ triple-bonded complexes **16** and **17**, respectively. The metal–metal triple bonds of these complexes readily add two molecules of CO to reform **13** and **14**, or one molecule of *t*Bu–N≡C to give **18** and **19**. The X-ray crystal structure analysis of the $Mo_2Cp_2(CO)_4$ complex **13a**, with the 2-$P(OEt)_2$-phosphinine, shows a *gauche* orientation of the two Cp rings and very short P–Mo bonds of 2.3565(4) and 2.406(2) Å to the phosphinine and $P(OEt)_2$ groups, respectively.

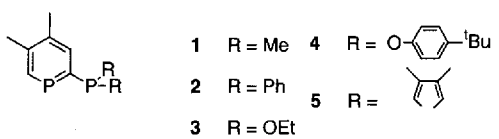
Currently, the well-established coordination chemistry of 2-phosphanylpyridines (P^N)[1] is not paralleled by knowledge concerning the 2-phosphanylphosphinines (P^P). The replacement of the σ-donor nitrogen centre of the former by the π-acceptor phosphorus centre of the latter can induce a sharply different reactivity while keeping the geometrical constraints associated with the PN system. In particular, a wide range of dinuclear complexes, either with or without metal–metal bonds, might be accessible. The coordination chemistry of 2-phosphanylphosphinines is not totally unprecedented, but still remains poorly developed. There have, however, been some reports on complexes of 2-diphenylphosphanylphosphinines. The first example, which was published by Hughes in 1988, concerns platinum and nickel(II) complexes of a 2,3-bis(diphenylphosphanyl) derivative[2a]. However, these complexes cannot really be considered as very representative since the lone pair of phosphinine is not involved in the coordination of the MCl_2 metal fragments. Chelate $M(CO)_4$ (M = Cr, Mo, W) complexes were reported by Märkl in 1990[2b]. Finally, more classical complexes, in which a 2-diphenylphosphanyl derivative binds one or two $W(CO)_5$ fragments are also known[2c,d].



As is apparent from this brief survey, the bridging behavior of 2-phosphanylphosphinines has yet to be realized. The recent discovery of a straightforward route to 2-dibromophosphanylphosphinines[3] has provided us an easy access to a wide range of 2-phosphanylphosphinines. Considering the strong π-acceptor properties of the phosphinine phosphorus[4], our work was first directed toward the low oxidation states of transition metals. We report here on our results with dinuclear carbonyls.

Results and Discussion

We selected a series of 2-phosphanyl-4,5-dimethylphosphinines **1**–**4** and a 2-phospholyl derivative **5** as starting ligands. Thus, the electronic characteristics of the phosphanyl group were varied from those of a good σ-donor **1** to those of a good π-acceptor **4**. Apparently, the better balanced phosphonites **3** and **4** give more stable complexes as we shall see later. The phosphole **5**[5] was added to the list because it offers additional possibilities as an η^5 ligand[6].



As a preliminary experiment, we chose to treat phosphonite **3** and phosphole **5** with manganesecarbonyl. The reactions afforded the very stable $Mn_2(CO)_8$ complexes **6** and **7**, in which **3** and **5** adopt a bridging mode, akin to the dppm ligand [dppm = bis(diphenylphosphanyl)methane]. This result underlines the difference between 2-phosphanylphosphinines and their nitrogen counterparts. Indeed, under the same experimental conditions, it has been shown

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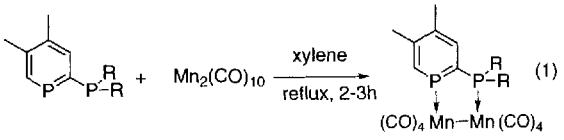
that the 2-diphenylphosphanylpyridine ligand behaves as a chelate towards one $Mn(CO)_3$ unit in the complex $[Mn_2(CO)_8(Ph_2Ppy)]$[7]

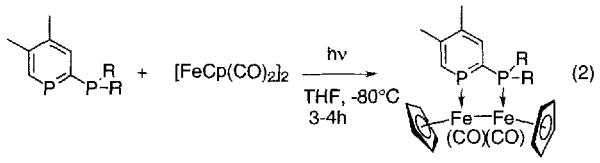


(1)

3 **6** R = OEt (50%)

5 **7** R = (55%)

The structures of **6** and **7** were unambiguously confirmed by a combination of NMR and IR experiments and by elemental analysis. No 4-electron bridging CO was detected in the IR spectra of **6** and **7**. Even in refluxing xylene, neither **3** nor **5** produced any of the $Mn_2(CO)_5$ complexes analogous to that obtained from dppm under similar conditions[8]. In marked contrast to the situation with 1-arylphospholes under strictly identical conditions[6], the cleavage of the phosphinine-phosphole C–P bond by $Mn_2(CO)_{10}$ to give a phosphacymantrene was not observed. More interesting results were obtained with $[Fe_2Cp_2(CO)_4]$. Under UV irradiation at low temperature, both **3** and **5** reacted, to afford the dinuclear complexes **8** and **9**, respectively. As for the manganese complexes, the structures of **8** and **9** were confirmed by NMR studies and elemental analysis for **9**.

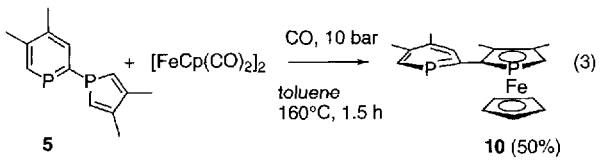


(2)

3 **8** R = OEt (60%)

5 **9** R = (65%)

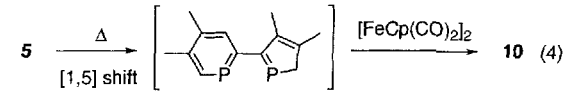
However, at high temperature under CO pressure, the reaction of **5** with $[Fe_2Cp_2(CO)_4]$ followed a different course and produced the phosphaferrocene **10**.



(3)

5 **10** (50%)

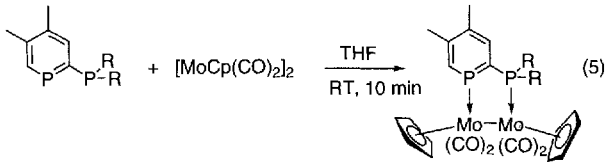
The mechanism involves a [1,5]-sigmatropic shift of the phosphinine nucleus around the phosphole ring. As for the synthesis of 2-phenylphosphaferrocenes[9] we found that CO pressure is necessary to slow down the complexation so that it does not take place before the shift. Without CO pressure, 3,4-dimethyl-1-phosphaferrocene is formed by cleavage of the P(phosphole)–C(phosphinine) bond.



(4)

The existence of the intermediate *2H*-phosphole has previously been demonstrated by trapping experiments with alkynes[5]. It is fascinating to observe that the phosphinine does not alter the course of the phosphole complexation under such drastic conditions. The ^{31}P-NMR spectrum of **10** displays the characteristic high-field resonance of phosphaferrocenes: $\delta^{31}P$ (**10**) = −68.70 (phosphaferrocene unit) and +190.70 (phosphinine unit), $^3J_{PP}$ = 30.90 Hz. These data are quite similar to those of the phenyl analogues, i.e. 2-phenyl-4,5-dimethylphosphinine ($\delta^{31}P$ = +181.00)[10] and 2-phenyl-3,4-dimethylphosphaferrocene ($\delta^{31}P$ = −72.50)[11].

A systematic study of the reaction of 2-phosphanylphosphinines with $Cp(CO)_2Mo{\equiv}(CO)_2Cp$ was also carried out. As expected, an addition across the Mo≡Mo triple bond takes place.



(5)

1 - 5 **11 a,b** R = Me (55%)
12 R = Ph (75%)
13 a,b R = OEt (75%)

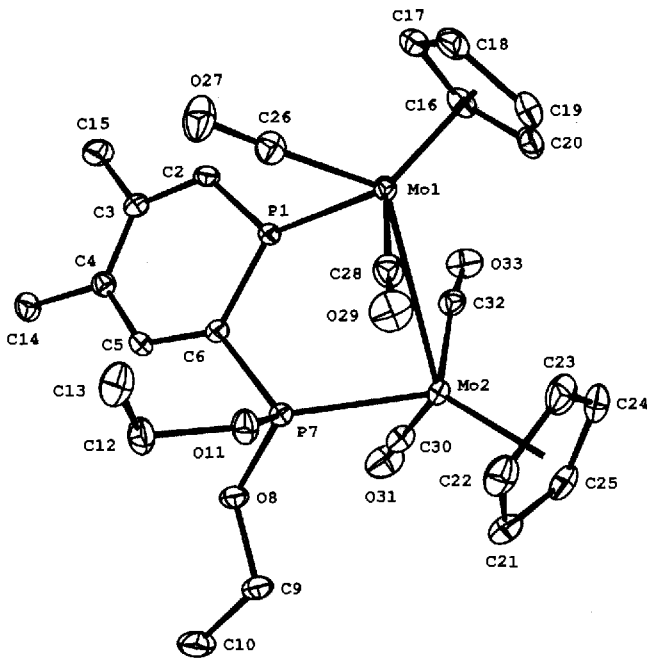
14 R = O-C6H4-tBu (80%)

15 R = (75%)

These results merit several comments. Firstly, 2-phosphanylphosphinines act here as bidentate bridging ligands whereas 2-phosphanylpyridines only act as monodentate P ligands toward $[Mo_2Cp_2(CO)_4]$[12]. Secondly, in most cases, only one isomer is obtained in these additions across the triple bond. A second isomer, corresponding to a *syn* disposition of the two Cp rings with respect to the Mo_2P_2 pseudoplane, appears only when the smallest R groups are used in the phosphanyl substituent (R = Me, **11**; R = OEt, **13**). This observation suggests that the discrimination between the two isomers is mainly of steric origin. Two earlier reports disagree on the steric vs. electronic origin of this preference[13,14]. Our findings at least prove that a set of two π acceptors (**4** and **5**) does not necessarily favour the formation of the *syn* isomer, as has been suggested[14]. We were able to crystallize the major isomer **13a** and to perform its X-ray crystal structure analysis. An ORTEP drawing of the structure is presented in Figure 1. The phosphinine geometry is normal and deserves no special comment[15]. At 3.2660(2) Å, the Mo–Mo separation is almost identical to that recorded in the analogous $Ph_2PCH_2PPh_2$ (dppm) complex[16]. This is in accordance with the fact that the P–C–P angle in **13a** [109.9(1)°C] is very close to the tetrahedral value, despite the sp^2 hybridization of the carbon bridge C2. The two P–Mo bond lengths are significantly different at 2.365(4) (P1) and 2.406(2) Å (P7). The shorter contact between phosphinine and molybdenum does not necessarily reflect a higher bond strength, but rather the sp^2 hybridization of phosphorus. This point being

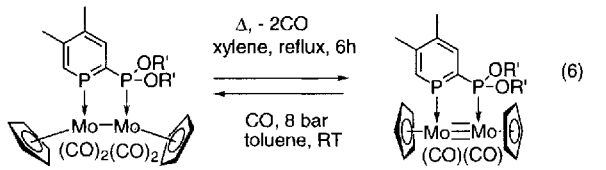
taken into account, it appears that the phosphanylphosphinine **3** is more strongly bound to the Mo_2 unit than dppm in the analogous complex [P–Mo: 2.430(3) and 2.445(3) Å][16]. This is most probably a consequence of the higher π acceptor capacity of **3** compared to dppm. Finally, the P–Mo–Mo–P torsion angles are almost equal in **13a** and in the dppm complex [41.39 (± 0.01)° vs. 42.90°[16]]. On the other hand, whereas the two Cp rings, which lie on both sides of the Mo_2P_2 pseudoplane, show a *trans* conformation in the dppm complex[16], they display a *gauche* conformation in **13a** [Cp(centroid)–Mo–Mo–Cp(centroid) torsion angle: 65.36 (± 0.01)°] as in the analogous *t*BuPH–CH_2–PH*t*Bu complex[13]. The comparison between the ^{31}P-NMR data of the **13a**-*gauche* and the **13b**-*syn* complexes is also interesting; **13a**: $\delta^{31}P$ = 240.70 and 176.10, $^2J_{PP}$ = 156.20 Hz; **13b**: $\delta^{31}P$ = 240.20 and 187.90, $^2J_{PP}$ = 179.90 Hz. Only the $P(OEt)_2$ resonance and the $^2J_{PP}$ coupling are affected by the change of stereochemistry. This observation suggests that the change takes place on Mo2.

Figure 1. ORTEP drawing of one molecule of **13a**, as determined by a single-crystal X-ray diffraction study; ellipsoids are scaled to enclose 50% of the electron density; hydrogen atoms are omitted for clarity[a]



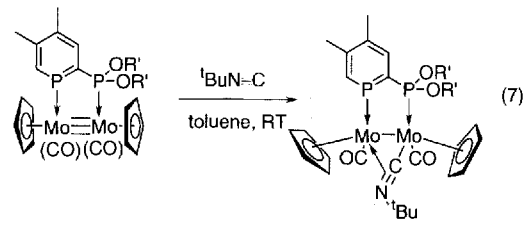
[a] Selected bond lengths [Å] and angles [°]: Mo1–Mo2 3.2660(2), Mo1–P1 2.3565(4), Mo1–C26 1.942(2), Mo1–C28 1.971(2), Mo2–P7 2.406(2), Mo2–C30 1.947(2), Mo2–C32 1.95(1), P1–C2 1.715(2); P1–C6 1.709(2), P7–O8 1.630(2), P7–O11 1.607(2), P7–C6 1.806(3); C2–C3 1.397(3), C3–C4 1.414(2), C4–C5 1.393(2), C5–C6 1.393(3); Mo2–Mo1–P1 77.32(1), Mo2–Mo1–C26 125.95(5), Mo2–Mo1–C28 68.13(4), P1–Mo1–C26 75.06(5), P1–Mo1–C28 108.71(5), C26–Mo1–C28 78.10(7), Mo1–Mo2–P7 80.62(4), Mo1–Mo2–C30 124.68(5), Mo1–Mo2–C32 65.59(4), P7–Mo2–C30 77.98(6), P7–Mo2–C32 109.00(6), C30–Mo2–C32 74.32(7), Mo1–P1–C2 130.00(6), Mo1–P1–C6 124.78(7), C2–P1–C6 103.05(9), Mo2–P7–C6 113.9(1), P1–C6–P7 109.9(1).

It is known that $[Mo_2Cp_2(dppm)(CO)_4]$ readily decomposes upon heating[14]. Besides, the direct substitution of the CO ligands of $[Mo_2Cp_2(Co)_4]$ without disruption of the Mo≡Mo triple bond has been demonstrated only in very special cases[17]. Hence, a study of the thermolysis of complexes **11**–**15** seemed appropriate. Decomposition was observed for complexes **11**, **12**, and **15**, but with the phosphonite complexes **13** and **14** a clean conversion to the Mo≡Mo triple-bonded complexes **16** and **17** was achieved.



13 a,b **16** R' = Et (55%)
14 **17** R' = –C6H4–^{t}Bu (50%)

The formation of the Mo≡Mo triple bond induces significant downfield shifts of the ^{31}P-NMR resonances and an increase of the $^2J_{PP}$ couplings, e.g.: **14**: $\delta^{31}P$ = 236.40 and 180.50, $^2J_{PP}$ = 171 Hz; **17**: $\delta^{31}P$ = 254.60 and 226.20, $^2J_{PP}$ = 207.40 Hz. In the ^{13}C-NMR spectra, the CO resonances, which appear as triplets at room temperature, indicate that a fast exchange takes place on the NMR time scale. This exchange process has been discussed for the mixed $[Cp(CO)_2Mo{\equiv}W(CO)_2Cp]$ complex[18]. The IR spectrum shows a shift toward the longer wavelengths of the CO stretches in comparison with that of the $[Mo_2Cp_2(CO)_4]$ complex; in **16**: ν(CO) 1856 and 1806 cm^{-1} vs. 1900 and 1850 cm^{-1} for $[Mo_2Cp_2(Co)_4]$. Clearly, the most significant observation is the fact that both **16** and **17** quantitatively fix two molecules of CO at room temperature to reform **13(a,b)** and **14**[19]. Similarly, both **16** and **17** readily add one molecule of *tert*-butyl isocyanide to give **18** and **19**, thus demonstrating that the high reactivity of the metal–metal triple bond is preserved.



16 **18** R' = Et (90%)
17 **19** R' = –C6H4–^{t}Bu (90%)

This kind of addition has been described for $[Mo_2Cp_2(CO)_4]$[20] and its dppm derivative[21]. Since the phosphonite group exhibits an upfield shift in the range from −33 to −36 ppm upon addition of the isocyanide, whereas the phosphinine resonance remains almost unaffected, it is clear that the isocyanide carbon is connected to the molybdenum bearing the $P(OR)_2$ group in **18** and **19**. The chemistry depicted in Equations (6) and (7) illustrates the exceptional strength of the coordination between the Mo_2 core an the 2-phosphanylphosphinines. The weaker

bond obviously lies between the phosphanyl groups and the corresponding molybdenum, as shown by the failure of the thermolysis of **11**, **12**, and **15**.

The original aim of this work was to demonstrate that 2-phosphanylphosphinines can be used as bridging ligands. From our experiments it appears that the P=C−P geometry in these compounds is sufficiently flexible to accommodate various metal−metal separations. Additionally, the series of results obtained demonstrates that the coordination chemistry of 2-phosphanylphosphinines toward dinuclear transition metal carbonyl complexes is markedly different from that of their isostructural analogues, the 2-phosphanylpyridines. In one respect, a different behavior from that of dppm has also been observed. The existence of complexes **16** and **17** underlines the unique electronic properties of phosphonites **3** and **4**. To the best of our knowledge, these complexes are the first examples of diphosphanyl-bridged $Mo_2(CO)_2Cp_2$ units. Investigations are currently in progress to further extend the coordination chemistry of 2-phosphanylphosphinines toward other metallic centres such as nickel(0) and copper(I).

Experimental Section

All reactions were routinely performed under either nitrogen or argon by using Schlenk techniques and dry, deoxygenated solvents. Dry THF, toluene, xylene, hexane, and pentane were obtained by distillation from Na/benzophenone, dry CH_2Cl_2 was obtained by distillation from P_2O_5, and triethylamine by distillation from KOH. Dry Celite was used for filtration. − Nuclear magnetic resonance spectra were obtained with a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts are expressed in ppm downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in Hz. The following abbreviations are used; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. − Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif-sur-Yvette, France. − $[Mo_2Cp_2(CO)_4]$ was prepared according to published methods[22].

2-(Diethoxyphosphanyl)-4,5-dimethylphosphinine (**3**): 2-Dibromophosphanyl-4,5-dimethylphosphinine (2.00 g, 6.36 mmol) was dissolved in a mixture of THF (30 ml) and triethylamine (3.85 g, 38.16 mmol, 6 equiv.). After cooling of the mixture to 0°C, a solution of EtOH (0.60 g, 12.70 mmol) in THF (5 ml) was added dropwise. Following this addition, the reaction mixture was stirred for 10 min, and then slowly allowed to warm to room temperature. After evaporation of the solvents and excess triethylamine, phosphinine **3** was extracted with dry hexane (3 × 20 ml) and the extract was filtered under nitrogen. Phosphinine **3** was recovered as a yellow, oxygen-sensitive oil after evaporation of the solvent. Yield: 1.23 g (80%). − ^{31}P NMR (C_6D_6): δ = 202.00 (d, $^2J_{PP}$ = 85.10, P of C_7H_8P), 156.95 [P of $P(OEt)_2$]. − ^1H NMR (C_6D_6): δ = 1.31 (t, 6H, $^3J_{HH}$ = 7.04, Me of OEt), 2.40 (d, 3H, J_{HP} = 3.54, Me of C_7H_8P), 2.43 (s, 3H, Me of C_7H_8P), 3.95 (m, 4H, CH_2 of Et), 7.91 (dd, 1H, $^3J_{HP}$ = 11.11, $^3J_{HP}$ = 7.06, 3-H), 8.57 (dd, $^2J_{HP}$ = 39.07, $^4J_{HP}$ = 2.84, 6-H). − ^{13}C NMR (C_6D_6): δ = 17.25 (d, ^3J = 5.0, Me of OEt), 22.05 (s, Me of C_7H_8P), 23.10 (d, J_{CP} = 2.80, Me of C_7H_8P), 62.10 (d, $^2J_{CP}$ = 9.50, CH_2 of OEt), 138.70 (C-4 or C-5 masked by C-3), 138.70 (dd, $^2J_{CP}$ = 26.15, $^2J_{CP}$ = 13.70, C-3), 144.20 (d, J_{CP} = 13.75, C-4 or C-5), 155.95 (dd, ^1JCP = 55.80, $^3J_{CP}$ = 5.40, C-6), 169.75 (dd, $^1J_{CP}$ = 68.65, $^1J_{CP}$ = 35.10, C-2). − MS, *m/z* (%): 244 (1) [M^+], 123 (100) [M^+ − $P(OEt)_2$], 121 (41) [$P(OEt)_2^+$]. − Phosphinine **3** was too sensitive toward hydrolysis to give satisfactory analytical data.

2-[Bis(p-tert-butylphenoxy)phosphanyl]4,5-dimethylphosphinine (**4**): The procedure was identical to that used for the synthesis of phosphinine **3**. Starting from 2-dibromophosphanyl-4,5-dimethlylphosphinine (2.00 g, 6.36 mmol) and *p-tert*-butylphenol (5.72 g, 12.70 mmol), phosphinine **4** was recovered as a yellow, oxygen-sensitive oil after evaporation of the solvent. Yield: 2.43 g (85%). − ^{31}P NMR (THF): δ = 204.05 (d, $^2J_{PP}$ = 128.60, P of C_7H_8P), 161.61 [d, P of $P(OC_6H_4tBu)_2$]. − ^1H NMR ($CDCl_3$): δ = 1.34 (s, 18H, Me of *t*Bu), 2.47 (d, 3H, J_{HP} = 3.50, Me of C_7H_8P), 2.51 (s, 3H, Me of C_7H_8P), 7.09 (dd, 4H, $^3J_{HH}$ = 8.70, $^4J_{HP}$ = 1.20, H *ortho* of C_6H_4tBu), 7.34 (d, 4H, $^3J_{HH}$ = 8.70, H *meta* of C_6H_4tBu), 8.18 (dd, 1H, $^3J_{HP}$ = 11.73, $^3J_{HP}$ = 6.40, 3-H of C_7H_8P), 8.67 (dd, 1H, $^2J_{HP}$ = 39.85, $^4J_{HP}$ = 3.74, 6-H of C_7H_8P). − ^{13}C NMR ($CDCl_3$): δ = 22.90 (s, Me of C_7H_8P), 24.10 (s, Me of C_7H_8P), 32.05 (s, Me of *t*Bu), 34.75 (s, Cq of *t*Bu), 120.10 (d, $^3J_{CP}$ = 8.20, CH *ortho* of C_6H_4tBu), 126.90 (s, CH *meta* of C_6H_4tBu), 138.85 (dd, $^2J_{CP}$ = 25.15, $^2J_{CP}$ = 13.20, C-3 of C_7H_8P), 145.80 (d, J_{CP} = 13.90, C-4 or C-5 of C_7H_8P), 146.70 (s, Cq of C_6H_4tBu), 153.50 (d, J_{CP} = 5.80, C-4 or C-5 of C_6H_4tBu), 154.95 (Cq of C_6H_4tBu masked by C-6), 155.75 (dd, $^1J_{CP}$ = 58.10, $^3J_{CP}$ = 10.20, C-6 of C_7H_8P), 167.70 (dd, $^1J_{CP}$ = 64.60, $^1J_{CP}$ = 27.35, C-2 of C_7H_8P). MS, *m/z* (%): 452 (10) [M^+], 123 (100) [M^+ − $P(OC_{10}H_{13})_2$]. − Phosphinine **4** was too sensitive toward hydrolysis to give satisfactory analytical data.

[Mn2(CO)8{μ-(2-(diethoxyphosphanyl)-4,5-dimethylphosphinine)}] (**6**): A solution of phosphinine **3** (0.14 g, 0.57 mmol) and $Mn_2(CO)_{10}$ (0.22 g, 0.57 mmol) in xylene was heated under reflux. After 2 h, ^{31}P-NMR control indicated the end of the complexation. The xylene was then evaporated and the red powder obtained was washed twice with pentane (2 × 15 ml), thereby removing unreacted **3** and traces of $Mn_2(CO)_{10}$. After drying, complex **6** was obtained as a poorly soluble orange powder. Yield: 0.16 g (50%), m.p. 200°C (dec.). − IR (CH_2Cl_2): ν(CO) = 2065 (m) cm^{-1}, 1997 (s), 1982 (s), 1950 (s), 1925 (s). − ^{31}P NMR ($CDCl_3$): δ = 240.55 (broad signal, P of C_7H_8P), 190.30 [broad signal, P of $P(OEt)_2$]. − ^1H NMR ($CDCl_3$): δ = 1.31 (t, 6H, $^3J_{HH}$ = 6.70, Me of OEt), 2.33 (d, 3H, J_{HP} = 5.63, Me of C_7H_8P), 2.42 (s, 3H, Me of C_7H_8P), 3.83−4.04 (m, 4H, CH_2 of OEt), 7.70 (dd, 1H, $^3J_{HP}$ = 20.98, $^3J_{HP}$ = 11.51, 3-H), 8.28 (dd, 1H, $^2J_{HP}$ = 23.91, $^4J_{HP}$ = 6.74, 6H). − ^{13}C NMR ($CDCl_3$): δ = 16.05 (s, Me of OEt), 22.35 (s, Me of C_7H_8P), 24.30 (s, Me of C_7H_8P), 62.30 (s, CH_2 of OEt), 135.35 (m, C-4 or C-5 of C_7H_8P), 139.10 (d, $^1J_{CP}$ = 13.15, C-6), 150.25 (C-4 or C-5, partially masked by C-3), 150.60 (dd, $^2J_{CP}$ = 22.90, $^2J_{CP}$ = 13.75, C-3), 171.15 (b, C-2), 222.00−228.00 (m, CO). − $C_{19}H_{18}Mn_2O_{10}P_2$ (578.2): calcd. C 39.47, H 3.14; found C 39.55, H 3.28.

[Mn2(CO)8{μ-(2-[di-(p-tert-butylphenoxy)phosphanyl]-4,5-dimethylphosphinine)}] (**7**): A solution of phosphinine **5** (0.30 g, 1.28 mmol) was heated with $Mn_2(CO)_{10}$ (0.50 g, 1.28 mmol) in xylene under reflux. After 3 h, ^{31}P-NMR control indicated the end of the reaction. Celite (2 g) was then added and the solvent was evaporated yielding an orange powder. The resulting coated Celite was then loaded onto the top of a silica gel column and subjected to flash chromatography. A first fraction eluted with hexane yielded traces of unreacted $Mn_2(CO)_{10}$. Complex **7** was then eluted with a mixture of hexane and dichloromethane (2:1). After evaporation of the solvents, **7** was obtained as an orange powder. Yield: 0.40 g (55%), m.p. 200°C (dec.). − IR (CH_2Cl_2) ν(CO): 2059 (s) cm^{-1}, 1997 (s), 1974 (s), 1951 (s), 1925 (s). − ^{31}P NMR ($CDCl_3$): δ = 247.10 (d, $^2J_{PP}$ = 146.06, C_7H_8P), 54.50 (d, C_6H_8P). − ^1H NMR

($CDCl_3$): δ = 2.22 (s, 6H, Me of C_6H_8P), 2.25 (s, 3H, Me of C_7H_8P), 2.39 (s, 3H, Me of C_7H_8P), 6.56 (d, 2H, $^2J_{HP}$ = 36.77, CH of C_6H_8P), 7.09 (dd, 1H, J_{HP} = 19.86, J_{HP} = 13.58, 3-H or 6-H), 8.25 (dd, 1H, J_{HP} = 23.18, J_{HP} = 6.03, 6-H or 3-H). – ^{13}C NMR ($CDCl_3$): δ = 18.25 (d, $^3J_{CP}$ = 11.80, Me of C_6H_8P), 22.50 (d, J_{CP} = 3.0, Me of C_7H_8P), 24.60 (d, J_{CP} = 9.05, Me of C_7H_8P), 130.70 (dd, $^1J_{CP}$ = 42.55, $^3J_{CP}$ = 7.50, =CH of C_6H_8P), 136.55 (dd, J_{CP} = 26.05, J_{CP} = 6.30, C-5 or C-4), 140.15 (dd, $^1J_{CP}$ = 13.35, $^3J_{CP}$ = 2.65, C-6), 150.60 (d, $^2J_{CP}$ = 16.80, C-4 or C-5), 151.25 (dd, $^2J_{CP}$ = 14.90, $^2J_{CP}$ = 8.55, C-3), 152.55 (d, $^2J_{CP}$ = 9.05, =C– of C_6H_8P), 165.50 (dd, $^1J_{CP}$ = 28.25, $^1J_{CP}$ = 20.50, C-2), 220–230 (m, 4 × CO). – $C_{21}H_{16}Mn_2O_8P_2$ (568.2): calcd. C 44.40, H 2.84; found C 44.28, H 3.03.

[Fe_2{μ-(CO)}$_2${η^5(C_5H_5)}$_2${μ-[2-(diethoxyphosphanyl)-4,5-dimethylphosphinine]}] (**8**): A solution of phosphinine **3** (0.18 g, 0.74 mmol) and [$FeCp(CO)_2]_2$ (0.26 g, 0.74 mmol) in THF (25 ml) was irradiated for 3 h at −80°C. After this period, ^{31}P-NMR control indicated the end of the complexation. The solvent was then evaporated yielding a black powder, which was washed twice with hexane (2 × 15 ml), thereby removing traces of unreacted dimer and ligand. The black powder thus obtained was then dissolved in dichloromethane (20 ml) and the resulting solution was filtered through Celite under nitrogen. After evaporation of the solvent, complex **8** was recovered as a black powder, which was recrystallized from a mixture of dichloromethane and hexane (1:1). Yield: 0.24 g (60%). – ^{31}P NMR ($CDCl_3$): δ = 266.90 (d, $^2J_{PP}$ = 181.90, P of C_7H_8P), 213.35 [d, P of $P(OEt)_2$]. – ^1H NMR ($CDCl_3$): δ = 1.17–1.57 (m, 6H, 2 × Me of OEt), 2.06 (d, 3H, J_{HP} = 3.32, Me of C_7H_8P), 2.15 (s, 3H, Me of C_7H_8P), 3.51–4.15 (m, 4H, CH_2 or OEt), 4.68 (s, 5H, C_5H_5), 4.75 (s, 5H, C_5H_5), 7.25 (3-H masked by $CHCl_3$), 7.76 (dd, 1H, $^2J_{HP}$ = 25.57, $^4J_{HP}$ = 7.13, H-6). – ^{13}C NMR ($CDCl_3/C_6D_6$): δ = 16.80 (s, Me of OEt), 16.95 (s, Me of OEt), 21.85 (s, Me of C_7H_8P), 24.35 (d, J_{CP} = 8.60, Me of C_7H_8P), 61.05 (s, CH_2 of OEt), 86.05 (s, C_5H_5), 86.90 (s, C_5H_5), 128.00 (C-4 or C-5 of C_7H_8P masked by C_6D_6), 135.30 (d, $^1J_{CP}$ = 10.70, C-6 of C_7H_8P), 142.40 (t, $^2J_{CP}$ = $^2J_{CP}$ = 12.20, C-3 of C_7H_8P), 149.75 (d, J_{CP} = 12.20, C-4 or C-5), 185.00 (t, $^1J_{CP}$ = $^1J_{CP}$ = 18.30, C-2), 218.00–220.00 (bm, CO). – Complex **8** was too sensitive toward hydrolysis to give satisfactory analytical data.

[Fe_2{μ-(CO)}$_2${η^5(C_5H_5)}$_2${μ-[2-(3,4-dimethylphospholyl)-4,5-dimethylphosphinine]}] (**9**): A solution of phosphinine **5** (0.20 g, 0.85 mmol) and [$FeCp(CO)_2]_2$ (0.30 g, 0.85 mmol) in THF (30 ml) was irradiated for 4 h at −80°C. After evaporation of the solvent, the oxygen-sensitive brown powder obtained was washed with hexane (3 × 20 ml) in order to remove traces of unreacted dimer and ligand. After drying, **9** was crystallized from a mixture of dichloromethane and hexane (1:1). The product was stored at −20°C. Yield: 0.28 g (65%). – ^{31}P NMR ($CDCl_3$): δ = 277.25 (d, $^2J_{PP}$ = 152.95, P of C_7H_8P), 78.50 (d, P of C_6H_8P). – ^1H NMR ($CDCl_3$): δ = 1.69–2.25 (m, 12H, Me), 4.35 (s, 5H, C_5H_5), 4.71 (s, 5H, C_5H_5), 6.32 (d, 2H, $^2J_{HP}$ = 33.56, =CH of C_7H_8P), 6.61 (m, 1H, 3-H), 7.66 (dd, 1H, J_{HP} = 25.23, J_{HP} = 5.28, 6-H). – $C_{25}H_{26}Fe_2O_2P_2$ (532.1): calcd. C 56.43, H 4.92; found C 56.25, H 4.64.

2-(4,5-Dimethylphosphinyl)-3,4-dimethylphosphaferrocene (**10**): Phosphinine **5** (1 g, 4.27 mmol) and [$FeCp(CO)_2]_2$ (0.76 g, 2.14 mmol) were dissolved in toluene (25 ml) under nitrogen and the resulting mixture was transferred to an autoclave. The autoclave was then pressurized with CO (10 bar) and then heated at 160°C. After 90 min, the CO pressure was slowly reduced. This operation required about 1 h. When no CO remained in the autoclave, the reaction mixture was slowly cooled to room temperature. The resulting brown solution was then transferred via a syringe onto a frit and filtered under nitrogen. After evaporation of the solvent, complex **10** was obtained as a dark-orange solid, which contained traces (<5%) of 3,4-dimethylphosphaferrocene ($\delta^{31}P$ = −72.50). Complex **10** was purified by chromatography on dry and deoxygenated silica gel as rapidly as possible, so as to remove traces of phosphaferrocene, which was eluted first. Yield: 0.76 g (50%). – ^{31}P NMR (C_6D_6): δ = 190.65 (d, $^3J_{PP}$ = 30.90, P of C_7H_8P), −68.70 (d, P of C_6H_7P). – ^1H NMR (C_6D_6): δ = 1.97 (m, 9H, 3 × Me), 2.16 (s, 3H, Me of C_7H_8P), 3.80 (d, 1H, $^2J_{HP}$ = 35.53, 5′-H of C_6H_7P), 4.12 (s, 5H, CH of C_5H_5), 7.61 (d, 1H, $^3J_{HP}$ = 5.15, 3-H of C_7H_8P), 8.23 (d, 1H, $^2J_{HP}$ = 38.36, 6-H of C_7H_8P). – ^{13}C NMR (C_6D_6): δ = 15.85 (d, Me of C_6H_7P), 18.00 (s, Me of C_6H_7P), 22.90 (s, Me of C_7H_8P), 23.45 (d, J_{CP} = 3.60, Me of C_7H_8P), 74.30 (d, $^2J_{CP}$ = 2.15, C_5H_5), 78.40 (d, $^2J_{CP}$ = 60.40, C-5′ of C_6H_7P), 92.50 (d, J_{CP} = 2.95, C-3′ or C-4′ of C_6H_7P), 97.00 (d, J_{CP} = 6.30, C-3′ or C-4′ of C_6H_7P), 104.80 (dd, $^1J_{CP}$ = 57.75, $^2J_{CP}$ = 25.65, C-2′ of C_6H_7P), 138.70 (d, J_{CP} = 15.55, C-4 or C-5), 139.90 (dd, $^2J_{CP}$ = 10.70, $^3J_{CP}$ = 7.60, C-3), 141.35 (d, J_{CP} = 15.20, C-4 or C-5), 155.25 (d, $^1J_{CP}$ = 51.55, C-6), 170.00 (dd, $^1J_{CP}$ = 48.05, $^2J_{CP}$ = 17.55, C-2). – $C_{18}H_{20}FeP_2$ (354.1): calcd. C 61.05, H 5.69; found C 61.55, H 5.72.

General Procedure for the Synthesis of Complexes **11**, **12**, **13**, **14**, *and* **15**

[$Mo_2(CO)_4${η^5C_5H_5)}$_2${μ[2-(dimethylphosphanyl)-4,5-dimethylphosphinine]}] (**11**): Phosphinine **1** (0.10 g, 0.55 mmol) was added to a solution of [$Mo_2Cp_2(CO)_4$] (0.24 g, 0.55 mmol) in THF (2 ml). After 10 min of stirring, ^{31}P-NMR control indicated the end of the complexation. The brown solid, obtained after the evaporation of the solvent, was washed twice with pentane (2 × 5 ml). After drying, complex **11(a,b)** was obtained as a red-brown solid. Yield: 0.19 g (55%), m.p. 120°C (dec.). – IR (CH_2Cl_2): ν(CO) = 1958 (s) cm^{-1}, 1913 (s), 1884 (s). – ^{31}P NMR (CD_2Cl_2) (major isomer): δ = 250.45 (d, $^2J_{PP}$ = 122.20, P of C_7H_8P), 24.35 (d, P of PMe_2), (minor isomer): 243.15 (d, $^2J_{PP}$ = 119.40, P of C_7H_8P), 20.18 (d, P of PMe_2). – ^1H NMR (CD_2Cl_2) (mixture of two isomers): δ = 1.93 (d, 3H, $^2J_{HP}$ = 8.66, P-Me), 1.98 (d, 6H, $^2J_{HP}$ = 8.12, 2 × P-Me), 2.09 (d, 3H, $^2J_{HP}$ = 7.90, P-Me), 2.54 (s, 6H, 2 × Me of C_7H_8P), 2.59 (s, 6H, 2 × Me of C_7H_8P), 5.57–5.67 (bs, 20H, C_5H_5), 7.36 (dd, 1H, $^3J_{HP}$ = 21.40, $^3J_{HP}$ = 13.98, 3-H of C_7H_8P in minor isomer), 7.40 (dd, 1H; $^3J_{HP}$ = 21.21, $^3J_{HP}$ = 13.87, 3-H of C_7H_8P in major isomer), 7.90 (dd, 1H, $^2J_{HP}$ = 22.58, $^4J_{HP}$ = 5.85, 6H of C_7H_8P in minor isomer), 8.01 (m, 1H, H-6 of C_7H_8P in major isomer). – ^{13}C NMR (CD_2Cl_2) (mixture of two isomers): δ = 19.05–21.40 (m, 4 × Me of PMe_2), 22.00 (m, 2 × Me of C_7H_8P), 24.10 (m, 2 × Me of C_7H_8P), 90.15 (s, C_5H_5), 91.05 (s, C_5H_5), 92.25 (bs, 2 × C_5H_5), 130.50 (dd, J_{CP} = 24.40, J_{CP} = 6.10, C-4 or C-5 of C_7H_8P), 130.55 (m, C-4 or C-5), 134.65 (m, $^1J_{CP}$ = 10.70, $^3J_{CP}$ = 4.60, 2 × C-6 of C_7H_8P), 147.15 (m, 2 × C-4 or C-5 and C-3 of C_7H_8P), 147.70 (t, $^2J_{CP}$ = $^2J_{CP}$ = 9.15, C-3), 164.00 (m, C-2), 166.50 (t, $^1J_{CP}$ = $^1J_{CP}$ = 27.45, C-2), 207.35 (d, $^2J_{CP}$ = 29.00, CO), 210.75 (d, $^2J_{CP}$ = 29.00, CO), 216.00–218.00 (m, CO), 223.20 (s, CO), 227.00 (d, $^2J_{CP}$ = 4.55, CO). – $C_{23}H_{24}Mo_2O_4P_2$ (618.3): calcd. C 44.68, H 3.91; found C 44.35, H 3.85.

[$Mo_2(CO)_4${η^5(C_5H_5)}$_2${μ-[2-(diphenylphosphanyl)-4,5-dimethylphosphinine]}] (**12**): Starting from phosphinine **2** (0.11 g, 0.35 mmol) and [$Mo_2Cp_2(CO)_4$] (0.15 g, 0.35 mmol) in THF (15 ml), complex **12** was isolated as a red-brown solid. Yield: 0.19 g (75%), m.p. 150°C (dec.). – IR (CH_2Cl_2) ν(CO) = 1924 (s) cm^{-1}, 1888 (s). – ^{31}P NMR ($CDCl_3$): δ = 244.75 (d, $^2J_{PP}$ = 148.70, P of C_7H_8P), 60.05 (P of PPh_2). – ^1H NMR ($CDCl_3$): δ = 2.24 (d, 3H, J_{HP} = 5.74, Me of C_7H_8P), 2.31 (s, 3H, Me of C_7H_8P), 4.65 (s, 5H, C_5H_5), 4.90 (s, 5H, C_5H_5), 6.99–7.76 (m, 11H, 2 × C_6H_5 and 3-H), 8.19 (dd, 1H, $^2J_{HP}$ = 21.40, $^4J_{HP}$ = 6.47, 6-H). – ^{13}C NMR

($CDCl_3$): δ = 22.45 (d, J_{CP} = 4.15, Me of C_7H_8P), 24.35 (d, J_{CP} = 2.15, Me of C_7H_8P), 89.90 (s, C_5H_5), 92.45 (s, C_5H_5), 128.75 (d, J_{CP} = 8.95, CH of C_6H_5), 129.35 (d, J_{CP} = 9.10, CH of C_6H_5), 131.05 (s, CH of C_6H_5), 132.75 (s, CH of C_6H_5), 132.95 (s, CH of C_6H_5), 139.50 (dd, $^1J_{CP}$ = 12.30, $^3J_{CP}$ = 4.10, C-6), 140.45 (d, $^1J_{CP}$ = 12.40, Cq of C_6H_5), 141.30 (d, $^1J_{CP}$ = 12.70, Cq of C_6H_5), 147.40 (d, J_{CP} = 15.30, C-4 or C-5), 149.25 (dd, $^2J_{CP}$ = 19.25, $^2J_{CP}$ = 12.05, C-3), 179.30 (dd, $^1J_{CP}$ = 25.15, $^1J_{CP}$ = 19.20, C-2), 212.70 (d, $^2J_{CP}$ = 27.10, CO), 221.50 (d, $^2J_{CP}$ = 29.20, CO), 223.80 (s, CO), 225.80 (s, CO). – $C_{33}H_{28}Mo_2O_4P_2$ (742.4): calcd. C 53.39, H 3.80; found C 52.61, H 3.81.

[$Mo_2(CO)_4\{\eta^5(C_5H_5)\}_2\{\mu$-[2-(diethoxyphosphanyl)-4,5-dimethylphosphinine]}] (**13a, b**): Starting from phosphinine **3** (1 g, 4.15 mmol) and [$Mo_2Cp_2(CO)_4$] (1.80 g, 4.15 mmol) in THF (70 ml), complex **13(a,b)** was isolated as a red-brown solid. Yield: 2.11 g (75%), m.p. 130°C (dec.). – IR (CH_2Cl_2) ν(CO) = 1928 (s) cm^{-1}, 1895 (s), 1852 (s). – ^{31}P NMR ($CDCl_3$) (major *gauche* isomer): δ = 240.75 (d, $^2J_{PP}$ = 156.20, P of C_7H_8P), 176.10 [d, $P(OEt)_2$], (minor *syn* isomer): 240.20 (d, $^2J_{PP}$ = 179.90, P of C_7H_8P), 187.90 [d, $P(OEt)_2$]. – ^1H ($CDCl_3$) NMR (mixture of two isomers): δ = 1.11–1.47 (m, 12H, Me of OEt), 2.22 (d, 6H, J_{HP} = 4.98, Me of C_7H_8P), 2.25 (s, 6H, Me of C_7H_8P), 3.49–4.14 (m, 8H, CH_2 of OEt), 4.95 (s, 5H, C_5H_5), 5.10 (s, 5H, C_5H_5), 5.30 (d, 5H, $^3J_{HP}$ = 3.02, C_5H_5), 5.32 (d, 5H, $^3J_{HP}$ = 3.51, C_5H_5), 7.25 (dd, 2H, $^3J_{HP}$ = 21.42, $^3J_{HP}$ = 13.65, 3-H of C_7H_8P), 7.70 (dd, 1H, $^2J_{HP}$ = 23.31, $^4J_{HP}$ = 7.27, 6-H), 8.12 (dd, 1H, $^2J_{HP}$ = 22.17, $^4J_{HP}$ = 7.51, 6-H). – ^{13}C NMR ($CDCl_3$) (mixture of two isomers): δ = 16.90 (m, Me of OEt), 22.40 (m, Me of C_7H_8P), 24.60 (d, $^3J_{CP}$ = 9.05, Me of C_7H_8P), 60.80 (m, CH_2 of OEt), 90.15 (s, C_5H_5), 91.55 (s, C_5H_5), 91.65 (s, C_5H_5), 92.25 (s, C_5H_5), 131.20 (m, C-4 or C-5), 136.05 (t, $^1J_{CP}$ = $^3J_{CP}$ = 9.90, C-6 of C_7H_8P), 147.60 (m, C-3 and C-4 or C-5), 164.65 (dd, $^1J_{CP}$ = 45.80, $^1J_{CP}$ = 29.00, C-2 of C_7H_8P), 220.80–230.35 (m, CO). $C_{25}H_{28}Mo_2O_6P_2$ (678.3): calcd. C 44.27, H 4.16; found C 44.44, H 4.39.

[$Mo_2(CO)_4\{\eta^5(C_5H_5)\}_2\{\mu$-(2-[di-(p-tert-butylphenoxy)-phosphanyl]-4,5-dimethylphosphinine)}] (**14**): Starting from phosphinine **4** (1 g, 2.21 mmol) and [$Mo_2Cp_2(CO)_4$] (0.95 g, 2.21 mmoL) in THF (50 ml), complex **14** was isolated as a red-brown solid. Yield: 1.56 g (80%), m.p. 160°C (dec.). – IR (CH_2Cl_2) ν(CO) = 1904 (s) cm^{-1}, 1852 (s). – ^{31}P NMR ($CDCl_3$): δ = 236.40 (d, $^2J_{CP}$ = 171.05, P of C_7H_8P), 180.50 [d, $P(OC_6H_4tBu)_2$]. – ^1H NMR ($CDCl_3$): δ = 1.20 (s, 9H, Me of *t*Bu), 1.37 (s, 9H, Me of *t*Bu), 2.04 (d, 3H, J_{HP} = 5.15, Me of C_7H_8P), 2.22 (s, 3H, Me of C_7H_8P), 4.95 (s, 5H, C_5H_5), 5.38 (s, 5H, C_5H_5), 6.95–7.42 (m, 9H, H of C_6H_4tBu and 3-H), 7.69 (dd, 1H, $^1J_{HP}$ = 24.19, $^4J_{HP}$ = 8.16, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 22.10 (s, Me of C_7H_8P), 24.70 (d, J_{CP} = 8.94, Me of C_7H_8P), 32.05 (s, Me of *t*Bu), 32.25 (s, Me of *t*Bu), 34.90 (s, Cq of *t*Bu), 35.10 (s, Cq of *t*Bu), 92.15 (s, C_5H_5), 92.60 (s, C_5H_5), 121.55 (d, $^3J_{CP}$ = 2.75, CH *ortho* of C_4H_6tBu), 121.90 (d, $^3J_{CP}$ = 5.90, CH *ortho* of C_4H_6tBu), 126.55 (s, CH *meta* of C_4H_6tBu), 126.90 (s, CH *meta* of C_4H_6tBu), 131.15 (dd, J_{CP} = 25.70 , J_{CP} = 7.30, C-4 or C-5 of C_7H_8P), 136.90 (d, $^1J_{CP}$ = 14.15, C-6), 147.65 (m, C-3 and C-4 or C-5 and Cq of C_4H_6tBu), 151.75 (s, Cq of C_4H_6tBu), 152.10 (s, Cq of C_4H_6tBu), 164.30 (dd, $^1J_{CP}$ = 48.85, $^1J_{CP}$ = 29.00, C-2 of C_7H_8P), 231.00 (s, CO), 231.65 (s, CO), 232.80 (s, CO), 233.60 (d, $^2J_{CP}$ = 17.40, CO). – $C_{41}H_{44}Mo_2O_6P_2$ (886.6): calcd. C 55.54, H 5.00; found C 55.45, H 4.84.

[$Mo_2(CO)_4\{\eta^5(C_5H_5)\}_2\{\mu$-[2-(3,4-dimethylphospholyl)-4,5-dimethylphosphinine]}] (**15**): Starting from phosphinine **5** (0.14 g, 0.58 mmol) and [$Mo_2Cp_2(CO)_4$] (0.25 g, 0.58 mmol) in THF (15 ml), complex **15** was isolated as a red-brown solid. Yield: 0.29 g (75%), m.p. 140°C (dec.). – IR (CH_2Cl_2) ν(CO) = 1924 (m) cm^{-1}, 1884 (s), 1826 (s). – ^{31}P NMR ($CDCl_3$): δ = 244.40 (d, $^2J_{PP}$ = 118.20, P of C_7H_8P), 51.80 (d, P of C_6H_8P). – ^1H NMR ($CDCl_3$): δ = 2.04 (s, 3H, Me of C_6H_8P), 2.7 (s, 3H, Me of C_6H_8P), 2.14 (s, 3H, of C_7H_8P), 2.16 (s, 3H, Me of C_7H_8P), 5.12 (s, 5H, C_5H_5), 5.30 (s, 5H, C_5H_5), 6.48 (d, 2H, $^2J_{HP}$ = 33.74, =CH of C_6H_8P), 6.75 (dd, 1H, $^3J_{HP}$ = 20.81, J_{HP} = 14.52, 3-H of C_7H_8P), 7.62 (m, 1H, 6-H of C_7H_8P). – ^{13}C NMR ($CDCl_3$): δ = 18.10 (d, $^3J_{CP}$ = 11.25, Me of C_6H_8P), 22.10 (d, J_{CP} = 3.10, Me of C_7H_8P), 24.35 (d, J_{CP} = 8.90, Me of C_7H_8P), 92.10 (bs, C_5H_5), 134.80 (bs, C-6 of C_7H_8P), 130.95 (dd, $^1J_{CP}$ = 44.95, $^3J_{CP}$ = 11.0, =CH of C_6H_8P), 146.90 (d, J_{CP} = 15.25, C-4 or C-5 of C_7H_8P), 147.95 (dd, $^2J_{CP}$ = 16.55, $^2J_{CP}$ = 10.20, C-3 of C_7H_8P), 152.90 (m, =C– of C_6H_8P), 161.40 (m, C-2 of C_7H_8P), 235.00–237.00 (m, CO), 241.75 (d, $^2J_{CP}$ = 35.10, CO), 242.00–244.00 (m, CO), 251.00–253.00 (m, CO). – $C_{27}H_{26}Mo_2O_4P_2$ (668.3): calcd. C 48.52, H 3.92; found C 48.28, H 4.04.

[$Mo_2(CO)_2\{\eta^5(C_5H_5)\}_2\{\mu$-[2-(diethoxyphosphanyl)-4,5-dimethylphosphinine]}] (**16**): A solution of complexes **13a, b** (0.50 g, 0.74 mmol) in xylene (20 ml) was heated at reflux under a flow of nitrogen (the Schlenk tube was connected to a bubbler to monitor the evolution of CO). After 6 h, ^{31}P-NMR control indicated the end of the reaction and the solvent was evaporated. The brown powder thus obtained was then washed twice with pentane (2 × 20 ml) in order to remove any traces of unreacted complex **13**. Complex **16** was collected on a frit after the evaporation of the solvent. After drying, **16** was recovered as a red-brown solid. Yield: 0.25 g (55%), m.p. 160°C (dec.). – IR (CH_2Cl_2) ν(CO): 1856 (m) cm^{-1}, 1806 (m). – ^{31}P NMr (C_6D_6): δ = 256.35 (d, $^2J_{PP}$ = 188.95, P of C_7H_8P), 223.75 [d, $P(OEt)_2$], ^1H NMR (C_6D_6): δ = 1.13 (t, 6H, $^3J_{HH}$ = 7.04, Me of OEt), 1.88 (s, 3H, Me of C_7H_8P), 1.96 (d, 3H, J_{HP} = 3.47, Me of C_7H_8P), 4.00 (m, 4H, CH_2 of OEt), 4.94 (d, 5H, $^3J_{HP}$ = 1.81, C_5H_5), 4.96 (d, 5H, $^3J_{HP}$ = 1.60, C_5H_5), 7.16 (dd, 1H, $^2J_{HP}$ = 24.49, $^4J_{HP}$ = 7.80, 6-H), 7.45 (dd, 1H, $^3J_{HP}$ = 22.30, $^3J_{HP}$ = 15.03, 3-H). – ^{13}C NMR (C_6D_6): δ = 17.35 (d, $^3J_{CP}$ = 8.84, Me of OEt), 21.70 (s, Me of C_7H_8P), 21.90 (s, Me of C_7H_8P), 61.50 (s, CH_2 of OEt), 89.10 (s, C_5H_5), 90.00 (s, C_5H_5), 132.30 (dd, J_{CP} = 22.15, J_{CP} = 6.85, C-4 or C-5), 136.90 (d, $^1J_{CP}$ = 9.16, C-6), 143.75 (dd, $^2J_{CP}$ = 22.85, $^2J_{CP}$ = 9.10, C-3), 149.25 (d, J_{CP} = 12.20, C-4 or C-5), 168.20 (t, $^1J_{CP}$ = $^1J_{CP}$ = 23.65, C-2), 227.15 (t, $^2J_{CP}$ = 6.85, 2 × CO). – $C_{23}H_{28}Mo_2O_4P_2$ (622.3): calcd. C 44.39, H 4.54; found C 44.60, H 4.56.

[$Mo_2(CO)_2\{\eta^5(C_5H_5)\}_2\{\mu$-(2-[di-(p-tert-butylphenoxy)-phosphanyl]-4,5-dimethylphosphinine)}] (**17**): A solution of complex **12** (0.40 g, 0.45 mmol) in xylene (15 ml) was heated at reflux under a flow of nitrogen. After 6 h, when no more CO was evolved, ^{31}P-NMR control indicated the end of the reaction. The solvent was then evaporated and the brown powder thus obtained was redissolved in hexane (40 ml). After filtration under nitrogen and evaporation of the hexane, complex **17** was recovered as a red-brown solid. Yield: 0.19 g (50%), m.p. 160°C (dec.). – IR (CH_2Cl_2) ν(CO): 1869 (m) cm^{-1}, 1781 (s). – ^{31}P NMR ([D_8]THF): δ = 254.60 (d, $^2J_{PP}$ = 207.40, P of C_7H_8P), 226.20 [d, $P(OC_6H_4tBu)_2$]. – ^1H NMR ([D_8]THF): δ = 1.24 (s, 9H, Me of *t*Bu), 1.27 (s, 9H, Me of *t*Bu), 2.22 (d, 3H, J_{HP} = 4.60, Me of C_7H_8P), 2.28 (s, 3H, Me of C_7H_8P), 4.20 (d, 5H, $^3J_{HP}$ = 1.09, C_5H_5), 5.11 (d, 5H, $^3J_{HP}$ = 1.67, C_5H_5), 6.99–7.51 (m, 9H, CH of C_6H_4tBu and 3-H), 7.67 (dd, 1H, $^2J_{HP}$ = 25.09, $^4J_{HP}$ = 8.88, 6-H). – ^{13}C NMR ([D_8]THF): δ = 22.75 (s, Me of C_7H_8P), 25.70 (d, J_{CP} = 10.35, Me of C_7H_8P), 33.20 (s, Me of *t*Bu), 33.40 (s, Me of *t*Bu), 36.30 (s, Cq of *t*Bu), 90.35 (s, C_5H_5), 91.50 (s, C_5H_5), 123.95, 124.10, 128.00, 128.05 (m, CH of C_6H_4tBu), 134.65 (dd, J_{CP} = 23.20 J_{CP} = 8.15, C-4 or C-5), 139.30 (d, $^1J_{CP}$ = 9.90, C-6), 145.10 (dd, $^2J_{CP}$ = 23.30, $^2J_{CP}$ = 10.70, C-3), 148.65 (s, Cq of C_6H_4tBu), 151.50 (d, J_{CP} = 14.75, C-

4 or C-5), 152.95 (s, Cq-O of C_6H_4tBu), 153.00 (s, Cq-O of C_6H_4tBu), 171.35 (dd, $^1J_{CP}$ = 24.35, $^1J_{CP}$ = 18.55, C-2), 211.90 (t, $^2J_{CP}$ = 6.95, CO). – $C_{39}H_{44}Mo_2O_4P_2$ (830.6): calcd. C 56.40, H 5.34; found C 56.25, H 5.30.

General Procedure for the Synthesis of Complexes **18** *and* **19**

[$Mo_2(CO)_2\{\eta^5(C_5H_5)\}_2\{\mu$-(σ,π-CNtBu)$\}\{\mu$-[2-(diethoxyphosphanyl)-4,5-dimethylphosphinine]$\}$] (**18**): *tert*-Butyl isocyanide (0.025 g, 0.30 mmol) was added at room temperature to a solution of complex **16** (0.19 g, 0.30 mmol) in toluene. After 5 min, ^{31}P-NMR control indicated the end of the reaction. Evaporation of the solvent yielded a black-green solid, which was redissolved in hexane (20 ml) and the resulting solution was filtered under nitrogen. Evaporation of the hexane yielded **18** as a dark-green solid. Yield: 0.19 g (90%), m.p. 130°C (dec.). – IR (toluene) ν(CO): 1955 (m) cm^{-1}, 1900 (m), 1865 (m), 1847 (s), 1821 (s), 1798 (s), 1678 (m, CN*t*Bu). – ^{31}P NMR (C_6D_6): δ = 249.75 (d, $^2J_{PP}$ = 158.75, P of C_7H_8P), 190.95 [d, $P(OEt)_2$]. – ^{1}H NMR (C_6D_6): δ = 1.11 (t, 6H, $^3J_{HH}$ = 7.09, Me of OEt), 1.24 (s, 9H, Me of *t*Bu), 1.80 (s, 3H, Me of C_7H_8P), 1.96 (d, 3H, J_{HP} = 5.35, Me of C_7H_8P), 3.44–4.00 (m, 4H, CH_2 of OEt), 4.91 (s, 5H, C_5H_5), 5.17 (d, 5H, $^3J_{HP}$ = 1.31, H of C_5H_5), 7.08–7.25 (m, 1H, 3-H), 8.08 (dd, 1H, $^2J_{HP}$ = 20.26, $^4J_{HP}$ = 7.61, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 16.15 (d, $^3J_{CP}$ = 7.05, Me of OEt), 17.00 (d, $^3J_{CP}$ = 7.58, Me of OEt), 21.85 (s, Me of C_7H_8P), 24.35 (d, J_{CP} = 9.20, Me of C_7H_8P), 31.70 (s, Me of *t*Bu), 60.10 (m, CH_2 of OEt), 61.40 (s, Cq of *t*Bu), 90.45 (s, C_5H_5), 93.80 (s, C_5H_5), 128.70 (C-4 or C-5 partially masked by C_6D_6), 134.20 (d, $^1J_{CP}$ = 10.70, C-6), 143.70 (t, $^2J_{CP}$ = 19.10, C-3), 147.05 (d, J_{CP} = 15.25, C-4 or C-5), 180.95 (dd, $^1J_{CP}$ = 38.15, $^1J_{CP}$ = 19.84, C-2), 216.60 (s, CN), 223.45 (d, $^2J_{CP}$ = 36.60, CO), 236.15 (d, $^2J_{CP}$ = 22.90, CO). – $C_{28}H_{37}Mo_2NO_4P_2$: (705.4) calcd. C 47.67, H 5.29; found C 47.85, H 5.35.

[$Mo_2(CO)_2\{\eta^5(C_5H_5)\}_2\{\mu$-(σ,π-CNtBu)$\}\{\mu$-(2-(di-(p-tert-butylphenoxy)phosphanyl)-4,5-dimethylphosphinine)$\}$] (**19**): Starting from complex **17** (0.12 g, 0.14 mmol), **19** was isolated as a dark-green solid. Yield: 0.11 g (90%), m.p. 150°C (dec.). – IR (toluene) ν(CO): 1950 (m) cm^{-1}, 1905 (s), 1872 (s), 1852 (s), 1824 (s), 1794 (s). – ^{31}P NMR ($CDCl_3$): δ = 247.55 (d, $^2J_{CP}$ = 176.50, P of C_7H_8P), 189.95 [d, $P(OC_6H_4tBu)_2$]. – ^{1}H NMR ($CDCl_3$): δ = 1.28 (m, 18H, Me of *t*Bu), 2.07 (s, 3H, Me of C_7H_8P), 2.19 (d, 3H, J_{HP} = 5.10, Me of C_7H_8P), 4.57 (s, 5H, C_5H_5), 5.27 (s, 5H, C_5H_5), 7.02–7.29 (m, 9H, CH of C_6H_4tBu and 3-H), 7.57 (dd, 1H, $^2J_{HP}$ = 21.18, $^4J_{HP}$ = 8.46, 6-H). – ^{13}C NMR (C_6D_6): δ = 22.10 (s, Me of C_7H_8P), 24.35 (d, J_{CP} = 9.20, Me of C_7H_8P), 32.00 (s, Me of *t*Bu), 32.15 (s, Me of *t*Bu), 32.20 (s, Me of *t*Bu), 34.80 (s, Cq of *t*Bu), 34.90 (s, Cq of *t*Bu), 60.00 (s, Cq of N-*t*Bu), 90.05 (s, C_5H_5), 94.20 (s, C_5H_5), 120.70 (d, J_{CP} = 6.95, CH of C_6H_4tBu), 121.30 (d, J_{CP} = 4.65, CH of C_6H_4tBu), 126.35–130.0 (m, partially masked by C_6D_6, CH of C_6H_4tBu and C-4 or C-5 of C_7H_8P), 135.05 (d, $^1J_{CP}$ = 14.50, C-6 of C_7H_8P), 142.75 (t, $^2J_{CP}$ = $^2J_{CP}$ = 20.30, C-3), 147.10 (s, Cq of C_6H_4tBu), 152.55 (s, Cq of C_6H_4tBu), 182.35 (dd, $^1J_{CP}$ = 38.15, $^1J_{CP}$ = 19.84, C-2 of C_7H_8P), 211.70 (d, $^2J_{CP}$ = 36.60, CO), 215.85 (s, CN), 224.40 (d, $^2J_{CP}$ = 22.90, CO). – Complex **19** was too oxygen sensitive to give satisfactory analytical data.

Crystal Structure Analysis[23]: Crystals of **13a**, $C_{25}H_{28}Mo_2O_6P_2$, were grown from a THF/hexane solution of the compound. Data were collected at –150 ± 0.5°C with an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P\bar{1}$(no. 2), a = 10.143(1), b = 10.950(1), c = 11.914(1) Å, α = 80.05(1), β = 84.26(1), γ = 87.48(1)°; V = 1296.39(28) Å^3; Z = 2; $d_{calcd.}$ = 1.738 g/cm^3; μ = 11.0 cm^{-1}; $F(000)$ = 6.80. A total of 7886 unique reflections were recorded in the range 2° ≤ 2Θ ≤ 60.0°, of which 1129 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 6757 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.06. The final agreement factors were R = 0.022, R_w = 0.037, G.O.F. = 1.03.

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[23] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100093. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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