(η^3-Phosphaallyl)iron Complexes: Synthesis and Preliminary Chemical Study

François Mercier, Catherine Hugel-Le Goff, and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH-Ecole Polytechnique, 91128 Palaiseau Cedex, France

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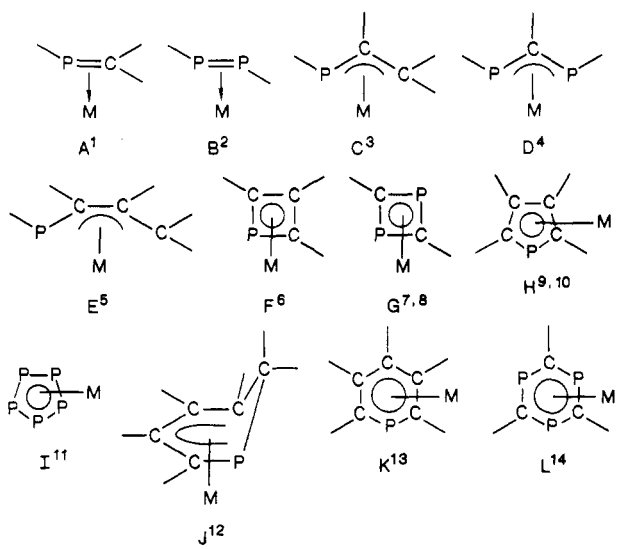
Vinylchlorophosphine P–$W(CO)_5$ complexes react in boiling toluene with $[CpFe(CO)_2]_2$ to give μ_2-vinylphosphido complexes whose phosphorus atom bridges a $W(CO)_5$ and a $Fe(CO)_2Cp$ unit. Upon short irradiation, these μ_2-complexes yield (η^3-1-phosphaallyl)Fe(CO)Cp complexes as mixtures of two isomers. These two series of isomers undergo a slow equilibration in solution. This equilibration takes place via the decoordination and the upside-down rotation of the vinyl unit followed by a recomplexation of this unit by the iron atom. These two series of isomers differ mainly in the magnitude of the $^2J(P\text{–}C\text{–}H)$ coupling constants within the phosphaallyl unit. The constant is high (ca. 30 Hz) when the W–P–C–H dihedral angle is close to 0° and low (ca. 0 Hz) when this angle is close to 180°. A slightly different synthetic scheme is devised for preparing the η^3-(*t*-Bu)P($CH{=}CH_2$) complex. In that case, the pure anti isomer is obtained as the sole product (W–P–C–H $\simeq$ 180°). The replacement of the $W(CO)_5$ protecting group by $Fe(CO)_4$ met with only limited success. The η^3-phosphaallyl structure seems to need a bulky P-complexing group to achieve kinetic stability. The vinyl subunit of the η^3-phosphaallyl complexes is displaced from the coordination sphere of iron by CO under pressure, PPh_3, and $P(OMe)_3$. In the last two cases, the external phosphine or phosphite ligand ends up in the coordination sphere of tungsten, contrary to expectation. Iodine completely breaks the η^3-phosphaallyl–iron bond and gives a vinyliodophosphine P–$W(CO)_5$ complex.

During the last few years, numerous phosphorus analogues of classical transition-metal π-complexes have been described in the literature[1–14] as evidenced by the 12 generic formulas which are listed here (A–L) (triple-deckers have been excluded). This flurry of new discoveries clearly demonstrates the exceptional ability of phosphorus to replace carbon in the skeleton of any typical unsaturated hydrocarbon π-complex.[15] At the moment, however, the chemistry of these species remains practically unknown except in the case of the so-called phosphametallocenes (type H).[10] Thus, in order to expand our knowledge concerning the chemical behavior of such π-phospha complexes, we decided to perform a thorough investigation of the synthesis and chemical properties of one new type of the class, i.e., the (η^3-1-phosphaallyl)iron complexes (type C) which have been recently discovered in our laboratory.[3] The first results of this study are reported here.



Results and Discussion

In our preliminary work,[3] we used a rather lengthy route to prepare the desired η^3-complexes (eq 1). The overall yield was low, and a mixture of three main types of complexes was finally obtained. Our first aim was thus to prepare **6** via a more selective and efficient scheme. We found that it was possible to avoid the reduction step (**2** → **3**) and to use directly the chloro complex **2** as the

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(15) This topic is discussed in some depth in ref 10.

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(19) Deschamps, B.; Mathey, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.* **1984**, *23*, 3455.

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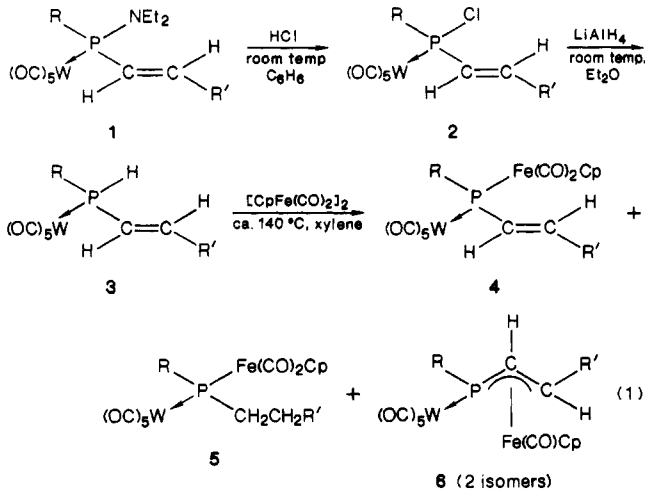
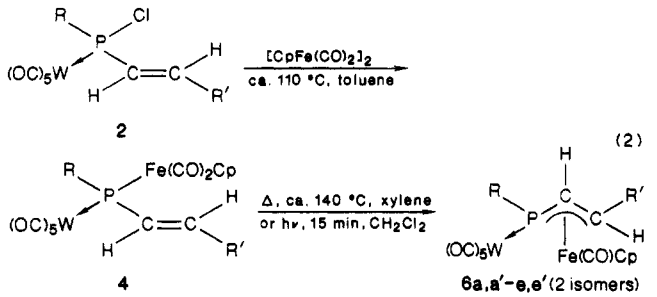


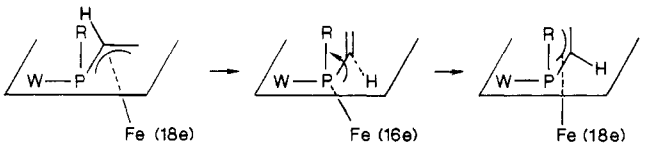
starting material (eq 2). In so doing, we also avoided the



a,a', R=Ph, R'=H; b,b', R=R'=Ph; c,c', R=Me, R'=H; d,d', R=-CH=CH_2, R'=H; e,e', R=*trans*-CH=CHPh, R'=Ph

hydrogenation of the vinyl group (apparently, the P–H bond of **3** was at the origin of this reduction) and greatly improved the overall yields of **6**. Using this modified scheme, we were then able to prepare a series of complexes, **6a,a'–e,e'**, with different R and R' groups.

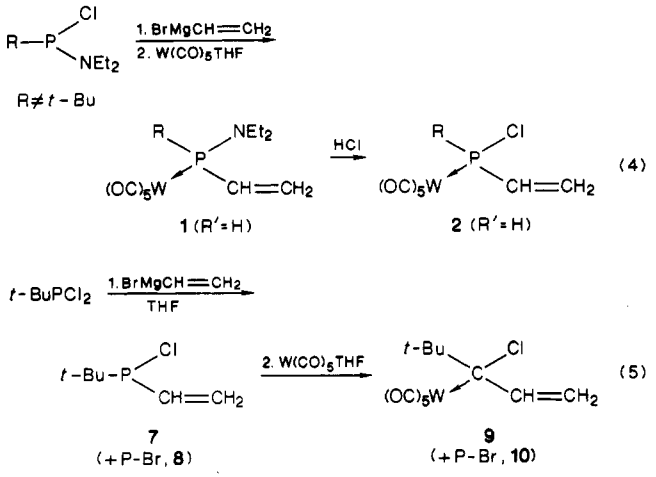
The most striking observation concerning these η^3-complexes **6a,a'-e,e'** is that they are always obtained as mixtures of two isomers. The ratio and the relative stabilities of these isomers, of course, depend on the substitution pattern. In all cases, the **a–e** isomers are obtained as the major products by the thermal route whereas the **a'–e'** isomers are the main products of the UV route. All our experiments indicate that **6a–e** are the thermodynamically most stable isomers. Indeed, a slow conversion of **6a'–e'** into **6a–e** is observed in solution, the speed of which increases with the temperature. In the cases of **6a,a'** and **6b,b'** the two isomers are sufficiently stable so that it is possible to isolate both of them in the pure state. Before the nature of the **6a'–e'** ⇌ **6a–e** interconversion is discussed, the main features of the molecular structures of **6a** and **6b** as established by X-ray analysis in our preliminary note[3] must be recalled. The tungsten atom and the phosphaallyl unit are practically coplanar; the R substituent at phosphorus lies on the side of this plane opposite to the side of the iron atom. Besides, the α-hydrogen atom of the phosphaallyl unit is *syn* to the tungsten atom in both cases. Unfortunately, we have not been able to grow satisfactory crystals of **6a'** or **6b'** for X-ray analysis. Thus, the nature of the isomerization **6a',b'** → **6a,b** must be discussed on the basis of a comparison between the NMR data of these isomers. This comparison is made for **6a,a'** in Tables I and II. It immediately appears that the ^1H and ^{13}C NMR characteristics of both isomers are remarkably similar except in one case. The ^2J(H–P) coupling between the α-vinylic hydrogen H_c and phosphorus is extremely high in **6a** (29.8 Hz) and extremely low in **6a'** (2.0 Hz). A similar phenomenon is observed in the case of **6b** and **6b'**. A priori, the equilibration between **6a–e** and **6a'–e'** can take place via the decoordination of either the C=C bond, the phosphorus atom, or the whole phosphaallyl ligand. The reactivity experiments which are described later in this paper convincingly show that external ligands easily displace the C=C double bond from the coordination sphere of iron without cleaving the P—Fe bond. Thus, the first mechanism is by far the most likely (eq 3).



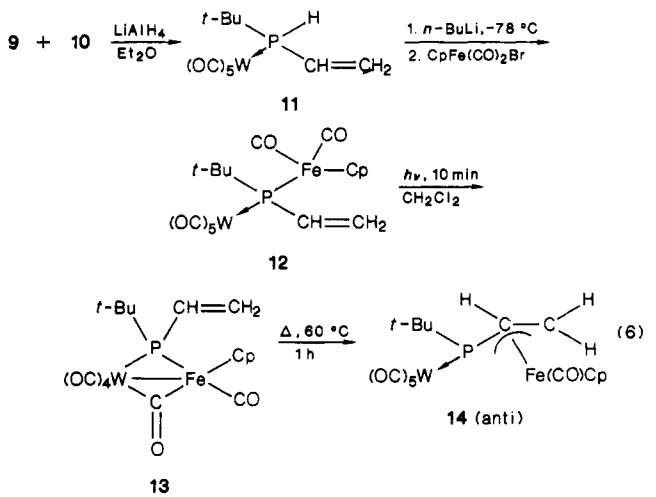
If we accept this isomerization mechanism, then the α-hydrogen atom that is syn to W in **6a–e** becomes anti to W in **6a'–e'**. The problem is now to check whether or not this hypothesis fits the drastic decrease of the ^2J(H–P) coupling constants that is observed when the ^1H NMR spectra of **6a–e** are compared with those of **6a'–e'**. The only comparable data that are available in the literature concern the ^2J(H–P) couplings in a series of phosphorus-containing π-complexes. In a free phosphaalkene such as Cl—P=CH_2, the ^2J(H–P) coupling is high for the hydrogen that is syn to the lone pair and low for the hydrogen which is anti[16] (see Table III). A similar observation holds true for related phosphorus-containing π-complexes even when the lone pair at phosphorus is σ-bonded to another metallic center (Table III). Thus, we can consider that the ^1H NMR data provide a strong additional argument in favor of the isomerization scheme depicted in eq 3. Other, less compelling evidence can be drawn from the ^{13}C NMR data. Quin has shown that the well-known stereospecificity of the ^2J(P–C) couplings in phosphines (^2J(P–C) is large when C is close to the lone pair and small when remote) holds for phosphine complexes.[20,21] In our case, ^2J(P–CH_2) is small for **6a** when CH_2 is anti to W (7.3 Hz) and higher for **6a'** when CH_2 is syn to W (11.0 Hz). Of course, the difference is small and **6a,a'** are not strictly similar to classical phosphine complexes. Before leaving the subject, it is interesting to note the shielding of the Cp hydrogens in **6a'**. This may be related to steric compression. Indeed in **6a'**, the cyclopentadienyl ring comes close to the carbonyls of the $W(CO)_5$ group.

Coming back now to the synthetic problems, it soon appeared that the schemes depicted in eq 1 and 2 did not work conveniently when R = *tert*-butyl. Since this case was especially interesting due to the expected additional stability provided to the various complexes by this bulky substituent, we tried to improve the situation. We thus found that it was not necessary any more to protect by aminolysis one of the P–Cl bonds during the reaction of *t*-$BuPCl_2$ with the vinylmagnesium compound. The standard and the *t*-Bu cases are compared in eq 4 and 5. The chlorophosphine **7** was always mixed in various proportions with the corresponding bromophosphine **8** formed by metathetical exchange with $MgBr_2$ as evidenced by ^{31}P NMR spectroscopy and mass spectrometry (**7**, $\delta(^{31}P)$ +105, m/z 150 (M^+, ^{35}Cl); **8**, $\delta(^{31}P)$ +99, m/z 195 (M^+)). Com-

(20) Quin, L. D.; Mesch, K. A.; Stone-Berger Pinault, F.; Crumbliss, A. L. *Inorg. Chim. Acta* **1981**, *53*, L223.
(21) Crumbliss, A. L.; Topping, R. J.; Quin, L. D. *Tetrahedron Lett.* **1986**, *27*, 889.

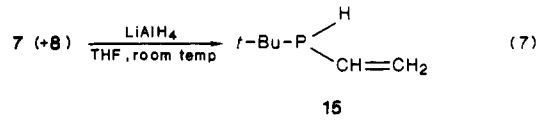


pound **7** was used as such without further purification, and thus the chloro complex **9** was always contaminated by the bromo complex **10**. The following steps were again different from the standard scheme (eq 6). Contrary to the

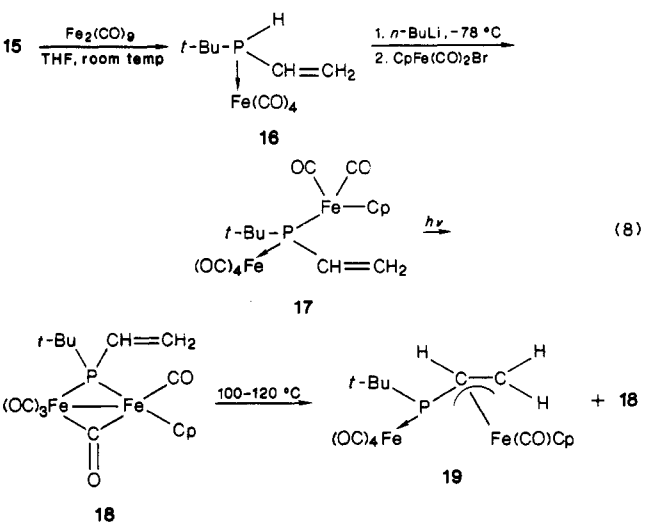


normal case where it spontaneously dimerizes to give a 1,4-diphosphacyclohexane ring,[22] the P anion from **11** is reasonably stable due to steric protection by the *tert*-butyl group. Thus, it became possible to use it to prepare the η^1-iron complex **12** analogous to **4**. The last steps were classical. However, in that case, we were able to isolate and fully characterize an intermediate μ_2 complex, **13**, which is similar to a series of phosphido-bridged bimetallic complexes recently described by King.[23] In the standard case, complexes analogous to **13** were transiently observed during the UV irradiation of complexes **4**, but we were unable to purify them owing to their instability. Their formation was just monitored by ^{31}P NMR and IR spectroscopy. Finally, the most noteworthy feature of this synthetic sequence is that it afforded only one pure η^3-phosphaallyl complex **14** which has clearly the anti structure. Indeed, all the protons of the vinyl unit of **14** show H–H and H–P couplings very similar to those of **6a'** including a $^2J(H\text{–}C\text{–}P)$ coupling constant close to 0 Hz. No isomerization of **14** into its syn counterpart was ever observed in our experiments. It seems that in the *t*-Bu case, the anti complex is both the kinetic and the thermodynamic isomer. It probably means that the anti structure is less hindered than the syn one.

The next step of our synthetic effort concerned the following question: is it possible to replace the $W(CO)_5$ phosphorus protecting group by another group such as $Fe(CO)_4$, for example? Ultimately, would it be possible to suppress the protecting group? After various unsuccessful trials in the Ph–P series, we decided to work in the *t*-Bu–P series. Our approach relied on the possibility of getting pure secondary *tert*-butylvinylphosphine (**15**) by reduction of the corresponding chlorophosphine (**7**) (eq 7).

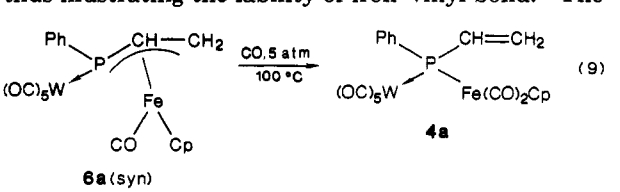


Since the work of Ripoll,[24] who showed that primary vinylphosphine is reasonably stable at room temperature when pure, it is not so surprising to find that pure **15** can be also easily obtained. Then, the next steps of the scheme were very similar to those depicted in eq 6 (eq 8). The



phosphido-bridged diiron complex **18** showed good thermal stability. Upon heating at 100–120 °C, it partly isomerized to give an inseparable mixture of **18** and of the expected η^3-phosphaallyl complex **19**. An analysis of the ^1H NMR spectrum of the mixture **18** + **19** did not lead to clear-cut conclusions concerning the structure of **19**. Indeed, the H–P coupling constants of the vinylic protons of **19** are very different from those of both **6a** and **6a'**. The limited success of these experiments with the $Fe(CO)_4$ protecting group convincingly demonstrates the need for an efficient and bulky stabilizing group such as $W(CO)_5$ at least when working on weakly substituted η^3-phosphaallyl complexes such as those described here.

Finally, in order to get an overall picture of the chemical properties of these η^3-phosphaallyl complexes, we undertook a preliminary study of the reactivity of **6a**. The reaction with CO gives back easily the η^1-complex **4a** (eq 9), thus illustrating the lability of iron–vinyl bond. The



reaction with phosphines and phosphites follows the same

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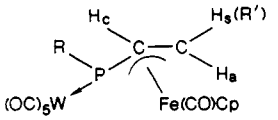
(23) King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 3094; **1986**, *25*, 2394.
(24) Lasne, M.-C.; Ripoll, J.-L.; Thuillier, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1428.

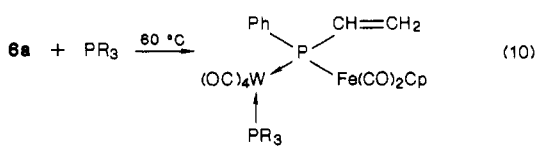
Table I. ^{31}P and ^{1}H NMR Data of η^3-Phosphaallyl Complexes 6 and 14



products (solv)	^{31}P NMR δ	^{31}P NMR $^1J(^{31}P-^{183}W)$, Hz	^{1}H NMR[a] H_a H_s	H_c	Cp
6a	−6.9	224.6	1.72 3.66 7.6 = ^3J(H-P) = 24.4 1.2 = ^2J(H-H) = 1.2 12.5 = ^3J(H-H) = 8.8	4.32 ^2J(H-P) = 29.8 ^3J(H-H) = 12.5 ^3J(H-H) = 8.8	4.86
6a′	−25.6	231.9	1.74 3.47 9.3 = ^3J(H-P) = 34.2 1.9 = ^2J(H-H) = 1.9 12.4 = ^3J(H-H) = 9.0	5.10 ^2J(H-P) = 2.0 ^3J(H-H) = 12.4 ^3J(H-H) = 9.0	4.45
6b (CD_2Cl_2)	−20.5	227.0	3.39 ^3J(H-P) = 7.6 ^3J(H-H) = 12.2	5.10 ^2J(H-P) = 27 ^3J(H-H) = 12.2	4.59
6b′ (CD_2Cl_2)	−36.4	231.9	3.45 ^3J(H-P) = 10.2 ^3J(H-H) = 12.4	5.86 ^2J(H-P) ≃ 0 ^3J(H-H) ≃ 12.4	4.16
6c	−27.5	228.5	1.63 3.52 8.0 = ^3J(H-P) = 24.7 1.9 = ^2J(H-H) = 1.9 12.5 = ^3J(H-H) = 8.5	4.22 ^2J(H-P) = 29.8 ^3J(H-H) = 12.5 ^3J(H-H) = 8.5	4.12
6d	−17.7	234.4	1.81 3.43 7.6 = ^3J(H-P) = 23.9 1.7 = ^2J(H-H) = 1.7 12.2 = ^3J(H-H) = 8.5	4.20 ^2J(H-P) = 30.3 ^3J(H-H) = 12.2 ^2J(H-H) = 8.5	4.75
6d′	−37.4	234.0	1.66 3.39 10.1 = ^3J(H-P) = 34.0 1.7 = ^2J(H-H) = 1.7 11.1 = ^3J(H-H) = 8.1	4.75 ^2J(H-P) ≃ 0 ^3J(H-H) = 11.1 ^3J(H-H) = 8.1	4.66
6e (C_6D_6)	−35.6	234.6	3.43 ^3J(H-P) = 7.8 ^3J(H-H) = 12.0	4.92 ^2J(H-P) = 28.1 ^3J(H-H) = 12.0	4.07
6e′ (C_6D_6)	−52.5	234.6	3.48 ^3J(H-P) = 9.8 ^3J(H-H) = 12.5	5.17 ^2J(H-P) ≃ 0 ^3J(H-H) = 12.5	3.68
14	20.0	224.6	1.78 3.38 10.01 = ^3J(H-P) = 30.28 1.71 = ^2J(H-H) = 1.71 12.21 = ^3J(H-H) = 9.03	4.76 ^2J(H-P) ≃ 0 ^3J(H-H) = 12.21 ^2J(H-H) = 9.03	4.81

[a] Chemical shifts in δ and J values in Hz.

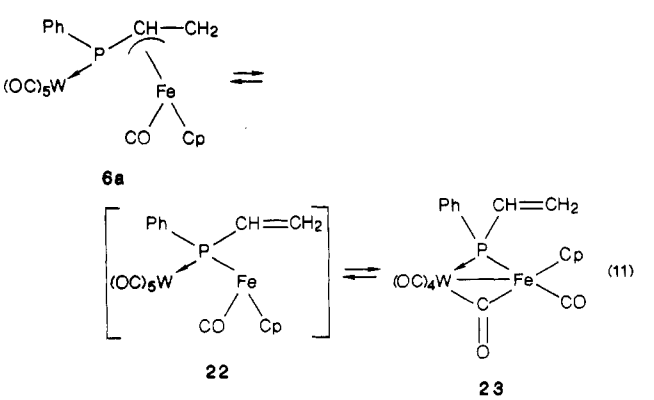
course, but, curiously, the phosphorus ligand is bonded to tungsten and not to iron in the final η^1-complexes (eq 10) as demonstrated by the existence of huge $^1J(^{31}P-^{183}W)$ couplings. The two phosphorus atoms of **20b** and **21** are



(10)

20a,b, R=Ph
21, R=OMe

cis in the coordination sphere of tungsten as indicated by the weak ^2J(P–P) coupling constants (respectively 26.9 and 31.7 Hz for **20b** and **21**).[25] In contrast, the additional complex **20a** has probably the trans stereochemistry (^2J(P–P) = 53.7 Hz). The formation of **20** and **21** suggests the existence of an equilibrium between **6a** and a phosphido-bridged complex, **23**, similar to **13** (eq 11) via the intermediate unstable 16-electron complex **22** which very likely intervenes in the syn–anti equilibration **6a** ⇌ **6a′** (vide supra). The attack of PR_3 would take place on the



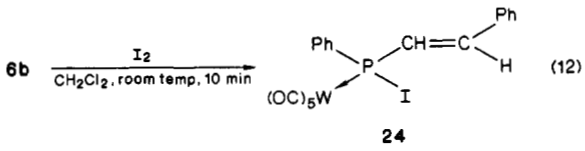
(11)

tungsten atom of **23** with displacement of the bridging CO leading to the observed cis structure as the only stereochemistry except when PR_3 is too bulky. It must be remembered here that **23** has been transiently observed by ^{31}P NMR [(CH_2Cl_2) δ +142.57 ($^1J(^{31}P-^{183}W)$ = 200.2 Hz)] and IR spectroscopy during the UV irradiation of **6a**.

The lability of the η^3-bonding between the phosphaallyl group and the iron atom is again illustrated by the reaction

(25) Recorded couplings are in the range 0–38 Hz for *cis*-$L_2W(CO)_4$ and in the range 65–315 Hz for *trans*-$L_2W(CO)_4$ (L = monodentate phosphorus ligand), see: Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; pp 116, 118.

of **6b** with iodine at room temperature (eq 12). In complex



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24, the P–W bond is preserved as indicated by the huge (^{31}P–^{183}W) coupling, but the P–Fe bond has been broken as checked by ^{13}C NMR, IR, and mass spectrometry.

This lability of the η^3-structure suggests some possible uses of similar complexes in homogeneous catalysis.

Experimental Section

All reactions were carried out under dry oxygen-free argon atmosphere. All solvents were freshly distilled over appropriate drying agents. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13, 20.15, and 32.435 MHz, respectively. Some ^{1}H and ^{13}C spectra were recorded on a Bruker 200-MHz ACSY instrument. Chemical shifts are given in parts per million downfield from internal Me_4Si for ^{1}H and ^{13}C shifts and from external 85% H_3PO_4 for ^{31}P shifts whereas coupling constants are given in hertz (Hz). NMR spectra were obtained in $CDCl_3$ unless otherwise stated. Infrared spectra were recorded in decalin solutions or in NaCl pellets on a Perkin-Elmer 297 spectrophotometer and mass spectra on a Shimadzu GCMS-QP1000 spectrometer at 70 eV. Elemental analyses were performed by the Service Central de Microanalyse of the CNRS, France.

General Data. Chromatographic separations were performed on silica gel columns (70–230 mesh, Merck). $W(CO)_6$, $Fe_2(CO)_9$, and $[CpFe(CO)_2]_2$ were purchased from Strem Chemical Inc. $PhPCl_2$, PCl_3, $MePCl_2$, PPh_3, $P(OMe)_3$, $BrCH{=}CH_2$, $PhCH{=}CHBr$, *n*-BuLi, *t*-BuLi, $LiAlH_4$, I_2, and Br_2 were used as received without further purification. Et_2NPCl_2,[26] *t*-$BuPCl_2$,[27] $CpFe(CO)_2Br$,[28] $RPCl(NEt_2)$,[26] and $RP(NEt_2)(CH{=}CHR')$[26] were obtained as previously described. UV irradiations were performed with 125-W medium-pressure mercury lamp.

General Procedure for the Synthesis of $(OC)_5W[RP(NEt_2)(CH{=}CHR')]$ (1). A THF solution of 1 equiv of $BrMgCH{=}CHR'$ (25 mL, 0.4 M) at −78 °C was added dropwise to a 10-mL THF solution of 1 equiv (10 mmol) of $RPCl(NEt_2)$; the resulting mixture was stirred for 0.5 h at this temperature and then allowed to warm to room temperature. The crude reaction mixture was poured into a solution of $W(CO)_5$·THF (from 3.5 g (10 mmol) of $W(CO)_6$ in 250 mL of THF under UV irradiation for 1 h at room temperature) and then stirred for 2 h. The solvent was removed under vacuum, and the residue was extracted twice with Et_2O (50 mL) and chromatographed rapidly on a short column of silica gel (20 g) with Et_2O.

$(CO)_5W[PhP(NEt_2)(CH{=}CH_2)]$ (1a). This procedure applied to 2.15 g of $PhPCl(NEt_2)$ yielded after chromatography a pale yellow oil (4.0 g, 75%): ^{1}H NMR δ 1.06 (t, ^3J(H–H) = 7.1 Hz, 6 H, CH_3), 3.20 (dq, ^3J(H–P) = 11.5 Hz, 4 H, CH_2N), 5.66–6.86 (m, ABCX, 3 H, vinyl), 7.44 (br s, 5 H, Ph); ^{31}P NMR δ 68.1 ($^1J(^{31}P–^{183}W)$ = 258.8 Hz); IR ν(CO) 2070 (w), 1940–1945 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 531 (M, 48), 317 (100). Anal. Calcd for $C_{17}H_{18}NO_5PW$: C, 38.34; H, 3.42; N, 2.64; P, 5.83. Found: C, 38.97; H, 3.49; N, 2.45; P, 5.68.

$(CO)_5W[PhP(NEt_2)(CH{=}CHPh)]$ (1b). The same procedure gave a yellow oil (1.8 g, 30%) that was not pure enough for correct elemental analysis: ^{1}H NMR (C_6D_6) δ 0.84 (t, ^3J(H–H) = 7.0 Hz, 6 H, CH_3), 3.0 (dq, ^3J(H–P) = 11.4 Hz, 4 H, CH_2N), 6.71–6.89 (dd, J(H–P) = 17.18 Hz, 2 H, vinyl ABX), 7.0–7.47 (m, 10 H, Ph); ^{31}P NMR δ 67.1 ($^1J(^{31}P–^{183}W)$ = 262.7 Hz); IR ν(CO) 2075 (w), 1938–1942 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 607 (M, 12), 495 (M − 4CO, 55), 353 (100).

$(CO)_5W[MeP(NEt_2)(CH{=}CH_2)]$ (1c). The general procedure applied to 1.53 g yielded a yellow oil (2.5 g, 53%): ^{1}H NMR δ 1.09 (t, ^3J(H–H) 7.1 Hz, 6 H, $MeCH_2$), 1.82 (d, ^2J(H–P) = 5.6 Hz, 3 H, Me), 3.10 (dq, ^3J(H–P) = 11.5 Hz, 4 H, CH_2N), 5.3–6.5 (m, ABCX, 3 H, vinyl); ^{31}P NMR δ 52.0 ($^1J(^{31}P–^{183}W)$ = 256.3 Hz); IR ν(CO) 2070 (w), 1940–1945 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 469 (M, 55), 385 (M − 3CO, 60), 327 (100). Anal. Calcd for $C_{12}H_{16}NO_5PW$: C, 30.73; H, 3.44; N, 2.98; P, 6.60; W, 39.20. Found: C, 30.98; H, 3.17; N, 2.92; P, 6.84; W, 39.19.

$(CO)_5W[P(NEt_2)(CH{=}CH_2)_2]$ (1d): see ref 22.

$(CO)_5W[P(NEt_2)(CH{=}CHPh)_2]$ (1e). The above procedure was applied to 1.74 g of Et_2NPCl_2 with 2 equiv of Grignard reagent. After chromatography, complex **1e** was obtained as an orange oil (1.3 g, 20%): ^{1}H NMR δ 1.13 (t, ^3J(H–H) = 7.1 Hz, 6 H, $MeCH_2$), 3.25 (dq, ^3J(H–P) = 11.5 Hz, 4 H, CH_2N), 6.76 (d, ABX, J(H–P) = 21.7 Hz, 2 H, vinyl), 6.82 (d, ABX, J(H–P) = 17.6 Hz, 2 H, vinyl), 7.31 (b s, 10 H, Ph); ^{31}P NMR δ 59.2 ($^1J(^{31}P–^{183}W)$ = 258.8 Hz); IR (CH_2Cl_2) ν(CO) 2060 (w), 1930 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 633 (M, 15), 493 (M − 5CO, 70), 420 (100). Anal. Calcd for $C_{25}H_{24}NO_5PW$: C, 47.43; H, 3.82; N, 2.21. Found: C, 47.64; H, 3.91; N, 1.86.

General Procedure for the Synthesis of $(CO)_5W[RPCl(CH{=}CHR')]$ (2). Gaseous hydrogen chloride was bubbled through a solution of complex **1** in benzene for 10 min. Removal of the solvent from the filtered pale yellow solution gave crude **2** as an oil in almost quantitative yield. The products thus obtained were practically pure according to their ^{31}P NMR spectra. $\delta(^{31}P)$ in C_6H_6 [$^1J(^{31}P–^{183}W)$, Hz]: **2a**, 87.0 [283.2]; **2b**, 87.8 [283.2]; **2d**, 78.4 [278.3]; **2e**, 81.6 [280.7]. Only the complex **2c** was completely characterized; the others were directly used for further reactions.

2c: ^{1}H NMR δ 2.32 (d, ^2J(H–P) = 4.64 Hz, 3 H, Me), 5.79–6.78 (m, ABCX, 3 H, vinyl); ^{31}P NMR δ 78.5 ($^1J(^{31}P–^{183}W)$ = 275.9 Hz); $^{13}C\{^1H\}$ NMR δ 28.47 (d, ^1J(C–P) = 21.22 Hz, Me), 128.74 (d, ^2J(C–P) = 4.94 Hz, $CH_2{=}$), 138.94 (d, ^1J(C–P) = 27.78 Hz, PCH), 195.34 (d, ^2J(C–P) = 7.35 Hz, cis CO), 198.55 (d, ^2J(C–P) = 30.0 Hz, trans CO); IR ν(CO) 2080 (w), 1955 (w), 1950 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 432 (M, 50), 348 (M − 3CO, 52), 392 (M − 5CO, 100). Anal. Calcd for $C_8H_6ClO_5PW$: C, 22.24; H, 1.40. Found: C, 22.47; H, 1.46.

General Procedure for the Preparation of $[(OC)_5WP(R)(CH{=}CHR')]Fe(CO)_2Cp$ (4). A mixture of the crude chlorophosphine **2** and 1 equiv of dimeric $[CpFe(CO)_2]_2$ was heated in toluene with magnetic stirring at 110 °C for 1 h. The solvent was removed under vacuum after filtration, and the resulting residue was chromatographed.

$[(OC)_5WP(Ph)(CH{=}CH_2)]Fe(CO)_2Cp$ (4a). This procedure applied to 5.0 g (10 mmol) of complex **2a** in 50 mL of toluene gave after elution with hexane/toluene (50:50) complex **4a** as a yellow-orange oil which was crystallized from 90:10 hexane/toluene (4.3 g, 68%): bright yellow solid; mp 125 °C; IR ν(CO) 2060 (w), 2020 (m), 1983 (m), 1935 (vs), 1920 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 636 (M, 3), 440 (M − 6CO), 100). Anal. Calcd for $C_{20}H_{13}FeO_7PW$: C, 37.77; H, 2.06; Fe, 8.78; P, 4.87. Found: C, 38.44; H, 1.94; Fe, 8.55; P, 4.87.

$[(OC)_5WP(Ph)(CH{=}CHPh)]Fe(CO)_2Cp$ (4b). The same experimental procedure was applied to 2.8 g of **2b** (5 mmol) and 1.7 g (5 mmol) of $[CpFe(CO)_2]_2$ to yield after chromatography (eluent hexane/toluene, 70:30) 1.9 g (54%) of **4b** as an orange oil: IR ν(CO) 2060 (w), 2020 (m), 1985 (m), 1938 (vs), 1925 (vs) cm^{-1}. Anal. Calcd for $C_{26}H_{17}FeO_7PW$: C, 43.86; H, 2.40; Fe, 7.84; P, 4.35. Found: C, 45.05; H, 2.49; Fe, 7.41; P, 4.34.

$[(OC)_5WP(Me)(CH{=}CH_2)]Fe(CO)_2Cp$ (4c). The same procedure applied to 2.15 g (5 mmol) of **2c** gave 0.71 g (25%) of **4c** as a pale yellow oil after purification by chromatography with hexane/toluene (90:10): IR ν(CO) 2060 (w), 2020 (m), 1988 (m), 1940 (vs), 1925 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 574 (M, 15), 434 (M − 5CO, 75), 362 (100). Anal. Calcd for $C_{15}H_{11}FeO_7PW$: C, 31.38; H, 1.92; Fe, 9.73; P, 5.39. Found: C, 31.31; H, 2.04; Fe, 9.42; P, 5.30.

$[(OC)_5WP(CH{=}CH_2)_2]Fe(CO)_2Cp$ (4d). The general procedure applied to 4.4 g (10 mmol) of **2d** yielded after chromatography with hexane/toluene (70:30) a yellow oil that was recrystallized from hexane/toluene (95:5): 3.0 g (52%); mp 132 °C; bright yellow solid; IR ν(CO) 2060 (m), 2020 (m), 1988 (m), 1935 (vs), 1925 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 586 (M,

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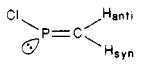
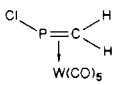
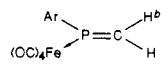
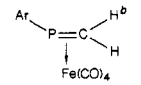
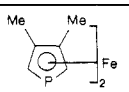
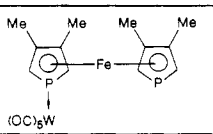
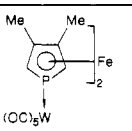
(27) Fild, M.; Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1973**, *14*, 4.
(28) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *Inorg. Synth.* **1955**, *1*, 165.

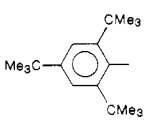
Table II. ^{13}C NMR Data[a] of η^3-Phosphaallyl Complexes 6 and 14

products (solv)	CHR′ (^2J(C–P))	CHP (^1J(C–P))	Cp	R	CO δ	CO ^2J(C–P)	
6a	47.84	61.62	83.22		198.48	8.5	cis
(CD_2Cl_2)	(7.3)	(3.7)			201.24	22.4	trans
					219.14	13.4	Fe
6a′	41.53	66.94	82.27		196.92	8.5	cis
	(11.0)	(7.3)			200.04	25.5	trans
					218.13	17.0	Fe
6b	58.59	69.41	84.79		198.51	7.3	cis
	(3.7)	(4.9)			201.15	25.6	trans
					219.75	13.4	Fe
6b′	64.14	64.17	84.67		197.90	7.3	cis
	(14.64)	(6.10)			200.0	22.2	trans
					219.55	19.5	Fe
6c	43.86	62.06	82.46	16.23	197.52	7.6	cis
	(7.2)	(6.5)		^1J(C–P) = 8.0	199.96	34.5	trans
					217.28	16.9	Fe
6d	45.47	61.29	82.29	125.3	197.38	7.3	cis
	(6.7)	(0)		136.3	199.63	24.0	trans
				^1J(C–P) = 12.7	218.16	12.5	Fe
6d′	41.18	67.48	81.45	126.3	196.41	7.5	cis
	(9.3)	(0)		142.0	198.3	25.6	trans
				^1J(C–P) = 15.1	212.45	16.5	Fe
6e	59.50	68.01	84.91		198.5	8.5	cis
(CD_2Cl_2)	(3.7)	(4.9)			200.0	25.6	trans
					220.0	13.4	Fe
6e′	63.65	65.95	84.24		197.90	7.5	cis
(CD_2Cl_2)					201.1	22.2	trans
					219.5	17.0	Fe
14	36.62	68.0	80.38	30.4 (6.8)	199.41	7.4	cis
(C_6D_6)	(0)	(17.16)		39.4 (6.8)			

[a] Chemical shifts in δ and J values in Hz.

Table III. Some Characteristic Syn and Anti ^2J(H–P) Couplings in Various Phosphorus-Containing π-Complexes[a]

				
^2J(H–P) syn	44.9	49.6	25.8	34.7
^2J(H–P) anti	14.4	7.6	9.6	9.0
ref	16	17	18	18
				
^2J(H–P) syn	36.1	33.4 and 36.1		33.9
ref	19	19		19

[a] J in Hz. [b] Ar = 

12), 390 (M – 7CO, 88), 388 (100). Anal. Calcd for $C_{16}H_{11}FeO_7PW$: C, 32.79; H, 1.89; Fe, 9.53; P, 5.28. Found: C, 33.04; H, 1.89; Fe, 9.40; P, 5.13.

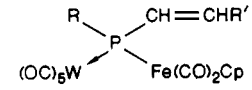
[(OC)$_5$WP(CH=CHPh)$_2$]Fe(CO)$_2$Cp (4e). The same procedure as above applied to 3.0 g (5 mmol) of chlorophosphine **2c** gave a colorless oil (eluent hexane/toluene, 50:50): yield 2.4 g (65%); IR ν(CO) 2060 (w), 2020 (m), 1982 (m), 1938 (vs), 1922 (vs) cm^{-1}; MS (^{184}W), m/z (relative intensity) 738 (M, 2), 598 (M – 5CO, 51), 542 (M – 7CO, 86), 540 (100). Anal. Calcd for $C_{28}H_{19}FeO_7PW$: C, 45.57; H, 2.59; P, 4.20. Found: C, 45.92; H, 2.64; P, 3.93.

Synthesis of [(OC)$_5$WP(Ph)(CH$_2$CH$_3$)]Fe(CO)$_2$Cp (5a). The secondary phosphine complex $(CO)_5WP(H)(Ph)CH{=}CH_2$ (2.3 g, 5 mmol) and 0.9 g of $[CpFe(CO)_2]_2$ (2.5 mmol) were heated in 25 mL of boiling xylene for 5 h. The solvent was removed in vacuo after filtration and the product isolated from the residual mixture by chromatography. The first orange-red fraction was eluted with hexane/toluene (90:10) and gave after crystallization 0.76 g (25%) of the complex **6a**; the second orange fraction (eluted just before **4a** and **6a′**) contained the complex **5a** as a red oil (0.32 g, 10%): ^{1}H NMR δ 1.20 (dt, ^3J(H–P) = 16.60 Hz, ^3J(H–H) = 7.32 Hz, 3 H, CH_3CH_2), 2.24 (m, 1 H, CH_2CH_3), 2.84 (m, 1 H, CH_2CH_3), 4.67 (d, ^3J(H–P) = 1.22 Hz, 5 H, Cp), 7.19–7.79 (m, 5 H, Ph); ^{31}P NMR δ –8.5 ($^1J(^{31}P–^{183}W)$ = 212.4 Hz); ^{13}C NMR δ 12.78 (s, CH_3CH_2), 30.30 (d, ^1J(C–P) = 12.21 Hz, CH_2), 87.23 (s, Cp), 199.10 (d, ^2J(C–P) = 6.11 Hz, cis CO), 201.62 (d, ^2J(C–P) = 18.6 Hz, trans CO), 213.30 (d, ^2J(C–P) = 24.42 Hz, CO), 214.10 (d, ^2J(C–P) = 21.98 Hz, CO); IR ν(CO) 2060 (w), 2018 (m), 1975 (m), 1935 (vs), 1920 (vs) cm^{-1}; MS (^{184}W), m/z (relative intensity) 638 (M, 2), 412 (100). Anal. Calcd for $C_{20}H_{15}FeO_7PW$: C, 37.65; H, 2.37; P, 4.85; W, 28.81. Found: C, 37.50; H, 2.43; P, 4.80; W, 28.44.

General Procedure for the Synthesis of [η^3-(OC)$_5$WP(R)(CH=CHR′)]Fe(CO)Cp (6, 6′). Method A. A solution of complex 4 was refluxed in xylene for 1 h. After evaporation of xylene under vacuum, complexes 6 and 6′ were isolated by chromatography like in method B.

Method B. A solution of complex 4 in 150 mL of CH_2Cl_2 was irradiated at room temperature for 15 min. The solvent was evaporated at 60 °C and the residual oil heated at this temperature

Table IV. NMR[a] Data of μ_2-Vinylphosphido Complexes 4



products (solv)	^{31}P NMR δ	$^{1}J(^{31}P-^{183}W)$	^{1}H NMR Cp	vinyl	R
4a	−14.57	207.52	4.71	5.44–6.94[b]	7.24–7.72
4b (CD_2Cl_2)	−17.3	208.0	4.77	6.91 (^2J(H-P) = 15.9)[c] 7.12	7.29–7.73
4c	−47.4	205.1	4.92	5.18–6.76[b]	1.92 (^2J(H-P) = 5.8)
4d	−30.6	205.1	4.88	5.40–6.70[b]	
4e	−30.9	207.5	4.87	6.90 (^2J(H-P) = 17.3[d]	7.17–7.41

products (solv)	^{13}C NMR Cp	CHR' (^2J(C-P))	PCH (^1J(C-P))	CO δ	^1J(C-P)	
4a	87.35	123.52 (0)	144.22 (15.9)	198.92	6.10	cis
				201.32	19.54	trans
				213.06	17.09	Fe
				213.46	17.09	Fe
4b (CD_2Cl_2)	88.36	135.80 (17.09)	137.35 (13.43)	200.08	4.89	cis
				202.50	19.53	trans
				214.50	15.87	Fe
4c	86.60	118.25 (5.53)	145.78 (12.19)	199.03	6.05	cis
				201.62	18.60	trans
				213.03	10.90	Fe
4d	87.17	122.92 (~0)	142.42 (14.65)	198.6	6.10	cis
				201.7	19.54	trans
				212.34	14.65	Fe
4e	88.18	135.17 (17.09)	137.25 (12.21)	199.93	6.10	cis
				202.39	19.53	trans
				214.13	13.09	Fe

[a] Chemical shifts in δ and J values in Hz. [b] ABCX system. [c] ABX system. [d] ABM system.

for an additional 0.5 h. Complexes **6** and **6'** were isolated by column chromatography. The syn isomer **6** was eluted first and then the anti isomer **6'**.

[η^3-(OC)$_5$WP(Ph)(CH=CH$_2$)]Fe(CO)Cp (6a, 6a'). Method B applied to 3.2 g of **4a** (5 mmol) yielded after elution with hexane/toluene (90:10) a first complex, **6a**, that was crystallized in CH_2Cl_2/MeOH (10:90): 0.8 g of orange crystals (27%); mp 124 °C dec. Then a second fraction contained complex **6a'** that was crystallized in cyclohexane: 1.3 g of red-orange crystals (43%); mp 138 °C dec. **6a**: IR ν(CO) 2080 (w), 2075 (w), 1980–1970 (sh m), 1940 (s), 1933 (s), 1925 (s) cm^{-1}; MS (^{184}W), m/z (relative intensity) 608 (M, 12), 440 (M − 6CO, 100). Anal. Calcd for $C_{19}H_{13}FeO_6PW$: C, 37.53; H, 2.15; Fe, 9.18; P, 5.10. Found: C, 37.54; H, 2.03; Fe, 9.05; P, 5.03. **6a'**: IR ν(CO) 2070 (w), 1990 (m), 1943–1940 (sh vs) cm^{-1}; MS (^{184}W), m/z (relative intensity) 608 (M, 8), 440 (M − 6CO, 100). Anal. Calcd for $C_{19}H_{13}FeO_6PW$: C, 37.53; H, 2.15; Fe, 9.18; P, 5.10. Found: C, 37.70; H, 2.08; Fe, 9.14; P, 5.14.

[η^3-(OC)$_5$WP(Ph)(CH=CHPh)]Fe(CO)Cp (6b, 6b'). From 0.7 g (1 mmol) of **4b** via method B and after elution with hexane/toluene (70:30) and crystallization from hexane/cyclohexane (90:10) were obtained 0.14 g (~20%) of complex **6b** as orange crystals and 0.4 g (~60%) of complex **6b'** as an orange oil. Anal. Calcd for $C_{25}H_{17}FeO_6PW$ (**6b, 6b'**): C, 43.89; H, 2.50; Fe, 8.16. Found: C, 44.71–44.87; H, 2.55–2.63; Fe, 8.06–8.38.

[η^3-(OC)$_5$WP(Me)(CH=CH$_2$)]Fe(CO)Cp (6c). The same procedure applied to 1.2 g (2 mmol) of **4c** gave after elution with hexane/toluene (90:10) 0.22 g (20%) of complex **6c** as a brown oil. This complex was too unstable for satisfactory elemental analysis: IR ν(CO) 2070 (w), 1978 (m), 1945–1930 (s) cm^{-1}; MS (^{184}W), m/z (relative intensity) 546 (M, 20), 406 (M − 5CO, 45), 362 (100).

[η^3-(OC)$_5$WP(CH=CH$_2$)$_2$]Fe(CO)Cp (6d, 6d'). Procedure B was applied to 1.5 g of **4d** (2.5 mmol). An orange fraction was first eluted with hexane/toluene (80:20) giving a red-orange oil, **6d** (0.42 g, 30%); then a red fraction was isolated with hexane/toluene (50:50) giving a red oil. This oil consisted mainly of the expected compound **6d'** (0.30 g, ~20%) and of undesirable complexes that were not identified. **6d/6d'**: IR ν(CO) 2065 (w), 1982 (m), 1945–1930 (vs)/2070 (w), 1990 (m), 1945–1935 (vs) cm^{-1}; MS (^{184}W), m/z (relative intensity) 558 (M, 3), 390 (M − 6CO, 100). Anal. Calcd for $C_{15}H_{11}FeO_6CPW$: C, 32.28; H, 1.98. Found: C, 31.98; H, 2.24.

[η^3-(OC)$_5$WP(CH=CHPh)$_2$]Fe(CO)Cp (6e, 6e'). The same procedure applied to 1.47 g (2 mmol) of complex **4e** gave after separation of the two isomers with hexane/toluene (80:20) first complex **6e** (400 mg, 28%) and then **6e'** (300 mg, 21%). Complexes **6e** and **6e'** equilibrated at room temperature, and it was not possible to have correct analytical samples of each. **6e/6e'**: IR ν(CO) 2090 (w), 1990 (m), 1955 (s), 1945 (s), 1935 (s)/2065 (w), 1985 (m), 1940 (s), 1935 (s) cm^{-1}; MS (^{184}W), m/z (relative intensity) 710 (M, 3), 682 (M − CO, 14), 121 (100). Anal. Calcd for $C_{27}H_{19}FeO_6PW$ (**6e, 6e'**): C, 45.67; H, 2.70; Fe, 7.86. Found: C, 44.71; H, 2.55; Fe, 8.06.

Vinyl-*tert*-butylchloro- and Vinyl-*tert*-butyl-bromophosphine (7 and 8, Respectively). The dropwise addition of a THF solution of 1 equiv of $BrMgCH=CH_2$ (25 mL, 10 mmol) to a 10 mL THF solution of 1 equiv of t-$BuPCl_2$ (1.6 g, 10 mmol) was performed at −78 °C. Then the solution was allowed to warm to room temperature while being stirred, and a mixture of **7** and **8** in various proportions was obtained. After filtration, the solvent was removed under vacuum while the temperature was kept below 50 °C to avoid decomposition.

7: ^{1}H NMR δ 1.16 (d, ^3J(H-P) = 13.71 Hz, 9 H, t-Bu), 5.8–6.1 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 105.84; ^{13}C NMR δ 25.09 (d, ^2J(C-P) = 17.68 Hz, C(CH$_3$)$_3$), 33.13 (d, ^1J(C-P) = 25.96 Hz, $C(CH_3)_3$), 131.21 (d, ^2J(C-P) = 33.41 Hz, CH=CH$_2$), 136.64 (d, ^1J(C-P) = 39.71 Hz, CH=CH$_2$); MS, m/z (relative intensity) 150 (M, 8), 131 (100).

8: ^{1}H NMR δ 1.11 (d, ^3J(H-P) = 13.66 Hz, 9 H, t-Bu), 6.3–6.8 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 100.72; ^{13}C NMR δ 25.64 (d, ^2J(C-P) = 17.67 Hz, C(CH$_3$)$_3$), 31.89 (d, ^1J(C-P) = 29.17 Hz, $C(CH_3)_3$), 132.15 (d, ^2J(C-P) = 36.40 Hz, CH=CH$_2$), 135.54 (d, ^1J(C-P) = 42.12 Hz, CH=CH$_2$); MS, m/z (relative intensity) 194–196 (M − 1, M + 1, 3.7), 131 (100).

(CO)$_5$W[t-BuPCl(CH=CH$_2$)] (9) and (CO)$_5$W[t-BuPBr(CH=CH$_2$)] (10). The preceding crude mixture of **7** and **8** (10 mmol) was poured into a solution of W(CO)$_5$·THF (10 mmol) (see synthesis of **1**) and stirred for 1 h. After removal of the solvent under vacuum, the residue was first extracted with diethyl ether (50 mL) and then with hexane/toluene (80:20, 100 mL). This procedure led to 2.8 g of a brown oil that was a mixture of **9** and **10** in various proportions. Treatment of this mixture with 0.4 mL of DBU allowed the elimination of **10** and gave, after rapid chromatography on silica gel, 1.2 g of almost pure **9** (4.7 g, yield ≃25%).

9: ^{1}H NMR δ 1.40 (d, ^3J(H-P) = 17.69 Hz, 9 H, t-Bu), 5.5–7.0 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 120.37 ($^1J(^{31}P-^{183}W)$ = 266.11 Hz); ^{13}C NMR δ 25.01 (d, ^2J(C-P) = 7.82 Hz, C(CH$_3$)$_3$), 39.22 (d, ^1J(C-P) = 13.17 Hz, $C(CH_3)_3$), 129.90 (s, CH=CH$_2$), 134.19 (d, ^1J(C-P) = 20.14 Hz, CH=CH$_2$), 196.20 (d, ^2J(C-P) = 7.06 Hz, cis CO), 198.64 (d, ^2J(C-P) = 29.75 Hz, trans CO); MS (^{184}W), m/z (relative intensity) 474 (M, 32), 390 (M − 3CO, 100). Anal. Calcd for $C_{11}H_{12}ClO_5PW$: C, 27.84; H, 2.55; C., 7.47; P, 6.53. Found: C, 28.37; H, 2.45; Cl, 7.24; P, 6.79.

10: ^{1}H NMR δ 1.44 (d, ^3J(H-P) = 17.90 Hz, 9 H, t-Bu), 5.5–7.0 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 109.53 ($^1J(^{31}P-^{183}W)$ = 263.68 Hz); ^{13}C NMR δ 25.52 (d, ^2J(C-P) = 7.64 Hz, C(CH$_3$)$_3$), 38.61 (d, ^1J(C-P) = 12.98 Hz, $C(CH_3)_3$), 131.64 (s, CH=CH$_2$), 133.45 (d, ^1J(C-P) = 16.92 Hz, CH=CH$_2$), 196.62 (d, ^2J(C-P) = 7.14 Hz, cis CO), 197.39 (d, ^2J(C-P) = 29.84 Hz, trans CO); MS (^{184}W), m/z (relative intensity) 518 (M, 13), 392 (M − 3CO, 100). **10** could not be separated from **9** for analysis.

9 and **10**: IR ν(CO) 2068 (w), 1958 (s, br), 1943 (s, br) cm^{-1}.

(CO)$_5$W[t-BuP(H)(CH=CH$_2$)] (11). A solution of $LiAlH_4$ in 10 mL of Et_2O was added to 2.8 g of the preceding crude mixture of **9** and **10** (about 6 mmol) in 20 mL of Et_2O and 10 mL of n-pentane. After being stirred for half an hour, the solution was filtered, hydrolyzed with 10 mL of HCl (2 N), washed with H_2O, dried over Na_2SO_4, and evaporated. The resulting oil was

chromatographed on a column of silica gel with hexane, and 1.7 g of the phosphine **11** (dark green oil) was obtained (2.6 g, yield 65%): ^{1}H NMR δ 1.25 (d, ^3J(H–P) = 16.11 Hz, 9 H, *t*-Bu), 5.12 (dd, ^1J(H–P) = 329.59 Hz, ^3J(H–H) = 8.05 Hz, 1 H, PH), 5.5–6.5 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 9.58 (^1J(^{31}P–^{183}W) = 222.17 Hz, ^1J(P–H) = 329.59 Hz); ^{13}C NMR δ 27.85 (d, ^2J(C–P) = 5.55 Hz, C(*C*H$_3$)$_3$), 31.15 (d, ^1J(C–P) = 26.28 Hz, *C*(CH$_3$)$_3$), 130.68 (s, C=*C*H$_2$), 129.14 (d, ^1J(C–P) = 34.06, *C*H=CH$_2$), 196.46 (d, cis CO), 198.98 (trans CO) (^2J(C–P) could not be determined for the CO); IR ν(CO) 2065 (w), 1938 (s, br) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 440 (M, 100), 384 (M – 2CO, 85). Anal. Calcd for $C_{11}H_{13}O_5PW$: C, 30.02; H, 2.98; P, 7.04. Found: C 30.12; H, 3.21; P, 7.24.

[η^1-(CO)$_5$WP(*t*-Bu)(CH=CH$_2$)]Fe(CO)$_2$Cp (12). The metalation of 1.8 g of **11** (4 mmol) in 20 mL of THF with 2.6 mL of *n*-BuLi (1.5 N, 4 mmol) was carried out at −78 °C. After a 5 min of stirring, a solution of 1.0 g of BrCpFe(CO)$_2$ (4 mmol) in 5 mL of THF was added and the mixture was allowed to warm to room temperature. Then the mixture was evaporated and chromatographed on silica gel, **12** being obtained with hexane/toluene (80:20). The procedure gave 1.3 g of dark brown crystals (2.6 g, yield 50%): mp 94 °C dec; ^{1}H NMR δ 1.33 (d, ^3J(H–P) = 13.92 Hz, 9 H, *t*-Bu), 5.08 (s, 5 H, Cp), 5.5–7.0 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 21.55 (^1J(^{31}P–^{183}W) = 209.96 Hz); ^{13}C NMR δ 30.37 (d, ^2J(C–P) = 5.70 Hz, C(*C*H$_3$)$_3$), 37.27 (d, ^1J(C–P) = 4.31 Hz, *C*(CH$_3$)$_3$), 85.94 (s, Cp), 126.05 (s, CH=*C*H$_2$), 142.52 (d, ^1J(C–P) = 9.08 Hz, *C*H=CH$_2$), 199.62 (d, ^2J(C–P) = 5.75 Hz, W(CO)$_4$ cis), 213.22 (d, ^2J(C–P) = 14.1 Hz, Fe–CO), 214.21 (d, ^2J(C–P) = 13.3 Hz, Fe–CO); IR ν(CO) 2060 (m), 2020 (m), 1990–1970 (m, br), 1960 (m), 1945–1920 (s, br) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 616 (M, 6.5), 362 (100). Anal. Calcd for $C_{18}H_{17}FeO_7PW$: C, 35.09; H, 2.78; Fe, 9.06. Found: C, 35.19; H, 2.93; Fe, 8.38.

(CO)$_4$W[(μ_2-CO)(μ_2-*t*-BuP(CH=CH$_2$))]Fe(CO)Cp (13). Irradiation for 10 min of a solution of 0.62 g of **12** (1 mmol) in 70 mL of CH_2Cl_2 gave only **13**. After evaporation, the residue was chromatographed on silica gel with *n*-pentane/CH_2Cl_2 (90:10). A dark brown crystalline product was obtained nearly quantitatively (0.53 g, 90%): mp 160–165 °C dec; ^{1}H NMR δ 1.31 (d, ^3J(H–P) = 15.87 Hz, 9 H, *t*-Bu), 4.51 (s, 5 H, Cp), 5.5–7.5 (m, 3 H, CH=CH$_2$); ^{31}P NMR δ 193.45 (^1J(^{31}P–^{183}W) = 205.08 Hz); ^{13}C NMR δ 30.84 (s, C(*C*H$_3$)$_3$), 39.29 (d, ^1J(C–P) = 22.69 Hz, *C*(CH$_3$)$_3$), 85.24 (s, Cp), 128.92 (s, CH=*C*H$_2$), 139.82 (d, ^1J(C–P) = 25.01 Hz, *C*H=CH$_2$); IR ν(CO) 2055 (m), 1973 (m), 1967 (s), 1956 (s), 1932 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{17}FeO_6PW$: C, 34.73; H, 2.91. Found: C, 34.55; H, 3.64.

[η^3-(OC)$_5$WP(*t*-Bu)(CH=CH$_2$)]Fe(CO)Cp (14). A solution of 0.59 g of **13** (1 mmol) in 10 mL of hexane was heated 2 h at 60 °C. The residue was chromatographed after being evaporated and **14** eluted with hexane/toluene (80:20). After crystallization from hexane, 0.29 g (50%) of yellow-brown crystals of the pure anti isomer was obtained; mp 137 °C; IR ν(CO) 2065 (w), 1984 (m), 1941 (s), 1930–1925 (s, br) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 588 (M, 25.5), 362 (100). Anal. Calcd for $C_{17}H_{17}FeO_6PW$: C, 34.73; H, 2.91; Fe, 9.50. Found: C, 34.57; H, 2.87; Fe, 8.61.

Synthesis of *t*-BuP(H)(CH=CH$_2$) (15). A solution of the crude mixture of **7** and **8** obtained from 20 mmol of *t*-BuPCl$_2$ was reduced by an excess of LiAlH$_4$ in Et$_2$O for 30 min at 0 °C under stirring. The solution was treated with 10 mL of 2 N HCl. The solution was washed, dried over CaCl$_2$, and evaporated on a short vertical fractionating column. The residual oil was purified by a rapid distillation (Kugelrohr) at 60 °C. The phosphine **15** (400 mg) was kept at 0 °C to avoid decomposition: ^{1}H NMR δ 1.13 (d, ^3J(H–P) = 12.2 Hz, 9 H, *t*-Bu), 3.57 (dd, ^1J(H–P) = 195.32 Hz, ^3J(H–H) = 6.6 Hz, 1 H, PH), 5.57–6.46 (m, 3 H, vinyl); ^{31}P NMR δ −20.8 (^1J(P–H) = 195.32 Hz); ^{13}C NMR (C$_6$D$_6$) δ 29.92 (d, ^2J(C–P) = 12.7 Hz, CH$_3$ and CP), 130.48 (d, ^1J(C–P) = 20.52 Hz, PCH), 132.16 (d, ^2J(C–P) = 19.5 Hz, CH$_2$); MS, *m/z* (relative intensity) 132 (M + O, 80), 131 (M + O – H, 100), 117 (M + H, 95). **15** was too unstable and oxidizable for correct elemental analysis.

(CO)$_4$Fe[(*t*-Bu)PH(CH=CH$_2$)] (16). At 25 °C, 3.6 g of Fe$_2$(CO)$_9$ (10 mmol) in 20 mL of THF were directly added to the crude solution of **15** (20 mmol) (after drying over Na$_2$SO$_4$). After being stirred during 45 min, the solution was evaporated, chromatographed with hexane, and gave 2.0 g (35%) of **16** as a yellow oil: ^{1}H NMR (C$_6$D$_6$) δ 0.87 (d, ^3J(H–P) = 16.58 Hz, 9 H, *t*-Bu), 4.54 (dd, ^1J(H–P) = 351.56 Hz, ^3J(H–H) = 7.15 Hz, 1 H, P*H*), 5.0–6.0 (m, 3 H, CH=CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 60.23 (^1J(P–H) = 351.56 Hz); ^{13}C NMR (C$_6$D$_6$) δ 27.72 (s, C(*C*H$_3$)), 33.46 (d, ^1J(C–P) = 28.55 Hz, *C*(CH$_3$)$_3$), 213.71 (d, ^2J(C–P) = 18.91 Hz, (CO)$_4$) (the vinyl resonances are hidden by C$_6$D$_6$); IR ν(CO) 2045 (s), 1975 (s, br), 1945–1935 (vs, br) cm^{-1}; MS, *m/z* (relative intensity) 284 (M, 5), 174 (100). Anal. Calcd for $C_{10}H_{13}FeO_4P$: C, 42.29; H, 4.61. Found: C, 42.37; H, 4.58.

(CO)$_4$Fe[μ_2-*t*-BuP(CH=CH$_2$)]Fe(CO)$_2$Cp (17). Metalation was performed via the dropwise addition of 4.7 mL of *n*-BuLi (1.5 M, 7 mmol) to 2 g of **16** (7 mmol) in 50 mL of THF at −78 °C. The solution was stirred 5 min, and 1.8 g of BrFeCp(CO)$_2$ (7 mmol) in 50 mL of THF was poured into it. Then the resulting mixture was allowed to warm to room temperature, evaporated, and chromatographed on silica gel. Elution with hexane/toluene (70:30) gave 1.5 g of **17** as red-brown crystals obtained from hexane (yield 47%): ^{1}H NMR (C$_6$D$_6$) δ 1.18 (d, ^3J(H–P) = 14.41 Hz, 9 H, *t*-Bu), 4.29 (s, 5 H, Cp), 5.5–7.0 (m, 3 H, CH=CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 87.48; ^{13}C NMR (C$_6$D$_6$) δ 31.48 (s, C(*C*H$_3$)$_3$), 42.22 (d, ^1J(C–P) = 5.75 Hz, *C*(CH$_3$)$_3$), 87.22 (s, Cp), 127.81 (s, CH=*C*H$_2$), 141.21 (d, ^1J(C–P) = 14.10 Hz, *C*H=CH$_2$), 212.93 (d, ^2J(P–C) = 15.95 Hz, CO), 215.16 (d, ^2J(P–C) = 14.06 Hz, CO), 217.27 (d, ^2J(P–C) = 14.83 Hz, CO); IR ν(CO) 2040 (m), 2022 (s), 1984 (s), 1960 (m), 1928 (s), 1910 (s) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 460 (M, 4), 208 (100). Anal. Calcd for $C_{17}H_{17}Fe_2O_6P$: C, 44.39; H, 3.72; Fe, 24.28; P, 6.73. Found: C, 44.15; H, 3.79; Fe, 24.51; P, 6.63.

(CO)$_3$Fe[μ_2-*t*-BuP(CH=CH$_2$)](μ_2-CO)Fe(CO)Cp (18). **17** (1.15 g, 2.5 mmol) in 100 mL of THF was irradiated during 20 min and evaporated, and **18** was obtained by chromatography on silica gel with hexane/CH_2Cl_2 (90:10). The procedure yielded 0.8 g of a dark blue solid (1.08 g, yield 74%): ^{1}H NMR (C$_6$D$_6$) δ 1.03 (d, ^3J(H–P) = 15.62 Hz, 9 H, *t*-Bu), 4.19 (s, 5 H, Cp), 5.4–6.7 (m, 3 H, CH=CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 218.59; ^{13}C NMR (C$_6$D$_6$) δ 28.49 (s, C(*C*H$_3$)$_3$), 37.79 (d, ^1J(H–P) = 7.0 Hz, *C*(CH$_3$)$_3$), 84.11 (s, Cp), 130.07 (s, CH=*C*H$_2$), 138.09 (d, ^1J(C–P) = 21.10 Hz, *C*H=CH$_2$), 223.78 (d, ^2J(C–P) = 10.81 Hz, (CO)$_3$); IR ν(CO) 2025 (m), 1965 (s, br), 1953 (m, br) cm^{-1}; MS, *m/z* (relative intensity) 432 (M, 5), 208 (100). Anal. Calcd for $C_{16}H_{17}Fe_2O_5P$: C, 44.48; H, 3.897; Fe, 25.85. Found: C, 44.13; H, 4.09; Fe, 26.64.

[η^3-(OC)$_4$FeP(*t*-Bu)(CH=CH$_2$)]Fe(CO)Cp (19). A solution of 0.86 g of **18** (2 mmol) in 20 mL of methylcyclohexane was heated for 1 h at 90 °C. After evaporation, the residue was chromatographed on silica gel with hexane/CH_2Cl_2 (70:30) and gave a mixture of **18** and **19**, the total yield being 50% (0.43 g): ^{1}H NMR (C$_6$D$_6$) δ 1.16 (d, ^3J(H–P) = 15.55 Hz, 9 H, *t*-Bu), 3.92 (s, 5 H, Cp), 1.6–2.4–3.8 (m, 3 H, CH=CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 64.15; ^{13}C NMR (C$_6$D$_6$) δ 30.86 (s, C(*C*H$_3$)), 88.12 (s, Cp). These data were collected from a mixture of **18** and **19** with only a small amount of **19**. This is the reason why some signals were undetectable and are not reported.

Reaction of 6a under Pressure of CO. Complex **6a** (1.2 g, 2 mmol) in 25 mL of toluene was heated at 100 °C for 1 h under 5 atm of CO in an autoclave. After the solution was cooled to room temperature, the solvent was removed and the residue chromatographed and identified by comparison with an authentic sample of **4a**.

Synthesis of [η^1-(Ph$_3$P)W(CO)$_4$P(Ph)(CH=CH$_2$)]Fe(CO)$_2$Cp (20). A solution of 1.2 g of **6a** (2 mmol) in 25 mL of toluene was heated with 0.5 g (2 mmol) of triphenylphosphine for 3 h at 60 °C. Evaporation of the solvent and chromatography of the red residue gave in a first fraction eluted with hexane/toluene (60:40) 0.5 g (28%) of the isomer **20a** that was recrystallized from toluene/hexane (50:50): mp 170 °C dec; red crystals. A second fraction contained **20b** as an oil (0.35 g, 20%) which was not pure enough for correct elemental analysis.

20a: ^{1}H NMR (C$_6$D$_6$) δ 4.08 (s, 5 H, Cp), 5.30–5.90 (m, 3 H, vinyl), 7.02–7.98 (m, 20 H, Ph); ^{31}P NMR (C$_6$D$_6$) δ(P$_A$) +26.62 (^1J(^{31}P–^{183}W) = 288.10 Hz), δ(P$_B$) −10.23 (^1J(^{31}P–^{183}W) = 239.26 Hz), ^2J(P$_A$–P$_B$) = 53.71 Hz; ^{13}C NMR (C$_6$D$_6$) 87.37 (s, Cp), 121.51 (s, CH$_2$), 145.40 (d, ^1J(C–P) = 14.33 Hz, CHP), 206.07 (s, CO), 214.25 (d, ^2J(C–P) = 24.63 Hz, CO), 215.15 (d, ^2J(C–P) = 15.54

Hz, CO); IR ν(CO) 2020 (m), 2005 (w), 1975 (m), 1880 (s) cm^{-1}; MS (^{184}W), m/z (relative intensity) 842 (M - CO, 2), 702 (M - 6CO, 45), 442 (100). Anal. Calcd for $C_{37}H_{28}FeO_6P_2W$: C, 51.09; H, 3.24. Found: C, 51.02; H, 3.32.

20b: ^{1}H NMR (C_6D_6) δ 4.0 (s, 5 H, Cp), 5.08-6.20 (m, 3 H, vinyl), 6.94-8.0 (m, 20 H, Ph); ^{31}P NMR δ (P_A) 20.31 ($^1J(^{31}P-^{183}W)$ = 224.61 Hz), δ (P_B) -16.8 ($^1J(^{31}P-^{183}W)$ = 200.19 Hz), $^2J(P_A-P_B)$ = 26.86 Hz; ^{13}C NMR (C_6D_6) δ 87.33 (Cp), 122.52 (s, CH_2), 143.58 (d, ^1J(C-P) = 8.0 Hz, HCP), 205-206 (m, $(CO)_4$), 213.05 (d, ^2J(C-P) = 16.39 Hz, CO), 214.64 (d, ^2J(C-P) = 14.94 Hz, CO); IR ν(CO) 2022 (m), 2005 (w), 1980 (m), 1910 (s), 1890 (s) cm^{-1}.

Synthesis of [η^1-[(MeO)$_3$P]W(CO)$_4$P(Ph)(CH=CH$_2$)]Fe(CO)$_2$Cp (21). A solution of 0.6 g (1 mmol) of **6a** and 0.12 g of $P(OMe)_3$ (1 mmol) in 25 mL of toluene was heated at 60 °C for 1.5 h. Addition of hexane precipitated red crystals that were recrystallized from hexane/toluene (90:10) to give **21** (0.5 g, 68%): mp 156 °C dec; ^{1}H NMr δ 3.40 (d, ^3J(H-P) = 11.0 Hz, 9 H, OCH_3), 4.69 (d, ^3J(H-P) = 1.5 Hz, 5 H, Cp), 5.32-6.99 (m, ABCX, 3 H, vinyl), 7.18-7.77 (m, 5 H, Ph); ^{31}P NMR δ 139.20 ($^1J(^{31}P-^{183}W)$ = 373.5 Hz), -14.4 ($^1J(^{31}P-^{183}W)$ = 212.4 Hz) ($^2J(P_A-P_B)$ = 31.7 Hz); ^{13}C NMR δ 51.2 (d, ^2J(C-P) = 3.7 Hz, OCH_3), 87.3 (s, Cp), 121.7 (s, CH_2=), 143.4 (d, ^1J(C-P) = 12.2 Hz, PCH), 201.205 (m, COW), 213.10 (d, ^2J(C-P) = 15.87 Hz, CO), 213.85 (d, ^2J(C-P) = 14.65 Hz, CO); IR ν(CO) 2022 (m), 2010 (m), 1978 (m), 1925-1890 (sh, s); MS (^{184}W), m/z (relative intensity) 678 (M - 2CO + 2H, 85), 566 (M - 6CO + 2H, 100). Anal. Calcd for $C_{22}H_{22}FeO_9P_2W$: C, 36.09; H, 3.03; Fe, 7.63; P, 8.46. Found: C, 36.31; H, 2.69; Fe, 7.28; P, 8.41.

Synthesis of (CO)$_5$W[P(Ph)(CH=CHPh)I] (24). A solution of 0.68 g (1 mmol) of **6a** was stirred for 10 min at room temperature in 25 mL of CH_2Cl_2 with 0.25 g (1 mmol) of I_2. The solvent was removed, and the residue was chromatographed rapidly on a short column (eluent toluene), yielding a red-orange oil (180 mg, 27%) which was not pure enough to give correct elemental analysis: ^{1}H NMR δ 6.96-7.35 (m, ABX, 2 H, vinyl), 7.39-7.79 (m, 10 H, Ph); ^{31}P NMR δ 12.7 ($^1J(^{31}P-^{183}W)$ = 271.0 Hz); ^{13}C NMR δ 125.28 (d, ^2J(C-P) = 28.36 Hz, CH_2=); 147.31 (d, ^1J(C-P) = 13.2 Hz, CHP), 196.88 (d, ^2J(C-P) = 7.0 Hz, cis CO), 199.5 (d, ^2J(C-P) = 28.4 Hz, trans CO); IR ν(CO) 2070 (w), 1955 (vs), 1948 (vs) cm^{-1}; MS (^{184}W), m/z (relative intensity) 662 (M, 22), 535 (M - I, 65), 395 (M - (I + 5CO), 100).

Registry No. **1a**, 101078-12-0; **1b**, 101078-13-1; **1c**, 112712-67-1; **1d**, 99331-07-4; **1e**, 112712-68-2; **2a**, 101078-19-7; **2b**, 101078-20-0; **2c**, 112712-69-3; **2d**, 99331-09-6; **2e**, 112712-70-6; **4a**, 112712-71-7; **4b**, 101078-16-4; **4c**, 112712-73-9; **4d**, 112712-74-0; **4e**, 112712-75-1; **5a**, 112712-76-2; **6a**, 101144-76-7; **6a'**, 112712-84-2; **6b**, 101078-17-5; **6b'**, 101078-18-6; **6c**, 112712-85-3; **6d**, 112712-86-4; **6d'**, 112791-08-9; **6**, 112712-87-5; **6e'**, 112863-66-8; **7**, 112712-89-7; **8**, 112712-90-0; **9**, 112712-91-1; **10**, 112712-77-3; **11**, 112712-78-4; **12**, 112712-79-5; **13**, 112739-91-0; **14**, 112712-88-6; **15**, 112712-92-2; **16**, 112712-80-8; **17**, 112712-81-9; **18**, 112739-92-1; **19**, 112712-82-0; **20a**, 112739-93-2; **20b**, 112835-50-4; **21**, 112739-94-3; **24**, 112712-83-1; W(CO)$_5$·THF, 36477-75-5; $[CpFe(CO)_2]_2$, 12154-95-9; $(CO)_5WP(H)(Ph)CH=CH_2$, 101078-14-2; $BrCpFe(CO)_2$, 12078-20-5; $Fe_2(CO)_9$, 15321-51-4; $BrMgCH=CH_2$, 1826-67-1; BrMgCH=CHPh, 30094-01-0; $PhPCl(NEt_2)$, 4073-31-8; $MePCl(NEt_2)$, 40467-94-5; Et_2NPCl_2, 1069-08-5; t-$BuPCl_2$, 25979-07-1.

Clusters Containing Carbene Ligands. 3. The Transformations of a (Dimethylamino)methyl Ligand in a Triosmium Cluster. The Synthesis and Structural Characterizations of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$, $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$, and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$

Richard D. Adams* and James E. Babin

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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The reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $CH_2(NMe_2)_2$ at 25 °C has yielded the compound $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (**1**, 32%). Compound **1** was characterized by X-ray diffraction methods: space group $P2_1/n$, a = 9.396 (4) Å, b = 14.362 (9) Å, c = 15.175 (8) Å, β = 105.57 (3)°, V = 1972 (1) Å^3, Z = 4. The structure was solved by direct methods and was refined (1706 reflections) to the final values of the residuals R = 0.032 and R_w = 0.033. The molecule contains a triangular cluster of three osmium atoms with a (dimethylamino)methyl ligand bridging an edge of the cluster, C-N = 1.53 (2) Å. At 98 °C **1** was converted into two products, $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (**2**, 28%) and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**3**, 60%). Both products were characterized by X-ray diffraction methods. For **2**: space group $P2_12_12_1$, a = 13.769 (6) Å, b = 14.841 (8) Å, c = 9.058 (3) Å, V = 1851 (1) Å^3, Z = 4. The structure was solved by direct methods and was refined (1362 reflections) to the final values of the residuals R = 0.054 and R_w = 0.054. Compound **2** contains a triangular cluster of three osmium atoms with a triply bridging η^2-(dimethylamino)carbene ligand, HC(NMe$_2$), C-N = 1.40 (5) Å. For **3**: space group $P\bar{1}$, a = 9.147 (2) Å, b = 13.036 (2) Å, c = 8.969 (2) Å, α = 104.42 (2)°, β = 109.13 (2)°, γ = 90.07 (2)°, V = 974.5 (8) Å, Z = 2. The structure was solved by the heavy-atom method and was refined (2649 reflections) to the final values of the residuals R = 0.042 and R_w = 0.048. Compound **3** consists of a triangular cluster of three osmium atoms with a (dimethylamino)carbyne ligand bridging one edge, C=N = 1.28 (2) Å. Compound **2** can be converted to **3** at 125 °C under 1 atm of CO, but not under the conditions of its formation from **1**. Two routes to **3** that involve multicenter metal C-H activation processes have been proposed.

Introduction

The ability of transition-metal cluster compounds to produce unusual ligand transformations by multicenter activation processes has been a subject of great interest.[1-3] In our recent studies, we have been investigating the coordination behavior and reactivity of heteroatom-substi-

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