1796 *Organometallics* 1988, *7*, 1796–1801

Introducing New Phosphorus Substituents in Terminal Phosphinidene Complexes. An Illustration with [(Ethoxycarbonyl)phosphinidene]-, (*tert*-Butoxyphosphinidene)-, and (Fluorenylphosphinidene)pentacarbonyltungsten Complexes

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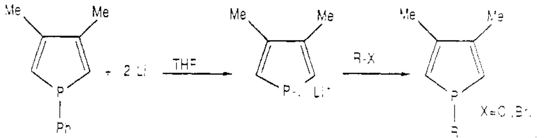
The reaction of ethyl chloroformate with the [(3,4-dimethylphospholyl)lithium(*P–W*)]pentacarbonyltungsten complex yields the corresponding 1-(ethoxycarbonyl)phosphole complex. Upon reaction with dimethyl acetylenedicarboxylate, this phosphole derivative gives the corresponding 7-phosphanorbornadiene complex which in turn appears to be a good precursor for the transient (ethoxycarbonyl)phosphinidene complex [EtO—C(O)—P=W(CO)$_5$]. This transient species cleanly reacts with methanol, diethylamine, and tolan to give the expected phosphinite and phosphirene complexes. However, it appears impossible to perform the P–CO$_2$Et → P–H conversion via the attack of OH$^-$ at the carbonyl group without destroying the phosphinite and phosphirene structures. Thus [EtO—C(O)—P=W(CO)$_5$] cannot be used as a masked [HP=W(CO)$_5$]. In order to vary the substituent at phosphorus in the transient phosphinidene complexes, it is possible to start with 1-cyano-3,4-dimethylphosphole which is easily obtained from BrCN and the appropriate phospholyl anion. This 1-cyanophosphole provides for the first time an easy access to 1-alkoxy-, 1-amino-, 1-aryl-, and 1-alkynyl-3,4-dimethylphospholes. Using the same basic scheme as with the ethoxycarbonyl substituent, it is possible to prepare from these new phospholes the corresponding 7-phosphanorbornadiene complexes. The precursors of [*t*-BuO—P=W(CO)$_5$] and [9-fluorenyl—P=W(CO)$_5$] are thus prepared and tested as an example.

Recently, we have demonstrated that it is possible to activate phosphinidenes [RP] by complexation with M(CO)$_5$ (M = Cr, Mo, W). Thus it has been possible to develop a versatile carbene-like chemistry with the resulting terminal phosphinidene complexes [RP=M(CO)$_5$].[1] From a synthetic standpoint, the full use of this technique depends on the following conditions: (1) the development of a large array of high-yield reactions between these terminal phosphinidene complexes and the most common organic functionalities. Such reactions have been found with alcohols, amines, olefins, alkynes, conjugated dienes, α,β-unsaturated ketones, azadienes, enamines, and ferrocene (see ref 1) and, more recently, with oxiranes,[2] aziridines,[2] carbene,[3] and carbyne complexes;[4] (2) the development of reliable techniques for removing the organophosphorus species from the coordination sphere of the metal after their synthesis [such a technique has been devised for W(CO)$_5$ (see ref 1)]; (3) the development of versatile methods for introducing new substituents in the phosphinidene complexes. This work describes a new solution to this problem.

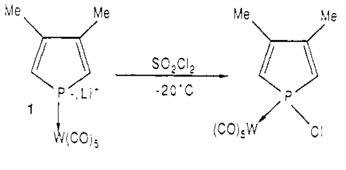
Results and Discussion

In practice, when the phosphole–7-phosphanorbornadiene route to terminal phosphinidene complexes is used,[1] the choice of the R substituent at phosphorus is made on the initial R-substituted-3,4-dimethylphosphole. The most obvious technique for selecting R consists in treating RX with the easily obtained 3,4-dimethylphospholyl anion (eq 1).



(1)

This method has a good versatility for alkyl substituents. However, it becomes practically useless for aromatic and heteroatomic substituents (RO, R$_2$N, etc....). In a first attempt to solve this problem, we studied the synthesis of 1-chloro-3,4-dimethylphosphole but this product soon appeared to be highly unstable and we were obliged to carry out its synthesis directly in the coordination sphere of tungsten in order to achieve a sufficient stability[5] (eq 2).



(2)

As may be guessed, this chlorination is quite delicate since it is necessary to avoid the oxidation of tungsten. Thus, at best, the reproducibility of this reaction is rather low. In order to overcome this problem, we decided to investigate the possible replacement of chlorine by various electronegative substituents. Our first significant success was achieved with the ethoxycarbonyl substituent. The required phosphole complex **2** is easily obtained from **1**[6] according to eq 3.

Complex **2** then smoothly reacts with neat acetylenedicarboxylate to afford the expected 7-phosphanor-

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[1] The chemistry of these transient terminal phosphinidene complexes has been reviewed: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. Recently, Lappert and co-workers have described stable terminal phosphinidene complexes RP=MCp$_2$ where M stands for Mo or W and R for bulky alkyl or aryl groups: Hitchcock, P. B.; Lappert, M. F.; Leung W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. The chemistry of these nucleophilic phosphorus species is certainly very different from the chemistry of the electrophilic transient species that are used in this work. The relationship between [RP=M(CO)$_5$] and RP=MCp$_2$ probably parallels the relationship between electrophilic and nucleophilic carbene complexes (Fischer and Schrock types).

[2] Marinetti, A.; Mathey, F. *Organometallics* **1987**, *6*, 2189.

[3] Tran Huy, N. H.; Mathey, F. *Organometallics* **1987**, 6, 207. Tran Huy, N. H.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1987**, *109*, 3475.

[4] Tran Huy, N. H.; Fischer, J.; Mathey, F. *Organometallics* **1988**, *7*, 240.

[5] Alcaraz, J.-M.; Svara, J.; Mathey, F. *Nouv. J. Chim.* **1986**, *10*, 321.

[6] Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.

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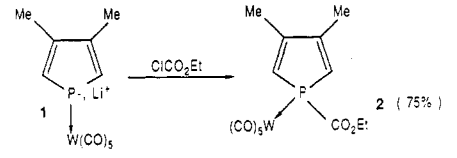
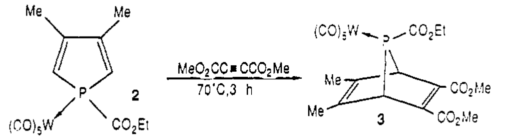


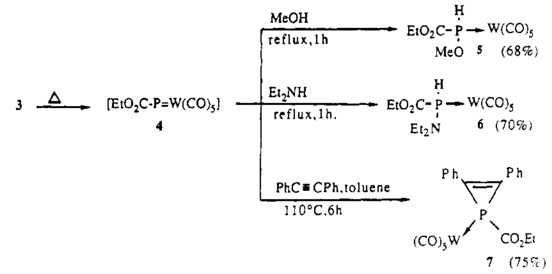
(3)

bornadiene complex **3** (eq 4).



(4)

The cycloaddition takes place on the less hindered side of the phosphole complex as usual. The stereochemistry at the bridge is monitored by comparing the $^2J(\text{Me}-C\cdots P)$ and $^2J(\text{MeO}_2\text{C}-C\cdots P)$ coupling constants within the 7-phosphanorbornadiene ring for **3** with those of similar complexes of known structures[7] (^2J = ca. 17 and 5 Hz, respectively). Complex **3** ($\delta(^{31}\text{P})$ +194 vs H_3PO_4) is always accompanied by a minor byproduct ($\delta(^{31}\text{P})$ +220) which probably is the 7-phosphanorbornadiene complex with the reverse stereochemistry at the bridge phosphorus. Complex **3** is a good precursor for the nonconventional (ethoxycarbonyl)phosphinidene complex **4**. Various typical trapping reactions of **4** were indeed successfully carried out with MeOH, Et_2NH, and PhC≡CPh (eq 5–7).

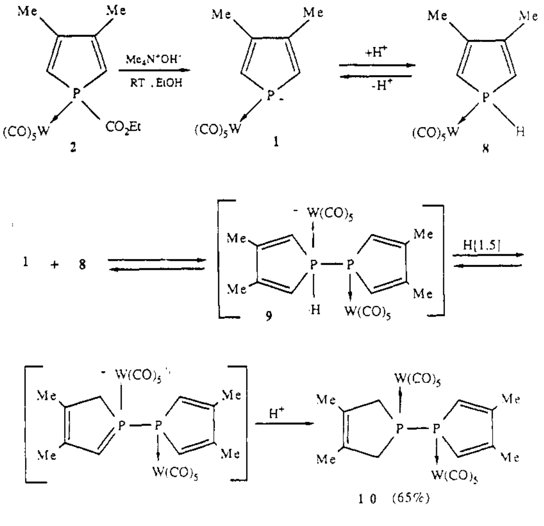


(5)

(6)

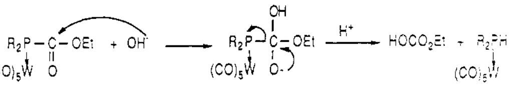
(7)

According to our initial program it was then necessary to devise a technique for replacing the $P-CO_2Et$ by other P substituents in order to achieve the fullest possible use of this first series of results. The preliminary experiments were performed with complex **2**. The $P-CO_2Et$ bond of **2** was easily cleaved by basic hydrolysis (eq 8).



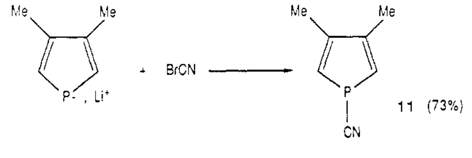
(8)

The final product **10** was unambiguously characterized by comparison of its ^{31}P NMR spectrum with the data of the literature ($\delta(^{31}\text{P})$ +7.7 and −6.2 in CH_2Cl_2, $^1J(\text{P-P})$ = 178 Hz, see ref 6). Since **10** is very probably formed via the mechanism which is outlined in eq 8, this result meant that the $P-CO_2Et$ bond might be viewed as a masked P–H bond. This cleavage almost certainly involves the attack of the hydroxide ion at the carbonyl carbon (eq 9) as for the hydrolysis of acylphosphonium salts.[8]



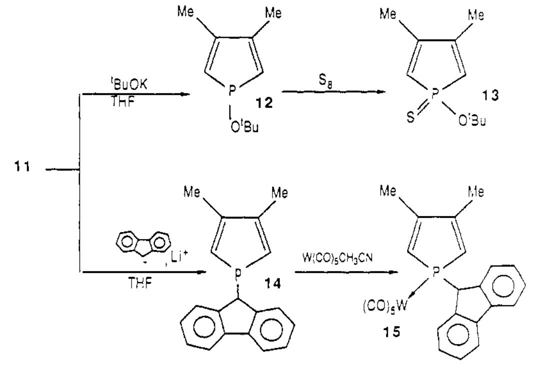
(9)

Unfortunately, this mild cleavage reaction proved to be useless in the case of our compounds. Under the same conditions, the phosphirene complex **7** gives a complicated mixture of products in which the ring is obviously broken ($\delta(^{31}\text{P})$ between +108 and +178). On the other hand, complex **6** gives an unstable primary phosphine complex according to the ^{31}P NMR spectrum of the crude reaction mixture ($\delta(^{31}\text{P})$ +11.1 in MeOH, triplet, $^1J(\text{P-H})$ = 316 Hz, $^1J(^{31}\text{P}-^{183}\text{W})$ = 240 Hz), but the data do not fit those of the expected compound $(Et_2N-PH_2)W(CO)_5$ which was already known.[9] Thus, we came back to our initial problem and decided to investigate the P–CN series. Contrary to the 1-chloro derivative, the 1-cyano-3,4-dimethylphosphole proved to be surprisingly stable (eq 10).



(10)

As expected, the C=C double bonds of **11** appear to be more polarized than those of the corresponding 1-phenyl-3,4-dimethylphosphole: $\delta(C_\alpha)$ +120.5 and $\delta(C_\beta)$ +155.5 in **11** versus $\delta(C_\alpha)$ +129.5 and $\delta(C_\beta)$ +148.6 in the PPh compound.[10] On the other hand, the carbon of the cyano group of **11** shows the huge $^1J(\text{P-C})$ coupling constant (83 Hz) which has been already observed with other cyanophosphines.[11] The cyanophosphole **11** can serve as an efficient substitute for the unknown 1-chloro-3,4-dimethylphosphole. It cleanly reacts with alkoxy and aryl anions as exemplified by eq 11 and 12.



(11)

(12)

Phospholes **12** and **14** were previously unknown and probably would be difficult to obtain by another route. They have been fully characterized as their sulfide **13** and their $W(CO)_5$ complex **15**, respectively. The $P-W(CO)_5$ complex of **11** can be obtained via the reaction of BrCN with the phospholyllithium complex **1** (eq 13).

Complex **16** is a very versatile synthetic tool. We have briefly investigated its reactions with various oxyanions

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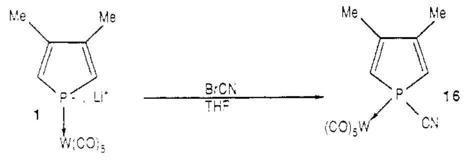
[7] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

[8] Issleib, K.; Priebe, E. *Chem. Ber.* **1959**, *92*, 3183.

[9] Mercier, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1984**, 782.

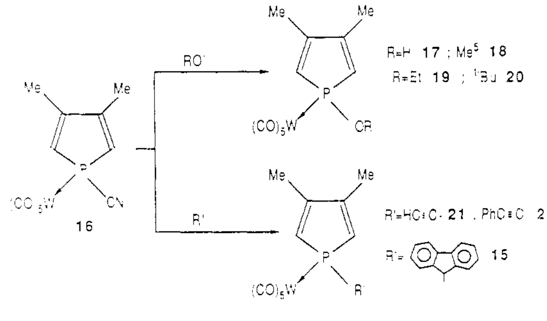
[10] Gray, G. A.; Nelson, J. H. *Org. Magn. Reson.* **1980**, *14*, 14. Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5025.

[11] Wilkie, C. A.; Parry, R. W. *Inorg. Chem.* **1980**, *19*, 1499.



(13)

and carbanions by ^{31}P NMR spectroscopy (eq 14 and 15).



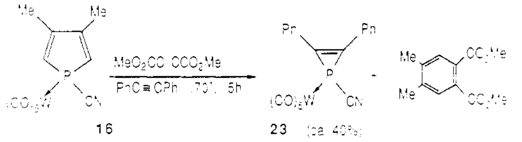
(14)

(15)

In all cases, clean reactions were observed, but only complexes **15** and **20** were isolated and fully characterized. Indeed, considering either their synthetic versatility or their steric bulk, we selected the PCN complex **16**, the P–O-*t*-Bu complex **20**, and the P–fluorenyl complex **15** for further investigation as potential precursors of the corresponding terminal phosphinidene complexes.

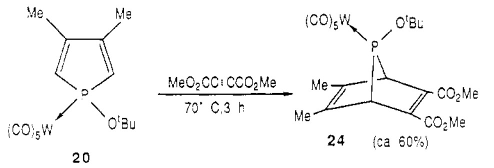
The attempted [4 + 2] cycloaddition between **16** and dimethyl acetylenedicarboxylate gave rather disappointing results. Only a minor amount of the expected 7-phosphanorbornadiene complex was obtained ($\delta(^{31}P)$ +180) probably because various side reactions can take place at the P–CN bond upon heating.

However, it was possible to combine the synthesis of the 7-phosphanorbornadiene and the trapping of the cyanophosphinidene complex which results from its collapse by reacting **16** directly with a mixture of dimethyl acetylenedicarboxylate and tolan (eq 16).



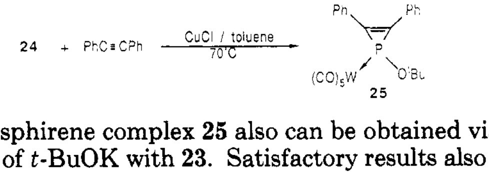
(16)

More satisfactory results were obtained in the *tert*-butoxy case. On the basis of previous data,[7] we feared a strong adverse effect of the steric bulk of the *tert*-butoxy substituent upon the [4 + 2] cycloaddition. This is not the case (eq 17).



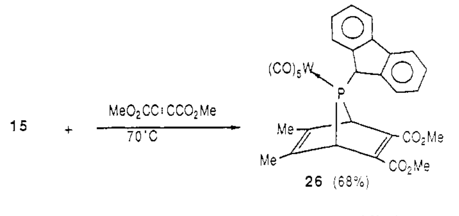
(17)

Obviously, the activating effect of the alkoxy substitution at P upon the diene overcompensates the negative effect of the steric congestion. The 7-phosphanorbornadiene complex **24** is a convenient precursor of [*t*-BuO—P=W(CO)$_5$] as shown by its reaction with tolane (eq 18). The collapse of **24** is catalyzed by CuCl as usual.[1]



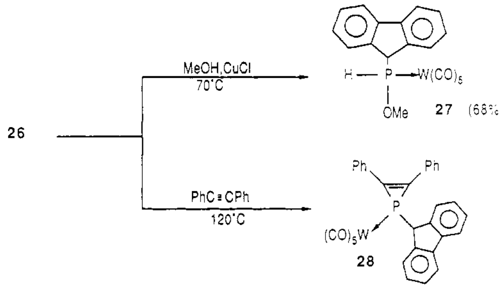
(18)

The phosphirene complex **25** also can be obtained via the reaction of *t*-BuOK with **23**. Satisfactory results also were obtained in the 9-fluorenyl case. The phosphole complex **15** cleanly reacts with dimethyl acetylenedicarboxylate to give the expected 7-phosphanorbornadiene complex **26** (eq 19).



(19)

In turn, complex **26** can serve as an efficient precursor of the fluorenylphosphinidene complex as demonstrated by its reactions with MeOH and PhC≡CPh (eq 20 and 21).



(20)

(21)

The phosphirene complex **28** is better made, however, by the direct reaction of complex **15** with a mixture of $MeO_2CC{\equiv}CCO_2Me$ and PhC≡CPh. In that case, yields as high as 80% were observed.

At this point of our research program on terminal phosphinidene complexes, it is quite clear that the only limitation which remains for the choice of the R substituent in [RP=W(CO)$_5$] is the compatibility of the P–R bond with the [4 + 2] cycloaddition between the phosphole dienic system and dimethyl acetylenedicarboxylate. On the other hand, this work once again demonstrates the high versatility of terminal phosphinidene complexes as synthons in organophosphorus chemistry. Indeed, it appears possible to transfer reactive functionalities such as P–CO$_2$Et or bulky groups such as P–O-*t*-Bu or P–9-fluorenyl without any difficulty.

Experimental Section

NMR spectra (chemical shifts in parts per million from internal Me_4Si for ^1H and ^{13}C and from external H_3PO_4 for $^{31}P\{^1H\}$; positive for downfield shifts in all cases) were recorded on a Bruker WP80 instrument respectively at 80.13, 20.15, and 32.44 MHz. Mass spectra (electronic impact, EI) were recorded on a Shimadzu QP1000 spectrometer. All reactions were carried out under argon. Chromatographic separations were performed on deoxygenated silica gel columns (70–230 mesh, Riedel de Haën).

[η^1-3,4-Dimethyl-1-(ethoxycarbonyl)phosphole-*P*]pentacarbonyltungsten (2). To a solution of the phospholyllithium complex **1**[6] (30 mmol in 200 mL of THF) was added at room temperature 3.25 g (30 mmol) of ethyl chloroformate. After vacuum distillation of the THF, a large amount of diethyl ether was first added to the residue and then, successively under vigorous stirring, 10 mL of water and anhydrous sodium sulfate. The mixture was filtered on a column of diatomaceous silica. After evaporation of the filtrate, the residue was chromatographed successively with hexane and toluene leading to 12.5 g (yield 75%) of pale yellow solid, mp 69 °C. An analytical sample was recrystallized from ethanol; mp 71 °C; ^{31}P NMR ($CDCl_3$) δ 9.3 ($^1J_{PW}$ = 215 Hz); ^1H NMR ($CDCl_3$) δ 1.21 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3), 2.15 (s, 6 H, CH_3), 4.27 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 6.30 (d, $^2J_{HP}$ = 36.8 Hz, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ 14.2 (s, CH_3CH_2), 17.5 (d, $^3J_{CP}$ = 11.9 Hz, CH_3), 63.0 (s, CH_2), 123.9 (d, $^1J_{CP}$ = 43.6 Hz, =CH), 153.8 (d, $^2J_{CP}$ = 10.0 Hz, =C<), 171.8 (d, $^1J_{CP}$ = 61.0 Hz, COO), 195.1 (d, $^2J_{CP}$ = 6.2 Hz, CO cis), 198.4 (d, $^2J_{CP}$ = 20.0 Hz, CO trans); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 508 (M, 55). Anal. Calcd for $C_{14}H_{13}O_7PW$: C, 33.08; H, 2.58; P, 6.09; W, 36.19. Found: C, 33.22; H, 2.63; P, 6.26; W, 36.35.

[η^1-5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-(ethoxycarbonyl)-7-phosphanorbornadiene-*P*]pentacarbonyltungsten (3). To 4.0 g (7.85 mmol) of phosphole complex **2** was added 4 mL of dimethyl acetylenedicarboxylate. The mixture was heated for 2 h at 75 °C. The excess of alkyne was removed under 0.1 Torr at 60 °C and the residue chromatographed first with hexane–dichloromethane (70:30) and then with dichloromethane: yield 5.1 g (75%) of pale yellow solid; mp 124 °C; ^{31}P NMR (CDCl$_3$) δ 193.9 ($^1J_{PW}$ = 234 Hz), minor isomer 220.4 ($^1J_{PW}$ = 224 Hz); ^{1}H NMR (CDCl$_3$) δ 1.28 (t, $^3J_{HH}$ = 7.15 Hz, 3 H, CH_3CH$_2$), 2.0 (d, $^4J_{HP}$ = 1.4, 6 H, CH$_3$), 3.8 (s, 6 H, CH$_3$O), 3.94 (s, 2 H, CH), 4.28 (q, $^3J_{HH}$ = 7.15, 2 H, CH$_3$$CH_2$); ^{13}C NMR (CDCl$_3$) δ 14.1 (s, CH_3CH$_2$), 15.6 (s, =CCH_3), 52.5 (s, CH$_3$O), 58.6 (d, $^1J_{CP}$ = 22.9 Hz, CHP), 62.1 (s, OCH$_2$), 136.9 (d, $^2J_{CP}$ = 16.9 Hz, =CCH$_3$), 147.2 (d, $^2J_{CP}$ = 5.1 Hz, CCO$_2$Me), 164.2 (d, $^3J_{CP}$ = 2.7 Hz, CO$_2$Me), 173.9 (d, $^1J_{CP}$ = 26.5 Hz, PCO$_2$Et), 195.7 (d, $^2J_{CP}$ = 6.1 Hz, cis CO), 196.7 (d, $^2J_{CP}$ = 27.2 Hz, trans CO); mass spectrum (70 eV, ^{184}W), m/z (relative intensity) 650 (M, 5). Anal. Calcd for C$_{20}$H$_{19}$O$_{11}$PW: C, 36.94; H, 2.94; P, 4.76; W, 28.28. Found: C, 37.05; H, 2.95; P, 4.77; W, 28.47.

[η^1-*O*-Methyl (ethoxycarbonyl)phosphinite-*P*]pentacarbonyltungsten (5). To a solution of 3.25 g (5 mmol) of phosphanorbornadiene complex **3** in 15 mL of methanol was added a catalytic amount of cuprous chloride. The mixture was refluxed for 2 h. After evaporation of the solvent, the residue was chromatographed with toluene: yield 1.55 g (79.9%) of a yellow oil; ^{31}P NMR (CDCl$_3$) δ 78.3 ($^1J_{PW}$ = 278 Hz); ^{1}H NMR (CDCl$_3$) δ 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3CH$_2$), 3.8 (d, $^3J_{HP}$ = 12.5 Hz, 3 H, CH$_3$O), 4.38 (m, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2CH$_3$), 7.44 (d, $^1J_{HP}$ = 365.5 Hz, 1 H, HP); ^{13}C NMR (CDCl$_3$) δ 14.2 (s, CH_3CH$_2$), 62.4 (s, CH$_3$O), 62.7 (s, CH$_2$O), 173.1 (d, $^1J_{CP}$ = 59.9 Hz, CO$_2$Et), 194.3 (d, $^2J_{CP}$ = 7.0 Hz, cis CO), 197.8 (d, $^2J_{CP}$ = 28.2 Hz, trans CO); mass spectrum (70 eV, ^{184}W), m/z (relative intensity) 459 (M − H, 95), 386 (M − CO$_2$Et − H, 25), 348 (M − 4CO, 100).

[η^1-*N*,*N*-Diethyl(ethoxycarbonyl)phosphinous amide-*P*]pentacarbonyltungsten (6). A solution of 3.25 g (5 mmol) of compound **3** in 3 mL of diethylamine was refluxed for 1 h. The excess of amine then was removed under vacumm and the residue chromatographed with toluene: yield 1.75 g (70%) of pale yellow oil; ^{31}P NMR (C$_6$D$_6$) δ 29.7 ($^1J_{PW}$ = 249 Hz); ^{1}H NMR (C$_6$D$_6$) δ 0.85 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, CH_3CH$_2$N), 0.97 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3CH$_2$O), 2.85 (dq, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 12.5 Hz, 4 H, CH$_2$N), 3.98 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH$_2$O), 6.70 (d, $^1J_{HP}$ = 388.8 Hz, 1 H, PH); ^{13}C NMR (C$_6$D$_6$) δ 13.6 (d, $^3J_{CP}$ = 2.9 Hz, CH_3CH$_2$N), 13.9 (s, CH_3CH$_2$O), 46.6 (d, $^2J_{CP}$ = 4.2 Hz, CH$_2$N), 62.1 (s, CH$_2$O), 175.2 (d, $^1J_{CP}$ = 48.9 Hz, CO$_2$Et), 196.1 (d,2J_{CP} = 5.9 Hz, cis CO), 198.7 (d, $^2J_{CP}$ = 24.4 Hz, trans CO); mass spectrum (70 eV, ^{184}W), m/z (relative intensity) 501 (M, 28), 429 (M − NEt$_2$, 25).

[η^1-2,3-Diphenyl-1-(ethoxycarbonyl)phosphirene-*P*]-pentacarbonyltungsten (7). A solution of 4 g (6.1 mmol) of phosphanorbornadiene **3** and 3.2 g (18 mmol) of tolan in 8 mL of mesitylene was heated 6 h at 120 °C. Filtration of the cooled solution gave 2.9 g (77.7%) of crystals: mp 146 °C; a recrystallization of the solid from a mixture of dichloromethane and hexane did not change the melting point; ^{31}P NMr (CDCl$_3$) δ −171.1 ($^1J_{PW}$ = 273 Hz); ^{1}H NMR (DDCl$_3$) δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH$_3$), 4.22 (q, $^3J_{HH}$ = 7.1, 2 H, CH$_2$), 7.5 (m, 6 H, meta and para aromatic H), 7.8 (m, 4 H, ortho-aromatic H); ^{13}C NMR (CDCl$_3$) δ 14.1 (s, CH$_3$), 63.4 (s, CH$_2$), 124.1 (d, $^1J_{CP}$ = 13.0 Hz, =CP), 172.7 (d, $^1J_{CP}$ = 18.0 Hz, CO$_2$Et), 195.1 (d, $^2J_{CP}$ = 9.3 Hz, cis CO), 196.8 (d, $^2J_{CP}$ = 35.1 Hz, trans CO), aromatic carbons 126.2 (d, J_{CP} = 6.1 Hz), 129.3 and 130.4 (s), 130.8 (d, J_{CP} = 21.9 Hz); mass spectrum (70 eV, ^{184}W), m/z (relative intensity) 606 (M, 35), 470 (M − 5CO, 90). Anal. Calcd for C$_{22}$H$_{15}$O$_7$PW: C, 43.59; H, 2.49; P, 5.11; W, 30.33. Found: C, 43.64; H, 2.46; P, 5.20; W, 30.37.

(η^1,η^1-3,3′,4,4′-Tetramethyl-2,5-dihydro-1,1′-biphospholyl-*P*,*P*′)decacarbonylditungsten (10). To 1.4 g (2.7 mmol) of phosphole **2** in 20 mL of ethanol was added 1.5 mL of a 20% solution (3.3 mmol) of tetramethylammonium hydroxide in methanol. The pale yellow solid formed was filtered and recrystallized from dichloromethane–ethanol: yield 0.78 g (65.2%); mp 193 °C.[6]

3,4-Dimethyl-1-cyanophosphole (11). To 3.25 g (30 mmol) of cyanogen bromide in 50 mL of toluene and 10 mL of THF was added at −50 °C a solution of phospholyllithium complex **1** (26.6 mmol in 150 mL of THF).[6] The reaction mixture was concentrated under vacuum, and 50 mL of toluene, 50 mL of hexane, and sodium sulfate were successively added with vigorous stirring. The mixture then was filtered over a small quantity of silica gel. Vacuum distillation of the filtrate led to 2.65 g (72.8%) of white crystals. Purification of the phosphole **11** also was performed by chromatography with hexane (yield 70%). An analytical sample was purified by sublimation at 80 °C under 20 Torr: mp 52 °C; ^{31}P NMR (CDCl$_3$) δ −54.7; ^{1}H NMR (CDCl$_3$) δ 2.13 (dd, $^4J_{HH}$ = 0.7 Hz, $^4J_{HP}$ = 3.6 Hz, 6 H, CH$_3$), 6.27 (dd, $^4J_{HH}$ = 0.7 Hz, $^2J_{HP}$ = 42.0 Hz, 2 H, =CH); ^{13}C NMR (CDCl$_3$) δ 17.3 (d, $^3J_{CP}$ = 3.6 Hz, CH$_3$), 115.9 (d, $^1J_{CP}$ = 83.0 Hz, CN), 120.5 (s, =CH), 155.5 (d, $^2J_{CP}$ = 8.5 Hz, =C); IR (KBr) ν(CN) 2160 cm^{-1}; mass spectrum (70 eV), m/z (relative intensity) 137 (M, 100). Anal. Calcd for C$_7$H$_8$NP: C, 61.31; H, 5.88; N, 10.22; P, 22.59. Found: C, 61.38; H, 5.96; N, 9.99; P, 22.56.

3,4-Dimethyl-1-*tert*-butoxyphosphole (12) and 3,4-Dimethyl-1-*tert*-butoxyphosphole Sulfide (13). To 0.4 g (2.9 mmol) of the cyanophosphole **11** in 8 mL of THF was added 0.33 g (2.9 mmol) of solid potassium *tert*-butoxide at −40 °C. The reaction mixture was stirred for 20 min at room temperature, and the formation of compound **12** was monitored by ^{31}P NMR (without ^{1}H decoupling): δ 82.6 (m, $^2J_{PH}$ = 39.0 Hz). Elemental sulfur (0.28 g, 1.1 mmol) then was added, and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was chromatographed with hexane–toluene (3/1) to remove the excess of S$_8$ and then with hexane–dichloromethane (1/1): yield 0.57 g (91.9%) of white crystals: mp 95.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.53 (s, 9 H, *t*-Bu), 2.0 (dd, $^4J_{HH}$ = 1.0 Hz, $^4J_{HP}$ = 1.7 Hz, 6 H, CH$_3$), 5.88 (dd, $^4J_{HH}$ = 1.0 Hz, $^2J_{HP}$ = 29.1 Hz, 2 H, =CH); ^{13}C NMR (CDCl$_3$) δ 16.9 (d, $^3J_{CP}$ = 20.5 Hz, CH$_3$), 30.5 (d, $^3J_{CP}$ = 3.9 Hz, $(CH_3)_3$C), 83.5 (d, $^2J_{CP}$ = 9.8 Hz, CO), 123.5 (d, $^1J_{CP}$ = 107.5 Hz, =CH), 149.3 (d, $^2J_{CP}$ = 24.4 Hz, =C); mass spectrum (70 eV), m/z (relative intensity) 216 (M, 22), 160 (M + 1 − *t*-Bu). Anal. Calcd for C$_{10}$H$_{17}$OPS: C, 55.53; H, 7.92; P, 14.32; S, 14.82. Found: C, 55.42; H, 7.88; P, 14.00; S, 14.60.

3,4-Dimethyl-1-(9-fluorenyl)phosphole (14) and [η^1-3,4-Dimethyl-1-(9-fluorenyl)phosphole-*P*]pentacarbonyltungsten (15). Method A. To a solution of 9-fluorenyllithium (10 mmol; from 1.66 g of fluorene and 0.08 g of Li) in 20 mL of THF was added at −10 °C a solution of 1.0 g (7.2 mmol) of cyanophosphole **11** in 6 mL of THF. After 15 min of stirring at room temperature, the reaction mixture was neutralized with a few drops of acetic acid and the solvent removed. The residue was rapidly chromatographed with toluene leading to 1.8 g of partly crystallized phosphole **14**; ^{31}P NMR (toluene) without ^{1}H irradiation, gave a splitted signal: δ 1.0 (t, $^2J_{PH}$ = 37.6 Hz). To the phosphole **14** (ca. 6.4 mmol) in 20 mL of THF was added 2.3 g (6.4 mmol) of pentacarbonyl(acetonitrile)tungsten, and the solution was heated 3 h at 60 °C. After evaporation of the solvent, the residue was chromatographed with toluene, leading to 2.6 g (overall yield 60.2%) of yellow crystals: mp 220 °C dec; ^{31}P NMR (CDCl$_3$) δ 18.3 ($^1J_{PW}$ = 225 Hz); ^{1}H NMR (CDCl$_3$) δ 2.25 (d, $^4J_{HH}$ = 0.85 Hz, 6 H, CH$_3$), 4.18 (d, $^2J_{HP}$ = 15.6 Hz, 1 H, CHP), 6.75 (dd, $^4J_{HH}$ = 0.75 Hz, $^2J_{HP}$ = 36.7 Hz, 2 H, =CH), 7.35–7.85 (m, 8 H, aromatic H); ^{13}C NMR (CDCl$_3$) δ 17.2 (d, $^3J_{CP}$ = 11.0 Hz, CH$_3$), 49.3 (d, $^1J_{CP}$ = 15.9, >CHP), 129.8 (d, $^1J_{CP}$ = 37.8 Hz, =CH), 151.0 (d, $^2J_{CP}$ = 7.3 Hz, =C), 194.7 (d, $^2J_{CP}$ = 6.1 Hz, cis CO), 198.1 (d, $^2J_{CP}$ = 19.1 Hz, trans CO), secondary aromatic C 120.7 (s), 125.2 (d, J_{CP} = 3.7 Hz), 127.2 (d, J_{CP} = 2.5 Hz), 128.4 (d, J_{CP} = 2.5 Hz), tertiary aromatic C 141.6 (s), 142.4 (d, J_{CP} = 4.9 Hz); mass spectrum (70 eV, ^{184}W, m/z (relative intensity) 600 (M, 25). Anal. Calcd for C$_{24}$H$_{17}$O$_5$PW: C, 48.02; H, 2.86; P, 5.56; W, 30.63. Found: C, 48.00; H, 2.94; P, 5.16; W, 31.13.

Method B. To a solution of 14.3 mmol of 9-fluorenyllithium in 30 mL of THF was added at −40 °C 6.0 g (13 mmol) of complexed cyanophosphole **16**. The mixture was stirred for 30 min at room temperature and the solvent distilled under vacuum. The residue was chromatographed first with hexane and then with toluene: yield 6.2 g (79.5%); mp 220 °C dec; ^{31}P NMR (CH$_2$Cl$_2$) δ 20.2 ($^1J_{PW}$ = 224.5 Hz).

(η^1-3,4-Dimethyl-1-cyanophosphole-*P*)pentacarbonyltungsten (16). To 4.8 g (0.047 mol) of cyanogen bromide in 50 mL of THF was added at −40 °C a solution of 0.042 mol of complexed phospholyllithium **1**. The mixture was stirred for 30 min, and then the solvent was distilled under vacuum. The residue was chromatographed first with hexane and then with toluene: yield 10.2 g (52%) of yellow crystals which darkened in air; mp 119 °C; ^{31}P NMR (CDCl$_3$) δ -23.2 ($^1J_{PW}$ = 237 Hz); ^{1}H NMR (CDCl$_3$) δ 2.30 (s, 6 H, CH$_3$), 6.42 (d, $^2J_{HP}$ = 40.5 Hz, 2 H, =CH); ^{13}C NMR (CDCl$_3$) δ 17.6 (d, $^4J_{CP}$ = 12 .8 Hz, CH$_3$), 115.6 (d, $^1J_{CP}$ = 104.5 Hz, CN), 122.5 (d, $^1J_{CP}$ = 48.2, =CH), 156.9 (d, $^2J_{CP}$ = 11.4 Hz, =C), 193.9 (d, $^2J_{CP}$ = 6.0 Hz, cis CO), 196.9 (d, $^2J_{CP}$ = 23.9 Hz, trans CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 461 (M, 18). Anal. Calcd for $C_{12}H_8NO_5PW$: C, 31.26; H, 1.75; N, 3.04; P, 6.72. Found: C, 31.47; H, 1.81; N, 3.02; P, 6.83.

General Procedure for (η^1-3,4-Dimethyl-1-alkoxyphosphole-*P*)-, (η^1-3,4-Dimethyl-1-hydroxyphosphole-*P*)-, and (η^1-3,4-Dimethyl-1-alkynylphosphole-*P*)pentacarbonyltungsten. To a solution of 2.3 g (5 mmol) of the complexed cyanophosphole **16** in 30 mL of THF was added 0.95 equiv of the corresponding solid sodium or potassium alcoholate (compounds **18**, **19**, and **20**) or of a 30% aqueous sodium hydroxide solution (compound **17**) or 1.2 equiv of the lithium or bromomagnesium monoacetylide in THF (compounds **21** and **22**) at -20 °C. After 15 min of stirring at room temperature, the products were purified and their formation was monitored by ^{31}P NMR of the reaction mixtures.

(η^1-3,4-Dimethyl-1-*tert*-butoxyphosphole-*P*)pentacarbonyltungsten (20). The reaction mixture was evaporated under vacuum and the residue chromatographed with toluene: yield 1.55 g (62.3%) of an orange oil; ^{31}P NMR (CDCl$_3$) δ 89.2 ($^1J_{PW}$ = 254 Hz); ^{1}H NMR (CDCl$_3$) δ 1.24 (s, 9 H, *t*-Bu), 2.1 (d, $^4J_{HH}$ = 0.7 Hz, 6 H, CH_3C=), 6.26 (dd, $^4J_{HH}$ = 0.7 Hz, $^2J_{HP}$ = 36.1 Hz, 2 H, =CH); ^{13}C NMR (CDCl$_3$) δ 16.4 (d, $^3J_{CP}$ = 12.3 Hz, CH_3C=), 29.4 (d, $^3J_{CP}$ = 4.9 Hz, $(CH_3)_3$C), 83.6 (d, $^2J_{CP}$ = 18.3 Hz, CO), 130.0 (d, $^1J_{CP}$ = 36.6 Hz, =CH), 146.0 (d, $^2J_{CP}$ = 14.6 Hz, =C), 196.4 (d, $^2J_{CP}$ 7.3 Hz, cis CO), 199.3 (d, $^2J_{CP}$ = 20.8 Hz, trans CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 508 (M, 20), 368 (M - 5CO, 28), 340 (M - 5CO - C$_4$H$_8$, 100).

(η^1-3,4-Dimethyl-1-methoxyphosphole-*P*)pentacarbonyltungsten (18): ^{31}P NMR (THF) δ 111.8 ($^1J_{PW}$ = 262 Hz) [lit.[5] δ 110.0 ($^1J_{PW}$ = 263.7 Hz)].

(η^1-3,4-Dimethyl-1-ethoxyphosphole-*P*)pentacarbonyltungsten (19): ^{31}P NMR (THF) δ 107.1 ($^1J_{PW}$ = 260 Hz); presence of a minor signal at 76.9 ppm corresponding to the oxyanion of the phosphole **17** (see later).

(η^1-3,4-Dimethyl-1-hydroxyphosphole-*P*)pentacarbonyltungsten (17). The ^{31}P NMR spectrum of the reaction mixture showed a triplet at 76.9 ppm ($^2J_{PH}$ = 34.2 Hz, $^1J_{PW}$ = 222 Hz) corresponding to the oxyanion of the phosphole **17**. Acidification by dilute hydrochloric acid gave the hydroxyphosphole: ^{31}P NMR (THF) δ 92.5 ($^2J_{PH}$ = 36.4 Hz, $^1J_{PW}$ = 250 Hz).

(η^1-3,4-Dimethyl-1-ethynylphosphole-*P*)pentacarbonyltungsten (21): purified by chromatography with toluene; yield 0.9 g (40%); light yellow solid; mp 183 °C dec; ^{31}P NMR (THF) δ -23.5 ($^1J_{PW}$ = 222 Hz); ^{1}H NMR (CDCl$_3$) δ 2.15 (d, $^4J_{HH}$ = 1.0 Hz, 6 H, CH$_3$), 3.05 (d, $^3J_{HP}$ = 7.3 Hz, 1 H, CH), 6.3 (dd, $^4J_{HH}$ = 1.0 Hz, $^2J_{HP}$ = 38.3 Hz, 2 H, =CH); ^{13}C NMR (CDCl$_3$) δ 17.3 (d, $^3J_{CP}$ = 12.6 Hz, CH$_3$), 94.8 (d, $^2J_{CP}$ = 11.4 Hz, ≡CH), 116.8 (s, ≡CP), 126.5 (d, $^1J_{CP}$ = 50.1 Hz, =CH), 152.4 (d, $^2J_{CP}$ = 12.1 Hz, =C), 195.6 (d, $^2J_{CP}$ = 6.6 Hz, cis CO).

[η^1-3,4-Dimethyl-1-(phenylethynyl)phosphole-*P*]pentacarbonyltungsten (22): purified by chromatography with toluene; yield 1.45 g (55%) of pale yellow solid; mp 101 °C; ^{31}P NMR (CH$_2$Cl$_2$) δ -25.6 ($^1J_{PW}$ = 220 Hz); ^{1}H NMR (CDCl$_3$) δ 2.2 (d, $^4J_{HH}$ = 0.9 Hz, 6 H, CH$_3$), 6.37 (dd, $^4J_{HH}$ = 0.9 Hz, $^2J_{HP}$ = 38.1 Hz, 2 H, =CH), 7.3–7.5 (m, 5 H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$) δ 17.3 (d, $^3J_{CP}$ = 12.6 Hz, CH$_3$), 107.8 (d, $^2J_{CP}$ = 13.6 Hz, ≡CPh), 121.2 (s, ≡CP), 126.8 (d, $^1J_{CP}$ = 50.6 Hz, =CH), 128.4, 129.9, 132.3 (s, C$_6$H$_5$), 151.7 (d, $^2J_{CP}$ = 12.2 Hz, =C), 195.9 (d, J_{CP} = 6.1 Hz, cis CO), 199.1 (d, J_{CP} = 20.1 Hz, trans CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 536 (M, 15), 368 (M - 4CO, 100).

(η^1-1-Cyano-2,3-diphenylphosphirene-*P*)pentacarbonyltungsten (23). A mixture of 2.08 g (4.5 mmol) of cyanophosphole complex **16**, 1.6 g (9 mmol) of tolan, and 1.3 g (9 mmol) of dimethyl acetylenedicarboxylate was heated 5 h at 70 °C. The reaction mixture was chromatographed first with hexane and then with dichloromethane: yield 1.1 g (44.0%) of yellow crystals; mp 136 °C; ^{31}P NMR (toluene) δ -206.8 ($^1J_{PW}$ = 312.5 Hz); ^{13}C NMR (CDCl$_3$) δ 119.8 (d, $^1J_{CP}$ = 69.1 Hz, CN), 124.3 (d, $^1J_{CP}$ = 12.0 Hz, =CP), 124.9 (d, $^2J_{CP}$ = 5.3 Hz, aromatic C$_1$), 129.8, 130.6, 132.1 (s, ortho, meta, para aromatic C), 193.8 (d, $^2J_{CP}$ = 8.0 Hz, cis CO), 195.5 (d, $^2J_{CP}$ = 42.2 Hz, trans CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 559 (M, 6). Anal. Calcd for $C_{20}H_{10}NO_5PW$: C, 42.96; H, 1.80; N, 2.50; P, 5.54; W, 32.88. Found: C, 42,50; H, 1.95; N, 2.38; P, 6.21; W, 33.17.

[η^1-5,6-Dimethyl-7-*tert*-butoxy-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene-*P*]pentacarbonyltungsten (24). A mixture of 5.08 g (10 mmol) of phosphole **20** and 7.1 g (50 mmol) of dimethyl acetylenedicarboxylate was heated 8 h at 65 °C. The excess of acetylenic compound was distilled under pump vacuum at 60 °C. The residue was chromatographed successively with toluene, dichloromethane, and ethyl acetate and led to the following. The starting material **20**: 0.9 g (18%); δ (^{31}P) (toluene) 88.9 ppm. *syn*-Phosphanorbornadiene **24**: 1.95 g (38.2%); mp 100 °C; ^{31}P NMR (toluene) δ 214.5 ($^1J_{PW}$ = 270 Hz); ^{1}H NMR (CDCl$_3$) δ 1.45 (d, $^4J_{HP}$ = 0.5 Hz, 9 H, *t*-Bu), 2.0 (d, $^4J_{HP}$ = 2.2 Hz, 6 H, CH_3C=), 3.73 (d, $^2J_{HP}$ = 1.0 Hz, 2 H, CHP), 3.80 (s, 6 H, CH$_3$O); ^{13}C NMR (CDCl$_3$) δ 16.0 (s, *t*-Bu), 30.6 (s, CH$_3$), 52.3 (s, OCH$_3$), 135.4 (d, $^2J_{CP}$ = 22.7 Hz, =CCH$_3$), 143.8 (d, $^2J_{CP}$ = 9.4 Hz, =CCO$_2$Me), 165.4 (s, CO$_2$Et), 196.4 (d, $^2J_{CP}$ = 6.9 Hz, cis CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 650 (M, 50), 372 ((CO)$_5$W←P O-*t*-Bu, 38). Anal. Calcd for $C_{21}H_{23}O_{10}PW$: C, 38.79; H, 3.57. Found: C, 38.81; H, 3.33.

(η^1-2,3-Diphenyl-1-*tert*-butoxyphosphirene-*P*)pentacarbonyltungsten (25). Method A. *tert*-Butoxyphosphanorbornadiene **24** (0.56 g, 1 mmol), 0.3 g of tolan, and 0.05 g of cuprous chloride in 2 mL of toluene were heated 1 h at 70 °C. Chromatography with hexane and then with toluene led to 0.3 g (50.0%) of orange crystals, mp 80 °C.

Method B. To 0.6 g of cyanophosphirene **23** in 5 mL of THF was added 0.15 g (1.3 mmol) of solid potassium *tert*-butoxide. After evaporation of the solvent, the residue was chromatographed with toluene: yield 0.34 g (56.6%) of orange crystals; mp 80 °C; ^{31}P NMR (CDCl$_3$) δ -89.0 ($^1J_{PW}$ = 237 Hz); ^{1}H NMR (CDCl$_3$) δ 1.16 (s, 9 H, *t*-Bu), 7.53 (m, 6 H, ortho and para aromatic H), 7.90 (m, 4 H, meta aromatic H); ^{13}C NMR (CDCl$_3$) δ 30.4 (d, $^3J_{CP}$ = 12.5 Hz, $(CH_3)_3$C), 81.2 (d, $^2J_{CP}$ = 16.7 Hz, C(CH$_3$)$_3$), 128.4 (d, $^2J_{CP}$ = 4.4 Hz, aromatic C$_1$), 129.3 (s), 129.8 (d, $^3J_{CP}$ = 5.5 Hz), 129.9 (s, meta, para, and ortho aromatic C), 149.1 (d, $^1J_{CP}$ = 21.3 Hz, =CP), 196.1 (d, $^2J_{CP}$ = 10.8 Hz, cis CO), mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 606 (M, 20), 466 (M - 5CO, 40), 410 (M - 5CO - C$_4$H$_8$, 100).

[η^1-5,6-Dimethyl-7-(9-fluorenyl)-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene-*P*]pentacarbonyltungsten (26). A mixture of 3.2 g (5.3 mmol) of 9-fluorenylphosphole **15** and 4 mL of dimethyl acetylenedicarboxylate was heated overnight at 80 °C. The reaction mixture was cooled, giving a pale yellow solid which was recrystallized from dichloromethane–methanol: yield 2.6 g (67.6%); mp 205 °C dec; ^{31}P NMR (CDCl$_3$) δ 225.5 ($^1J_{PW}$ = 250 Hz); ^{1}H NMR (CDCl$_3$) δ 2.04 (d, $^4J_{HP}$ = 1.5 Hz, 6 H, CH$_3$), 3.85 (s, 6 H, CH$_3$O), 4.15 (d, $^2J_{HP}$ = 3.2 Hz, 2 H, CHP), 5.10 (d, $^2J_{HP}$ = 12.0 Hz, 1 H, CHP), 7.4 and 7.8 (m, 8 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 16.2 (d, $^3J_{CP}$ = 2.4 Hz, CH$_3$), 52.6 (d, $^1J_{CP}$ = 7.3 Hz, fluorenyl CH), 52.7 (s, CH$_3$O), 60.8 (d, $^1J_{CP}$ = 15.8 Hz, CHP), 138.9 (d, $^2J_{CP}$ = 15.9 Hz, =CMe), 145.9 (d, $^2J_{CP}$ = 3.6 Hz, =CCO$_2$Me), aromatic C 121.0 (s), 124.6 (d, J_{CP} = 2.5 Hz), 127.7 (s), 128.4 (s), 141.4 (d, J_{CP} = 2.4 Hz), 142.8 (d, J_{CP} = 3.2 Hz), 165.3 (s, CO$_2$Me), 195.0 (d, $^2J_{CP}$ = 6.1 Hz, cis CO); mass spectrum (70 eV, ^{184}W), *m/z* (relative intensity) 742 (M, 10). Anal. Calcd for $C_{30}H_{23}O_9PW$: C, 48.54; H, 3.12; P, 4.17; W, 24.77. Found: C, 48.43; H, 3.19; P, 3.99; W, 24.91.

(η^1-*O*-Methyl 9-fluorenylphosphinite-*P*)pentacarbonyltungsten (27). Phosphanorbornadiene **26** (3.4 g, 4.6 mmol) in 50 mL of dry methanol was heated 10 h at 120 °C in a stainless-steel autoclave. The methanol was distilled under vacuum and the residue chromatographed with hexane–dichloromethane (4/1) leading to 1.7 g (68%) of white crystals: mp 146 °C; ^{31}P NMR (CDCl$_3$) δ 111.0 ($^1J_{PW}$ = 290 Hz); ^{1}H NMR (acetone-d_6) δ 4.18 (d, $^3J_{HP}$ = 12.0 Hz, 3 H, CH$_3$O), 5.60 (dd, $^3J_{HH}$ = 3.5 Hz, $^2J_{HP}$ = 16.7 Hz, 1 H, CH), 7.9 (dd, $^3J_{HH}$ = 3.5 Hz, $^1J_{HP}$ = 336 Hz, 1 H, PH), 7.3–7.9 (m, 8 H, aromatic); ^{13}C NMR (acetone-d_6) δ 47.1 (d, $^1J_{CP}$ = 16.6 Hz, fluorenyl CH), 60.5 (d, $^2J_{CP}$ = 13.4 Hz, CH$_3$O), 194.3 (d, $^2J_{CP}$ = 7.7 Hz, cis CO), aromatic C 121.0 (d, J_{CP} = 12.1 Hz), 122.7 (s), 125.6 (s), 127.7 (d, J_{CP} = 10.4 Hz), 128.7 (s), 142.7

Organometallics 1988, 7, 1801-1806 1801

(d, J_{CP} = 20.6 Hz); mass spectrum (70 eV, ^{184}W), m/z (relative intensity) 552 (M, 25), 387 (M − fluorenyl, 20).

[η^1-2,3-Diphenyl-1-(9-fluorenyl)phosphirene-*P*]pentacarbonyltungsten (28). The 9-fluorenylphosphanorbornadiene **26** (0.74 g, 1 mmol) and 0.71 g (4 mmol) of tolan in 7 mL of mesitylene were heated 5 h at 125 °C. The solid obtained at room temperature was suction-filtered and then recrystallized from dichloromethane by slow evaporation of the solvent: yield 0.5 g (70%); mp 228 °C; ^{31}P NMR (CH_2Cl_2) δ −140.8 ($^1J_{PW}$ = 268 Hz); ^{1}H NMR ($CDCl_3$) δ 4.25 (d, $^2J_{HP}$ = 7.2 Hz, 1 H, CH), 7.2–7.9 (m, 18 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.2 (d, $^1J_{CP}$ = 9.3 Hz, CH), 125.4 (d, $^1J_{CP}$ = 3.7 Hz, =CP), 195.0 (d, $^2J_{CP}$ = 4.2 Hz, cis CO), aromatic carbons 127.5, 128.1, 129.1, 129.8 (d, J_{CP} = 3.1 Hz), 130.4, 140.9, 141.8; mass spectrum (46 eV, ^{184}W), m/z (relative intensity) 698 (M, 3), 533 (M − fluorenyl, 30). Anal. Calcd for $C_{32}H_{19}O_5PW$: C, 55.02; H, 2.74; P, 4.43; W, 26.33. Found: C, 54.95; H, 2.69; P, 4.41; W, 26.42.

Registry No. **1**, 105857-15-6; **2**, 115076-19-2; **3**, 115076-20-5; **5**, 115076-21-6; **6**, 115076-22-7; **7**, 115076-23-8; **10**, 105812-22-4; **11**, 115076-24-9; **12**, 115076-25-0; **13**, 115076-26-1; **14**, 115076-27-2; **15**, 115076-28-3; **16**, 115076-29-4; **17**, 115076-30-7; **18**, 108504-07-0; **19**, 115076-31-8; **20**, 115076-32-9; **21**, 115076-33-0; **22**, 115076-34-1; **23**, 115076-35-2; **24**, 115076-36-3; **25**, 115076-37-4; **26**, 115076-38-5; **27**, 115076-39-6; **28**, 115076-40-9; $ClCO_2Et$, 541-41-3; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; BrCN, 506-68-3; $W(CO)_5CH_3CN$, 15096-68-1; $LiC{\equiv}CH$, 1111-64-4; $PhC{\equiv}CMgBr$, 6738-06-3; tolan, 501-65-5; 9-fluorenyllithium, 881-04-9.

Synthesis and X-ray Crystal Structures of the Mono- and Binuclear Arylmanganate Complexes $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$, $[Li(THF)_4]_2[Mn_2Ph_6]$, and $[Li(THF)_4][MnMes_3]$

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The synthesis and X-ray crystal structures of the arylmanganate complexes $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ (**1**), $[Li(THF)_4]_2[Mn_2Ph_6]$ (**2**), and $[Li(THF)_4][MnMes_3]$ (**3**) are reported. They are the first X-ray structural characterizations of compounds of the type $LiMnR_3$ which are, in conjunction with neutral organomanganous species, of growing importance in organic synthesis. The complex "$LiMnPh_3$", derived from a manganese dihalide and 3 equiv of PhLi, crystallizes as a centrosymmetric dimer in the case of both **1** and **2**. The structure of **1** may be described as a linear array of the four metals LiMnMnLi. Each metal is located at the centers of four edge-sharing distorted tetrahedra. Thus, both manganese atoms are surrounded by four bridging phenyls, and the two outer lithiums are coordinated to two bridging phenyls and two ethers. The ionic complex **2** has a similar structure except that the more strongly coordinating THF's effect separation of the lithium ions as $[Li(THF)_4]^+$ leaving the free dimeric $[Mn_2Ph_6]^{2-}$ ion with a core structure similar to that seen in **1**. Use of the bulkier mesityl group affords the mononuclear ionic species $[Li(THF)_4][MnMes_3]$ (Mes = 2,4,6-$Me_3C_6H_2$) featuring a trigonal-planar structure for the $[MnMes_3]^-$ ion. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K are as follows: **1**, a = 14.764 (6) Å, b = 15.496 (6) Å, c = 21.889 (8) Å, Z = 4, orthorhombic, space group $Pbca$, R = 0.059; **2**, a = 10.494 (5) Å, b = 15.746 (8) Å, c = 19.659 (9) Å, β = 97.17 (4)°, Z = 2, monoclinic, space group $P2_1/n$, R = 0.081; **3**, a = 15.089 (5) Å, b = 16.288 (5) Å, c = 17.249 (6) Å, Z = 4, orthorhombic, space group $P2_12_12_1$, R = 0.073.

Introduction

σ-Bonded organomanganese complexes were first reported by Gilman, who used the reagents "$MnPh_2$" and "MnPhI" in situ.[1,2] Unfortunately, no structures were reported and definitive characterizations could not be claimed. In a more recent paper Andersen, Wilkinson, and co-workers described the syntheses and characterization of several neutral and ionic manganese(II) alkyls.[3] In addition, the first X-ray structures of σ-bonded, homoleptic, Mn(II) alkyls $[\{Mn(CMe_2Ph)_2\}_2]$ (**4**) and $[\{Mn(CH_2SiMe_3)_2\}_\infty]$ (**5**) were reported. Subsequent work by a number of groups has involved the synthesis of several new complexes. Examples include $[LiMnMes_3\cdot 2dioxane\cdot 2THF]$,[4] $[\{Mn(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}_2]$,[5] $[\{MnMes_2\}_3]$,[6] $[Li(THF)_4][\{(Me_3Si)_3C\}_3Mn_3Cl_4(THF)]$,[7] $[Mn\{C(SiMe_3)_3\}_2]$,[8] $[Mn(CH_2\text{-}t\text{-}Bu)_2]$,[9] and $[MnPh_2\{P(C_6H_{11})_3\}]$[10] as well as the dimeric tertiary phosphine adducts of the manganese(II) alkyls $[Mn_2R_4(PMe_3)_2]$ (R = CH_2SiMe_3, CH_2CMe_3, and CH_2Ph) and $[Mn_2(CH_2SiMe_3)_2(PR_3)_2]$ (R = Et_3, Me_2Ph, $MePh_2$, and $(C_6H_{11})_3$).[11] Some were structurally characterized, and those of $[Mn\{C(SiMe_3)_3\}_2]$[8] and $[Mn(CH_2\text{-}t\text{-}Bu)_2]$[9] are particularly interesting since their structures were the first authenticated examples of two-coordination in a transition metal which did not have a d^{10} electron configuration. In spite of this activity there is, at present, little structural information available for ionic "ate" complexes. In a recent review,[12] Normant and Cahiez have shown that organomanganous reagents, both neutral and ionic, i.e. RMnX, MnR_2, or $LiMnR_3$ (R = alkyl, aryl; X = halide), have considerable synthetic utility in organic chemistry. Their advantages compared with organo-

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