Generation and Trapping of Transient *cis*-(η^1-Phosphinidene)(η^1-carbene)tetracarbonyltungsten Complexes

Pascal Le Floch, Ngoc Hoa Tran Huy, and François Mathey*

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

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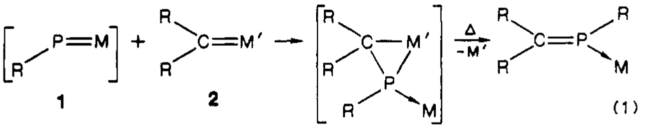
The reaction of *n*-butyl- or phenyllithium with (3,4-dimethyl-1-phenylphosphole)pentacarbonyltungsten followed by O-alkylation with $[Et_3O]BF_4$ gives the corresponding *cis*-(phosphole)(ethoxycarbene)$W(CO)_4$ complexes. The [4 + 2] cycloaddition of the phosphole dienic system of these complexes with dimethyl acetylenedicarboxylate then affords the corresponding *cis*-(7-phosphanorbornadiene)(ethoxycarbene)$W(CO)_4$ complexes. These 7-phosphanorbornadiene complexes can serve as precursors of transient *cis*-(phenylphosphinidene)(ethoxycarbene)$W(CO)_4$ complexes under mild conditions. These transient species selectively react at phosphorus with alcohols and amines to give the corresponding *cis*-[PhP(H)A](ethoxycarbene)-$W(CO)_4$ complexes (A = OR, NHR). When the amino group is sufficiently nucleophilic, intramolecular exchange takes place between the amino group at phosphorus and the ethoxy group of the carbene. No satisfactory trapping of the phosphinidene is observed with diphenylacetylene.

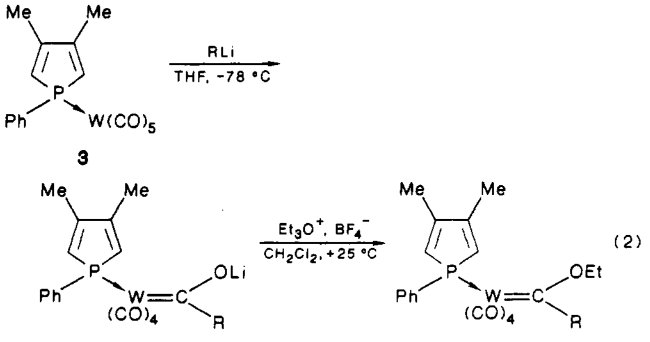
Recently, we have started to investigate the reaction of transient terminal phosphinidene complexes **1**[1] with carbene complexes **2**. Although both species show more or less pronounced electrophilic properties, in some cases, a condensation takes place as depicted in eq 1.[2] As a logical step further, we decided to try to generate a phosphinidene in the same coordination sphere as a carbene in order to investigate the competition between a possible intramolecular condensation and the reactions of both the phosphinidene and the carbene ligands with external reagents. We report here on the results of this study.



1 **2** (1)

Results and Discussion

For practical reasons, all our work has been performed with tetracarbonyltungsten complexes since both phosphinidene and carbene complexes with tungsten(0) are readily accessible. Following the phosphole–7-phosphanorbornadiene route to terminal phosphinidene complexes,[1] we first prepared two (phosphole)(carbene)tetracarbonyltungsten complexes (eq 2). The lithium salts **4** have only been characterized in situ by ^{31}P NMR spectroscopy. On the other hand, the ethoxycarbene complexes **5** have been fully characterized by mass spectrometry and IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Both IR and ^{13}C NMR spectroscopy demonstrate that the phosphole (P) and the carbene (C) are cis in the coordination sphere of tungsten. For example, the CO resonances appear as follows for **5a**: δ 201.88, $^2J_{CP}$ = 5.5 Hz, 2CO cis to (P) and (C); δ 205.8, $^2J_{CP}$ = 18.5 Hz, CO trans to (P); δ 210.6, ^2J(C–P) = 5.5 Hz, CO trans to (C). On the other hand, the carbenic carbon resonates at very low field (δ 319.9) as expected and shows no coupling with phosphorus. The reaction of **5** with neat dimethyl acetylenedicarboxylate then afforded the required 7-phosphanorbornadiene complexes **6** (eq 3). These complexes show the characteristic low-field shift of the ^{31}P resonance that is normally associated with the 7-phosphanorbornadiene skeleton[3] (for example, $\delta(^{31}P)$ (**6a**) +215.7 in CH_2Cl_2 vs H_3PO_4). The cis stereochemistry around the metal is retained. From another standpoint, it is interesting to note that the mass spectrum of **6a** (EI, 70 eV, ^{184}W) shows a peak at *m*/*z* 538 corresponding to the expected (phosphinidene)(carbene)tetracarbonyltungsten complex. The thermal decomposition of these 7-phosphanorbornadiene complexes was studied in the case of **6a**. In the presence of CuCl as a catalyst, the decomposition of **6a** takes place rapidly at 45

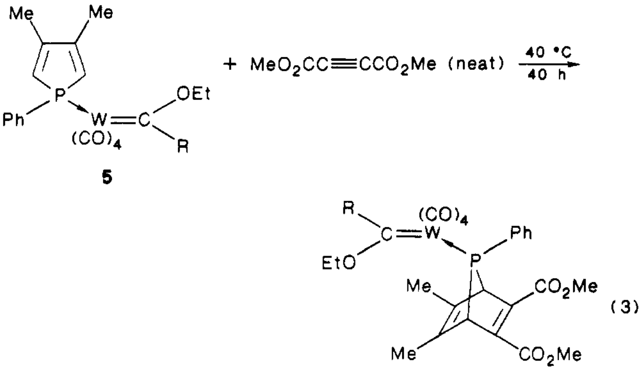


3

(2)

4a: R = Ph
b: R = *n*-Bu

5a: R = Ph (91%)
b: R = *n*-Bu (81%)



5

(3)

6a: R = Ph (70%)
b: R = *n*-Bu (40%)

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[1] The chemistry of transient terminal phosphinidene complexes has been recently reviewed: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275.

[2] Tran Huy, N. H.; Mathey, F. *Organometallics* **1987**, *6*, 207.

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

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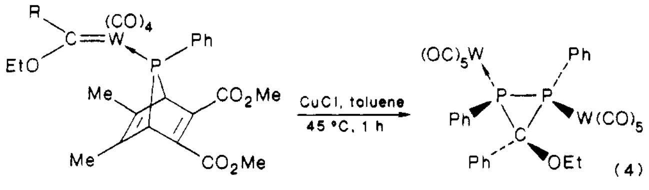
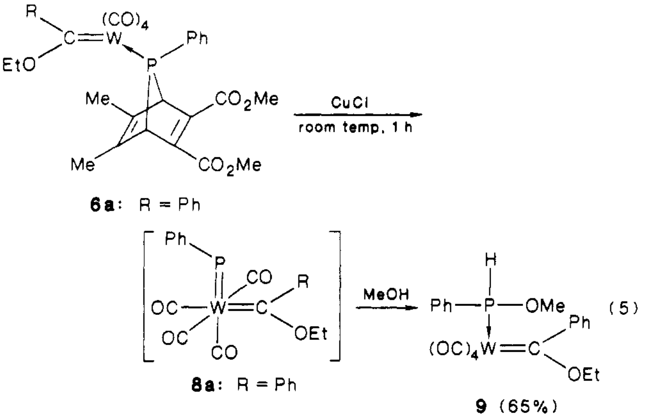
°C to give as the sole characterizable product the diphosphirane complex **7** in very modest yield (eq 4). Owing to its low thermal stability, the mass spectrum of **7** (EI, 20 eV) does not contain the molecular peak but the base peak at m/z 350 corresponds to the free diphosphirane ligand. The ^{31}P NMR spectrum of **7** is also very significant. The two different substituents at the ring carbon break the C_2 symmetry, and the two inequivalent phosphorus atoms give a AB system: δ(A) − 111.6, δ(B) − 122.5, and $^{1}J_{AB}$ = 122 Hz. The high-field shifts of these resonances suggest that the phosphorus atoms are included in a three-membered ring whereas the large coupling constant indicates the presence of a P–P bond. Finally, the ^{1}H NMR spectrum establishes that the EtO:Ph ratio is 1:3 and the IR spectrum that practically equivalent W(CO)$_5$ groups are present. Obviously, compound **7** results from a complicated series of reactions, and it is clear that the phosphinidene–carbene coupling observed previously[2] has a low efficiency within a single coordination sphere. Whereas the intramolecular coupling appears to be difficult, efficient trapping reactions of the postulated (phosphinidene)(carbene)tetracarbonyltungsten complexes **8** were observed with methanol (eq 5) and aniline (eq 6). The cis stereochemistry around tungsten is preserved in all these reactions.



6a: R = Ph

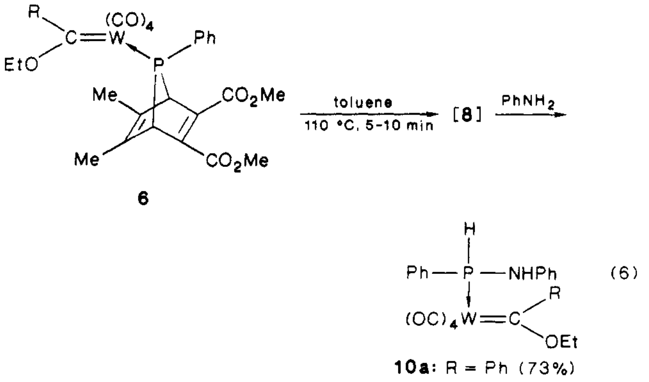
7 (~76%)



6a: R = Ph

8a: R = Ph

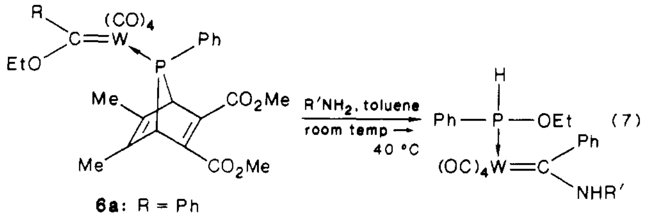
9 (65%)



6

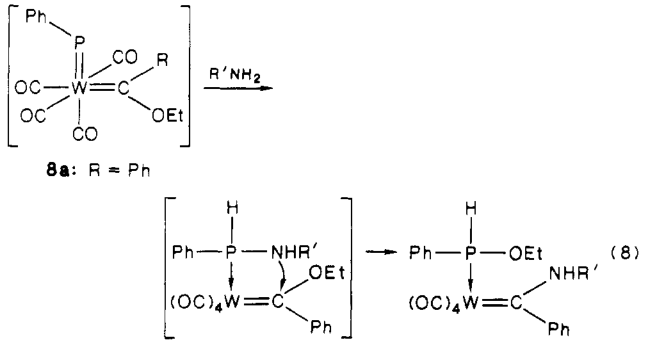
10a: R = Ph (73%)
b: R = n-Bu (50%)

A completely unexpected result was found when trying to extend this first series of experiments with aniline to other primary amines. When alkyl- or benzylamines were used, we obtained the compounds resulting from an exchange of the ethoxy and amino groups between the phosphorus and the carbenic carbon in the expected products (eq 7). Compounds **11** and **12** have the expected empirical formulas according to their mass spectra. However, the EtO→NHR′ exchange has clearly taken place on the basis of the following evidence: (1) whereas the carbenic carbon resonates at 320 ± 1 ppm in the ^{13}C NMR spectra of all the derivatives containing the C(Ph)OEt carbene (**5a**, **6a**, **9**, and **10a**), here the carbene resonance is observed at 262 ppm in **11** and 261.9 ppm in **12**; (2) the OCH$_2$ carbon is now coupled to phosphorus in **11** ($^{2}J_{CP}$ = 14.6 Hz) and **12** ($^{2}J_{CP}$ = 13 Hz). Since we used a great excess of amine in all these reactions, the aminolysis of the carbene with release of ethanol followed by the reaction of ethanol with the phosphinidene is obviously ruled out. Such a mechanism would lead to (aminophosphine)(aminocarbene)tetracarbonyltungsten complexes as the main products. The only acceptable possibility is the intramolecular aminolysis of the carbene by the aminophosphine in the initially expected products via nucleophilic attack at the carbenic carbon by the nitrogen lone pair (eq 8). This exchange does not take place in **10** probably because the nucleophilicity of nitrogen is too low. This mechanism seems all the more likely since it is now known that the nitrogen is far more nucleophilic in complexes than in free aminophosphines.[4]



6a: R = Ph

11: R′ = PhCH$_2$ (90%)
12: R′ = n-Bu (76%)



8a: R = Ph

Less satisfactory results were obtained when diphenylacetylene was as a trap. In order to be able to detect the formation of a phosphirene–carbene complex such as **14**, we first prepared it via the classical route already used for the synthesis of the phosphole–carbene complexes **5** (eq 9). The phosphirene and the carbene are cis in the tungsten coordination sphere of **14** as monitored by ^{13}C NMR. The ^{31}P resonance of **14** appears at −153 ppm in toluene vs −161 ppm for **13**.[5] When the phosphanorbornadiene–carbene complex **6a** was heated with tolan in excess at 110 °C in toluene for 1 h, a complicated mixture of products was obtained. According to the ^{31}P NMR spectrum of the crude reaction mixture, the main product was the diphosphirane complex **7** easily detected by its characteristic AB spectrum. This means that the efficiency

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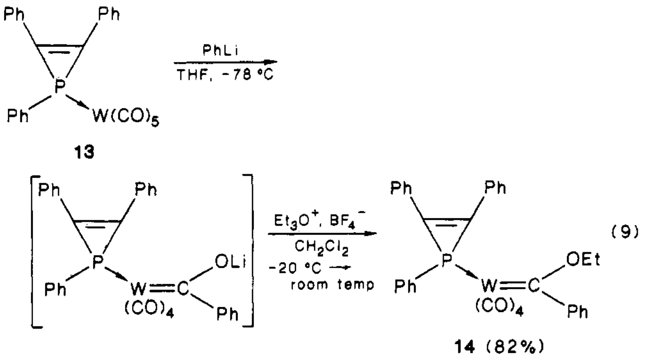
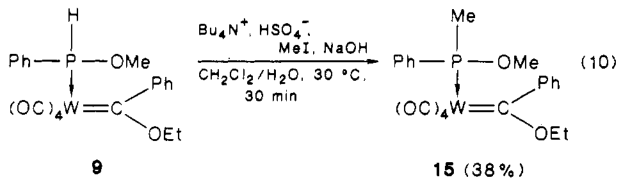
(4) Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 7985.

(5) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.



of tolan as a trap is low. In addition, three other resonances at −156, −161, and −189 ppm could be reasonably assigned to the expected product 14, to the phosphirene–$W(CO)_5$ complex 13, and to the free triphenylphosphirene,[6] respectively. We think that the low efficiency of this trapping reaction may be ascribed to some steric congestion around the phosphinidene phosphorus in 8a due to the cis stereochemistry. Besides, the electrophilicity of 8a is probably reduced by comparison with the corresponding phosphinidene–$W(CO)_5$ complex. Anyhow, it clearly appears that the versatility of 8 as a synthetic tool is less broad than for classical phosphinidene–$W(CO)_5$ complexes. Nevertheless, compounds such as 9–12 would be practically impossible to obtain via conventional routes[7] owing to the instability of the corresponding free phosphorus ligands and to the presence of a P–H bond. The novelty of these new complexes prompted us to investigate the alkylation of their P–H bond as a preliminary evaluation of their synthetic potential. The attempts were made with 9. Conventional metalation of 9 with *n*-BuLi in THF at low temperatures completely destroyed the product. However, using a mild phase-transfer technique, it proved possible to methylate the P–H bond (eq 10).



Experimental Section

All reactions were carried out under argon. Solvents and silica gel (70–230 mesh Merck) were used after being degassed with argon. ^{31}P NMR spectra were recorded on a Bruker WP 80 spectrometer at 32.43 MHz and ^{13}C and ^{1}H NMR spectra on a Bruker WP 200 spectrometer. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4; ^{1}H and ^{13}C chemical shifts are internally referenced to Me_4Si and are positive for downfield shifts in all cases. IR spectra were recorded on a Perkin-Elmer 297 spectrometer and mass spectra on a Shimadzu GCMS-QP1000 spectrometer (EI, 70 eV, ^{184}W).

Preparation of *cis*-(Phenylethoxycarbene)(1-phenyl-3,4-dimethylphosphole)tetracarbonyltungsten (5a). To a solution of 20 g (39 mmol) of **3** in 70 mL of THF cooled at −78 °C was added 26.8 mL (42.9 mmol) of phenyllithium. After 10 min, the formation of the intermediate lithium acylate salt **4a** was monitored by ^{31}P NMR [δ(^{31}P) 18.6, $^{1}J_{PW}$ = 205 Hz]. The solvent was vacuum distilled and the residue dissolved in 50 mL of CH_2Cl_2. Then, 8.15 g (42.9 mmol) of $[Et_3O][BF_4]$ was added in this solution at −20 °C. The mixture was warmed slowly to 25 °C. After evaporation, the residue was chromatographed on silica gel with hexane/CH_2Cl_2 (3:1). Compound **5a** was recovered in 91% yield as a red-orange solid: mp 100 °C; ^{1}H NMR ($CDCl_3$) δ 1.5 (t, 3 H, CH_3), 2.1 (s, 6 H, CH_3), 4.7 (q, 2 H, OCH_2), 6.3 (d, $^{2}J_{HP}$ = 36 Hz, 2 H, CHP), 7.1–7.5 (m, 10 H, Ph); ^{31}P NMR (CH_2Cl_2) δ 13.2 ($^{1}J_{PW}$ = 210 Hz); ^{13}C NMR ($CDCl_3$) δ 15 (s, CH_3), 17.1 (d, $^{3}J_{CP}$ = 10 Hz, $\mathit{C}H_3C$:), 78.1 (s, OCH_2), 125.3–136.1 (Ph), 149.8 (d, $^{2}J_{CP}$ = 10 Hz, :$\mathit{C}CH_3$), 157.3 (s, C_1(Ph)), 201.8 (d, $^{2}J_{CP}$ = 5.5 Hz, CO cis api), 205.8 (d, $^{2}J_{CP}$ = 18.6 Hz, CO cis equ), 210.6 (d, $^{2}J_{CP}$ = 5.5 Hz, CO trans), 319.9 (d, $^{2}J_{CP}$ = nondetected, W=C); IR (pentane) ν(CO) 2015 (s), 1930 (vs), 1905 (vs) cm^{-1}; mass spectrum (200 °C), *m/e* (relative intensity) 618 (M, 40), 590 (M − CO, 11), 562 (M − 2CO, 17), 506 (M − 4CO, 23), 462 (M − 4CO − OEt, 100). Anal. Calcd for $C_{25}H_{23}PO_5W$: C, 48.56; H, 3.75. Found: C, 48.67; H, 3.60.

***cis*-(Butylethoxycarbene)(1-phenyl-3,4-dimethylphosphole)tetracarbonyltungsten (5b).** The same procedure as for **5a** was used with butyllithium [^{31}P NMR of **4b**: δ 19.1 ($^{1}J_{P-W}$ = 205 Hz)]: yield from 5.12 g (10 mmol) of **3**, 4.9 g (81%); red oil; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, CH_3), 1.3 (m, 4 H, CH_2CH_2), 1.4 (t, CH_3), 2.1 (s, 6 H, CH_3), 2.9 (t, =CH_2), 4.6 (q, OCH_2), 6.4 (d, $^{2}J_{HP}$ = 36 Hz, CHP), 7.2–7.6 (m, Ph); ^{31}P NMR (CH_2Cl_2) δ 14.3 ($^{1}J_{PW}$ = 210 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9 (s, CH_3), 14.7 (s, CH_3), 17.1 (d, $^{3}J_{CP}$ = 10.5 Hz, CH_3), 22.4 (s, CH_2), 28.9 (s, CH_2), 64.18 (s, :$\mathit{C}CH_2$), 78.6 (s, OCH_2), 128.4–132.5 (Ph + PC:), 149.65 (d, $^{2}J_{CP}$ = 8.5 Hz, :$\mathit{C}CH_3$), 202.2 (d, $^{2}J_{CP}$ = 8 Hz, CO cis api), 205.9 (d, $^{2}J_{CP}$ = 19.1 Hz, CO cis equ), 210 (d, $^{2}J_{CP}$ = 6 Hz, CO trans), 328.5 (d, $^{2}J_{CP}$ = nondetected, W=C); IR (CH_2Cl_2) ν(CO) 2000 (s), 1960 (vs), 1935 (vs), 1885 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 598 (M, 6). Anal. Calcd for $C_{23}H_{27}PO_5W$: C, 46.14; H, 4.53. Found: C, 46.39; H, 4.27.

***cis*-(Phenylethoxycarbene)[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]tetracarbonyltungsten (6a).** Compound **5a** (10 g, 16.2 mmol) and dimethyl acetylenedicarboxylate (20 mL, 162 mmol) were heated at 40 °C for 40 h. The mixture was chromatographed on silica gel with hexane/CH_2Cl_2 (1:5). Compound **6a** was recovered as a red solid in 70% yield: mp 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 1.4 (s, CH_3), 1.88 (d, $^{4}J_{HP}$ = 1.4 Hz, 6 H, CH_3), 3.61 (s, 6 H, OCH_3), 3.74 (d, $^{2}J_{HP}$ = 2.1 Hz, 2 H, CHP), 4.37 (q, OCH_2), 7.0–7.15 (m, 10 H, Ph); ^{31}P NMR (CH_2Cl_2) δ 215.7 ($^{1}J_{PW}$ = 239.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.75 (s, CH_3), 15.86 (s, CH_3), 52.1 (s, OCH_3), 59.9 (d, $^{1}J_{CP}$ = 18.4 Hz, CP), 78.2 (s, OCH_2), 124.8–129.6 (Ph), 137.6 (d, $^{2}J_{CP}$ = 17 Hz, MeC=CMe), 145.7 (d, $^{2}J_{CP}$ = 4 Hz, OOCC=CCOO), 157.4 (s, C_1(Ph)), 165.0 (s, COO), 201.7 (d, $^{2}J_{CP}$ = 5.45 Hz, CO cis api), 205.1 (d, $^{2}J_{CP}$ = 26.5 Hz, CO cis equ), 210.3 (d, $^{2}J_{CP}$ = 7.5 Hz, CO trans), 320.4 (d, $^{2}J_{CP}$ = 5.5 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2010 (s), 1935 (vs), 1900 (vs) cm^{-1}; mass spectrum (200 °C), *m/e* (relative intensity) 760 (M, 2), 648 (M − 4CO, 2), 538 (PhPW$(CO)_4$CPh(OEt), 5), 510 (538 − CO, 15), 482 (538 − 2CO, 9), 222 (M − PhPW$(CO)_4$CPh(OEt), 100). Anal. Calcd for $C_{31}H_{29}PO_9W$: C, 48.96; H, 3.84. Found: C, 48.93; H, 3.57.

***cis*-(Butylethoxycarbene)[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]tetracarbonyltungsten (6b).** Compound **6b** was prepared by the same method starting with 3 g (5 mmol) of **5b**. It was isolated as a red oil (1.48 g): ^{1}H NMR ($CDCl_3$) δ 0.8 (t, CH_3), 1.3 (m, 4 H, CH_2CH_2), 1.4 (t, CH_3), 2.0 (s, 6 H, :CMe), 2.9 (t, :CCh_2), 3.6 (s, 6 H, CO_2CH_3), 3.9 (d, 2 H, $^{2}J_{HP}$ = 2.1 Hz, PCH), 4.35 (q, OCH_2), 7.0–7.5 (Ph); ^{31}P NMR (CH_2Cl_2) δ 218.4 ($^{1}J_{PW}$ = 239.2 Hz); IR (CH_2Cl_2) ν(CO) 2020 (s), 1935 (vs), 1900 (vs) cm^{-1}; mass spectrum (200 °C), *m/e* (relative intensity) 740 (M, 4), 712 (M − CO, 2), 684 (M − 2CO, 2), 656 (M − 3CO, 5), 628 (M − 4CO, 5), 222 (M − PhP$(CO)_4$W=CBuOEt, 100).

(1,2,3-Triphenyl-3-ethoxy-1,2-diphosphirane)decacarbonylditungsten (7). Compound **6a** (0.5 g, 0.66 mmol) in toluene (5 mL) and CuCl (in catalytic amount) were heated at 45 °C for 1 h. After evaporation, the residue was chromatographed on silica gel with hexane. Compound **7** (25 mg) was recovered in 7.6% yield: mp 150 °C; ^{1}H NMR ($CDCl_3$) δ 0.6 (t, CH_3), 2.7 (m, 1 H, OCH_2), 3.4 (m, 1 H, OCH_2), 7.0–7.9 (m, 15 H, Ph); ^{31}P NMR (CH_2Cl_2) δ 111.6–122.5 ($^{1}J_{PP}$ = 122.1 Hz); IR (CH_2Cl_2) ν(CO) 2065 (s), 1950 (vs) cm^{-1}; mass spectrum (200 °C, *m/e* (relative intensity) 566 (M − PhPW$(CO)_5$, 2), 350 (M − 2W$(CO)_5$, 100).

***cis*-(Phenylethoxycarbene)(*O*-methyl phenylphosphinite)tetracarbonyltungsten (9).** Compound **6a** (1 g, 1.31 mmol) in MeOH (10 mL) with CuCl (in catalytic amount) was stirred at room temperature for 1 h. After evaporation, the

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[6] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 45.

[7] Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

residue was chromatographed on silica gel with hexane/CH_2Cl_2 (2:1). Compound **9** (0.49 g) was recovered as a red oil in 65% yield: ^{1}H NMR ($CDCl_3$) δ 1.5 (t, CH_3), 3.4 (d, $^{3}J_{HP}$ = 12.2 Hz, OCH_3), 4.7 (q, OCH_2), 6.9–7.6 (m, Ph), 7.58 (d, $^{1}J_{HP}$ = 337 Hz, PH); ^{31}P NMR (CH_2Cl_2) δ 113.3 ($^{1}J_{PW}$ = 278.3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.9 (CH_3), 59.6 (d, $^{2}J_{CP}$ = 14.6 Hz, OCH_3), 78.5 (OCH_2), 124.9–135.9 (Ph), 157.1 (s, C_1(Ph)), 201.4 (d, $^{2}J_{CP}$ = 7.7 Hz, CO cis api), 206.3 (d, $^{2}J_{CP}$ = 27.1 Hz, CO cis equ), 210 (d, $^{2}J_{CP}$ = 11.8 Hz, CO trans), 321.3 (d, $^{2}J_{CP}$ = 6 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2015 (s), 1935 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 570 (M, 25), 542 (M – CO, 23), 514 (M – 2CO, 23), 486 (M – 3CO, 53), 458 (M – 4CO, 15).

***cis*-(Phenylethoxycarbene)(*N*-phenylphenylphosphinous amide)tetracarbonyltungsten (10a).** Complex **6a** (3 g, 3.9 mmol) and aniline (1 mL, 12 mmol) were heated in toluene (10 mL) at 110 °C for 5 min. After evaporation, the residue was chromatographed on silica gel with pentane/CH_2Cl_2 (4:1). Compound **10a** was recovered as a red oil in 73% yield: ^{1}H NMR ($CDCl_3$) δ 1.5 (t, CH_3), 4.33 (m, NH), 4.63 (q, OCH_2), 6.43–7.56 (Ph), 7.35 (q, $^{1}J_{HP}$ = 356 Hz, $^{3}J_{HH}$ = 4.9 Hz, PH); ^{31}P NMR (CH_2Cl_2) δ 19 ($^{1}H_{PW}$ = 251.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.9 (CH_3), 78.4 (OCH_2), 116.3–130.1 (m, Ph), 135.7 (d, $^{1}J_{CP}$ = 48.3 Hz, PC), 143.9 (d, $^{2}H_{CP}$ = 11 Hz, NC), 157.0 (s, C_1(Ph)), 201.4 (d, $^{2}J_{CP}$ = 11 Hz, CO cis api), 205.9 (d, $^{2}J_{CP}$ = 24.5 Hz, CO cis equ), 210.5 (d, $^{2}J_{CP}$ = 6.4 Hz, CO trans), 321.3 (d, $^{2}J_{CP}$ = 5.8 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2015 (s), 1935 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 631 (M, 36), 603 (M – CO, 17), 575 (M – 2CO, 34), 547 (M – 3CO, 23), 519 (M – 4CO, 9). Anal. Calcd for $C_{25}H_{22}NO_5PW$: C, 47.56; H, 3.51. Found: C, 46.93; H, 3.55.

***cis*-(Butylethoxycarbene)(*N*-phenylphenylphosphinous amide)tetracarbonyltungsten (10b).** The same procedure as for **10a** was used: yield from 1 g (1.35 mmol) of **6b**, 0.41 g (49.7%); red oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (CH_3), 1.2–1.5 (m, 4 H, CH_2CH_2), 1.45 (CH_3), 3 (2 H, =CCH_2), 4.4–4.6 (m, 3 H, OCH_2, NH), 6.7–7.5 (Ph), 7.5 (q, $^{1}J_{HP}$ = 346.7 Hz, $^{3}J_{HH}$ = 5 Hz, 1 H, PH); ^{31}P NMR (CH_2Cl_2) δ 19.7 ($^{1}J_{PW}$ = 253.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 14.7 (CH_3), 22.6 (CH_2), 29.0 (CH_2), 64.3 (=CCH_2), 79 (OCH_2), 116.4–130.6 (Ph), 136.2 (d, $^{1}J_{CP}$ = 46.3 Hz, PC), 144.1 (d, $^{2}J_{CP}$ = 9.6 Hz, NC), 201.9 (d, $^{2}J_{CP}$ = 8 Hz, CO cis api), 205.9 (d, $^{2}J_{CP}$ = 24.4 Hz, CO cis equ), 209.9 (d, $^{2}J_{CP}$ = 6 Hz, CO trans), 334.8 (d, $^{2}J_{CP}$ = 6 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2020 (s), 1935 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 610 (M – 1, 7), 421 (M – C(OEt)Bu + 1, 100).

***cis*-[Phenyl(benzylamino)carbene](*O*-ethyl phenylphosphinite)]tetracarbonyltungsten (11).** A mixture of compound **6a** (0.2 g, 0.26 mmol), benzylamine (86 mg, 0.79 mmol), and toluene (5 mL) was heated at 40 °C for 2 h. After evaporation, the residue was chromatographed on silica gel with hexane/CH_2Cl_2 (2:1). Compound **11** was recovered as a yellow oil in 90% yield: ^{1}H NMR ($CDCl_3$) δ 0.9 (CH_3), 3.55 (q, OCH_2), 4.2 (NCH_2), 6.6–7.6 (Ph), 7.9 (d, $^{1}J_{HP}$ = 335.2 Hz, PH), 9.7 (NH); ^{31}P NMR (CH_2Cl_2) δ 103.7 ($^{1}J_{PW}$ 273.8 Hz); ^{13}C NMR ($CDCl_3$) δ 15.8 (CH_3), 54.1 (NCH_2), 68.5 (d, $^{2}J_{CP}$ = 14.6 Hz, OCH_2), 119.9–136.7 (Ph), 150.8 (C_1(Ph)), 202.6 (d, $^{2}J_{CP}$ = 7 Hz, CO cis api), 203 (d, $^{2}J_{CP}$ = 9 Hz, CO cis api), 208 (d, $^{2}J_{CP}$ = 33.2 Hz, CO cis equ), 209.7 (s, CO trans), 262 (d, $^{2}J_{CP}$ = 9 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2005 (s), 1920 (vs), 1890 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 645 (M, 21), 617 (M – CO, 19), 589 (M – 2CO, 8), 561 (M – 3CO, 27), 533 (M – 4CO, 6), 435 (M = HPPh(OEt) – 2CO, 100). Anal. Calcd for $C_{26}H_{24}NO_5PW$: C, 48.39; H, 3.75. Found: C, 48.56; H, 4.00.

***cis*-[Phenyl(*n*-butylamino)carbene](*O*-ethyl phenylphosphinite)tetracarbonyltungsten (12).** A mixture of compound **6a** (1 g, 1.31 mmol), butylamine (0.4 mL, 3.9 mmol), and toluene (10 mL) was stirred at room temperature for 15 min. After evaporation, the residue was chromatographed with hexane/AcOEt (5:1). Compound **12** was recovered as a yellow oil in 76% yield: ^{1}H NMR ($CDCl_3$) δ 0.9 (CH_3), 1.25 (m, 5 H, CH_3, CH_2), 1.5 (m, 2 H, CH_2), 3.1 (q, OCH_2), 3.7 (m, 2 H, NCH_2), 6.7–7.5 (Ph), 7.9 (d, $^{1}J_{HP}$ = 332 Hz, 1 H, PH); ^{31}P NMR (CH_2Cl_2) δ 104.8 ($^{1}J_{PW}$ = 273.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 16.5 (CH_3), 19.7 (CH_2), 31.5 (CH_2), 49.9 (CH_2), 68.5 (d, $^{2}J_{CP}$ = 13 Hz, OCH_2), 120–130.7 (Ph), 136.7 (d, $^{1}J_{CP}$ = 36.7 Hz, PC), 151 (C_1(Ph)), 202.7 (d, $^{2}J_{CP}$ = 6.5 Hz, CO cis api), 203.1 (d, $^{2}J_{CP}$ = 9.6 Hz, CO cis api), 208.1 (d, $^{2}J_{CP}$ = 33.2 Hz, CO cis equ), 209.6 (s, CO trans), 261.9 (d, $^{2}J_{CP}$ = 9.6 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2010 (s), 1920 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 611 (M, 40), 583 (M – CO, 36), 555 (M = 2CO, 36), 527 (M – 3CO, 11), 499 (M – 4CO, 53). Anal. Calcd for $C_{23}H_{26}NO_5PW$: C, 45.19; H, 4.29. Found: C, 45.18; H, 4.18.

***cis*-(Phenylethoxycarbene)(1,2,3-triphenylphosphirene)tetracarbonyltungsten (14).** The same procedure as for **5a** and **5b** was used [^{31}P NMR of the lithium acylate salt: δ –140.6 ($^{1}J_{PW}$ = 258.8 Hz)]: yield from 3.4 g (5.57 mmol) of **13**, 3.3 g (83%); red solid; mp 102 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (CH_3), 4.74 (OCH_2), 7.18–7.81 (Ph); ^{31}P NMR (CH_2Cl_2) δ –149.15 ($^{1}J_{PW}$ = 263.67 Hz); ^{13}C NMR ($CDCl_3$) δ 14.75 (CH_3), 78.5 (OCH_2), 125.4–138.6 (Ph), 157.2 (C_1(Ph)), 201.7 (d, $^{2}J_{CP}$ = 8.5 Hz, CO cis api), 204.6 (d, $^{2}J_{CP}$ = 31.2 Hz, CO cis equ), 210.6 (d, $^{2}J_{CP}$ = 7 Hz, CO trans), 320.2 (d, $^{2}J_{CP}$ = 8 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2005 (s), 1920 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 716 (M, 5), 688 (M – CO, 3), 660 (M – 2CO, 5), 632 (M – 3CO, 11), 286 (M – $(CO)_4W$=CPh(OEt), 100). Anal. Calcd for $C_{33}H_{25}PO_5W$: C, 55.32; H, 3.51. Found: C, 54.85; H, 3.44.

***cis*-(Phenylethoxycarbene)(*O*-methyl methylphenylphosphinite)tetracarbonyltungsten (15).** Complex **9** (0.45 g, 0.8 mmol), $[Bu_4N][HSO_4]$ (0.27 g, 0.8 mmol), NaOH (31 mg, 0.8 mmol), and MeI (2 mL) were heated at 30 °C for 30 min in a solution (6 mL) of H_2O/CH_2Cl_2 (1:1). After extraction and evaporation, the residue was chromatographed on silica gel with hexane/CH_2Cl_2 (4:1). Compound **15** was recovered as a red oil in 38% yield: ^{1}H NMR ($CDCl_3$) δ 1.5 (CH_3), 2 (d, $^{2}J_{HP}$ = 5 Hz, 3 H, PCH_3), 3.37 (d, $^{2}J_{HP}$ = 12.4 Hz, 3 H, OMe), 4.6 (OCH_2), 7.2–7.4 (Ph); ^{31}P NMR (CH_2Cl_2) δ 118 ($^{1}J_{PW}$ = 312.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.0 (CH_3), 22.4 (d, $^{1}J_{CP}$ = 23.6 Hz, PCH_3), 53.7 (d, $^{2}J_{CP}$ = 6.6 Hz, OCH_2), 78.15 (OCH_2), 124.9–131.2 (Ph), 140.3 (d, $^{1}J_{CP}$ = 36.2 Hz, PC), 157.43 (C_1(Ph)), 202.3 (d, $^{2}J_{CP}$ = 8 Hz, CO cis api), 206.3 (d, $^{2}J_{CP}$ = 25 Hz, CO cis equ), 211.11 (d, $^{2}J_{CP}$ = 8 Hz, CO trans), 320.5 (d, $^{2}J_{CP}$ = 8.2 Hz, W=C); IR (CH_2Cl_2) ν(CO) 2005 (s), 1920 (vs), 1900 (vs) cm^{-1}; mass spectrum (150 °C), *m/e* (relative intensity) 584 (M, 6), 556 (M – CO, 11), 528 (M – 2CO, 2), 500 (M – 3CO, 19), 472 (M – 4CO, 11).

Registry No. **3**, 74363-95-4; **4a**, 113860-33-6; **4b**, 113860-32-5; **5a**, 113892-45-8; **5b**, 113892-44-7; **6a**, 113860-34-7; **6b**, 113860-35-8; **7**, 113892-46-9; **9**, 113860-36-9; **10a**, 113860-37-0; **10b**, 113860-42-7; **11**, 113860-38-1; **12**, 113860-39-2; **13**, 82265-68-7; **14**, 113860-40-5; **15**, 113860-41-6; *cis*-benzoyl(1,2,3-triphenylphosaphirene)tetracarbonyltungsten, 113860-43-8.