Reaction of Terminal Phosphinidene Complexes with Enamines. A Method for Inserting a Phosphinidene Unit into a Carbonyl-Activated C–H Bond

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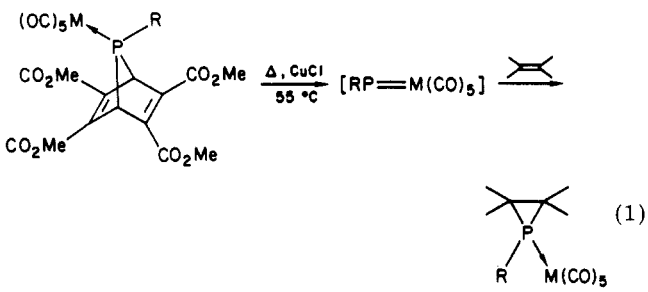
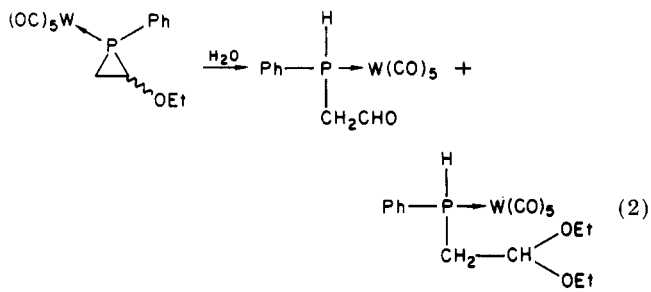
The reactions of a phosphanorbornadienic precursor for (phenylphosphinidene)pentacarbonyltungsten with enamines at 115–120 °C give three types of products according to the choice of the enamine. With 1-morpholinoisobutene, the expected phosphirane is obtained and can be hydrolyzed by hot water to give [α-(phenylphosphino)isobutyraldehyde]pentacarbonyltungsten. With a series of morpholinoalkenes derived from cyclohexanone, cyclopentanone, paramethylacetophenone, and isovaleraldehyde, the transient phosphirane cannot be observed and the final product results from an insertion of the (phenylphosphinidene)pentacarbonyltungsten unit into one of the carbon–hydrogen bonds adjacent to the carbonyl group of the starting ketone or aldehyde. In one particular case, the intermediate phosphirane rearranges to give an open-chain enamine with a (phenylphosphino)pentacarbonyltungsten substituent. These various observations can be rationalized if we assume that the 1:1 phenylphosphinidene–enamine adduct is not a classical phosphirane but has a partly zwitterionic, open-chain structure.

In a preceding paper[1] we demonstrated that terminal phosphinidene complexes, $RP{=}M(CO)_5$ (M = Cr, W), when generated by CuCl-catalyzed decomposition of the appropriate (7-phosphanorbornadiene)$M(CO)_5$ complexes, were able to react with olefins to give the corresponding phosphiranes (eq 1). On the other hand, we noted that



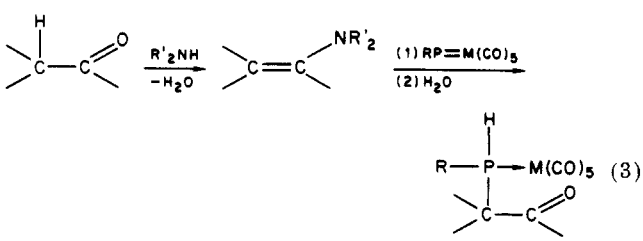
(1)

a 2-ethoxy-substituted phosphirane was readily hydrolyzed at room temperature with cleavage of the P–C(OEt) bond (eq 2). On the basis of these two observations, we thought



(2)

that it was perhaps possible to devise a general, two-step method for inserting a phosphinidene unit into a carbonyl-activated carbon–hydrogen bond on the basis of eq 3.

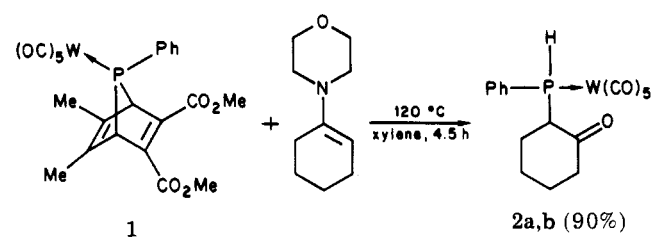


(3)

The first step involves the classical synthesis of enamines[2] from enolizable carbonyl compounds. The second step supposes the successful synthesis of a 2-amino-substituted phosphirane followed by hydrolysis of the $P–C(NR'_2)$ bond. We report hereafter on the work that we have done in order to check the possibility of this scheme.

Results and Discussion

All our experiments were performed with the 7-phosphanorbornadiene complex **1**. We immediately observed that the use of CuCl as a catalyst for the reaction of **1** with enamines was not effective. Very probably, CuCl gives complexes with the nitrogen lone pair of enamines[3] and becomes unable to promote the decomposition of the phosphanorbornadiene ring. Thus, we decided to work at the lowest possible temperature at which the generation of $PhP{=}W(CO)_5$ has been observed previously without a catalyst, that is, 115–120 °C. Under these conditions, we observed a clean reaction with 1-morpholinocyclohexene that produced directly the expected carbonyl-substituted secondary phosphine complex **2** as a mixture of two isomers (eq 4). Even after careful removal of traces of water



1 2a,b (90%)

(4)

from the reaction medium by azeotropic distillation, we were unable to detect the postulated transient phosphiranes. Similar observations were made with two other ketenamines (eq 5 and 6). However, when working with aldenamines, the intermediacy of a phosphirane was demonstrated in one case (eq 7). The presence of the

(1) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(2) For a recent review on the synthesis and chemistry of enamines, see: Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975, 3363.

(3) Recently some (enamine)Cu^I complexes have been used for catalytic purposes, see: Panova, G. V.; Pekshueva, E. G.; Potapov, V. M.; Ashkinadze, L. D. *Zh. Obshch. Khim.* **1981**, *51*, 1209.

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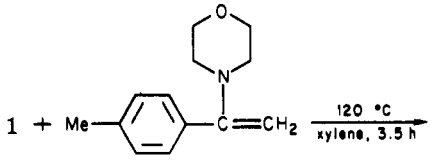
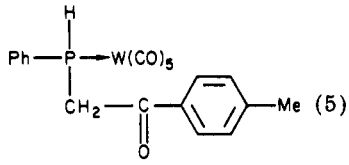
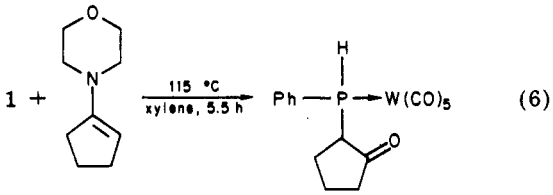
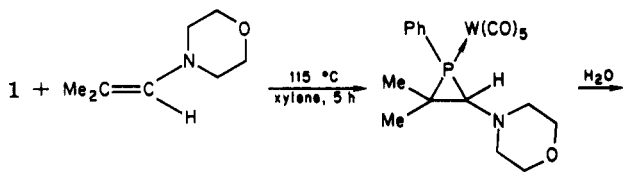


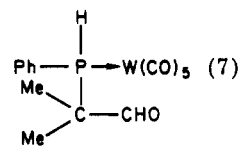


3 (67%)



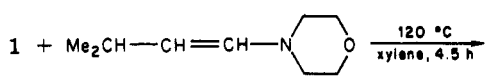
4a,b (75%)

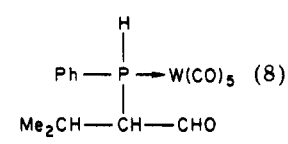




6 (overall yield 47%)

phosphirane intermediate **5** was clearly seen in the ^{31}P NMR spectrum of the crude reaction mixture. It gives a peak at −130 ppm (upfield from 85% H_3PO_4) in xylene [$^1J(^{31}P-^{183}W)$ = 256 Hz] with the characteristic shielding of three-membered carbon–phosphorus rings.[1] Upon addition of water to the reaction medium, the peak corresponding to **5** disappears upon heating and is replaced by a peak at −1.2 ppm that corresponds to **6**. Even with aldenamines, the observation of a transient phosphirane is critically dependent upon the substitution scheme. Indeed, in our only other attempt, we were unable to detect the three-membered ring (eq 8). The key factor governing

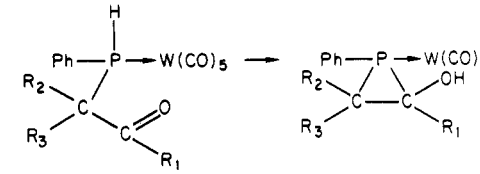




7 (42%)

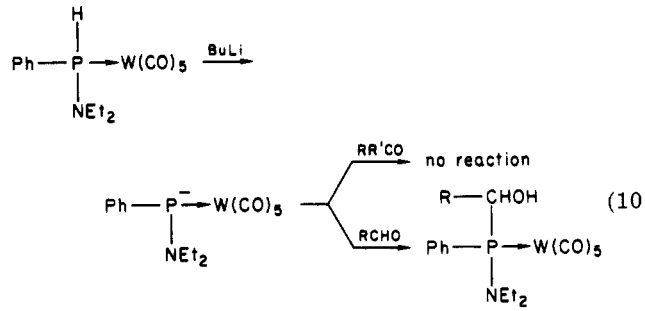
the observation of a transient phosphirane is obviously the stability and reactivity of the P–C(NR′$_2$) bond. We can gain some insight into the parameters that modulate this stability by envisaging the hypothetical reverse ring-closure reaction (eq 9).

In preceding work,[4] we noted that the anion derived from a complexed secondary phosphinamide reacted with



(9)

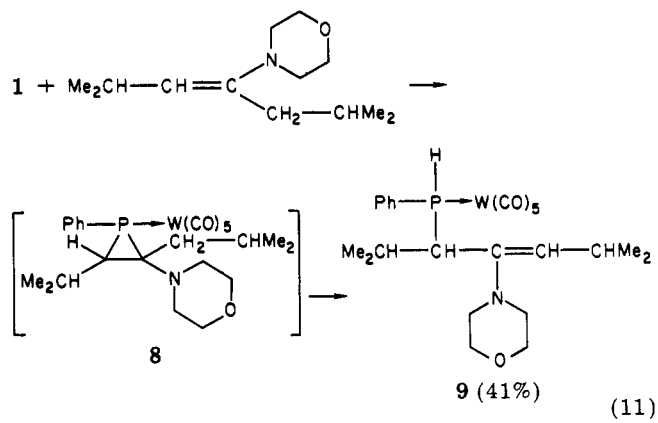
aldehydes but did not react with ketones (eq 10). The



(10)

failure of the reaction with ketones was ascribed to some steric congestion within the coordination sphere of tungsten. A similar phenomenon can explain the labilization of the P–C(NR′$_2$) bond of the intermediate phosphiranes derived from ketenamines ($R_1 \neq H$).

Instead of reacting with adventitious water, the transient phosphirane can also rearrange to give a ring-opened enamine. This rearrangement was observed in one case (eq 11). The empirical formula of **9** was unambiguously es-



(11)

tablished by C, H, P, and W elemental analysis and mass spectroscopy (EI, 70 eV, ^{184}W): *m/e* 643 (M, 17), 615 (M − CO, 10), 559 (M − 3CO, 31), 211 (M − $PhPW(CO)_5$, 89), 210 (100). The ^{31}P NMR spectrum of **9** [$\delta(^{31}P)$ −8.8 ($^1J(^{31}P-^{183}W)$ = 227 Hz, ^1J(P–H) = 347 Hz)] precludes a cyclic formulation such as **8** and demonstrates the presence of a P–H bond. No keto group is seen either in the IR or in the ^{13}C NMR spectra of **9** The ^1H NMR spectrum shows one vinyl proton at 4.76 ppm (in C_6D_6) as a characteristic doublet of doublets: ^3J(H–H) = 9.5 Hz and ^4J(H–P) = 3.9 Hz.

The **8** → **9** rearrangement strongly suggests the intervention of an intermediate carbocation. On the basis of that idea, it becomes possible to rationalize the apparent discrepancies between the various observations reported here. Due to the steric congestion within the coordination sphere of tungsten and to the carbocation stabilizing ability of the amino substituent, the 1:1 terminal phosphinidene–enamine addition product would lie somewhere between a true phosphirane ring and a zwitterionic product (eq 12). Of course, the zwitterionic formulation would be favored when C^+ is fully substituted (i.e., in the case of ketenamines). When α-hydrogens are available, the carbocation would stabilize itself by expelling a proton. The

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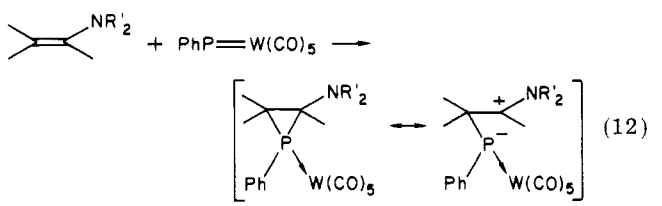
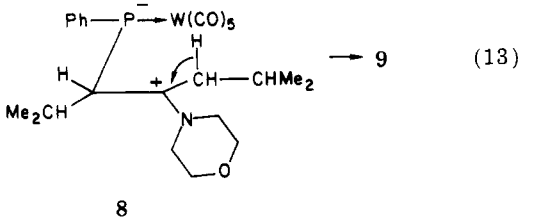
(5) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.
(6) Hünig, S.; Lücke, E.; Brenninger, W. *Org. Synth. 41*, 65.



rearrangement of **8** into **9** is easily explained in that way (eq 13).



8

In the case of **2**, **3**, and **4** a similar phenomenon could occur but the hydrolysis of the resulting enamine precludes its observation. On the contrary, in the case of **5**, the use of an aldenamine would favor the phosphirane formulation and the absence of α-hydrogens would forbid the rearrangement, thus allowing the observation of the three-membered ring.

Whatever the actual mechanism through which they are formed, ultimately we obtain the desired phosphinidene insertion products. Thus, starting from a monofunctional carbonyl compound, we create a new P–C bond and we obtain a bifunctional compound containing both a P—H and C=O reactive group. As far as we know, methods for building P—C bonds that at the same time create or preserve such useful functional groups as P—H or C=O are not numerous. In that sense, we think that the reaction of terminal phosphinidene complexes with enamines deserves some attention from the synthetic chemists.

Experimental Section

NMR spectra were recorded on a Bruker WP80 instrument at 80.13 MHz for ^{1}H, 32.435 MHz for ^{31}P, and 20.15 MHz for ^{13}C. Chemical shifts are reported in parts per million from internal Me_4Si for ^{1}H and ^{13}C and from external 85% H_3PO_4 for ^{31}P. Downfield shifts are noted positive in all cases. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Mass spectra were recorded on a VG 30 F spectrometer by Service Central d'Analyse du CNRS (Lyon). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**1**) is described in ref 5.

[2-(Phenylphosphino)cyclohexanone]pentacarbonyltungsten (2a,b). Complex **1** (2.1 g, 3.2 mmol) was heated at 120 °C for 4.5 h with 1-morpholinocyclohexene[6] (2.2 g, 13 mmol) in xylene (40 mL). The reaction mixture was then hydrolyzed at 70 °C. After evaporation, the residue was chromatographed with toluene (R_f ~0.4); yield 1.6 g (90%) of a mixture **2a** and **2b**. **2a** and **2b** were obtained in the pure state by crystallization from CH_2Cl_2–pentane.

2a: colorless solid; ^{31}P NMR (C_6D_6) δ −27.3 ($^1J(^{31}P-^{183}W)$ = 232 Hz); IR (decalin) ν(CO) 2072 (m), 1985 (m), 1948 (s), 1938 (vs) cm^{-1}, (KBr) ν(PH) 2350 cm^{-1}, ν(CO ketone) 1683 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.7–2.6 (m, 9 H), 5.49 (dd, ^1J(H–P) = 343.5 Hz, ^3J(H–H) = 4.9 Hz, 1 H, PH), 6.9–7.5 (m, 5 H, Ph); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 502 (M − CO, 55), 474 (M − 2CO, 13), 446 (M − 3CO, 29), 418 (M − 4CO, 17), 390 (M − 5CO, 89), 348 ($(CO)_2$WPPh, 90), 308 (100). Anal. Calcd for $C_{17}H_{15}O_6PW$: C, 38.52; H, 2.85; P, 5.84; W, 34.68. Found: C, 38.59; H, 2.81; P, 5.67; W, 34.68.

2b: ^{31}P NMR (C_6D_6) δ −27.1 ($^1J(^{31}P-^{183}W)$ = 232 Hz), IR (decalin) ν(CO) 2072 (m), 1985 (m), 1948 (s), 1937 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.8–2.6 (m, 9 H) 5.77 (dd, ^1J(H–P) = 350.8 Hz, ^3J(H–H) = 2.9 Hz, 1 H, PH), 6.9–7.5 (m, 5 H, Ph).

[α-(Phenylphosphino)-*p*-methylacetophenone]pentacarbonyltungsten (3). Complex **1** (1.5 g, 2.3 mmol) was heated at 120 °C for 3.5 h with 1-morpholino-*p*-methylstyrene (0.8 g, 3.9 mmol) in xylene (30 mL). After hydrolysis and evaporation of the solvent, the residue was chromatographed with hexane–toluene (70:30): R_f ~0.4; yield 0.9 g (67%) of colorless solid; mp 72 °C (CH_2Cl_2–pentane). 1-Morpholino-*p*-methylstyrene was obtained by refluxing under a water separator 1 equiv of ketone with 1.5 equiv of morpholine and 0.01 equiv of *p*-toluenesulfonic acid in benzene for 4 days. The enamine was used directly after removal of solvent and excess amine.[7]

3: ^{31}P NMR (C_6D_6) δ −39.3 ($^1J(^{183}W-^{31}P)$ = 234 Hz); IR (decalin) ν(CO) 2072 (m), 1985 (w), 1950 (sh), 1945 (vs) cm^{-1}, (KBr) ν(PH) 2345 cm^{-1}, ν(CO ketone) 1655 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.99 (s, 3 H, CH_3), 3.34 (pseudo t, ^2J(H–P) ≃ ^3J(H–H) = 6.1 Hz, 2 H, CH_2), 5.46 (dt, ^1J(H–P) = 354.5 Hz, 1 H, PH), 6.7–7.6 (m, 9 H, Ph); ^{13}C NMR (C_6D_6) δ 21.81 (s, CH_3), 39.74 (d, ^1J(C–P) = 24.4 Hz, CH_2), 145.10 (s, CO–*C*(phenyl)), 193.75 (d, ^2J(C–P) = 4.9 Hz, CO (ketone)), 196.96 (d, ^2J(C–P) = 7.3 Hz, cis CO), 199.66 (d, ^2J(C–P) = 23.19 Hz, trans CO); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 538 (M − CO, 36), 482 (M − 2CO, 100), 426 (M − 5CO, 96), 348 ($(CO)_2$WPPh, 45), 119 (CH_3PhCO, 54), 91 (C_7H_7, 73). Anal. Calcd for $C_{20}H_{15}O_6PW$: C, 42.43; H, 2.67; P, 5.47; W, 32.47. Found: C, 42.56; H, 2.51; P, 5.49; W, 32.18.

[2-(Phenylphosphino)cyclopentanone]pentacarbonyltungsten (4a,b). Complex **1** (3 g, 4.6 mmol) was heated at 115 °C for 5.5 h with 1-morpholinocyclopentene[8] (2.4 g, 16 mmol) in anhydrous xylene (50 mL). After hydrolysis and evaporation of the solvent, the residue was chromatographed with hexane–toluene (60:40): R_f ~0.4; yield 1.8 g (75%) of colorless solid. **4a** and **4b** were obtained in the pure state by crystallization from CH_2Cl_2–pentane.

4a: mp 137 °C; ^{31}P NMR (C_6D_6) δ −30.2 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1983 (m), 1953 (s), 1942 (vs) cm^{-1}, (KBr) ν(PH) 2340 cm^{-1}, ν(CO ketone) 1725 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.9–2.3 (m, 7 H), 6.05 (dd, ^1J(H–P) = 351.6 Hz, ^3J(H–H) = 2.4 Hz, 1 H, PH), 6.8–7.5 (m, 5 H, Ph); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity), 516 (M, 22), 488 (M − CO, 86), 460 (M − 2CO, 15), 432 (M − 3CO, 68), 404 (M − 4CO, 18), 376 (M − 5CO, 100), 348 ($(CO)_2$WPPh, 56). Anal. Calcd for $C_{16}H_{13}O_6PW$: C, 37.24; H, 2.54; W, 35.63. Found: C, 37.38; H, 2.58; W, 36.30.

4b: mp 144 °C; ^{31}P NMR (C_6D_6) δ −25.1 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1985 (m), 1953 (s), 1942 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.9–2.5 (m, 7 H), 5.85 (dd, ^1J(H–P) = 349.9 Hz, ^3J(H–H) = 3.2 Hz, 1 H, PH), 6.9–7.3 (m, 5 H, Ph).

[α-(Phenylphosphino)isobutyraldehyde]pentacarbonyltungsten (6). Complex **1** (3.6 g, 5.6 mmol) was heated at 115 °C for 5 h with 1-morpholinoisobutene[9] (3.3 g, 23 mmol) in anhydrous xylene (50 mL). The phosphirane complex **5** [^{31}P NMR δ −130.0 ($^1J(^{183}W-^{31}P)$ = 256 Hz)] was hydrolyzed with water at 80 °C. After evaporation, the residue was chromatographed with hexane–toluene (70:30): R_f ~0.5; yield 1.3 g (47%) of colorless solid; mp 62 °C (hexane); ^{31}P NMR (toluene) δ 0.7 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1985 (w), 1954 (s), 1945 (vs) cm^{-1} (KBr) ν(CH aldehyde) 2820, 2720 cm^{-1}, ν(PH) 2340 cm^{-1}, ν(CO aldehyde) 1700 cm^{-1}, ^{1}H NMR (C_6D_6) δ 0.88 (d, ^3J(H–P) = 16.4 Hz, 6 H, CH_3), 5.32 (d, ^1J(H–P) = 339.6 Hz, 1 H, PH), 6.8–7.2 (m, 5 H, Ph), 8.92 (d, ^3J(H–P) = 2.2 Hz, 1 H, CHO); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity), 504 (M, 25), 476 (M − CO, 53), 448 (M − 2CO, 13), 420 (M − 3CO, 31), 392 (M − 4CO, 12), 377 (M − 4CO − CH_3, 22), 364 (M − 5CO, 100). Anal. Calcd for $C_{15}H_{13}O_6PW$: C, 35.74; H, 2.60; P, 6.14; W, 36.47. Found: C, 35.69; H, 2.60; P, 6.11; W, 36.82.

[α-(Phenylphosphino)isovaleraldehyde]pentacarbonyltungsten (7a,b). Complex **1** (3 g, 4.6 mmol) was heated at 120 °C for 4.5 h with 1-morpholino-3-methyl-1-butene (3 g, 19 mmol) in anhydrous xylene (40 mL). The reaction mixture was then hydrolyzed at 80 °C. After evaporation, the residue was chro-

(7) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1961**, *85*, 207.
(8) Birkofer, L.; Barnikel, C. D. *Chem. Ber.* **1958**, *91*, 1996.
(9) Benzing, E. *Angew. Chem.* **1959**, *71*, 521.

matographed with hexane–toluene (70:30): $R_f \sim 0.5$; yield 1 g (42%) of a mixture **7a** and **7b**. **7a** and **7b** were obtained in the pure state by fractional crystallization from CH_2Cl_2–pentane. 1-Morpholino-3-methyl-1-butene was obtained by the same procedure as for 1-morpholinoisobutene.[9]

7a: ^{31}P NMR (C_6D_6) δ −33.4 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1985 (w), 1952 (sh), 1945 (vs) cm^{-1} (KBr) ν(PH) 2360 cm^{-1}, ν(CO aldehyde) 1710 cm^{-1}; ^1H NMR (C_6D_6) δ 0.72 (d, ^3J(H–H) 6.8 Hz, 3 H, CH_3), 0.74 (d, ^3J(H–H) = 6.8 Hz, 3 H, CH_3), 1.8–2.3 (m, 1 H, $CHMe_2$), 2.5–2.8 (m, 1 H, $CHCHO$), 5.70 (dd, ^1J(H–P) = 342.0 Hz, ^3J(H–H) = 7.8 Hz, 1 H, PH), 6.8–7.2 (m, 5 H, Ph), 9.17 (pseudo t, ^3J(H–P) $\simeq$ ^3J(H–H) = 3.7 Hz, 1 H, CHO), mass spectrum (EI, 70 eV, ^{184}W), m/e (relative intensity) 518 (M, 10), 490 (M − CO, 75), 462 (M − 2CO, 12), 434 (M − 3CO, 29), 406 (M − 4CO, 33), 378 (M − 5CO, 100). Anal. Calcd for $C_{16}H_{15}O_6PW$: C, 37.09; H, 2.92; P, 5.98; W, 35.48. Found: C, 37.32; H, 3.03; P, 6.01; W, 36.16.

7b: ^{31}P NMR (C_6D_6) δ −33.8 ($^1J(^{183}W-^{31}P)$ = 232 Hz); IR (decalin) ν(CO) 2070 (m), 1984 (w), 1950 (sh), 1945 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 0.5–0.8 (m, 6 H, CH_3), 1.6–2.1 (m, 1 H, $CHMe_2$), 2.5–2.8 (m, 1 H, $CHCHO$), 5.66 (dd, ^1J(H–P) = 346.2 Hz, ^2J(H–H) = 6.1 Hz, 1 H, PH), 6.8–7.3 (m, 5 H, Ph), 9.41 (dd, ^3J(H–P) = 4.9 Hz, ^3J(H–H) = 2.9 Hz, 1 H, CHO).

[4-Morpholino-5-(phenylphosphino)-1,6-dimethyl-3-heptene]pentacarbonyltungsten (9). Complex 1 (4.5 g, 6.9 mmol) was heated at 115 °C for 5 h with 4-morpholino-1,6-dimethyl-3-heptene (3.5 g, 15.6 mmol) in anhydrous xylene (50 mL). After hydrolysis and evaporation of the solvent, the residue was chromatographed with toluene ($R_f \sim 0.4$); yield 1.8 g (41%). The product thus obtained was a mixture of at least two isomers according to ^{31}P NMR: δ −7.2 and −13.8 (hexane). The major complex (δ −7.2) could be further purified by recrystallization in hexane. 4-Morpholino-1,6-dimethyl-3-heptene was synthesized by the same procedure as for 1-morpholino-*p*-methylstyrene.[7] Anal. Calcd for $C_{24}H_{30}NO_6PW$: C, 44.81; H, 4.70; P, 4.81; W, 28.58. Found: C, 44.80; H, 4.20; P. 4.64; W, 29.17.

Registry No. 1, 82265-64-3; **2a**, 91083-06-6; **2b**, 91176-75-9; **3**, 91083-07-7; **4a**, 91083-08-8; **4b**, 91176-76-0; **5**, 91110-39-3; **6**, 91083-09-9; **7a**, 91083-10-2; **7b**, 91176-77-1; **9**, 91110-38-2; 1-morpholinocyclohexene, 670-80-4; 1-morpholino-*p*-methylstyrene, 55949-65-0; 1-morpholinocyclopentene, 936-52-7; 1-morpholinoisobutene, 2403-55-6; 1-morpholino-3-methyl-1-butene, 53828-74-3; 4-morpholino-1,6-dimethyl-3-heptene, 78593-92-7.

Trapping of (Aryne)metallocene Complexes by Elemental Selenium. Crystal Structure of $(\eta^5$-*t*-$BuC_5H_4)_2ZrSe_2C_6H_4$-*o*

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Elemental selenium reacts with diarylmetallocenes $(\eta^5\text{-}RC_5H_4)_2M(C_6H_4R')_2$ (M = Zr, R = *t*-Bu, R′ = H and *p*-CH_3; M = Ti, R = R′ = H) in boiling heptane, leading to the corresponding phenylenediselenometallocenes $(\eta^5\text{-}RC_5H_4)_2MSe_2C_6H_4R'$-*o*. It is suggested that upon heating (aryne)metallocenes are generated in which the insertion of two selenium atoms occurs. The molecular structure of $(\eta^5$-*t*-$BuC_5H_4)_2ZrSe_2C_6H_4$-*o* is reported. The deep red crystals are monoclinic of space group $P2_1/n$ (a = 13.679 (3) Å, b = 22.649 (3) Å, c = 7.749 (3) Å, β = 103.06 (3)°, V = 2338.8 Å^3, Z = 4, F_{000} = 1128, D = 1611 Kg·m^{-3}). The central ring consists of one Zr atom, two Se atoms, and two aromatic carbon atoms. The Zr atom is 1.67 Å from the phenyl group plane. The dihedral angles between the two cyclopentadienyl rings and between the phenyl–Se–Se and Se–Zr planes are 53.8 and 56.1°, respectively. The distances from zirconium to cyclopentadienyl carbons lie within the range of 2.45–2.61 Å and show that the metal is displaced far from the ring centroids and the substituted carbon atoms.

Introduction

Metallic complexes containing chalcogenides in their framework are the subject of great attention due to their apparent implication in catalysis and biology and their potential application in organic synthesis as well as their interest in theoretical chemistry.[1-4] In a preceding paper[5] we reported the synthesis and the spectroscopic characterization of new selenium complexes of zirconium and hafnium, and we pointed out the insertion of elemental selenium into the M–CH_3 bond according to eq 1.

$$(\eta^5\text{-}RC_5H_4)_2M(CH_3)_2 + 2Se \xrightarrow{\text{boiling heptane}} \underset{\mathbf{1}}{(\eta^5\text{-}RC_5H_4)_2M(SeCH_3)_2} \quad (1)$$

M = Zr, Hf; R = H, *t*-Bu

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(5) Gautheron, B.; Tainturier, G.; Meunier, Ph. *J. Organomet. Chem.* **1981**, *209*, C49 and references therein.
(6) Surprisingly, when $Cp_2Zr(C_6H_4R)_2$ is allowed to react with Se under the same experimental conditions, an apparently polymeric insoluble red material is obtained while $Cp_2Ti(C_6H_5)_2$ gives the expected product.

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