construct a calibration curve. Additionally, in some experiments $^{14}CCl_4$ was added to the labeled samples as an internal calibration. Other ^{14}C analyses were calibrated by using similar techniques.

The filtrate from the above separation was also analyzed. The solvent and volatile halocarbons (CCl_4, C_2Cl_4, C_2Cl_6) were removed by vacuum distillation, and the resulting residue was checked for ^{14}C content. Also analyzed for labeled carbon was the tar from the precipitate above after being washed free of $FeCl_2$ with water. The resulting labeled carbon content was in agreement with the carbon content obtained from elemental analysis.

The $CpW(CO)_3Cl/CCl_4$ system was analyzed similarly although the carbon-containing tar was never isolated.

$CpW(CO)_2BrCl_2$. Irradiation ($\lambda > 400$ nm) of $CpW(CO)_3Cl$ (0.37 g, 1.0 mmol) in $CBrCl_3$ (6.0 mL) and acetone (6.0 mL) for 5 h resulted in disappearance of ca. 90% of the $CpW(CO)_3Cl$, as monitored by IR, and the production of an orange-yellow crystalline product. More product crystallized by keeping the reaction vessel at −20 °C for 12 h. The solution was filtered, and the resulting crystals (0.21 g) were washed with benzene and dried in vacuo. The product analyzed for $CpW(CO)_2BrCl_2$. Calcd for $C_7H_5BrCl_2W$: C, 18.45; H, 1.11; W, 40.34; Cl, 15.56; Br, 17.53; O, 7.02. Found: C, 18.18; H, 1.11; W, 39.95; Cl, 15.47; Br, 23.31; O, 1.99 (by difference). Repeated elemental analyses always gave variable amounts of Br but excellent C, H, W, and Cl values. The infrared spectrum of the product has bands at 2039 and 2089 cm^{-1} (acetone), a spectrum typical for $CpW(CO)_2X_3$-type complexes. Extinction coefficients (2039 (1450), 2089 cm^{-1} (980 M^{-1} cm^{-1})) calculated on the basis of 100% $CpW(CO)_2BrCl_2$ are also typical [$CpW(CO)_2Cl_3$ (acetone) 2044 (1400), 2094 cm^{-1} (900 M^{-1} cm^{-1})].

Reaction of $CpW(CO)_3Cl$ with Benzyl Chloride. Irradiation ($\lambda > 330$ nm) of $CpW(CO)_3Cl$ (0.6 g, 1.6 mmol) in $PhCH_2Cl$ (30 mL) under a CO atmosphere (the reaction was faster under Ar but yields were slightly lower) for approximately 20 h followed by filtration gave a dark blue solution, the infrared spectrum of which had bands at 2042 and 2092 cm^{-1}. The addition of 200 mL of petroleum ether formed a fluffy precipitate. Filtration followed by repeated washings with petroleum ether and then CCl_4 gave a dark blue solid (0.32 g) with bands in the infrared spectrum at 2030 and 2090 cm^{-1} (Nujol mull).

Acknowledgment. This work was supported by a University Exploratory Research Grant from the Procter and Gamble Co. We thank Professor T. J. Katz's research group for experimental assistance.

Registry No. $CpW(CO)_3Cl$, 12128-24-4; $CpW(CO)_2(PPh_3)Cl$, 12115-03-6; $CpW(CO)_2(THF)Cl$, 87937-33-5; $CpW(CO)_2Cl_3$, 12107-08-3; $[(MeCp)Mo(CO)_3]_2$, 33056-03-0; $Mn_2(CO)_{10}$, 10170-69-1; $(MeCp)Mo(CO)_3Cl$, 87937-34-6; $CpMo(CO)_3Cl$, 12128-23-3; $[CpW(CO)_3]_2$, 12091-65-5; $(MeCp)W(CO)_2Cl_3$, 87937-35-7; $[(MeCp)W(CO)_3]_2$, 68111-11-5; $CpW(CO)_2Br_3$, 12107-03-8; $CpW(CO)_2BrCl_2$, 87937-36-8; $CpW(CO)_2(PhCH_2)Cl_2$, 87937-37-9; $CpW(CO)_2(AsPh_3)Cl$, 12114-95-3; $Fe(CO)_5$, 13463-40-6; $Mn(CO)_5Cl$, 14100-30-2; $FeCl_2$, 7758-94-3; $(MeCp)W(CO)_3Cl$, 87937-38-0; CCl_4, 56-23-5; Ph_2CCl_2, 2051-90-3; $PhCCl_3$, 98-07-7; Ph_3CCl, 76-83-5; $PhCH_2Cl$, 100-44-7; $CBrCl_3$, 75-62-7; $:CCl_2$, 1605-72-7.

The Carbene-like Behavior of Terminal Phosphinidene Complexes toward Olefins. A New Access to the Phosphirane Ring

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In the presence of copper(I) chloride, (7-R-7-phosphanorbornadiene)P–$M(CO)_5$ complexes (M = Cr, W) decompose around 55 °C to give the corresponding terminal phosphinidene complexes $RP{=}M(CO)_5$. These transient phosphinidene complexes react in situ with olefins to give phosphirane complexes. The stereochemistry of the starting olefin is retained in the phosphirane ring, thus suggesting a concerted process. The reaction with 1,3-dienes yields 2-vinylphosphirane complexes that rearrange around 100 °C to the corresponding phospholenes. On the contrary, the reaction with α,β-unsaturated ketones gives directly the 1,2-oxaphospholene complexes, but the formation of an intermediate 2-acylphosphirane cannot be excluded. With methyl methacrylate, the 2-(methoxycarbonyl)phosphirane is formed and is apparently stable. With ethyl vinyl ether, the 2-ethoxyphosphirane transiently obtained is so reactive that neutral water cleaves the P–C(OEt) bond of the ring to give a secondary α-phosphinoacetaldehyde that is stabilized as its P–$W(CO)_5$ complex. An excess of vinyl ether also reacts with the 2-ethoxyphosphirane to give a 2,4-diethoxyphospholane. In all its reactions, $PhP{=}W(CO)_5$ apparently behaves as a singlet electrophilic carbene.

Introduction

Numerous six-electron species including carbenes, silylenes, nitrenes, etc. are known to react easily with olefins to give three-membered rings. On the contrary, it has never been possible up to now to condense a phosphinidene, RP, or a phosphinidene derivative, RP=Y (Y = O, S, ...), with an olefin to form a phosphirane.[1]

Recently, we have described[2-4] a new system based on the 7-phosphanorbornadiene skeleton (e.g., **1**) which generates terminal phosphinidene complexes, R—P=$M(CO)_5$ (M = Cr, Mo, W), around 150 °C. The reactions of these complexes with conjugated dienes and acetylenes form P–C rings much more efficiently and selectively than the corresponding reactions of phosphinidenes (eq 1) (these phosphinidenes are generated by thermal depolymerization of cyclopolyphosphines[1]). Thus, it was very tempting for us to study the reaction of these phosphinidene complexes with olefins: indeed, a significant extension of the scope of phosphinidene chemistry seemed to be at hand.

Results and Discussion

Reaction of Terminal Phosphinidene Complexes with Nonfunctional Olefins. Our preliminary attempts to react complex **1** with monoolefins around 150 °C pro-

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(1) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 14, 523 (1975).

(2) A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 667 (1982).

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

(4) A. Marinetti and F. Mathey, *Organometallics*, 1, 1488 (1982).

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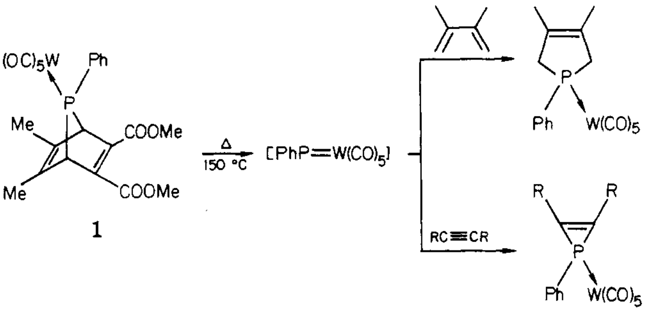
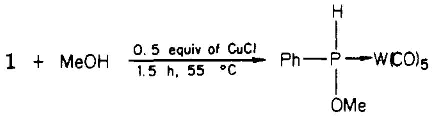


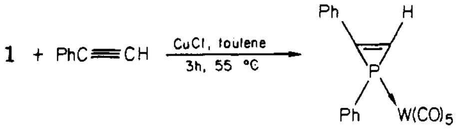
(1)

duced only very poor results; complicated mixtures of products were always obtained. Since the phosphirane ring is known to have low thermal stability, we suspected that one of the possible reasons for this failure was that the 7-phosphanorbornadiene generator was effective only at too high temperatures. Accordingly, we tried to catalyze the reaction by using heavy-metal derivatives with the assumption that the activation energy for generating PhP=W(CO)$_5$ from 1 would be lowered by heavy-metal π complexation of the double bonds of 1. We evaluated the catalytic effect by monitoring the reactions of 1 with methanol and phenylacetylene. Positive results were observed with Ag^{I}, Pd^{II}, and Cu^{I} but, for our purposes, Cu^{I} proved to be the best choice (eq 2 and 3). These new reaction conditions were much milder than the former ones (5–17 h at 150 °C) and allowed the synthesis of the new phosphirene 2, which had been difficult to obtain by using our former technique (only 21–46% yield).



$$1 + \mathrm{MeOH} \xrightarrow[\text{1.5 h, 55 °C}]{\text{0.5 equiv of CuCl}} \mathrm{Ph{-}\overset{H}{\underset{OMe}{P}}{\rightarrow}W(CO)_5} \quad (2)$$

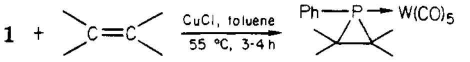
76%



(3)

75%

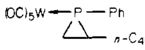
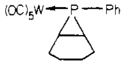
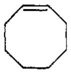
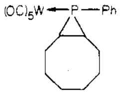
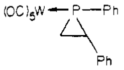
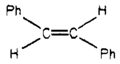
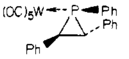
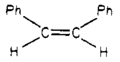
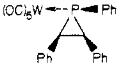
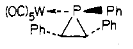
With this new technique in hand, we commenced a study of the reactions of 1 with monoolefins. This was an immediate success: in each case, the expected phosphirane was obtained in moderate to good yields (Table I) (eq 4).



(4)

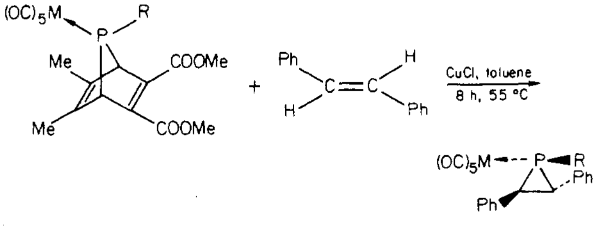
The reaction was generally performed with a threefold excess of olefin and 0.5 equiv of CuCl. The key data in demonstrating the formation of the phosphirane rings were the ^{31}P NMR chemical shifts given in Table I. The far upfield shifts that were observed are highly characteristic of three-membered rings containing tervalent phosphorus (see ref 5, p 211). Each time two isomers could be formed, they were indeed observed in the crude reaction mixture by ^{31}P NMR (see Table I). Pure isomers were obtained in the case of **5a**, **6a**, **7**, **8a**, and **8b**. The results obtained with *cis*- and *trans*-stilbene strongly suggest that the reaction is a concerted process with simultaneous formation of the two P–C bonds (no possible rotation around the former C=C double bond during the whole process). In the case of **8a** and **8b** (formed from *cis*-stilbene), the structural assignments are based upon the assumption that the well-known relationship between H–C–P lone-pair dihedral angles and ^{2}J(H–P) coupling constants in phosphines (maximum coupling for a dihedral angle close to 0°, see ref 5, p 325) holds true for (phosphine)W(CO)$_5$ complexes when the H–C–P–W angle is used. Whereas this is a questionable assumption with, as far as we know, no support from the literature, it suggests that the major isomer **8a** has, quite logically, the less hindered all-cis stereochemistry for the three phenyl substituents. Besides, even if this assignment is wrong, it does not question our conclusions on the possible concertedness of the condensation process.

Table I. Reactions of 1 with Olefins

olefin	products^a	overall yields,^{b} %	$\delta(^{31}P)$ (toluene) [$^{1}J(^{31}P-^{183}W)$, Hz]
n-$C_4H_9CH{=}CH_2$	 **3a,b**	71	a, −166.7 [257]; b, −166.2
	 **4a,b**	51	a, −154.9 [259]; b, −169 [254]
	 **5a,b**	95	a, −170.7 [249]; b, −161.2 [256]
$PhCH{=}CH_2$	 **6a,b**	92	a, −156.1 [259]; b, −151
	 **7**	60	−120.8 [264]
	 **8a**	25	−127.5 [264] (C_6D_6)
	 **8b**		−143 [259] (C_6D_6)

^{a} a for the major isomer; b for the minor one. ^{b} After purification by chromatography.

This phosphinidenation reaction is by no means limited to the grafting of the PhP=W(CO)$_5$ moiety onto C=C double bonds. We have checked that it is also possible to graft MeP=W(CO)$_5$ and PhP=Cr(CO)$_5$ moieties although the reaction appears to be less efficient especially in the latter case (eq 5).



(5)

9, R = Me, M = W, 39%
10, R = Ph, M = Cr, 21%

Reaction of Terminal Phosphinidene Complexes with Polyolefins and Functional Olefins. It is well-known that carbenes react with conjugated dienes to give

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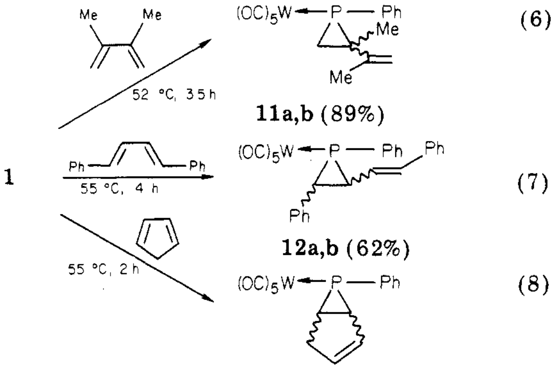
(5) L. D. Quin, "The Heterocyclic Chemistry of Phosphorus", Wiley-Interscience, New York, 1981.

vinylcyclopropanes through 1,2 cycloaddition.[6] Thus, after our initial success with monoolefins, we wondered immediately if the phospholenes obtained during the reactions of 1 with conjugated dienes around 150 °C (1,4 cycloaddition)[3] were not, in fact, secondary products produced through the thermal rearrangement of primary vinylphosphiranes. Indeed, the thermal conversion of vinylphosphiranes into phospholenes has been described in the literature very recently.[7] Thus, we decided to react 1 with 2,3-dimethylbutadiene, *trans,trans*-1,4-diphenylbutadiene, and cyclopentadiene around 55 °C in toluene with CuCl as the catalyst. The results confirmed our expectations since vinylphosphiranes were obtained in all cases (eq 6–8).

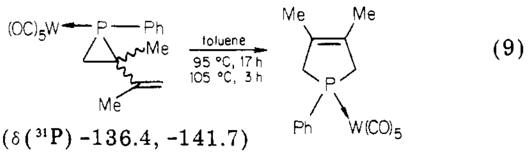


11a,b (89%)

12a,b (62%)

13a,b (66%)

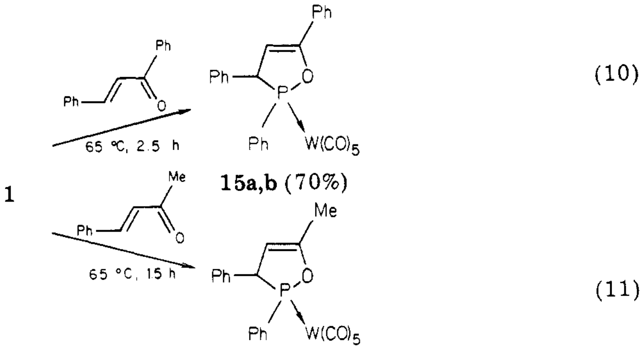
In each case, two isomeric phosphiranes were obtained, **a** designating the major isomer and **b** the minor one. We have been able to crystallize the major isomers **11a**, **12a**, and **13a** in the pure state. According to our results with *cis*- and *trans*-stilbene, only the phosphirane ring protons that are cis to the tungsten atom are significantly coupled with phosphorus (ca. 8 Hz). On this basis, the vinyl substituent of **12a** is cis to tungsten. In contrast, no straightforward conclusions can be drawn concerning the stereochemistry of **11a** and **13a**. When the mixture is heated in toluene around 100 °C, a slow conversion of the vinylphosphiranes **11a,b** into the corresponding phospholene **14** was observed (eq 9). Even though pure **14** was recovered in only 44% yield after chromatography, the conversion appeared to be almost quantitative when the reaction was monitored by ^{31}P NMR. Our initial hypothesis is thus fully supported by these experimental evidences.



11a,b ($\delta(^{31}P)$ -136.4, -141.7)

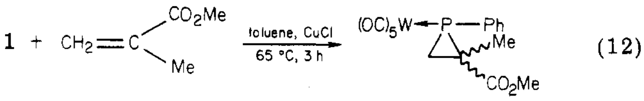
14 ($\delta(^{31}P)$-5.2)

The next step in our investigations dealt with the reactions of terminal phosphinidene complexes with α,β-unsaturated ketones. As usual, the reaction was performed in toluene with CuCl as the catalyst and, in each case, the 1,4-addition product was obtained (eq 10 and 11). Of course, we cannot exclude the initial formation of an acyl-substituted phosphirane followed by a very fast rearrangement into the corresponding 1,2-oxaphospholene: the formation of the very strong P–OC bond would be a powerful driving force for such a rearrangement. In fact, such a carbonyl-substituted phosphirane has been isolated in the reaction of 1 with methyl methacrylate (eq 12).



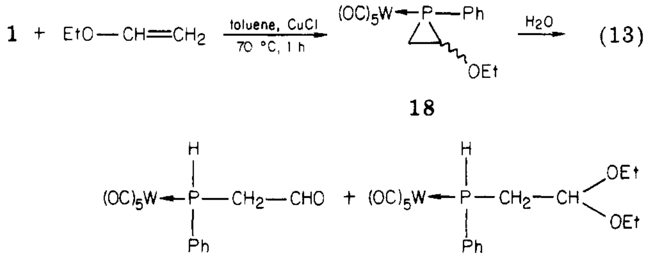
15a,b (70%)

16a,b (59%)



17a,b (40%)

Then, it was logical to try to extend this phosphinidenation reaction to an electron-rich olefin. The experiments were performed with ethyl vinyl ether. The expected phosphirane **18** was observed by ^{31}P NMR ($\delta(^{31}P)$ -168.3 in toluene) but was so reactive that we were unable to isolate it in the pure state. In fact, it reacted very rapidly with water to give the ring-opened products **19** and **20** (eq 13).



18

19 **20**

This ring-opening reaction is very similar to the hydrolysis of epoxides. It must be stressed that the cleavage of P–C bonds by reaction with neutral water at room temperature is a rather extraordinary reaction. From another standpoint, the stability of an aldehyde such as **19** once again illustrates the exceptional stabilizing power of the $W(CO)_5$ complexing group.[4] Only two very unstable tertiary α-phosphinoacetaldehydes have been described in the literature,[8,9] and no secondary α-phosphinoacetaldehyde is known. When an excess of vinyl ether is reacted with 1, the ethoxyphosphirane **18** was again transiently formed but the insertion of another molecule of vinyl ether into the phosphirane ring took place and the phospholane **21a** was finally obtained as the main product (eq 14). In the hydrolysis of **18**, the proton reacts with the phosphorus center, so that it is quite logical to find the positive end (+) of the olefin bonded to phosphorus in **21a**. Clearly, the reactivity of electron-rich phosphiranes deserves further investigations.

Conclusion

Finally, at this stage of our research work, we can conclude that terminal phosphinidene complexes behave as electrophilic singlet carbenes toward olefins: we observe faster reactions with electron-rich than with electron-poor

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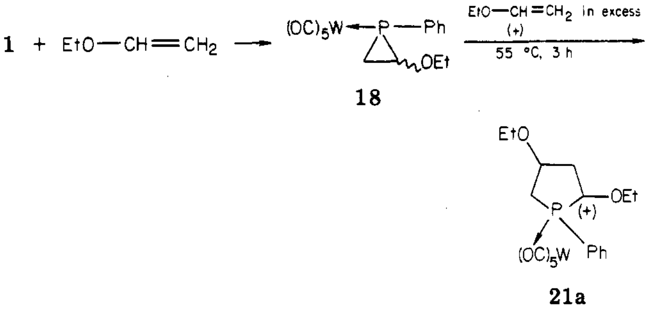
(6) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

(7) W. J. Richter, *Angew. Chem., Int. Ed. Engl.*, **21**, 292 (1982).

(8) M. Sokolov and K. Issleib, *Z. Chem.*, **17**, 365 (1977).

(9) F. Mathey and F. Mercier, *J. Organomet. Chem.*, **177**, 255 (1979).



(14)

olefins and we observe retention of the olefin stereochemistry in the phosphirane ring. With conjugated dienes, we note again a similarity between the behavior of terminal phosphinidene complexes and that of singlet carbenes since, in both cases, 1,2 cycloaddition is preferred. Of course, only a full theoretical analysis of these reactions could lend a definitive support to this comparison. From another standpoint, the broad demonstrated scope of this new olefin phosphinidenation reaction offers interesting synthetic opportunities that will be described in due course.

Experimental Section

NMR spectra were recorded on a Bruker WP 80 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 Nermag R10-10 spectrometer at 70 eV by Mr. Charré (SNPE). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën) under argon. Satisfactory elemental analyses have been difficult to obtain because all the complexes described hereafter are not stable over extended periods of time. Some analyses are given for the most stable crystalline products. The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten **1** is described in ref 4.

(*O*-Methyl phenylphosphinite)pentacarbonyltungsten. Complex **1** (1.5 g, 2.3 mmol) and CuCl (0.25 g, 2.5 mmol) were heated at 55 °C for 1.5 h with methanol (10 mL) and toluene (10 mL). After evaporation, the residue was chromatographed with hexane–toluene (90:10): yield, 0.8 g (76%) of colorless solid (see ref 3, 4).

(1,2-Diphenylphosphirene)pentacarbonyltungsten (2). Complex **1** (1.6 g, 2.4 mmol) and phenylacetylene (2 mL, 18 mmol) were heated at 55 °C for 3 h in toluene with CuCl (0.13 g, 1.3 mmol). After evaporation, the residue was chromatographed with hexane–toluene (90:10): $R_f \sim 0.6$; yield, 0.98 g (75%) of colorless solid; mp 88 °C (hexane); ^{31}P NMR (toluene) δ −155.8 ($^1J(^{31}P-^{183}W) = 276$ Hz); ^{13}C NMR (C_6D_6) δ 118.17 (d, $^1J(C-P) = 8.5$ Hz, PCH), 197.0 (d, $^2J(C-P) = 8.5$ Hz, cis CO), 198.5 (d, $^2J(C-P) = 31.7$ Hz, trans CO); IR (Decalin) ν(CO) 2072 (w), 1947 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 534 (M, 21), 478 (M − 2CO, 26), 450 (M − 3CO, 20), 422 (M − 4CO, 27), 394 (M − 5CO, 100), 348 ($PhPW(CO)_2$, 47), 320 (PhPWCO, 32), 292 (PhPW, 67).

(9-Phenyl-9-phosphabicyclo[6.1.0]nonane)pentacarbonyltungsten (5a,b). Complex **1** (2.5 g, 3.8 mmol) was heated with cyclooctene (2 mL, 15 mmol) and CuCl (210 mg, 2 mmol) in toluene (50 mL) at 55 °C for 3 h. After evaporation, the residue was chromatographed with hexane ($R_f \sim 0.8$); yield, 1.9 g (95%) of a mixture of **5a,b**. The major isomer **5a** was obtained in the pure state by crystallization from pentane: colorless solid; mp 104 °C; ^{13}C NMR (C_6D_6) δ 25.7 (d, $J(C-P) = 4.9$ Hz, CH_2), 26.5 (s, CH_2), 29.8 (d, $^1J(C-P) = 14.6$ Hz, CHP), 30.9 (d, $J(C-P) = 9.8$ Hz, CH_2), 197.1 (d, $^2J(C-P) = 8.5$ Hz, cis CO), 199.5 (d, $^2J(C-P) = 28.1$ Hz, trans CO); IR (decalin) ν(CO) 2070 (w), 1942 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 542 (M, 20), 432 ($PhPW(CO)_5$, 20), 404 ($PhPW(CO)_4$, 66), 402 (M − 5CO, 57), 376 ($PhPW(CO)_3$, 22), 348 ($PhPW(CO)_2$, 100), 320 (PhPW(CO), 42), 292 (PhPW, 50). Anal. Calcd for $C_{19}H_{19}O_5PW$: C, 42.09; H, 3.53; P, 5.71. Found: C, 42.10; H, 3.63; P, 5.70.

(1-Phenyl-2-*n*-butylphosphirane)pentacarbonyltungsten (3a,b). The same procedure as for **5a,b** was used, with 1-hexene replacing cyclooctene: yield from 2.5 g of **1**, 1.4 g (71%) of a mixture of **3a,b**; colorless oil; mass spectrum (^{184}W), *m/e* (relative intensity) 516 (M, 19), 432 ($PhPW(CO)_5$, 22), 404 ($PhPW(CO)_4$, 69), 376 ($PhPW(CO)_3$, 23), 348 ($PhPW(CO)_2$, 100), 320 (PhPW(CO), 36), 292 (PhPW, 55).

(7-Phenyl-7-phosphabicyclo[4.1.0]heptane)pentacarbonyltungsten (4a,b). The same procedure as for **5a,b** was used, with cyclohexene replacing cyclooctene: yield from 2.5 g of **1**, 1 g (51%) of a mixture of **4a,b**; colorless solid; mass spectrum (^{184}W), *m/e* (relative intensity) 514 (M, 11), 432 ($PhPW(CO)_5$, 27), 404 ($PhPW(CO)_4$, 60), 374 (M − 5CO, 18), 348 ($PhPW(CO)_2$, 100), 320 (PhPWCO, 41), 292 (PhPW, 67). Anal. Calcd for $C_{17}H_{15}O_5PW$: C, 39.72; H, 2.94; P, 6.02. Found: C, 39.71; H, 2.99; P, 6.10.

(1,2-Diphenylphosphirane)pentacarbonyltungsten (6a,b). The same procedure as for **5a,b** was used, with styrene replacing cyclooctene: yield from 2.5 g of **1**, 1.8 g (92%) of a mixture of **6a,b**. Pure **6a** was obtained by crystallization in pentane–CH_2Cl_2: mp 97 °C; ^{13}C NMR (C_6D_6) δ 14.5 (d, $^1J(C-P) = 11$ Hz, CH_2P), 31.5 (d, $^1J(C-P) = 18.3$ Hz, CHP), 196.6 (d, $^2J(C-P) = 7.3$ Hz, cis CO), 198.8 (d, $^2J(C-P) = 30.5$ Hz, trans CO); IR (Decalin) ν(CO) 2070 (w), 1947 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 536 (M, 25), 432 ($PhPW(CO)_5$, 31), 404 ($PhPW(CO)_4$, 53), 396 (M − 5CO, 18), 376 ($PhPW(CO)_3$, 16), 348 ($PhPW(CO)_2$, 93), 320 (PhPW(CO), 53), 292 (PhPW, 100). Anal. Calcd for $C_{19}H_{13}O_5PW$: C, 42.57; H, 2.44; P, 5.77; W, 34.29. Found: C, 42.60; H, 2.34; P, 5.90; W, 34.26.

(1,2,3-Triphenylphosphirane)pentacarbonyltungsten (Trans Isomer 7). The same procedure as for **5a,b** was used, with *trans*-stilbene replacing cyclooctene: yield from 2.5 g of **1**, 1.4 g (60%); colorless solid; mp 120 °C (hexane/ether); ^{1}H NMR (C_6D_6) δ 3.41 (*A*BX, $^3J(A-B) = 10$ Hz, $^2J(A-X) \approx 0$ Hz, H trans W), 3.66 (A*B*X, $^2J(B-X) = 7.6$ Hz, H cis W); ^{13}C NMR (C_6D_6) δ 33.9 (d, $^1J(C-P) = 15.9$ Hz, CHP), 37 (d, $^1J(C-P) = 18.3$ Hz, CHP), 196 (d, $^2J(C-P) = 8.5$ Hz, cis CO), 198.5 (d, $^2J(C-P) = 31.7$ Hz, trans CO); IR (Decalin) ν(CO) 2072 (w), 1954 (s), 1945 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 612 (M, 17), 472 (M − 5CO, 14), 432 ($PhPW(CO)_5$, 32), 404 ($PhPW(CO)_4$, 66), 376 ($PhPW(CO)_3$, 13), 348 ($PhPW(CO)_2$, 85), 320 (PhPW(CO), 36), 292 (PhPW, 55), 179 (Ph_2C_2H, 100). Anal. Calcd for $C_{25}H_{21}O_5PW$: C, 49.05; H, 2.80; P, 5.06. Found: C, 48.94; H, 2.75; P, 5.18.

(1,2,3-Triphenylphosphirane)pentacarbonyltungsten (Cis Isomers 8a,b). The same procedure as for **5a,b** was used, with *cis*-stilbene replacing cyclooctene: yield from 3.1 g of **1**, 0.7 g (25%) of **3a,b**. The mixture was chromatographed with hexane–toluene (95:5). The complex **8b** was eluted first ($R_f \sim 0.8$), and then **8a** was recovered ($R_f \sim 0.5$). **8b**: colorless solid; mp 100 °C (pentane/ether); ^{1}H NMR (C_6D_6) δ 3.21 (d, $^2J(H-P) = 1.5$ Hz, CHP); IR (Decalin) ν(CO) 2070 (w), 1946 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 612 (M, 11), 472 (M − 5CO, 7), 432 ($PhPW(CO)_5$, 30), 404 ($PhPW(CO)_4$, 70), 376 ($PhPW(CO)_3$, 15), 348 ($PhPW(CO)_2$, 74), 320 (PhPW(CO), 34), 292 (PhPW, 43), 179 (Ph_2C_2H, 100). Anal. Calcd for $C_{25}H_{21}O_5PW$: C, 49.05; H, 2.80; P, 5.06. Found: C, 49.32; H, 2.82; P, 5.03. **8a**: colorless solid; mp 151 °C (pentane/ether); ^{1}H NMR (C_6D_6) δ 3.10 (d, $^2J(H-P) = 7.8$ Hz, CMP); IR (Decalin) ν(CO) 2070 (w), 1950 (vs), 1942 (s) cm^{-1}.

(1-Methyl-2,3-diphenylphosphirane)pentacarbonyltungsten (9). [5,6,7-Trimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene]pentacarbonyltungsten (2.5 g, 4.2 mmol), *trans*-stilbene (2.2 g, 12.4 mmol), and CuCl (0.23 g, 2.3 mmol) were heated at 55 °C in toluene for 8 h. After evaporation, the residue was chromatographed first with hexane in order to remove the *trans*-stilbene and then with hexane–toluene (90:10) to recover **9**: yield 0.9 g (39%) of colorless oil; ^{31}P NMR (toluene) δ −142.1 ($^1J(^{31}P-^{183}W) = 261$ Hz); ^{1}H NMR (C_6D_6) δ 0.67 (d, $^2J(H-P) = 6.6$ Hz, Me), 2.80 (*A*BX, $^3J(A-B) = 9.8$ Hz, $^2J(A-X) = 7.3$ Hz, H cis W), 3.18 (A*B*X, $^2J(B-X) \approx 0$ Hz, H trans W); IR (Decalin)

ν(CO) 2070 (w), 1950 (s), 1944 (vs) cm^{-1}; mass spectrum (^{184}W), *m/e* (relative intensity) 550 (M, 28), 370 (MePW(CO)$_5$, 32), 342 (MePW(CO)$_4$, 100), 312 (MePW(CO)$_3$, 33), 284 (MePW(CO)$_2$, 34), 256 (MePW(CO), 26), 228 (MePW, 10), 178 (Ph$_2$C$_2$, 37).

(1,2,3-Triphenylphosphirane)pentacarbonylchromium (10). [5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonylchromium (1 g, 1.9 mmol), *trans*-stilbene (1 g, 5.5 mmol), and CuCl (0.19 g, 1.9 mmol) were heated in toluene (30 mL) at 55 °C for 8 h. After evaporation, the residue was chromatographed, first with hexane in order to remove the unreacted stilbene and then with hexane–toluene (90:10) to recover **10**: yield, 0.2 g (22%) of colorless solid; mp 133 °C (pentane); ^{31}P NMR (C_6D_6) δ −76.8; ^{1}H NMR (C_6D_6) δ 3.28 (*A*BX, ^3J(A–B) = 9.8 Hz, ^2J(A–X) $\approx$ 0 Hz, H trans W), 3.70 (A*B*X, ^2J(B–X) = 8.3 Hz, H cis W); IR (Decalin) ν(CO) 2065 (w), 1956 (s), 1947 (vs) cm^{-1}; mass spectrum, *m/e* (relative intensity) 480 (M, 32), 424 (M − 2CO, 38), 340 (M − 5CO, 100), 179 (Ph$_2$C$_2$H, 44). Anal. Calcd for $C_{25}H_{21}O_5PCr$: C, 62.51; H, 3.57; Cr, 10.82. Found: C, 62.37; H, 3.54; Cr, 10.81.

[1-Phenyl-2-methyl-2-(1-methylvinyl)phosphirane]pentacarbonyltungsten (11a,b). The same procedure as for **5a,b** was used, with 2,3-dimethyl-1,3-butadiene replacing cyclooctene: yield from 3 g of **1**, 1.86 g (78%) of a mixture of **11a,b**. Pure **11a** was obtained by crystallization in pentane: mp 48 °C; ^{31}P NMR (C_6D_6) δ −141.7 (^1J(^{183}W–^{31}P) = 254 Hz); IR (Decalin) ν(CO) 2070 (w), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.0 (*A*BX, ^2J(A–B) = 8.8 Hz, ^2J(A–X) $\approx$ 0 Hz, H trans W), 1.3 (d, ^3J(H–P) = 19 Hz, 3 H, PCCH$_3$), 1.4 (s, 3 H, CH$_2$=C—C*H*$_3$), 1.9 (A*B*X, ^2J(B–X) = 8.8 Hz, H cis W), 4.2 (pseudo s, 2 H, CH$_2$=C), 6.8–7.2 (m, 5 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 514 (M, 9), 486 (M − CO, 24), 430 (M − 3CO, 67), 402 (M − 4CO, 35), 374 (M − 5CO, 72), 348 (PhPW(CO)$_2$, 89), 320 (PhPW(CO), 52), 292 (PhPW, 100). **11b**: ^{31}P NMR (hexane) δ −136.4 (^1J(^{183}W–^{31}P) = 261 Hz).

[1,2-Diphenyl-3-(2-phenylvinyl)phosphirane]pentacarbonyltungsten (12a,b). The same procedure as for **5a,b** was used, with *trans,trans*-1,4-diphenyl-1,3-butadiene replacing cyclooctene: yield from 2.5 g of **1**, 1.5 g (62%) of a mixture of **12a,b**. Pure **12a** was obtained by crystallization in hexane: ^{31}P NMR (C_6D_6) δ −125.6 (^1J(^{183}W–^{31}P) = 261.2 Hz); IR (Decalin) ν(CO) 2073 (w), 1954 (s), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.0 (m, ^2J(H–P) $\approx$ 0 Hz, ^3J(*H*C$_3$–C$_2$*H*Ph) = 9.3 Hz, ^3J(*H*C$_3$–C*H*=) = 7.8 Hz, 1 H, PC$_3$H), 3.18 (m, ^2J(H–P) = 9.0 Hz, 1 H, PC$_2$HPh), 5.40 (m, ^3J(H–P) = 4.2 Hz, ^{3}J(*H*C=C*H*) = 15.9 Hz, 1 H, PhCH=C*H*), 6.31 (dd, ^4J(H–P) = 4.2 Hz, 1 H, PhC*H*=CH); mass spectrum (^{184}W), *m/e* (relative intensity) 638 (M, 7), 610 (M − CO, 11), 554 (M − 3CO, 25), 498 (M − 5CO, 15), 404 (PhPW(CO)$_4$, 24), 376 (PhPW(CO)$_3$, 10), 348 (PhPW(CO)$_2$, 43), 320 (PhPWCO, 24), 292 (PhPW, 30), 206 (Ph$_2$C$_4$H$_4$, 100). Anal. Calcd for $C_{27}H_{19}O_5PW$: C, 50.81; H, 3.00; P, 4.85; W, 28.80. Found: C, 51.04; H, 2.97; P, 4.84; W, 28.75. **12b**: ^{31}P NMR (C_6D_6) δ −125 (^1J(^{183}W–^{31}P = 261.2 Hz).

(6-Phenyl-6-phosphabicyclo[3.1.0]hex-2-ene)pentacarbonyltungsten (13a,b). The same procedure as for **5a,b** was used, with cyclopentadiene replacing cyclooctene: yield from 3 g of **1**, 1.5 g (66%) of a mixture **13a,b**. Pure **13a** was obtained by crystallization in pentane: colorless solid; mp 76 °C; ^{31}P NMR (C_6D_6) δ −153.5 ^1J(^{183}W–^{31}P) 263 Hz); IR(Decalin)ν(CO) 2072 (w), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.85 (m, 1 H), 2.2–2.6 (m, 3 H), 5.4 (m, 2 H, C*H*=C*H*), 6.8–7.2 (m, 5 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 498 (M, 26), 432 (PhPW(CO)$_5$, 35), 404 (PhPW(CO)$_4$, 50), 376 (PhPW(CO)$_3$, 13), 356 (M-5CO, 33), 348 (PhPW(CO)$_2$, 100), 320 (PhPW(CO), 48), 292 (PhPW, 91). **13b**: ^{31}P NMR (toluene) δ −147.4. Anal. Calcd for $C_{16}H_{11}O_5PW$: C, 38.58; H, 2.23; P, 6.22. Found: C, 38.85; H, 1.99; P, 6.57.

Vinylphosphirane–Phospholene Isomerization. Complex **11a,b** (2.3 g, 4.5 mmol) was heated in toluene at 95 °C for 24 h. After evaporation, complex **14** was purified by chromatography with hexane: yield, 1 g (44%) of colorless solid; mp 74 °C (hexane); ^{31}P NMR (C_6D_6) δ −5.2 ^1J(^{183}W–^{31}P) = 229.5 Hz); ^{1}H NMR (C_6D_6) δ 1.3 (s, 6 H, CH$_3$), 2.7 (m, 4H, PC*H*$_2$), 6.9–7.2 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{15}O_5PW$: C, 39.72; H, 2.94; P, 6.02. Found: C, 39.77; H, 3.00; P, 6.06.

(2,3,5-Triphenyl-1,2-oxaphosphol-4-ene)pentacarbonyltungsten (15a,b). Complex **1** (2.5 g, 3.8 mmol) was heated in toluene (50 mL) at 65 °C for 2.5 h with benzalacetophenone (1.7 g, 11.6 mmol) and CuCl (0.30 g, 3 mmol). After evaporation, the residue was chromatographed with pentane–ether (95:5): complex **15a** was eluted first (R_f ~0.8) and then complex **15b** was recovered (R_f ~0.5): total yield, 1.7 g (70%). **15a**: ^{31}P NMR (C_6D_6) δ 138.4 (^1J(^{183}W–^{31}P) = 283 Hz); IR (Decalin) ν(CO) 1974 (w), 1960 (s), 1947 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.25 (m, 1 H, CH=), 5.29 (dd, ^2J(H–P) = 17.3 Hz, ^3J(H–H) = 1.7 Hz, 1 H, CHP), 6.5–7.7 (m, 15 H, Ph). **15b**: ^{31}P NMR (pentane) δ 148.5 (^1J(^{183}W–^{31}P) = 288 Hz); IR (Decalin) ν(CO) 1976 (w), 1955 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.14 (dd, ^3J(P–H) $\approx$ ^3J(H–H) $\approx$ 4 Hz, 1 H, CH=); 5.30 (dd, ^2J(P–H) = 18 Hz, ^3J(H–H) = 4 Hz, 1 H, CHP), 7.0–7.7 (m, 15 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 640 (M, 26), 612 (M − CO, 13), 556 (M − 3CO, 67), 500 (M − 5CO, 100); colorless solid; mp 188 °C. Anal. Calcd for $C_{26}H_{17}O_6PW$: C, 48.78; H, 2.68; P, 4.84; W. 28.72. Found: C, 48.92; H, 2.66; P, 4.82; W. 28.43.

(2,3-Diphenyl-5-methyl-1,2-oxaphosphol-4-ene)pentacarbonyltungsten (16a,b). The same procedure as for **15a,b** was used, with benzalacetone replacing benzalacetophenone: yield from 2.5 g of **1**, 1.3 g (59%) of a mixture **16a,b**. Pure **16a** and **16b** were obtained by crystallization in pentane. **16a** (I): colorless solid; mp 135 °C (pentane); ^{31}P NMR (C_6D_6) δ 146.2 (^1J(^{183}W–^{31}P) = 288 Hz); IR (Decalin) ν(CO) 2075 (w), 1955 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.64 (m, 3 H, CH$_3$), 3.95 (m, ^3J(H–P) = 5 Hz, ^3J(H–H) = 3.4 Hz, 1 H, CH=), 4.52 (m, ^2J(H–P) = 17 Hz, 1 H, CHP), 7.0–7.5 (m, 10 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 578 (M, 24), 550 (M − CO, 13), 494 (M − 3CO, 70), 438 (M − 5CO, 100). Anal. Calcd for $C_{21}H_{15}O_6PW$: C, 43.63; H, 2.62; P, 5.36; W, 31.80. Found: C, 43.44; H, 2.67; P, 5.73; W, 31.42. **16b** (II): colorless solid, mp 85 °C (pentane); ^{31}P NMR (C_6D_6) δ 137.5 (^1J(^{183}W–^{31}P) = 281 Hz); IR (Decalin) ν(CO) 2075 (w), 1960 (s), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.67 (m, 3 H, CH$_3$), 4.49 (m, ^2J(H–P) = 18 Hz, ^3J(H–H) = 2.2 Hz, 1 H, CHP), 5.09 (m, ^3J(H–P) = 5 Hz, 1 H, CH=), 6.8–7.2 (m, 10 H, Ph). The methyl groups of both **16a** and **16b** are only weakly coupled (ca. 1 Hz) with the two protons of the oxaphospholene ring. Thus, the C=C double bond is necessarily between C$_4$ and C$_5$ in **16a** and **16b**.

[1-Phenyl-2-methyl-2-(methoxycarbonyl)phosphirane]pentacarbonyltungsten (17a,b). Complex **1** (3 g, 4.6 mmol) was heated with methyl methacrylate (2.5 mL, 23 mmol) and CuCl (0.3 g, 3 mmol) in toluene at 65 °C for 3 h. After evaporation, complex **17a** was purified by chromatography with hexane–toluene (70:30): yield, 1 g (40%) of colorless oil. ^{31}P NMR (hexane) δ −125.2 (^1J(^{183}W–^{31}P) = 268.6 Hz); IR (Decalin) ν(CO) 2076 (w), 1990 (vw), 1949 (vs) cm^{-1}, (KBr) ν(CO ester) 1700 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.93 (d, ^3J(P–H) = 10.5 Hz, 3 H, CCH$_3$), 1.29 (*A*BX, ^2J(A–B) $\approx$ ^2J(A–X) = 8.5 Hz, 1 H, CHP cis W), 2.13 (A*B*X, ^2J(A–B) = 8.5 Hz, ^2J(B–X) = 1 Hz, 1 H, CHP trans W), 3.49 (s, 3 H, CO$_2$CH$_3$), 6.94 (m, 5 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 532 (M, 15), 504 (M − CO, 30), 448 (M − 3CO, 24), 420 (M − 4CO, 18), 404 (PhPW(CO)$_4$, 28), 392 (M − 5CO, 50), 348 (PhPW(CO)$_2$, 93), 320 (PhPW(CO), 54), 292 (PhPW, 100). Minor product **17b**: ^{31}P NMR (hexane) δ −129.2.

[α-(Phenylphosphino)acetaldehyde]pentacarbonyltungsten (19) and [(2,2-Diethoxyethyl)phenylphosphine]pentacarbonyltungsten (20). Complex **1** (3 g, 4.6 mmol), ethyl vinyl ether (0.9 mL, 9.2 mmol), and CuCl (0.49 g, 4.9 mmol) were heated in toluene at 70 °C for 1 h. The phosphirane complex (^{31}P NMR δ −168.3) was hydrolyzed with water at room temperature. After evaporation, the residue was chromatographed first with petroleum ether–ether (95:5) and then with petroleum ether–ether (85:15). Complex **20** was eluted first: yield, 0.7 g (28%) of colorless oil; ^{31}P NMR (hexane) δ −37.9 (^1J(^{183}W–^{31}P) = 229 Hz); IR (Decalin) ν(CO) 2070 (w), 1980 (vw), 1946 (sh), 1940 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.97 (t, ^3J(H–H) = 7.1 Hz, CH$_3$), 1.00 (t, ^3J(H–H) = 7.0 Hz, CH$_3$), 2.3 (m, 2 H, PCH$_2$), 3.2 (m, 4 H, OC*H*$_2$CH$_3$), 4.40 (m, 1 H, CH$_2$C*H*), 5.74 (m, ^1J(P–H) = 352 Hz, ^3J(H–H) = 6.8 Hz, 1 H, PH), 6.9–7.3 (m, 5 H, Ph); mass spectrum (^{184}W), *m/e* (relative intensity) 550 (M, 15), 522 (M − CO, 63), 494 (M − 2CO, 13), 338 (100). Complex **19**: yield, 0.65 g (30%) of colorless oil; ^{31}P NMR (hexane) δ −43.1 (^1J(^{183}W–^{31}P) = 234 Hz); IR (Decalin) ν(CO) 1973 (w), 1945 (vs) cm^{-1}, (KBr) ν(PH) 2340 cm^{-1}, ν(CO aldehyde) 1710 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.4 (m, 2 H, PCH$_2$), 5.44 (ddd, ^1J(PH) = 350 Hz, ^3J(H–H) = 7.3 Hz, ^3J(H–H) = 5.5 Hz, 1 H, PH), 7.0 (m, 5 H, Ph), 8.8 (dt, ^3J(H–H) = 2.2 Hz, ^3J(H–P) = 4.9 Hz, 1 H, CHO); mass spectrum (^{184}W), *m/e* (relative in-

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tensity) 476 (M, 7), 448 (M – CO, 70), 422 (M – 2CO, 15), 392 (M – 3CO, 20), 364 (M – 4CO, 22), 348 ($PhPW(CO)_2$, 27), 336 (M – 5CO, 100), 320 (PhPW(CO), 15), 306 ($WPPhCH_2$, 76).

(1-Phenyl-2,4-diethoxyphospholane)pentacarbonyltungsten (21a). Complex 1 (2.5 g, 3.8 mmol), ethyl vinyl ether (2.2 mL, 23 mmol), and CuCl (0.38 g, 3.8 mmol) were heated in toluene at 55 °C for 3 h. After evaporation, the residue was chromatographed with hexane–toluene (80:20): R_f ~0.6; yield, 1.5 g (69%) of a mixture **21a**,**b**. Pure **21a** was obtained by chromatography with hexane–toluene (90:10) (R_f ~0.5) and crystallization in ethanol: colorless solid; mp 58 °C; ^{31}P NMR (C_6D_6) δ 19.5 ($^1J(^{183}W-^{31}P)$ = 236.8 Hz), IR (Decalin) ν(CO) 2070 (w), 1945 (vs), 1938 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 1.06 (t, ^3J(H–H) = 7.1 Hz, 3 H, CH_2CH_3), 1.15 (t, ^3J(H–H) = 6.8 Hz, 3 H, CH_2CH_3), 1.7–2.0 (m, 2 H, $CHCH_2CH$), 2.1–2.8 (m, 2 H, PCH_2), 2.9–3.5 (m, 5 H, OCH_2CH_3, CH_2CHCH_2), 3.83 (t, ^3J(H–H) = 6.3 Hz, ^2J(H–P) ≈ 0 Hz, 1 H, $PCHCH_2$); ^{13}C NMR (C_6D_6) δ 15.75 (s, CH_3), 16.00 (s, CH_3), 36.90 (d, ^1J(C–P) = 24.4 Hz, PCH_2), 39.20 (d, ^2J(CP) = 4.9 Hz, $PCHCH_2$), 65.25 (s, OCH_2CH_3), 67.43 (d, ^3J(C–P) = 9.8 Hz, OCH_2CH_3), 79.00 (s, CHOEt), 82.58 (d, ^1J(C–P) = 39.1 Hz, PCHOEt), 197.69 (d, ^2J(C–P) = 7.3 Hz, cis CO); mass spectrum (^{184}W), *m/e* (relative intensity) 576 (M, 63), 548 (M – CO, 20), 520 (M – 2CO, 89), 492 (M – 3CO, 20), 436 (M – 5CO, 30), 407 (M – 5CO – Et, 100). Anal. Calcd for $C_{19}H_{21}O_7PW$: C, 39.61; H, 3.67; P, 5.38; W, 31.91. Found: C, 39.35; H, 3.44; P, 5.29; W, 31.95. The phospholane **21a** is accompanied by a minor byproduct, **21b**, the formula of which has not been established. **21b** is very probably an isomeric compound of unknown structure: ^{31}P NMR (hexane) δ 1.71 ($^1J(^{183}W-^{31}P)$ = 239.2 Hz).

Registry No. **1**, 83603-06-9; **2**, 88000-28-6; **3** (isomer 1), 88000-29-7; **3** (isomer 2), 88080-13-1; **4** (isomer 1), 88000-30-0; **4** (isomer 2), 88080-14-2; **5** (isomer 1), 88000-31-1; **5** (isomer 2), 88081-26-9; **6** (isomer 1), 88000-32-2; **6** (isomer 2), 88080-15-3; **7**, 88000-33-3; **8a**, 88080-16-4; **8b**, 88080-17-5; **9**, 88000-34-4; **10**, 88000-35-5; **11** (isomer 1), 88000-36-6; **11** (isomer 2), 88080-18-6; **12a**, 88000-37-7; **12b**, 88080-19-7; **13** (isomer 1), 88000-38-8; **13** (isomer 2), 88080-20-0; **14**, 82281-49-0; **15** (isomer 1), 88000-39-9; **15** (isomer 2), 88080-21-1; **16** (isomer 1), 88000-40-2; **16** (isomer 2), 88080-22-2; **17** (isomer 1), 88080-23-3; **17** (isomer 2), 88000-41-3; **19**, 88000-42-4; **20**, 88015-24-1; **21a**, 88000-43-5; (*O*-methyl phenylphosphinite)pentacarbonyltungsten, 82265-66-5; [5,6,7-trimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene]pentacarbonyltungsten, 82265-65-4; [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonylchromium, 82265-63-2; phenylacetylene, 536-74-3; cyclooctene, 931-88-4; 1-hexene, 592-41-6; cyclohexene, 110-83-8; styrene, 100-42-5; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; *trans*,*trans*-1,4-diphenyl-1,3-butadiene, 538-81-8; cyclopentadiene, 542-92-7; benzalacetophenone, 94-41-7; benzalacetone, 122-57-6; methyl methacrylate, 80-62-6; ethyl vinyl ether, 109-92-2; CuCl, 7758-89-6.

A Mechanistic Study of the Reaction of the Dithiocarbene Complex $(CO)_5W[C(SMe)_2]$ with Amines

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The reactions of mono- and diamines (A) with $(CO)_5W[C(SMe)_2]$, 1, in THF solvent according to the equation $(CO)_5W[C(SMe)_2] + H_2NR \rightarrow (CO)_5WC{\equiv}NR + 2MeSH$ follow the two-term rate law rate = $k_1[1][A] + k_2[1][A]^2$. Monoamines (H_2NR) generally react by the k_2 pathway, which is proposed to involve initial amine nitrogen addition to the carbene carbon to give $(CO)_5W[C(SMe)_2(NH_2R)]$, followed by expulsion of the MeS^- group in a rate-determining step that is catalyzed by a second molecule of amine. The rate constant k_2 at 40.0 °C decreases with the amine in the order H_2N-*n*-Bu (41.9 $M^{-2}\,s^{-1}$) ≈ H_2N-*n*-Pr (40.2) > H_2NCH_2Ph (5.83) > $H_2NC_6H_{11}$ (0.800). The difference in rates for H_2N-*n*-Bu and $H_2NC_6H_{11}$ suggests that the bulkiness of the cyclohexyl group decreases the rate. In pyridine solvent, the reactions are still second order in the monoamine but are much faster than in THF. In MeOH solvent, the reaction with H_2NCH_2Ph is only first order in the amine concentration; in this case, MeOH instead of another molecule of H_2NCH_2Ph presumably catalyzes the breakdown of the intermediate in the rate-determining step. In cyclohexane solvent, the reaction becomes 4.1 order in the H_2NCH_2Ph concentration, which is interpreted to suggest that the amine is required to stabilize polar intermediates by solvation in this nonpolar solvent. In contrast with the second-order amine dependence of the monoamine reactions in THF solvent, the diamine $H_2N(CH_2)_nNH_2$ (n = 2 or 3) reactions in this solvent are much faster and are only first order in the diamine concentration. This result suggests that one end of the diamine attacks the carbene carbon while the other end promotes breakdown of the intermediate. The other diamines $H_2N(CH_2)_4NH_2$, $H_2N(CH_2)_2NMe_2$, and $H_2N(CH_2)_3NMe_2$ react not only by the pathway involving first-order dependence on the diamine concentration but also by one that is second order. The second-order pathway is probably similar to that for the monoamines but involves additional catalysis of the intermediate breakdown by the dangling amino groups at the other ends of the diamines. In general, the reactions appear to proceed by initial nucleophilic attack of the amine at the carbene carbon. A second mole of amine facilitates breakdown of the intermediate by removing a proton from the attacking amine and, where possible, protonating the departing MeS^-. Primary amines are much more effective than tertiary amines at promoting this breakdown. Details of the mechanisms are discussed.

Introduction

Although numerous reactions of transition-metal carbene complexes have been reported,[2-4] few kinetic studies of carbene ligand reactions are available.[5-8] A common reaction of carbene ligands is that involving addition of

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[2] Casey, C. P. "Transition Metal Organometallics in Organic Synthesis"; Wiley: New York, 1976; Vol. 1, p 1.

[3] Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

[4] Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857.

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