24, 108970-62-3; **25**, 108970-64-5; **26**, 108970-66-7; **27**, 108970-68-9; (η^5-C_5H_5)Ru(1,10-phen)Cl, 108970-69-0; (η^5-C_5H_5)Ru(5-NO_2-1,10-phen)Cl, 108970-70-3; (η^5-C_5H_5)Ru(4,4′-Me_2-2,2′-bpy)Cl, 108970-71-4; (η^5-C_5H_5)Ru(PPh_3)(η^1-dppm)Cl, 89298-92-0; [(η^5-C_5H_5)Ru(dppm)(η^1-dppm)]PF_6, 89298-97-5.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and bond lengths, and angles (12 pages); a listing of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

Ring Opening of Three-Membered Heterocycles by Terminal Phosphinidene Complexes

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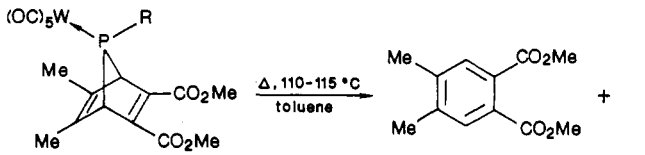
(Phenylphosphinidene)pentacarbonyltungsten as produced by thermal decomposition of the appropriate 7-phosphanorbornadiene complex reacts with phenyloxirane to give (2,4-diphenyl-1,3,2-dioxaphospholane)- and (1,2-diphenylphosphirane)pentacarbonyltungsten complexes. Their formation is explained by the insertion of the phosphinidene into the oxirane ring giving a transient 1,2-oxaphosphetane, which then undergoes a [2 + 2] cycloreversion. With 1-*tert*-butyl-2-phenylaziridine, the same insertion takes place but the isomeric 1,2-azaphosphetane complexes thus formed are thermally stable. With *trans*-2,3-diphenylthiirane, decomposition into stilbene and formation of phosphirane complexes take place in lieu of the expected insertion.

Two theoretical studies of [HP=$Cr(CO)_5$] are available at the moment.[1,2] Even though their results are somewhat different, both studies agree to predict that the phosphorus atom of this type of terminal phosphinidene complex will behave as a strong electrophilic center both in charge- and frontier-orbital-controlled reactions. A striking experimental confirmation of this electrophilicity has been provided inter alia by the recently discovered insertion of terminal phosphinidene complexes into the C–H bonds of ferrocene.[3]

On the other hand, classical three-membered heterocycles such as oxirane, thiiranes, and aziridines are well-known to open rings by reaction with electrophiles. This kind of considerations prompted us to study the reactions of terminal phosphinidene complexes with some representative examples of these heterocycles. We describe here the results of this study.

Results and Discussion

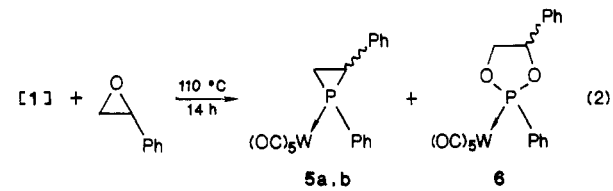
All our experiments have been carried out with the transient (phenylphosphinidene)- and (methylphosphinidene)pentacarbonyltungsten complexes [RP=$W(CO)_5$] which have been produced by thermal decomposition of the appropriate 7-phosphanorbornadiene complexes as described previously[4] (eq 1). We have first investigated the reaction of **1** with phenyloxirane (eq 2).



1: R = Ph
2: R = Me

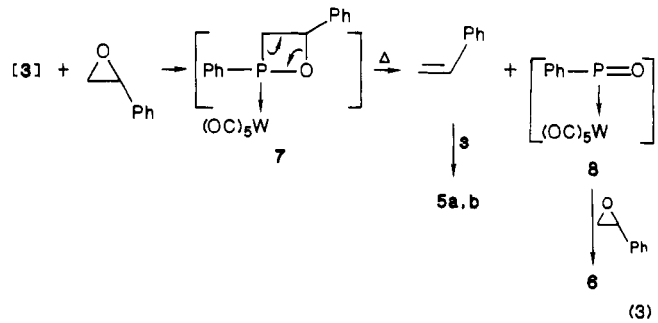
·[RP=$W(CO)_5$] (1)

3: R = Ph
4: R = Me



5a,b **6** (2)

The main products of this reaction are the two already known isomeric phosphirane complexes **5a,b**,[5] formally resulting from the condensation of **3** with styrene[5] and mainly characterized by their typical ^{31}P NMR resonances at high fields[5] together with several isomers of **6**, the most abundant of which has been obtained in the pure state and fully analyzed. The formation of these two series of products can be rationalized by the mechanism outlined in eq 3. The initial ring insertion leading to **7** would be



(3)

followed by a Wittig-like [2 + 2] cycloreversion giving styrene and the phenylphosphinidene oxide complex **8**. Even when the reaction is monitored by ^{31}P NMR, we have never been able to observe the appearance of **8** in the reaction mixture. Contrary to a bulky substituted aminophosphinidene oxide $Cr(CO)_5$ complex described by Niecke,[6] **8** is probably highly unstable and immediately cycloadds onto another molecule of phenyloxirane to give the dioxaphospholane complex **6**. Phosphirane complexes **5a,b** would be simultaneously formed through the already

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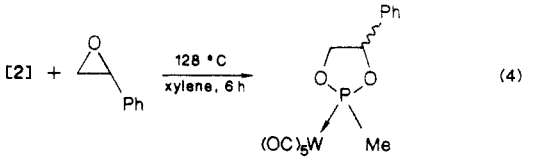
described reaction of **3** with styrene.[5] When the same reaction is performed with the methylphosphinidene complex **4**, only the dioxaphospholane complex **9** is recovered (eq 4). Under the relatively drastic reaction

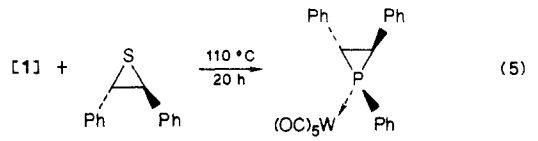


(4)

9

conditions, the isomeric (1-methyl-2-phenylphosphirane)pentacarbonyltungsten complexes either are unstable and decompose[4] or do not form because styrene evaporates. They can be detected in trace amounts, however, on the ^{31}P NMR spectrum of the crude reaction mixture ($\delta(^{31}P)$ −164.8 and −177.1 in xylene).

The reaction of **1** with *trans*-2,3-diphenylthiirane seems to follow another course (eq 5). Indeed, when the reaction

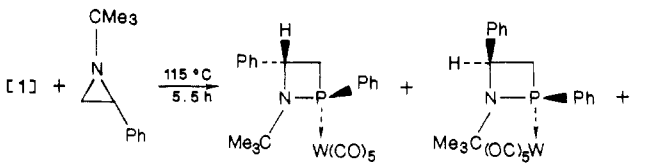


(5)

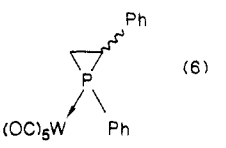
10

is monitored by ^{31}P NMR, the formation of only one product, the already described phosphirane complex **10**,[5] is observed. No trace of a 1,3,2-dithiaphospholane complex similar to **6** is detected. The most likely explanation is that, under the reaction conditions, the thiirane decomposes by extrusion of sulfur and gives *trans*-stilbene, which then reacts with **3**. The relatively low thiophilicity of phosphorus combined with the weak stability and nucleophilicity of the thiirane would explain why the expected insertion is unable to compete with the decomposition of the thiirane.

The story is again different with **1** and 1-*tert*-butyl-2-phenylaziridine (eq 6). In that case, we have been able



11a **11b**



(6)

5a, b

to isolate and characterize the postulated insertion product as a mixture of the two isomers **11a,b**. For the two isomers, the insertion has taken place selectively on the less hindered side of the three-membered ring. Indeed in both cases, we have observed a huge $^1J(P\text{–}CH_2)$ and a weak $^2J(P\cdots CHPh)$ coupling in the ^{13}C NMR spectrum: **11a** (minor isomer), $^1J(P\text{–}CH_2)$ = 39.3 Hz, $^2J(P\cdots CHPh)$ = 9.6 Hz; **11b** (major isomer), $^1J(P\text{–}CH_2)$ = 39.1 Hz, $^2J(P\cdots CHPh)$ = 10.0 Hz. On the basis of the stereochemical assignments made for a couple of tervalent phosphetanes,[7] we suggest that the minor isomer **11a** with no detectable $^3J(H\text{–}P)$ coupling between the C*H*Ph proton and the phosphorus atom corresponds to the more congested stereochemistry where the (Ph)C–H and P–Ph bonds are cis. Both mass spectra (EI, 70 eV, ^{184}W) suggest that these isomers can undergo a [2 + 2] cycloreversion like that of the postulated intermediate **7**: **11a**, *m/z* (relative intensity) 607 (M^+, 26), 467 (M^+ − 5CO, 80), 363 [467 − (PhCH=CH_2), 100]; **11b**, *m/z* (relative intensity) 607 (28), 467 (100), 363 (87). In practice, however, both **11a** and **11b** show no noticeable decomposition upon heating at 140 °C in boiling xylene for 8 h. Thus, the styrene which explains the formation of the phosphirane complexes **5a,b** is clearly formed through the thermal decomposition of the starting aziridine and not through the [2 + 2] cycloreversion of **11a,b**.

Experimental Section

NMR spectra were recorded on a Bruker WP 80 instrument at 80.13 MHz for ^1H and 32.435 MHz for ^{31}P. ^{13}C NMR spectra were recorded on a Bruker AC 200 SY at 50.32 MHz. Chemical shifts are reported in parts per million from internal Me_4Si for ^1H and ^{13}C and from external 85% H_3PO_4 for ^{31}P. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Mass spectra were recorded on VG 30F spectrometers by Serivce Central d'Analyse du CNRS (Lyon). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230mesh Riedel de Haën).

Reaction of Complex 1 with Phenyloxirane (Eq 2). Complex **1** (3.5 g, 5.4 mmol) and phenyloxirane (2.1 mL, 18.4 mmol) were heated in boiling toluene for 14 h. After evaporation, the residue was chromatographed with hexane/toluene (90:10). Complexes **5a,b** were recovered first: ^{31}P NMR (hexane) δ −149.5 and −154.6 (yield 0.25 g, 9%). Complex **6** was then eluted as an isomeric mixture. The major isomer was obtained in the pure state by chromatographic separation (hexane/ether, 98:2): yield 1.4 g, 46%; colorless oil; ^{31}P NMR (hexane) δ 174.2 ($^1J(^{31}P\text{–}^{183}W)$ = 336.9 Hz); ^1H NMR (C_6D_6) δ 3.57 (m, $^3J(H\text{–}P)$ = 9.9 Hz, $^3J(H\text{–}H)$ = 7.1 Hz, $^2J(H\text{–}H)$ = 9.0 Hz, 1 H, CH_2), 3.60 (m, $^3J(H\text{–}P)$ = 7.2 Hz, $^3J(H\text{–}H)$ = 7.1 Hz, $^2J(H\text{–}H)$ = 9.0 Hz, 1 H, CH_2), 4.62 (td, $^3J(H\text{–}P)$ = 1.7 Hz, $^3J(H\text{–}H)$ = 7.1 Hz, 1 H, C*H*–Ph), 6.9–7.6 (m, 10 H, Ph); IR (decalin) ν(CO) 2078 (m), 1960 (s), 1955 (vs) cm^{-1}; mass spectrum (^{184}W), *m/z* (relative intensity) 568 (M^+, 42), 484 (M^+ − 3CO, 44), 428 (M^+ − 5CO, 79), 324 ($W(CO)_5$ or $WPPhO_2$, 100). Anal. Calcd for $C_{25}H_{17}O_7PW$: C, 46.61; H, 2.66. Found: C, 46.83; H, 2.63.

Reaction of Complex 2 with Phenyloxirane (Eq 4). Complex **2** (2 g, 3.4 mmol) and phenyloxirane (1.2 mL, 10.1 mmol) were heated in xylene at 128 °C for 6 h. After evaporation, the residue was chromatographed with hexane/ether (97:3), and 0.34 g (20%) of **9** was obtained as a colorless oil: ^{31}P NMR (hexane) δ 191.8 ($^1J(^{31}P\text{–}^{183}W)$ = 332 Hz); ^1H NMR (C_6D_6) δ 1.36 (d, $^2J(H\text{–}P)$ = 3.7 Hz, 3 H, PMe), 3.17 (pst, $^2J(H\text{–}H) \simeq {}^3J(H\text{–}H)$ = 9.8 Hz, 1 H, CH_2), 3.72 (m, $^3J(H\text{–}P)$ = 21.5 Hz, $^3J(H\text{–}H)$ = 6.1 Hz, $^2J(H\text{–}H)$ = 9.8 Hz, 1 H, CH_2), 4.78 (m, $^3J(H\text{–}P)$ = 2.2 Hz, $^3J(H\text{–}H)$ = 9.8 Hz, $^3J(H\text{–}H)$ = 6.1 Hz, 1 H, C*H*Ph), 6.8–7.1 (m, Ph); IR (decalin) ν(CO) 2075 (m), 1965 (s), 1950 (sh), 1945 (vs) cm^{-1}; mass spectrum (^{184}W), *m/z* (relative intensity) 506 (M^+, 47), 422 (M^+ − 3CO, 28), 366 (M^+ − 5CO, 68), 316 (100).

Reaction of Complex 1 with 1-*tert*-Butyl-2-phenylaziridine (Eq 6). 1-*tert*-Butyl-2-phenylaziridine was prepared according to a literature procedure.[8]

Complex **1** (3 g, 4.6 mmol) and 1-*tert*-butyl-2-phenylaziridine (2 g, 11.4 mmol) were heated in xylene at 120 °C for 6 h. After partial evaporation of the solvent, the residue was passed through a short column of neutral alumina in hexane. A mixture of the two isomers **11a,b** and excess aziridine were eluted with hexane/ether (97:3). After several crystallizations in pentane the pure isomers **11a** and **11b** were obtained (yield 1.1 g, 40%).

11a: colorless solid, mp 140 °C; ^{31}P NMR (C_6D_6) δ 110.0 ($^1J(^{31}P\text{–}^{183}W)$ = 256 Hz); ^1H NMR (C_6D_6) δ 1.13 (s, 9 H, *t*-Bu), 3.87 (dd, $^2J(H\text{–}P)$ = 11.5 Hz, $^3J(H\text{–}H)$ = 7.6 Hz, 1 H, CH_2), 3.87 (dd, $^2J(H\text{–}P)$ = 9.5 Hz, $^3J(H\text{–}H)$ = 7.6 Hz, 1 H, CH_2), 4.39 (pst,

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^3J(H–H) = 7.6 Hz, 1 H, CHPh), 6.8–7.5 (m, Ph); ^{13}C NMR (C_6D_6) δ 27.56 (s, Me), 46.04 (d, ^1J(C–P) = 39.3 Hz, PCH_2), 51.9 (s, CMe_3), 53.43 (d, ^2J(C–P) = 9.6 Hz, *C*HPh), 198.12 (d, ^2J(C–P) = 7.0 Hz, cis CO); IR (decalin) ν(CO) 2070 (w), 1950 (m), 1940 (vs) cm^{-1}; mass spectrum (^{184}W), *m/z* (relative intensity) 607 (M^+, 26), 523 (M – 3CO, 26), 467 (M – 5CO, 80), 363 (WP(Ph)NC_4H_9, 100). Anal. Calcd for $C_{23}H_{22}NO_5PW$: C, 45.49; H, 3.65. Found: C, 45.30; H, 3.64.

11b: colorless solid, mp 104 °C; ^{31}P NMR (C_6D_6) δ 127.5 ($^1J(^{31}P–^{183}W)$ = 278 Hz); ^{1}H NMR (C_6D_6) δ 1.06 (s, 9 H, *t*-Bu), 3.7 (m, 2 H, CH_2), 3.97 (pseudo q, ^3J(H–P) $\simeq$ ^3J(H–H) = 7 Hz, 1 H, CHPh), 7.0–7.9 (m, Ph) (^{1}H NMR recorded at 200.13 MHz); ^{13}C NMR (C_6D_6) δ 27.66 (d, ^3J(C–P= 3.7 Hz, CH_3), 43.39 (d, ^1J(P–C) = 39.1 Hz, PCH_2), 52.54 (s, CMe_3), 55.41 (d, ^2J(C–P) = 10.0 Hz, *C*HPh), 197.34 (d, ^2J(C–P) = 7.4 Hz, cis CO), 199.03 (d, ^2J(C–P) = 25.9 Hz, trans CO); IR (decalin) ν(CO) 2075 (m), 1950 (sh), 1945 (vs) cm^{-1}; mass spectrum (^{184}W), *m/z* (relative intensity) 607 (M^+, 29), 579 (M^+ – CO, 15), 523 (M^+ – 3CO, 26), 467 (M^+–5CO, 100), 363 (WP(Ph)NC_4H_9, 87). Anal. Calcd for $C_{23}H_{22}NO_5PW$: C, 45.49; H, 3.65; N, 2.31; P, 5.10; W, 30.28. Found: C, 45.71; H, 3.45; N, 2.34; P, 5.15; W, 30.19.

Registry No. **1**, 82265-64-3; **2**, 82265-65-4; **3**, 82888-50-4; **4**, 82888-51-5; **5** isomer I, 88080-15-3; **5** isomer II, 88000-32-2; **6** isomer I, 109976-31-0; **6** isomer II, 110043-34-0; **9**, 109976-32-1; **10**, 88000-33-3; **11a**, 109976-33-2; **11b**, 109976-34-3; phenyloxirane, 96-09-3; *trans*-2,3-diphenylthiirane, 57694-36-7; 1-*tert*-butyl-2-phenylaziridine, 18366-49-9.

Reactions of $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$. H_2 Displacement by CO and H_2 Elimination Following Deprotonation

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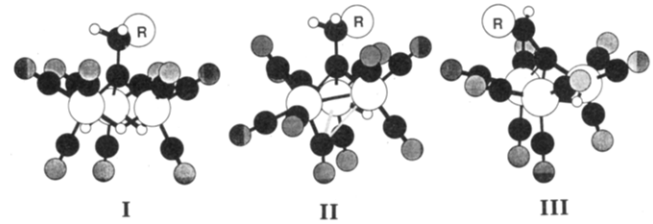
The conversion of $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ (I) to $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-CO})CCH_3$ (II) and the reverse reaction have been carried out via both direct and indirect routes. Direct H_2 displacement by CO and the reverse occur at 60 °C and 1–4 atm of pressure in an equilibrium process for which the equilibrium constant has been measured. The indirect route involves deprotonation of I in a reaction which is first order in I and first order in base. This is followed by a spontaneous, first-order cluster "oxidation" via H_2 elimination from an intermediate anion to yield $[(\mu\text{-H})Fe_3(CO)_9(CCH_2)]^-$ (III). Protonation of III followed by CO addition leads to II. On the other hand, protonation in the presence of H_2 at 1 atm of pressure leads to "reduction" of cluster III to I. These reactions are probed with isotopic labeling experiments that serve to define the mechanism for the indirect route relative to sites of deprotonation and dehydrogenation. Spectroscopic and kinetic evidence for the existence of intermediates in both processes is presented.

Although the metal cluster–metal surface analogy[1] has provided structural insight into the properties of organic fragments bound to multinuclear metal sites, it is perhaps most valuable in the area of chemical reactivity. Catalysts promote reactions, and, as has been pointed out in recent work,[2] stable structures need not be important species on a reaction pathway; i.e., characterized cluster complexes need not be relevant to a given reaction process. On the other hand, those aspects of a chemical reaction facilitated by interaction with more than a single metal atom will be important on surfaces as well as clusters. Hence, metal clusters provide a means of conveniently and clearly defining reactivity promoted by coordination to a multinuclear site.[3]

Due to the abundance of trinuclear systems that have been prepared and characterized,[4] reactions of organic fragments coordinated to the trimetal sites provided by these clusters constitute the most systematically studied systems.[5] For example, studies of the reactions of capped triosmium,[6,7] triruthenium,[8] triiron,[9–12] and mixed-metal

Chart I



I II III

clusters[13,14] have already revealed considerable information on reaction type. These studies clearly demonstrate the ease of making and breaking metal and main-group element bonds to hydrogen on the clusters.[5] However, there is more to reactivity than product definition or even stoichiometry, and research reports on mechanistic aspects of cluster reactivity are appearing more frequently.[15–18]

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