Organometallics 1986, *5*, 1161–1167

^1J(P–H) ≃ 350 Hz, 1 H, PH); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 604 (M$^+$, 38), 520 (M – 3CO, 12), 492 (M – 4CO, 15), 464 (M – 5CO, 8), 436 (M – 5CO – $\mathrm{H_2C{=}CH_2}$, 97), 400 (M – 5CO – $\mathrm{CH_2CH_2Cl}$, 30), 280 (ferrocenyl–$\mathrm{PCH_2CH_2Cl}$, 86), 217 (ferrocenyl–P, 100), 186 (ferrocene, 50). Anal. Calcd for $\mathrm{C_{17}H_{14}ClFeO_5PW}$: C, 33.78; H, 2.34; Cl, 5.87; P, 5.13; W, 30.42. Found: C, 33.39; H, 2.26; Cl, 5.55; P, 5.45; W, 30.82.

(Ferrocenylmethylphosphine)pentacarbonylmolybdenum (8). **2** (2.0 g, 3.97 mmol) was reacted with ferrocene (2.21 g, 11.9 mmol) in the presence of CuCl in toluene (4 mL) at 65 °C for 13 h. Ferrocene was removed by chromatography with hexane; **8** was isolated with hexane/$\mathrm{CH_2Cl_2}$ (90:10) and recrystallized from hexane: yield 0.47 g (25.3%) of brown crystals; mp 68 °C; ^{31}P NMR ($\mathrm{CH_2Cl_2}$) δ –38.3 (^{1}J(^{1}H–^{31}P) = 329.6 Hz); IR (decalin) ν(CO) 2064 (w), 1944 (s) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.17 (pseudo-t, ^3J(H–H) = 6.53 Hz, ^1J(P–H) ≃ 6.8 Hz, 3 H, $\mathrm{CH_3}$), 3.89–4.06 (m, $\mathrm{C_5H_4}$), 3.95 (s, $\mathrm{C_5H_5}$) (9 H), 4.87 (dq, ^1J(P–H) = 331.05 Hz, 1 H, PH); mass spectrum (EI, 70 eV, ^{98}Mo), *m/e* (relative intensity) 470 (M$^+$, 20), 386 (M – 3CO, 11), 330 (M – 5CO, 21), 314 (M – 5CO – $\mathrm{CH_4}$, 48), 232 (ferrocenyl–PHMe, 99), 217 (ferrocenyl–PH, 100), 186 (ferrocene, 41), 121 (CpFe, 55). Anal. Calcd for $\mathrm{C_{16}H_{13}FeMoO_5P}$: C, 41.06; H, 2.80; Fe, 11.93; Mo, 20.50; P, 6.62. Found: C, 41.23; H, 2.78; Fe, 11.95; Mo, 20.62; P, 6.47.

(Dimethylferrocenylphosphine)pentacarbonyltungsten (10). **7b** (0.42 g, 0.76 mmol) was metalated with 1.55 M butyllithium (0.49 mL, 0.76 mmol) in 30 mL of THF at –78 °C. After 15 min, MeI (0.11 g, 0.76 mmol) was added, and the mixture was warmed up to room temperature. Chromatography with $\mathrm{CH_2Cl_2}$ yielded a yellow oil which was crystallized from hexane: yield 0.33 g (76%); mp 56 °C; ^{31}P NMR ($\mathrm{CH_2Cl_2}$) δ –30.8 (^1J(^{31}P–^{183}W) = 251.47 Hz); IR (Nujol) ν(CO) 2064 (w), 1943 (s) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.38 (d, ^2J(P–H) = 7.32 Hz, 6 H, $\mathrm{CH_3}$), 3.94 (s, $\mathrm{C_5H_5}$), 3.86–4.0 (m, $\mathrm{C_5H_4}$) (9 H); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 570 (M$^+$, 90), 486 (M – 3CO, 66), 430 (M – 5CO, 100), 400 (M – 5CO – $\mathrm{2CH_3}$, 51), 246 (ferrocenyl–$\mathrm{PMe_2}$, 54), 231 (ferrocenyl–PMe, 36). Anal. Calcd for $\mathrm{C_{17}H_{15}FeO_5PW}$: C, 35.82; H, 2.65; Fe, 9.80; P, 5.43. Found: C, 35.77; H, 2.52; Fe, 9.74; P, 5.38.

(Ferrocenylmethylpivaloylphosphine)pentacarbonyltungsten (11). **7b** (0.35 g, 0.63 mmol) was metalated with 1.5 M butyllithium (0.42 mL, 0.63 mmol) in 20 mL of THF at –78 °C. After 30 min, pivaloyl chloride (0.09 g, 0.76 mmol) was added, and the mixture was warmed up to room temperature. Chromatography with pentane/$\mathrm{CH_2Cl_2}$ (70:30) yielded an orange solid which was washed with pentane: yield 0.39 g (97%); mp 148 °C; ^{31}P NMR ($\mathrm{CH_2Cl_2}$) δ –0.12 (^1J(^{31}P–^{183}W) = 227.0 Hz); IR (decalin) ν(CO) 2065 (w), 1948 (sh), 1941 (s) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.97 (s, 9 H, $\mathrm{C_4H_9}$), 1.90 (d, ^2J(P–H) = 6.84 Hz, 3 H, $\mathrm{CH_3}$), 3.66 (m, 1 H, CH_α), 3.95 (s, 5 H, $\mathrm{C_5H_5}$), 3.99 (m, 2 H, $\mathrm{CH}_{\beta\beta'}$), 4.50 (m, 1 H, $\mathrm{CH}_{\alpha'}$); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 640 (M$^+$, 12), 555 (M – 3CO – H, 32), 499 (M – 5CO, 41), 471 (M – 6CO – H, 22), 443 (M – 5CO – $\mathrm{C_4H_9}$, 14), 415 (M – 6CO – $\mathrm{C_4H_9}$, 48), 399 (M – 6CO – $\mathrm{C_4H_9}$ – $\mathrm{CH_4}$, 29), 231 (ferrocenyl–PMe, 100). Anal. Calcd for $\mathrm{C_{21}H_{21}FeO_6PW}$: C, 39.41; H, 3.31; Fe, 8.73; P, 4.84. Found: C, 39.31; H, 3.32; Fe, 8.73; P, 4.92.

(1-Ferrocenylphosphirane)pentacarbonyltungsten (12). To a solution of **7c** (0.36 g, 0.6 mmol) in 50 mL of THF at –78 °C was added 1.5 M butyllithium (0.4 mL, 0.6 mmol). After 30 min, the mixture was slowly warmed up to room temperature. **12** was isolated by chromatography with $\mathrm{CH_2Cl_2}$ as an orange oil, which crystallized upon standing at –20 °C. Recrystallization from hexane yielded 0.28 g (81%): mp 85 °C; ^{31}P NMR ($\mathrm{CH_2Cl_2}$) δ –195.8 ppm (^1J(^{31}P–^{183}W) = 261.2 Hz); IR (Nujol) ν(CO) 2066 (w), 1943 (s) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.95 (m, 4 H, $\mathrm{CH_2CH_2}$), 3.75–3.95 (m, 4 H, $\mathrm{C_5H_4}$), 3.99 (s, 5 H, $\mathrm{C_5H_5}$); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 568 (M$^+$, 34), 540 (M – CO, 21), 484 (M – 3CO, 27), 456 (M – 4CO, 30), 428 (M – 5CO, 52), 400 (M – 5CO – $\mathrm{C_2H_4}$, 93), 335 (M – 5CO – $\mathrm{C_2H_4}$ – $\mathrm{C_5H_5}$, 11), 244 (ferrocenyl–P($\mathrm{CH_2CH_2}$), 20), 216 (ferrocenyl–P, 100). Anal. Calcd for $\mathrm{C_{17}H_{13}FeO_5PW}$: C, 35.95; H, 2.31; Fe, 9.83; P, 5.45; W, 32.37. Found: C, 36.25; H, 2.41; Fe, 9.84; P, 5.56; W, 32.19.

Registry No. **1a**, 83603-06-9; **1b**, 83603-07-0; **1c**, 101200-20-8; **2**, 101200-21-9; **7a**, 101200-13-9; **7b**, 101200-14-0; **7c**, 101200-15-1; **8**, 101200-16-2; **10**, 101200-17-3; **11**, 101200-18-4; **12**, 101200-19-5; CuCl, 7758-89-6; ferrocene, 102-54-5; pivaloyl chloride, 3282-30-2.

A Preliminary Chemical Study of Terminal Allyl-, 3-Butenyl-, and 4-Pentenylphosphinidene Complexes. Thermal Rearrangement of 1-Allylphosphirene Complexes by Insertion of the Allylic C=C Double Bond into the Phosphirene Ring

Jürgen Svara, Angela Marinetti, and François Mathey*

Laboratoire CNRS-SNPE, BP No. 28, 94320 Thiais, France

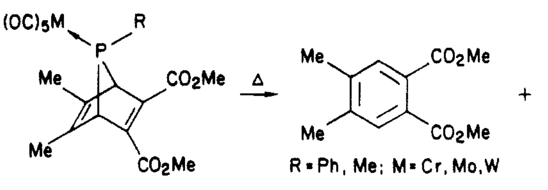
Received July 11, 1985

The reaction of dimethyl acetylenedicarboxylate with the appropriate phosphole complexes leads to the 7-allyl-, 7-(3-butenyl)-, and 7-(4-pentenyl)-7-phosphanorbornadiene P–W(CO)$_5$ complexes. In the 3-butenyl case, it is necessary to use a large excess of acetylenedicarboxylate in order to avoid an intramolecular [4 + 2] cycloaddition between the phosphole dienic system and the double bond of the butenyl P substituent. The thermal decomposition of the 7-phosphanorbornadiene complexes leads to the corresponding terminal phosphinidene tungsten pentacarbonyl complexes. The pentenylphosphinidene complex undergoes an internal cycloaddition involving the phosphorus atom and the C=C double bond to give a bicyclic phosphirane complex. The terminal allylphosphinidene complex reacts with olefins and acetylenes to give the expected phosphirane and phosphirene complexes. In the latter case, however, additional heating induces a brand new insertion of the allylic double bond within the phosphirene cycle leading to a new type of bicyclic phosphirane complex. The postulated mechanism implies an equilibrium between phosphirene complexes and 1-metalla-2-phosphacyclobutenes at high temperature. No such insertion has been observed with 1-(3-butenyl)phosphirene complexes nor with an external olefin and a phosphirene complex.

In a series of recent papers,[1-4] we demonstrated that it was possible to generate transient terminal phenyl- and methylphosphinidene complexes by thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene

0276-7333/86/2305-1161$01.50/0

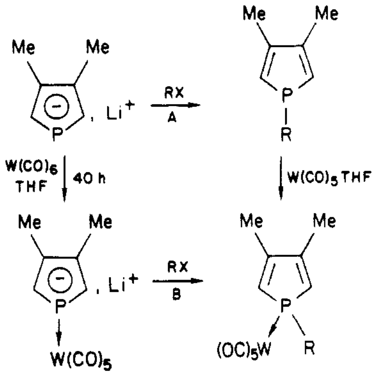
complexes (eq 1). These terminal phosphinidene complexes were trapped by alcohols,[2] alkenes,[3] alkynes,[1] and so on. In a subsequent step, it appeared quite logical to us to install a reactive functionality within the R group in order to investigate its interaction with the phosphinidene phosphorus. Along this line, we undertook the study of terminal phosphinidene complexes bearing an olefinic functionality at various distances from the phosphorus center. The results of this study are reported here.



$[RP{=}M(CO)_5]$ (1)

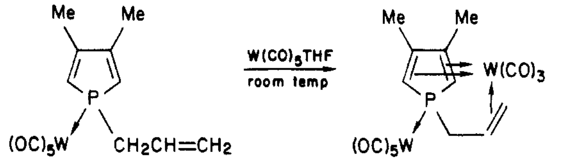
Results and Discussion

For practical reasons, we decided to restrict ourselves to the study of tungsten pentacarbonyl complexes. According to the previously described general scheme,[5] it was first necessary to prepare the appropriate phosphole tungsten pentacarbonyl complexes. This was achieved by two different routes, both starting from (3,4-dimethylphospholyl)lithium (eq 2). Route B is by far better than route A. However, its final yield is highly dependent on the method which is used for preparing the starting phospholyllithium. This anion is obtained by cleavage of the phosphorus–phenyl bond of 1-phenyl-3,4-dimethylphosphole[6] with lithium in THF. The phenyllithium which is a byproduct of the reaction must be destroyed by carefully controlled amounts of anhydrous $AlCl_3$ and *tert*-butyl chloride for optimum final yields (see Experimental Section). When this series of experiments was performed we unexpectedly discovered that 1-allyl-3,4-dimethylphosphole was able to chelate a metal between its dienic system and its allyl group. This observation was made when conducting the complexation of the free phosphole with an excess of $W(CO)_5THF$ (last step of route A). This excess reacts at room temperature with complex 1 to afford a new red complex (eq 3) to which we ascribed the chelate structure 4 on the following basis. The experimental formula of 4 was established by elemental and mass spectral analysis (CI, CH_4, ^{184}W): m/e (relative intensity) 744 (M, 97), 743 (M − H, 100), 475 (743 − $W(CO)_5$, 72). The high-field resonances (^1H and ^{13}C NMR) of the CH groups of the phosphole ring demonstrate the π-complexation of the dienic system. The olefinic CH_2 of the allyl group resonates at ca. δ 3.85 (^1H) and 72.46 (^{13}C) [vs. ca. δ 4.92 (^1H) for 1], in agreement with the complexation of the double bond. The aliphatic protons of the CH_2P group show a more pronounced inequivalency in 4 (δ 1.78 and 2.46) than in 1 (δ 2.30 and 2.39) due to the blocked rotation of the allyl group around the CH_2–P bond in 4. Finally, the *mer* configuration around $W(CO)_3$ is suggested by the strong inequivalency of the two sides of the phospholyl ring (δ (C*H*) 2.27 and 3.23).



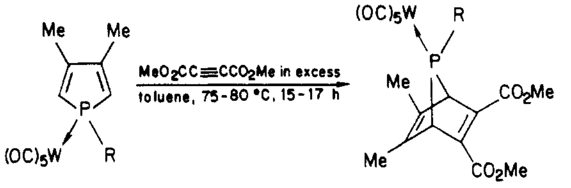
(2)

R = $CH_2CH{=}CH_2$, 1, route A, 25%; route B, 80%; R = $CH_2CH_2CH{=}CH_2$, 2, route B, 76%; R = $CH_2CH_2CH_2CH{=}CH_2$, 3, route B, 72%



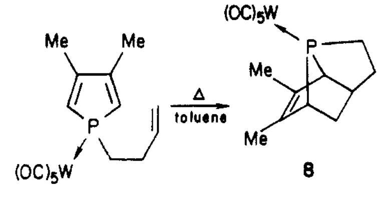
1 4 (3)

Always following the general scheme, we then studied the reaction of the phosphole complexes 1–3 with dimethyl acetylenedicarboxylate in excess at ca. 75 °C in toluene. Thus we obtained the expected 7-phosphanorbornadiene complexes in fair yields (eq 4). Once again, we discovered an unexpected reaction, here in the butenyl case. Indeed, upon heating in toluene, complex 2 undergoes an intramolecular Diels–Alder cycloaddition leading to the tricyclic complex 8 (eq 5). The elemental analysis and the mass spectrum of 8 [(EI, 70 eV, ^{184}W), m/e (relative intensity) 490 (M, 56)] demonstrate that 8 has the same empirical formula as 2. The ^1H NMR spectrum shows no olefinic proton, and the ^{13}C spectrum shows three aliphatic CH groups (δ 38.53, 52.13, 56.86; J(C–P) = 17, 25.6, 28.1 Hz) and three aliphatic CH_2 groups (δ 25.60, 33.23, 37.11; J(C–P) = 11, 3.7, 3.7 Hz), thus establishing that intramolecular cycloaddition has taken place. In order to avoid this side reaction and to obtain a good yield of the norbornadiene complex 6, it is necessary to perform the cycloaddition of 2 with a huge excess (fivefold) of acetylenedicarboxylate.



(4)

R = $CH_2CH{=}CH_2$, 5, 70%; R = $CH_2CH_2CH{=}CH_2$, 6, 70%; R = $CH_2CH_2CH_2CH{=}CH_2$, 7, 65%



2 8 (5)

Having these three P-functional 7-phosphanorbornadiene complexes (5–7) in hand, we then studied their thermal decomposition. Whereas no clean reaction was observed with 5 in the presence of copper(I) chloride at ca. 60 °C, decomposition of 5 in boiling toluene produced,

---

[1] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

[2] Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

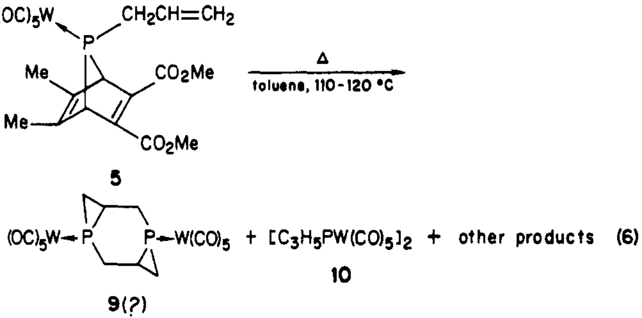
[3] Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456; **1984**, *3*, 1492.

[4] Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

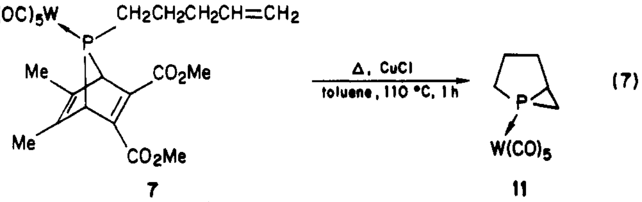
[5] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

[6] Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

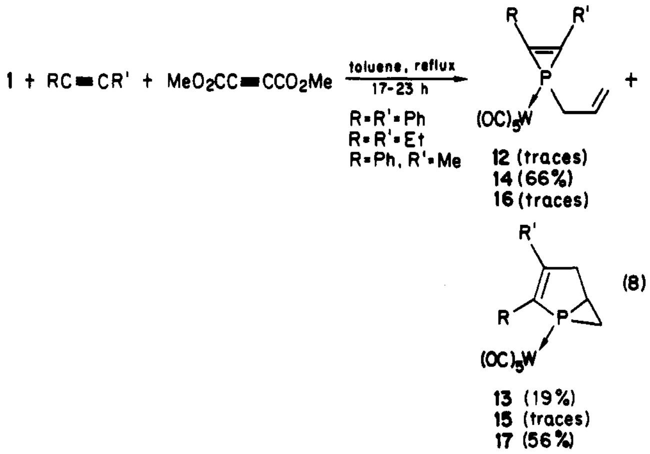
among other products, two dimers, **9** and **10**, of the transient allylphosphinidene tungsten pentacarbonyl complex (eq 6). Both **9** and **10** show a molecular peak at *m/e* 792 on their mass spectra (^{184}W). According to the ^{31}P NMR and IR spectra, the minor dimer **9** appears to be fully symmetrical whereas **10** appears to have two different tungsten atoms. The formula proposed for **9** is only tentative. The presence of the phosphirane rings is suggested by the high-field shift of the phosphorus resonance ($\delta(^{31}P)$ – 200) and by the presence of two types of highly shielded carbons at 12.35 and 14.49 ppm. In view of the very low yields of their syntheses (ca. 2 and 7%), we have not investigated these products further.

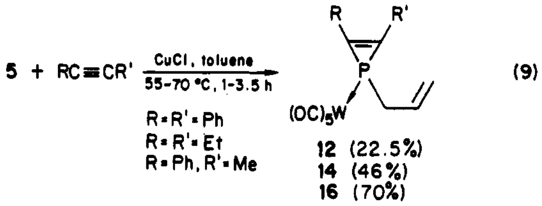


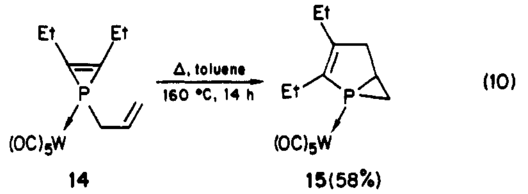
A more useful result was obtained when **7** was decomposed. According to ^{31}P NMR, this reaction led to the quantitative formation of the original bicyclic complex **11** (eq 7). In fact, complex **11** is always a byproduct of the synthesis of **7**. The empirical formula of **11** was easily established by elemental analysis and mass spectrometry (EI, 70 eV, ^{184}W): *m/e* (relative intensity) 424 (M, 64), 310 (100). The presence of the three-membered ring was indicated by the high-field shift of the ^{31}P resonance ($\delta(^{31}P)$ – 175). Finally, the ^{13}C NMR spectrum showed five sp^3-carbon resonances, including two at high field corresponding to the carbons of the three-membered ring and one at low field corresponding to the CH$_2$P group of the five-membered ring [$\delta(CH_2)$ 9.09 (^1J(C–P) = 14.6 Hz), δ(CH) 21.84 (^1J(C–P) = 15.8 Hz), and $\delta(CH_2)$ 26.9 (^1J(C–P) = 17.1 Hz)]. Apparently, the self-condensation of the transient terminal (4-pentenylphosphinidene)tungsten pentacarbonyl complex leading to **11** is so fast that it is impossible to trap it with external reagents such as alkynes. Our study of the reactivity of alkenylphosphinidene complexes was thus restricted to the allyl and 3-butenyl cases using **5** and **6** as generators.



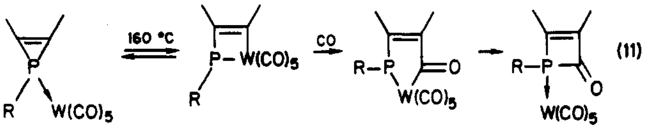
We first prepared a series of 1-allylphosphirene complexes **12**, **14**, and **16**, either through the direct reaction of a mixture of alkyne and dimethyl acetylenedicarboxylate with complex **1** according to a modified procedure described elsewhere[7] (eq 8) or by reaction of **5** with alkynes according to the classical procedure[1] (eq 9). The low-temperature catalytic process (eq 9) afforded the expected phosphirene complexes, thus showing that (allylphosphinidene)pentacarbonyltungsten displays a normal reactivity. Quite unexpectedly, however, the high-temperature direct process (eq 8) afforded, besides the same phosphirene complexes, new bicyclic phosphine complexes **13**, **15**, and **17** in variable yields according to the substitution scheme of the alkyne. We immediately checked that **13**, **15**, and **17** were produced by thermal rearrangement of **12**, **14**, and **16**, respectively. For example, when heated at 160 °C for 14 h in a sealed tube, the allylphosphirene complex **14** is indeed converted into the bicyclic phosphine complex **15** (eq 10). The experimental formula of **15** was established by elemental analysis and mass spectrometry (EI, 70 eV, ^{184}W): *m/e* (relative intensity) 478 (M, 29), 394 (M – 3CO, 40), 392 (64), 28 (CO, 100). The presence of the three-membered ring was indicated by the high-field shift of the ^{31}P resonance ($\delta(^{31}P)$ –154.3 in CDCl$_3$). The ^{1}H NMR spectrum of **15** showed only aliphatic protons, and the ^{13}C NMR spectrum displayed two sp^2-carbon resonances at 135.07 [^1J(C–P) = 25.6 Hz] and 149.97 ppm [^2J(C–P) = 6.1 Hz] together with two sets of resonances corresponding to the CH [δ 16.90 (^1J(C–P) = 8.5 Hz)] and CH$_2$ groups of the three-membered ring. In the case of the bicyclic phosphine complex **17**, the low value of the H···P coupling of the methyl group [^4J(H–P) = 1.2 Hz] demonstrated the β-substitution.







In other work,[8] we have recently demonstrated that it was possible to insert carbon monoxide into the three-membered ring of the phosphirene complexes. We postulated a mechanism involving an equilibrium between the phosphirene complex and the 1,2-metallaphosphacyclobutene at high temperature (eq 11). This mechanism suggested that it was possible to insert other small molecules within the phosphirene ring. In that respect, our present work describing the first intramolecular

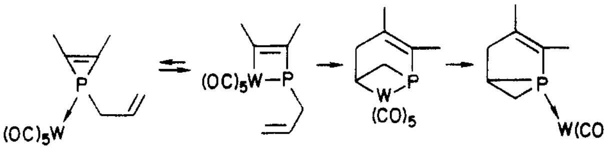


---

[7] Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700.

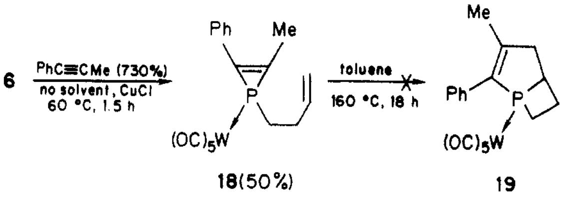
[8] Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.

insertion of an olefin into the phosphirene cycle can be considered as support for our initial hypothesis (eq 12).



(12)

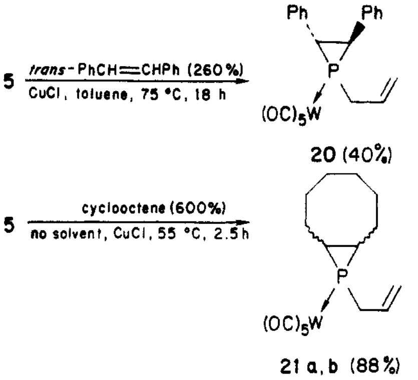
However, this type of insertion is apparently not a highly favored reaction since we found that is was impossible to insert an external olefin into the phosphirene complexes under the same experimental conditions even when a large excess of the olefin was used. In order to check if it was nevertheless possible to extend the scope of this insertion, we prepared the butenylphosphirene complex 18 (eq 13).



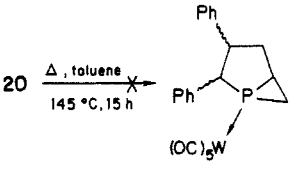
(13)

With use of the same experimental conditions as for the conversion of **14** into **15**, the rearrangement of **18** into **19** failed. The insertion was probably disfavored because a four-membered ring would be formed.

We finally checked whether or not it was possible to generalize the allyl insertion to the case of the saturated phosphirane ring. For that purpose, we prepared two 1-allylphosphirane complexes, **20** and **21**, according to the classical route[3] (eq 14). The attempted insertion of the allyl group into the phosphirane cycle of complex **20** was unsuccessful (eq 15). Only decomposition was observed, suggesting that the failure was due to the low thermal stability of the complex.



(14)



(15)

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 VG 30 F and VG 70-70 F spectrometers 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, Merck).

(1-Allyl-3,4-dimethylphosphole)pentacarbonyltungsten (1). Route A. A solution of 1-phenyl-3,4-dimethylphosphole (1.88 g, 10 mmol) in 70 mL of freshly distilled THF was stirred at room temperature with 0.35 g (50 mmol) of cut lithium wire for 3–4 h. The reaction was completed when the $^{31}P\{^1H\}$ NMR spectrum of the dark colored solution showed only the peak of (3,4-dimethylphospholyl)lithium at +55 ppm. Unreacted lithium was removed, and $AlCl_3$ (0.45 g, 3.33 mmol) was added. After being stirred for 30 min the solution was cooled to −40 °C and 0.76 g (10 mmol) of allyl chloride was added. After being warmed to room temperature, this solution was reacted (1 h) with $W(CO)_5 \cdot THF$ (prepared by irradiation of 3.52 g (10 mmol) of $W(CO)_6$ in 200 mL of THF). The solvent was evaporated and the residue chromatographed on a 20 × 2 cm column. **1** was eluted with hexane/toluene (95:5) (1.19 g, 25%): yellow solid; mp 49.5 °C (hexane); ^{31}P NMR (CH_2Cl_2) δ 3.5 ($^1J(^{31}P-^{183}W) = 212.4$ Hz); IR (decalin) ν(CO) 2064 (m), 1941 (vs), 1910 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.55 (dd, $^4J(H-H) = 0.98$ Hz, $^4J(P-H) \approx 0.9$ Hz, 6 H, CH_3), 2.34 (dd, $^2J(P-H) = 7.8$ Hz, $^3J(H-H) = 7.08$ Hz, 2 H, PCH_2), 4.6–5.5 (m, 3 H, $CH{=}CH_2$), 5.86 (dq ≈ dd, $^2J(P-H) = 36.63$ Hz, 2 H, CH(ring)); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 476 (M, 52), 407 (M − CO − C_3H_5, 57), 379 (M − 2CO − C_3H_5, 85), 349 (M − 3CO, C_3H_5, 100), 334 (M − 4CO − 2CH_3, 54), 321 (M − 5CO − CH_3, 41), 293 (M − 4CO − 2CH_3 − C_3H_5, 68), 265 (M − 5CO − 2CH_3 − C_3H_5, 26). Anal. Calcd for $C_{14}H_{13}O_5PW$: C, 35.22; H, 2.75; P, 6.51; W, 38.62. Found: C, 35.60; H, 2.75; P, 6.49; W, 38.13.

The byproduct **4** could be eluted with hexane/toluene (85:15) as an orange oil which solidified upon standing. Recrystallization from hexane yielded 0.22 g (3%) or orange crystals: mp 123 °C dec; ^{31}P NMR (C_6D_6) δ 162.3 ($^1J(^{31}P-^{183}W) = 200.2$ Hz); IR (decalin) ν(CO) 2063 (vw), 2004 (m), 1952 (m), 1939 (s), 1921 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.78 (ddd, $^2J(H-H) = 14.4$ Hz, $^3J(H-H) = 6.1$ Hz, $^2J(H-P) \approx 5$ Hz, 1 H, $^1/_2CH_2$), 2.06 (s, 3 H, CH_3), 2.15 (d, $^4J(H-H) = 1.22$ Hz, 3 H, CH_3), 2.27 (dd, $^2J(H-P) = 23.93$ Hz, $^4J(H-H) = 2.69$ Hz, 1 H, C–H(ring)), 2.46 (ddd, $^3J(H-H) = 7.0$ Hz, $^2J(H-P) = 3.2$ Hz, 1 H, $^1/_2CH_2$), 3.23 (dd, $^2J(H-P) = 21.0$ Hz, 1 H, C–H(ring)), 3.75–3.95 (m, 2 H, $=CH_2$), 5.9–6.4 (m, 1 H, CH=); ^{13}C NMR (C_6D_6) 16.24 (s, CH_3), 46.26 (d, $^1J(C-P) = 28.08$ Hz, CH_2P), 59.16 (d, $^1J(C-P) = 42.73$ Hz, C_α), 60.13 (d, $^1J(C-P) = 35.4$ Hz, $C_{\alpha'}$), 72.46 (s, $=CH_2$), 109.45 (d, $^2J(C-P) = 13.43$ Hz, C_β), 111.7 (d, $^2J(C-P) = 14$ Hz, $C_{\beta'}$), 112.72 (d, $^2J(C-P) = 11.0$ Hz, CH=), 198 (CO_{eq}, $W(CO)_5$), 202 (CO_{ax}, $W(CO)_5$), 214.0, 215.8, 220.0 ppm ($W(CO)_3$); mass spectrum (CI, CH_4, ^{184}W), *m/e* (relative intensity) 744 (M, 97), 716 (M − CO, 78), 688 (M − 2CO, 15), 660 (M − 3CO, 13), 632 (M − 4CO, 14), 476 (M − $W(CO)_3$, 72), 448 (M − $W(CO)_4$, 16), 435 (M − $W(CO)_3$ − C_3H_7, 35), 420 (M − $W(CO)_5$, 18), 407 (M − $W(CO)_4$ − C_3H_7, 12), 392 (M − $W(CO)_6$, 49), 379 (M − $W(CO)_5$ − C_3H_7, 46). Anal. Calcd for $C_{17}H_{13}O_8PW_2$: C, 27.45; H, 1.76; P, 4.16. Found: C, 28.01; H, 1.66; P, 5.03.

Route B. To a stirred solution of phospholyllithium (see route A), prepared from 17.36 g (92.24 mmol) of 1-phenyl-3,4-dimethylphosphole and 1.5 g (216 mmol) of lithium in 200 mL of THF, was added first 3.07 g (23.06 mmol) of $AlCl_3$ at 0 °C, followed after 20 min by 2.14 g (23.06 mmol) of *tert*-butyl chloride. After the solution was warmed to room temperature, solid $W(CO)_6$ (32.5 g (92.24 mmol)) was added and the mixture stirred for 40 h. The reaction can be followed by ^{31}P NMR spectroscopy (δ(phospholyllithium–$W(CO)_5$) −55). Then 11.16 g (92.24 mmol) of allyl bromide was added to the solution at −60 °C, and the mixture was stirred for 1 h. Evaporation of the solvent and chromatography of the brown residue with hexane/CH_2Cl_2 (90:10) yielded 35.4 g (80%) of **1** as yellow solid.

(1-(3-Butenyl)-3,4-dimethylphosphole)pentacarbonyltungsten (2). Compound **2** was prepared from 13.94 g (74.07 mmol) of phosphole, 1.5 g (216 mmol) of lithium, 2.47 g (18.72 mmol) of $AlCl_3$, 1.71 g (18.72 mmol) of *tert*-butyl chloride, 26.07 g (74.07 mmol) of $W(CO)_6$, and 10 g (74.07 mmol) of 4-bromobutene-1 in 250 mL of THF as described for **1**. After chromatography with hexane we obtained 27.5 g (76%) of **2** as yellow solid: mp 35 °C (hexane); ^{31}P NMR (toluene) δ 4.3 ($^1J(^{31}P-^{183}W) = 209.9$ Hz); IR (decalin) ν(CO) 2056 (m), 1931 (vs), 1907 (vw) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.58 (dd, $^4J(H-H) \approx {}^4J(P-H) \approx 1$ Hz, 6 H, CH_3), 1.76 (m, 4 H, $(CH_2)_4$), 4.75–5.0 (m, 2 H, $=CH_2$), 5.2–5.7 (m, 1 H, CH=), 5.85 (dq ≈ dd, $^2J(P-H) = 36.6$ Hz, $^4J(H-H) \approx 0.73$ Hz); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 490 (M, 24), 407 (M − CO − C_4H_7, 24), 406 (M − 3CO, 21), 378

(M – 4CO, 27), 350 (M – 5CO, 78), 348 (M – 4CO – $2CH_3$, 100), 320 (M – 5CO – $2CH_3$, 32), 293 (M – 4CO – $2CH_3$ – C_4H_7, 34), 265 (M – 5CO – $2CH_3$ – C_4H_7, 14). Anal. Calcd for $C_{15}H_{15}O_5PW$: C, 36.76; H, 3.09; P, 6.32; W, 37.51. Found: C, 36.94; H, 3.09; P, 6.36; W, 37.22.

(3,4-Dimethyl-1-(4-pentenyl)phosphole)pentacarbonyltungsten (3). Compound **3** was prepared from 7.95 g (42.27 mmol) of phosphole, 0.75 g (108 mmol) of lithium, 1.41 g (10.6 mmol) of $AlCl_3$, 0.38 g (10.6 mmol) of *tert*-butyl chloride, 14.87 g (42.27 mmol) of $W(CO)_6$, and 6.3 g (42.27 mmol) of 5-bromopentene-1 in 150 mL of THF as described for **1**. Chromatography of the crude product with heptane yielded 15.5 g (72%) of **3** as yellow oil, which crystallized upon standing at –20 °C: mp 20 °C; ^{31}P NMR (hexane) δ 6.0 ($^1J(^{31}P{-}^{183}W) = 212.4$ Hz); IR (decalin) ν(CO) 2063 (m), 1966 (w), 1940 (vs), 1906 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.0–1.9 (m, 6 H, $(CH_2)_3$, 1.58 (dd, $^4J(H{-}H) \approx {}^4J(P{-}H) \approx 1$ Hz, 6 H, CH_3), 4.7–5.1 (m, 2 H, $=CH_2$), 5.2–5.8 (m, 1 H, CH=), 5.89 (dq ≈ dd, $^2J(P{-}H) = 36.62$ Hz, $^4J(H{-}H) \approx 0.8$ Hz, 2 H, CH(ring)); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 504 (M, 32), 407 (M – C_5H_9 – CO, 46), 379 (M – C_5H_9 – 2CO, 51), 362 (M – 4CO – $2CH_3$, 91), 351 (M – C_5H_9 – 3CO, 35), 323 (M – C_5H_9 – 4CO, 20), 295 (M – C_5H_9 – 5CO, 25), 265 (M – C_5H_9 – 5CO – $2CH_3$, 15). Anal. Calcd for $C_{16}H_{17}O_5PW$: C, 38.12; H, 3.40; P, 6.14; W, 36.47. Found: C, 38.54; H, 3.33; P, 5.91; W, 34.83.

(7-Allyl-2,3-bis(methoxycarbonyl)-5,6-dimethyl-7-phosphanorbornadiene)pentacarbonyltungsten (5). A mixture of **1** (2.37 g, (4.98 mmol) and dimethyl acetylenedicarboxylate (DMAD) (2.83 g (19.91 mmol)) in 5 mL of toluene was heated at 70 °C for 16 h. The solvent was evaporated and the dark residue chromatographed with pentane/CH_2Cl_2 (70:30): yield 2.06 g (70%); yellow needles (hexane); mp 117 °C; ^{31}P NMR (CH_2Cl_2) δ 205.2 ($^1J(^{31}P{-}^{183}W) = 239$ Hz); IR (decalin) ν(CO) 2065 (w), 1952 (sh), 1944 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 1.64 (d, $^4J(P{-}H) = 1.47$ Hz, 6 H, CH_3), 2.88 (dd, $^3J(H{-}H) = 7.08$ Hz, $^2J(P{-}H) \approx 6$ Hz, 2 H, CH_2), 3.39 (s, OCH_3) and 3.4 (d, not resolved, CH) (8 H), 6.0–7.1 (m, 3 H, $H_2C{=}CH$); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 618 (M, 0.5), 493 (M – 3CO – C_3H_5, 6), 396 ($(OC)_5W{=}P{-}C_3H_5$, 4), 368 ($(OC)_4W{=}P{-}C_3H_5$, 2), 340 ($(OC)_3W{=}P{-}C_3H_5$, 4), 312 ($(OC)_2W{=}P{-}C_3H_5$, 9), 284 ($OCW{=}P{-}C_3H_5$, 2), 191 ($C_6H_4(COOMe)(CO)$, 100). Anal. Calcd for $C_{20}H_{19}O_9PW$: C, 38.86; H, 3.10; P, 5.01; W, 29.74. Found: C, 39.00; H, 3.07; P, 5.05; W, 29.20.

(2,3-Bis(methoxycarbonyl)-7-(3-butenyl)-5,6-dimethyl-7-phosphanorbornadiene)pentacarbonyltungsten (6). A mixture of **2** (8.61 g (17.58 mmol)) and DMAD (12.48 g (87.84 mmol)) was heated without solvent at 75 °C for 18 h. The crude product was chromatographed first with hexane to remove traces of **8** and then with hexane/CH_2Cl_2 (80:20) to recover **6**. Yellow oil crystallizes from hexane to yield 7.7 g (70%) of yellow solid: mp 77 °C; ^{31}P NMR (CH_2Cl_2) δ 214.1 ($^1J(^{31}P{-}^{183}W) = 234.38$ Hz); IR (decalin) ν(CO) 2065 (m), 1952 (sh), 1945 (vs), 1910 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.66 (d, $^4J(P{-}H) = 1.22$ Hz, 6 H, CH_3), 3.40 (s, OCH_3) and 3.41 (d, not resolved, CH) (8 H), 4.8–5.2 (m, 2 H, $=CH_2$), 5.4–5.9 (m, 1 H, CH=); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 632 (M, 4), 492 (M – 5CO, 9), 410 ($(OC)_5W{=}P{-}C_4H_7$, 25), 382 ($(OC)_4W{=}P{-}C_4H_7$, 47), 354 ($(OC)_3W{=}P{-}C_4H_7$, 65), 326 ($(OC)_2W{=}P{-}C_4H_7$, 38), 298 ($OCW{=}P{-}C_4H_7$, 39), 270 ($W{=}P{-}C_4H_7$, 22), 191 (C_6H_4-(COOMe)(CO), 100). Anal. Calcd for $C_{21}H_{21}O_9PW$: C, 39.90; H, 3.35; P, 4.90; W, 29.08. Found: C, 39.90; H, 3.22; P, 4.88; W, 28.54.

(2,3-Bis(methoxycarbonyl)-5,6-dimethyl-7-(4-pentenyl)-7-phosphanorbornadiene)pentacarbonyltungsten (7). Phosphole **3** (12.67 g (25.13 mmol) was heated with DMAD (5.36 g (37.70 mmol)) at 75 °C for 16 h. By chromatography with hexane/CH_2Cl_2 (60:40) 10.5 g (65%) of **7** was isolated as a yellow oil, which could be crystallized from hexane: mp 47 °C; ^{31}P NMR (CH_2Cl_2) δ 215.1 ($^1J(^{31}P{-}^{183}W) = 234.38$ Hz); IR (decalin) ν(CO) 2059 (m), 1936 (s), 1907 (vw) cm^{-1}; ^1H NMR (C_6D_6) δ 1.66 (d, $^4J(P{-}H) = 1.47$ Hz, 6 H, CH_3); 1.95 (m, 6 H, $(CH_2)_3$), 3.37 (d, $^2J(P{-}H) \approx 2.4$ Hz) and 3.40 (s, OCH_3) (8 H), 4.8–5.1 (m, 2 H, $H_2C{=}$), 5.3–6.0 (m, 1 H, CH=); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity), 646 (M, 0.5), 506 (M – 5CO, 0.7), 424 ($(OC)_5W{=}P{-}C_5H_9$, 11), 396 ($(OC)_4WP{-}C_5H_9$, 12), 368 ($(OC)_3W{=}P{-}C_5H_9$, 18), 340 ($(OC)_2W{=}P{-}C_5H_9$, 18), 312 ($OCW{=}P{-}C_5H_9$, 14), 191 ($C_6H_4(COOMe)(CO)$, 100). Anal. Calcd for $C_{22}H_{23}O_9PW$: C, 40.89; H, 3.59; P, 4.79; W, 28.45. Found: C, 40.98; H, 3.51; P, 4.77; W, 28.02.

(7,8-Dimethyl-1-phosphabicyclo[4.3.0.0^{4,9}]non-7-ene)pentacarbonyltungsten (8). **8** was isolated from the reaction of **2** (3.4 g, 7.14 mmol) with DMAD (3.05 g (21.43 mmol)) in 4 mL of toluene at 80 °C for 20 h by chromatography with hexane. It could be recrystallized from pentane at –20 °C to yield 1.45 g (41%) of colorless crystals. From the same reaction, 1.06 g (24%) of **6** could be isolated by chromatography with hexane/CH_2Cl_2 (80:20). When carried out in the absence of DAMD in toluene, the conversion of **2** into **8** was quantitative after 5 h at 85 °C: mp 72 °C; ^{31}P NMR (CH_2Cl_2) δ 71.4 ($^1J(^{31}P{-}^{183}W) = 229.5$ Hz); IR (decalin) ν(CO) 2064 (m), 1939 (vs), 1909 (w) cm^{-1}; ^1H NMR δ 1.50 (d, $^4J(P{-}H) = 1.46$ Hz, CH_3), 0.8–2.1 (m) cm^{-1}; ^{13}C NMR (C_6D_6) δ 13.54 (d, $^3J(P{-}C) = 3.66$ Hz, CH_3), 14.99 (d, $^3J(P{-}C) = 3.66$ Hz, CH_3), 25.60 (d, $J(P{-}C) = 10.99$ Hz, CH_2), 33.23 (d, $J(P{-}C) = 3.66$ Hz, CH_2), 37.11 (d, $J(C{-}P) = 3.66$ Hz, CH_2), 38.53 (d, $^2J(P{-}C) = 17.09$ Hz, CH), 52.13 (d, $^1J(C{-}P) = 25.64$ Hz, CH bridgehead), 58.86 (d, $^1J(P{-}C) = 28.08$ Hz, CH bridgehead), 130 (d, not resolved, C), 135.08 (d, $^2J(P{-}C) = 10.99$ Hz, C), 197.02 (d, $^2J(P{-}C) = 7.32$ Hz, CO_{eq}), 199.90 (d, $^2J(P{-}C) = 23.19$ Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 490 (M, 56), 434 (M – 2CO, 20), 406 (M – 3CO, 52), 378 (M – 4CO, 74), 376 (M – 3CO – $2CH_3$, 84), 350 (M – 5CO, 59), 348 (M – 4CO – $2CH_3$, 100), 320 (M – 5CO – $2CH_3$, 26). Anal. Calcd for $C_{15}H_{15}O_5PW$: C, 36.76; H, 3.09; P, 6.32; W, 37.51. Found: C, 37.02; H, 3.05; P, 6.32; W, 37.16.

Thermal Decomposition of 5. **5** (4.3 g (6.9 mmol)) in 300 mL of toluene was heated to reflux for 15 h. After evaporation of the solvent, the black residue was chromatographed over a 30 × 2 cm column with hexane/ethyl acetate mixtures of growing polarity. **9** was eluted with hexane/ethyl acetate (90:10). The crude product could be recrystallized from hexane/ethyl acetate to yield 100 mg (1.8%) of light brown needles: mp 180 °C dec; ^{31}P NMR (CH_2Cl_2) δ –198.8 ($^1J(^{31}P{-}^{183}W) = 258.8$ Hz); IR (decalin) ν(CO) 2065 (m), 1950 (s), 1913 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 0.3–0.8 (m, 6 H), 1.2–1.5 (m, 4 H); ^{13}C NMR (CD_2Cl_2) δ 12.35 (pseudo-t, $J(C{-}P) = 11.0$ Hz, CH), 14.49 (d, $J(C{-}P) = 5.5$ Hz, CH_2), 23.77 (t, $J(C{-}P) \approx 3$ Hz); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 792 (M^+, 14), 624 (M – 6CO, 12), 596 (M – 7CO, 16), 568 (M – 8CO, 21), 540 (M – 9CO, 5), 512 (M – 10CO, 16), 408 (M – $W(CO)_5$, 8). Anal. Calcd for $C_{16}H_{10}O_{10}P_2W_2$: C, 24.27; H, 1.27; P, 7.82. Found: C, 23.85; H, 1.28; P, 7.49.

10 was eluted with hexane/ethyl acetate (75:25) and rechromatographed with pentane/CH_2Cl_2 (85:15). Recrystallization from hexane/ethyl acetate yielded 380 mg (7%) of colorless crystals: mp 140 °C dec; ^{31}P NMR (CH_2Cl_2) δ –183.6 ($^1J(^{31}P{-}^{183}W_\alpha) = 295.4$ Hz, $^1J(^{31}P{-}^{183}W_\beta) = 227.05$ Hz); IR (decalin) ν(CO) 2077 (m), 2068 (m), 1988 (m), 1954 (vs), 1933 (s), 1917 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.1 (m); 2.6–3.3 (m); ^{13}C NMR ($CDCl_3$) δ 16.17 (pseudo-t, $J = 6.71$ Hz), 23.14 (m), 29.74 (pseudo-t, $J = 6.71$ Hz), 195.1 (m, CO_{eq}), 209.34 (d, $J(C{-}P)$ 8.5 Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 792 (M, 8), 708 (M – 3CO, 6), 680 (M – 4CO, 8), 652 (M – 5CO, 12), 624 (M – 6CO, 8), 576 (M – 7CO, 8), 568 (M – 8CO, 10), 512 (M – 10CO, 9), 144 ($(PC_3H_5)_2$, 25). Anal. Calcd for $C_{16}H_{10}O_{10}P_2W_2$: C, 24.27; H, 1.27; P, 782. Found: C, 24.45; H, 1.27; P, 7.84.

(1-Phosphabicyclo[3.1.0]hexane)pentacarbonyltungsten (11). **11** was prepared from **7** (4.55 g (7.04 mmol)) in the presence of CuCl in toluene (55–60 °C, 3 h). The product was purified by chromatography with hexane: yield 1.85 g (62%) of a pale yellow oil, which crystallizes upon standing at –20 °C; ^{31}P NMR (CH_2Cl_2) δ –175.0 ($^1J(^{31}P{-}^{183}W) = 244.14$ Hz); IR (decalin) ν(CO) 2066 (m), 1984 (vw), 1944 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 0.19–1.70 (m); ^{13}C NMR (C_6D_6) δ 9.09 (d, $^1J(C{-}P) = 14.6$ Hz, CH_2, C6), 21.75 (s, CH_2, C3/C4), 21.84 (d, $^1J(C{-}P) = 15.7$ Hz, CH, C5), 26.9 (d, $^1J(C{-}P) = 17.1$ Hz, CH_2, C2), 30.05 (s, CH_2, C3/C4), 196.3 (d, $^2J(C{-}P) = 8.5$ Hz, CO_{eq}), 198.8 (d, $^2J(C{-}P) = 30.5$ Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 424 (M, 64), 396 (M – CO, 20), 368 (M – 2CO, 38), 340 (M – 3CO, 54), 338 (M – 3CO – 2H, 92), 312 (M – 4CO, 79), 310 (M – 4CO – 2H, 100), 284 (M – 5CO, 45). Anal. Calcd for $C_{10}H_9O_5PW$: C, 28.33; H, 2.14; P, 7.31; W, 43.36. Found: C, 28.62; H, 2.14; P, 6.98; W, 43.19.

(1-Allyl-2,3-diphenylphosphirene)pentacarbonyltungsten (12). Complex **5** (2.4 g (3.87 mmol)) and PhC≡CPh (2.16 g (12.12 mmol)) in 5 mL of toluene were heated in the presence of a small amount of CuCl at 60–70 °C for 3.5 h. After evaporation of the solvent the crude product could be purified by chromatography with hexane: yield 500 mg (22.5%) of light brown oil; ^{31}P NMR (CH_2Cl_2) δ −157.0 ($^{1}J(^{31}P-^{183}W)$ = 258.8 Hz); IR (decalin) ν(CO) 2067 (m), 1984 (m), 1945 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.4 (ddd, ^{3}J(H–H) = 7.32 Hz, ^{4}J(H–H) = 0.98 Hz, ^{2}J(P–H) = 3.42 Hz, 2 H, CH_2P), 4.5–5.7 (m, 3 H, $CH{=}CH_2$), 7.0–7.3 (m) and 7.6–7.8 (m) (10 H, C_6H_5); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 574 (M, 11), 533 (M − C_3H_5, 18), 449 (M − 3CO − C_3H_5, 31), 434 (M − 5CO, 39), 396 (M − $PhC{\equiv}CPh$, 3), 284 (M − 3CO − $PhC{\equiv}CPh$, 7), 178 ($PhC{\equiv}CPh$, 100). Anal. Calcd for $C_{22}H_{15}O_5PW$: C, 46.02; H, 2.63; P, 5.39; W, 32.02. Found: C, 47.59; H, 2.94; P, 5.25; W, 32.02.

(1-Allyl-2,3-diethylphosphirene)pentacarbonyltungsten (14). (a) From 5. Complex **5** (6.19 g (10 mmol)) was heated with hexyne-3 (2.05 g (25 mmol)) in 10 mL of toluene in the presence of CuCl at 55–60 °C for 1 h. The crude product was chromatographed with hexane to yield 2.21 g (46%) of **14** as a colorless oil.

(b) From 1. **1** (4.76 g (10 mmol)), DMAD (2.84 g (20 mmol)), and hexyne-3 (2.05 g (25 mmol)) were heated in 5 mL of toluene at 115 °C for 17 h. Chromatography with hexane yielded 3.16 g (66%) of **14** contaminated with traces of **15**: ^{31}P NMR (CH_2Cl_2) δ −157.4 ($^{1}J(^{31}P-^{183}W)$ = 256.3 Hz); IR (decalin) ν(CO) 2064 (m), 1936 (s), 1909 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.95 (t, ^{3}J(H–H) = 7.32 Hz, 6 H, CH_3), 2.13 (m, ^{3}J(H–H) ≈ 7.1 Hz, ^{4}J(H–H) ≈ 1.2 Hz, CH_2(allyl)), 2.22 (m, CH_2 (ethyl)) (6 H), 4.6–5.4 (m, 3 H, $CH{=}CH_2$); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 478 (M, 38), 437 (M − C_3H_5, 33), 409 (M − CO − C_3H_5, 13), 353 (M − 3CO − C_3H_5, 19), 338 (M − 5CO, 98), 336 (M − 3CO − $2C_2H_5$, 100), 325 (M − 4CO − C_3H_7, 34), 297 (M − 5CO − C_3H_7, 30). Anal. Calcd for $C_{14}H_{15}O_5PW$: C, 35.17; H, 3.16; P, 6.48. Found: C, 35.45; H, 3.13; P, 6.44.

(1-Allyl-3-methyl-2-phenylphosphirene)pentacarbonyltungsten (16). **5** (5.07 g (8.19 mmol)) and $MeC{\equiv}CPh$ (2.38 g (20.47 mmol)) were heated in 5 mL of toluene in the presence of CuCl at 55 °C for 3 h. The product was isolated as a yellow oil by chromatography with hexane: yield 2.96 g (70%); ^{31}P NMR (CH_2Cl_2) δ −152.4 ($^{1}J(^{31}P-^{183}W)$ = 258.79 Hz); IR (decalin) ν(CO) 2058 (m), 1971 (w), 1936 (vs), 1904 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.06 (d, ^{3}J(P–H) = 9.5 Hz, 3 H, CH_3); 2.26 (dd, ^{3}J(H–H) = 7.3 Hz; ^{2}J(P–H) = 3.9 Hz, 2 H, CH_2), 4.6–5.6 (m, 3 H, $CH{=}CH_2$), 7.0–7.5 (m, 5 H, C_6H_5); mass spectrum (EI, 70 eV; ^{184}W), *m/e* (relative intensity) 512 (M, 41), 471 (M − C_3H_5, 35), 387 (M − 3CO − C_3H_5, 51), 372 (M − 5CO, 100), 327 ($P{=}W(CO)_4$, 49), 299 ($P{=}W(CO)_3$, 35), 271 ($P{=}W(CO)_2$, 27), 243 ($P{=}W(CO)$, 11). Anal. Calcd for $C_{17}H_{13}O_5PW$: C, 39.87; H, 2.56; P, 6.05. Found: C, 40.04; H, 2.59; P, 6.00.

(2,3-Diphenyl-1-phosphabicyclo[3.1.0]hex-3-ene)pentacarbonyltungsten (13). **1** (2.7 g (5.17 mmol)), DMAD (1.61 g (11.34 mmol)), and $PhC{\equiv}CPh$ (2.53 g (14.18 mmol)) were heated in 10 mL of toluene at 115 °C for 17 h. After evaporation of the solvent, the dark brown residue was chromatographed with heptane. **13** was obtained as a pale green oil, which crystallized from hexane to yield 0.63 g (19%) of colorless solid: mp 138 °C; ^{31}P NMR (CH_2Cl_2) δ −144.0 ($^{1}J(^{31}P-^{183}W)$ = 258.8 Hz); IR (decalin) ν(CO) 2066 (w), 1986 (vw), 1948 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.69 (m, $^{2}J(H_{A'}-H_{B'})$ ≈ $^{3}J(H_{A'}-H_{M'})$ ≈ 7 Hz, ^{3}J(H–P) not resolved, 1 H, $H_{A'}$), 0.96 (m, $^{2}J(H_{A'}-H_{B'})$ = 6.84 Hz, $^{3}J(H_{B'}-H_{M'})$ = 9.03, 1 H, $H_{B'}$), 2.72 (m, $^{2}J(H_A-H_B)$ = 18.55 Hz, $^{3}J(H_A-H_M)$ ≈ 0.73 Hz (not fully resolved), $^{3}J(H_A-P)$ = 12.70 Hz, 1 H, H_A), 3.23 (m ≈ ddd, $^{2}J(H_A-H_B)$ = 18.55 Hz, $^{3}J(H_B-H_M)$ = 6.84 Hz, $^{3}J(H_B-P)$ = 2.44 Hz, 1 H, H_B), 6.84 (s, 5 H, Ph), 7.03 (m, 5 H, Ph′); ^{13}C NMR ($CDCl_3$) δ 16.48 (d, ^{1}J(C–P) = 9.77 Hz, C5), 19.93 (d, ^{2}J(C–P) = 15.87 Hz, C6), 44.53 (s, C4), 127.77, 128.13, 128.62 (aromatic C), 129.89 (d, ^{3}J(C–P) = 6.1 Hz, C9 (Ph)), 134.86 (d, ^{1}J(C–P) = 18.31, C2), 136.43 (d, ^{2}J(C–P) ≈ 11 Hz, C7), 137.58 (s, C8), 145.82 (d, ^{2}J(C–P) = 8.55 Hz, C3), 194.9 (d, ^{2}J(C–P) = 7.3 Hz, CO_{eq}), 137.5 (d, ^{2}J(C–P) = 31.74 Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 574 (M, 32), 518 (M − 2CO, 41), 490 (M − 3CO, 26), 462 (M − 4CO, 14), 434 (M − 5CO, 85), 432 (M − 5CO − 2H, 100), 250 (M − $W(CO)_5$, 58). Anal. Calcd for $C_{22}H_{15}O_5PW$: C, 46.02; H, 2.63; P, 5.39; W, 32.02. Found: C, 46.52; H, 2.74; P, 5.25; W, 31.18.

(2,3-Diethyl-1-phosphabicyclo[3.1.0]hex-3-ene)pentacarbonyltungsten (15). A solution of **14** (2.42 g (5.06 mmol)) in 10 mL of toluene was heated in a sealed tube at 160 °C for 14 h. After evaporation of the solvent, the crude product was purified by chromatography with hexane: yield 1.41 g (58%) of yellow oil; ^{31}P NMR ($CDCl_3$) δ −154.3 ($^{1}J(^{31}P-^{183}W)$ = 246.6 Hz); IR (decalin) ν(CO) 2060 (m), 1981 (w), 1939 (vs), 1906 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.57 (t, ^{3}J(H–H) = 7.57 Hz, CH_3), 0.92 (t, ^{3}J(H–H) = 7.32 Hz, CH_3), 1.58 (q, ^{3}J(H–H) = 8.06 Hz, CH_2(ethyl)), 2.00 (q, ^{3}J(H–H) = 7.8 Hz, CH_2(ethyl)), 0.2–2.3 (m, CH_2CHCH_2), ^{13}C NMR ($CDCl_3$) δ 13.20 (s, CH_3, C10), 14.60 (d, ^{3}J(C–P) = 2.44 Hz, CH_3, C8), 16.90 (d, ^{1}J(C–P) = 8.55 Hz, CH, C5), 20.11 (d, ^{1}J(C–P) = 14.65 Hz, CH_2, C6), 20.84 (d, ^{2}J(C–P) = 21.97 Hz, CH_2, C7), 23.17 (d, ^{3}J(C–P) = 8.55 Hz, CH_2, C9), 42.04 (s, CH_2, C4), 135.07 (d, ^{1}J(C–P) = 25.64 Hz, C2), 149.97 (d, ^{2}J(C–P) = 6.10 Hz, C3), 195.41 (d, ^{2}J(C–P) = 8.55 Hz, CO_{eq}), 197.71 (d, ^{2}J(C–P) = 28.07 Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 478 (M, 29), 422 (M − 2CO, 22), 392 (M − 3CO − 2H, 64), 362 (M − 2CO − $2C_2H_6$, 43). Anal. Calcd for $C_{14}H_{15}O_5PW$: C, 35.17; H, 3.16; P, 6.48. Found: C, 36.13; H, 3.32; P, 6.32.

(3-Methyl-2-phenyl-1-phosphabicyclo[3.1.0]hex-3-ene)pentacarbonyltungsten (17). **1** (4.76 g (10 mmol)), DMAD (2.84 g (20 mmol)), and $MeC{\equiv}CPh$ (2.90 g (25 mmol)) in 5 mL of toluene were heated at 120 °C for 23 h. After evaporation of the solvent, **17** could be isolated by chromatography with hexane: yield 2.89 g (56%) of a pale yellow oil which crystallized slowly upon standing at −20 °C; mp 72 °C; ^{31}P NMR (CH_2Cl_2) δ −145.5 ($^{1}J(^{31}P-^{183}W)$ = 256.3 Hz); IR (decalin) ν(CO) 2066 (m), 1985 (w), 1946 (s), 1912 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.57 (m, $^{2}J(H_{A'}-H_{B'})$ ≈ $^{3}J(H_{A'}-H_M)$ ≈ 6 Hz, $H_{A'}$), and 0.85 (m, $^{2}J(H_{A'}-H_{B'})$ ≈ 6 Hz, $^{3}J(H_{B'}-H_M)$ ≈ 7 Hz, $H_{B'}$) (2 H), 1.26 (d, ^{4}J(P–H) = 1.22 Hz, 3 H, CH_3), 1.4–1.9 (m, 1 H, H_M), 2.1–2.8 (m, 2 H, $H_{A'}$ H_B), 7.12 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 16.93 (d, ^{3}J(C–P) = 8.55 Hz, CH_3, C7), 17.14 (d, ^{1}J(C–P) = 9.8 Hz, CH, C5), 20.23 (d, ^{1}J(C–P) = 14.65 Hz, CH_2, C6), 45.4 (s, CH_2, C4), 127.6 (d, ^{4}J(C–P) = 2.44 Hz, CH, C10/C12), 128.5 (s, CH, C11), 129.4 (d, ^{3}J(C–P) = 6.1 Hz, CH, C9/C13), 134.37 (d, ^{2}J(C–P) = 7.3 Hz, C8), 135.54 (d, ^{1}J(C–P) = 17.1 Hz, C2), 146.4 (d, ^{2}J(C–P) = 8.55 Hz, C3); 195.0 (d, ^{2}J(C–P) = 8.55 Hz, CO_{eq}), 197.7 (d, ^{2}J(C–P) = 30.53 Hz, CO_{ax}); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 512 (M, 55), 456 (M − 2CO, 50), 428 (M − 3CO, 81), 400 (M − 4CO, 24), 372 (M − 5CO, 64). Anal. Calcd for $C_{17}H_{13}O_5PW$: C, 39.87; H, 2.56; P, 6.05; W, 35.90. Found: C, 40.01; H, 2.49; P, 5.42; W, 34.29.

(1-(3-Butenyl)-2,3-diphenylphosphirene)pentacarbonyltungsten (18). A mixture of **6** (5.37 g (8.49 mmol)) and $MeC{\equiv}CPh$ (7.2 g (61.98 mmol)) was heated in the presence of CuCl at 60 °C for 1.5 h. Unreacted $MeC{\equiv}CPh$ was removed at 10^{-2} torr and the product isolated by chromatography with pentane: yield 2.27 g (50%) of colorless oil; ^{31}P NMR (CH_2Cl_2) δ −149.8 ($^{1}J(^{31}P-^{183}W)$ = 261.23 Hz); IR (decalin) ν(CO) 2064 (w), 1942 (s), 1907 (vw) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.63 (m, 4 H, $(CH_2)_2$), 2.01 (d, ^{3}J(P–H) = 9.5 Hz, 3 H, CH_3), 4.6–4.9 (m, 2 H, $H_2C{=}$), 5.1–5.7 (m, 1 H, $CH{=}$), 7.0–7.5 (m, 5 H, C_6H_5); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 526 (M, 37), 442 (M − CO − C_4H_7 − H, 14), 414 (M − 2CO − C_4H_7 − H, 20), 386 (M − 3CO − C_4H_7 − H, 87), 384 (M − 5CO − 2H, 100), 331 (M − 5CO − C_4H_7, 24). Anal. Calcd for $C_{18}H_{15}O_5PW$: C, 41.09; H, 2.87; P, 5.89; W, 34.94. Found: C, 41.40; H, 2.96; P, 6.04; W, 34.66.

(*trans*-1-Allyl-2,3-diphenylphosphirane)pentacarbonyltungsten (20). Complex **5** (2.0 g (3.23 mmol)) and *trans*-stilbene (1.52 g (8.41 mmol)) was heated in 3 mL of toluene with a small amount of CuCl at 75 °C for 18 h. After evaporation of the solvent the product was purified by chromatography with hexane/CH_2Cl_2 (90:10): yield 0.74 g (70%) of pale yellow oil; ^{31}P NMR (CH_2Cl_2) δ −128.8 ($^{1}J(^{31}P-^{183}W)$ = 263.7 Hz); IR (decalin) ν(CO) 2066 (m), 1985 (w), 1946 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.83 (dd ≈ t, ^{3}J(H–H) = 7.08 Hz, ^{2}J(H–P) = 7.33 Hz, 2 H, CH_2), 3.01 ($^{3}J(H_A-H_B)$ = 9.77 Hz, $^{2}J(H_B-P)$ = 7.32 Hz, 1 H, H_B), 3.31 ($^{3}J(H_A-H_B)$ = 9.77 Hz, $^{2}J(H_A-P)$ ≈ 0 Hz, 1 H, H_A), 4.6–5.7 (m, 3 H, $CH{=}CH_2$), 7.05 (s, 5 H, Ph), 7.12 (s, 5 H, Ph); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity), 576 (M, 19), 451 (M − 3CO − C_3H_5, 22), 396 ($(OC)_5W{=}PC_3H_5$, 43), 340 ($(OC)_3W{=}PC_3H_5$, 31), 327 ($(OC)_4W{=}P$, 47), 312 ($(OC)_2W{=}PC_3H_5$, 65), 299 ($(OC)_3W{=}P$, 31), 180 ($PhCH{=}CHPh$, 100). Anal. Calcd for $C_{22}H_{17}O_5PW$: C, 45.86; H, 2.97; P, 5.38; W, 31.91. Found: C, 46.31; H, 3.07; P, 5.35; W, 32.55.

(9-Allyl-9-phosphabicyclo[6.1.0]nonane)pentacarbonyltungsten (21a,b) (Mixture of Isomers). **5** (4.71 g (7.61 mmol))

Organometallics **1986**, *5*, 1167–1170

was heated with cyclooctene (5.02 g (45.55 mmol)) in the presence of a small amount of CuCl at 55 °C for 2.5 h. The crude product was purified by chromatography with heptane: yield 3.4 g (88%) of pale yellow crystalline solid; mp 141 °C (hexane); ^{31}P NMR (CH_2Cl_2) δ −168.7 ($^1J(^{31}P–^{183}W)$ = 253.9 Hz) (isomer a), δ −173.0 ($^1J(^{31}P–^{183}W)$ = 253.9 Hz) (isomer b); IR (decalin) ν(CO) 2064 (w), 1942 (s), 1908 (vw) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.16 (br m, $(CH_2)_6$), 1.4–1.75 (m, 2 H, CH), 1.90 (dd, ^3J(H–H) = 6.35 Hz, ^2J(P–H) $\approx$ 8 Hz, 2 H, PCH_2), 4.9–5.8 (m, 3 H, CH=CH_2); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 506 (M, 25), 478 (M − CO, 5), 396 ($(OC)_5WP—C_3H_5$, 15), 368 ($(OC)_4WP—C_3H_5$, 16), 340 ($(OC)_3WP—C_3H_5$, 35), 327 ($(OC)_4WP$, 38), 312 ($(OC)_2WP—C_3H_5$, 100), 299 ($(OC)_3WP$, 25), 284 ($OCWP—C_3H_5$, 22), 271 ($(OC)_2WP$, 19). Anal. Calcd for $C_{16}H_{19}O_5PW$: C, 37.97; H, 3.78; P, 6.12; W, 36.32. Found: C, 38.11; H, 3.85; P, 6.04; W, 35.26.

Registry No. 1, 101376-96-9; **2**, 101376-97-0; **3**, 101376-98-1; **4**, 101376-99-2; **5**, 101377-00-8; **6**, 101377-01-9; **7**, 101377-02-0; **8**, 101377-03-1; **9**, 101377-04-2; **11**, 101377-05-3; **12**, 101377-06-4; **13**, 101377-07-5; **14**, 101377-08-6; **15**, 101377-09-7; **16**, 101377-10-0; **17**, 101377-11-1; **18**, 101377-12-2; **20**, 101377-13-3; **21a**, 101377-14-4; **21b**, 101469-67-4; $W(CO)_6$, 14040-11-0; PhC≡CPh, 501-65-5; MeC≡CPh, 673-32-5; 1-phenyl-3,4-dimethylphosphole, 30540-36-4; allyl chloride, 107-05-1; 1-butyl chloride, 109-69-3; *tert*-butyl chloride, 507-20-0; allyl bromide, 106-95-6; 4-bromobutene-1, 5162-44-7; 5-bromopentene-1, 1119-51-3; dimethyl acetylenedicarboxylate, 762-42-5; hexyne-3, 928-49-4; *trans*-stilbene, 103-30-0; cyclooctene, 931-88-4.

Reactivity Profile of 1,3-Disubstituted Tetraorganodistannoxanes Assessed in Urethane Formation Reaction[1]

Junzo Otera,* Toru Yano, and Rokuro Okawara

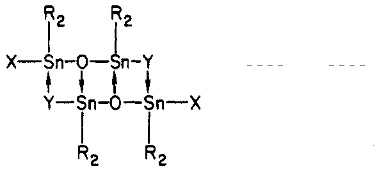
Okayama University of Science, Ridai-cho, Okayama 700, Japan

Received October 23, 1985

For the purpose of assessing general reactivity profiles of 1,3-disubstituted tetraorganodistannoxanes, the catalytic mechanism of the urethane formation reaction was investigated in detail. Apparently, the reaction is initiated by the formation of tin alkoxides which then add to isocyanates to give stannylcarbamates. Alcoholysis of these compounds furnishes urethane and regenerates tin alkoxides. In these reactions, an Sn–X (X = halogen, NCS) or Sn–OH bond in distannoxanes is easily cleaved by alcohols. The unique reactivity can be ascribed to the heteroatom-bridged dimerization of distannoxanes. For the reaction of alkoxydistannoxanes with isocyanates, a template effect is suggested by which addition reaction occurring at the tin attached to an alkoxyl group is accelerated by the tin of the other chain in the dimeric formulation.

Introduction

Among various organometallics of the group 14 elements, diorganotin dihalides are unique in that they can provide stable partial hydrolysis products, 1,3-disubstituted tetraorganodistannoxanes (1).[2] The facile formation and stability of these compounds are attributable to the dimeric ladder structure which has been confirmed both in the solid state and in solution.[3] Moreover, it is now apparent that replacement of one of the halogens in 1,3-dihalodistannoxanes with a hydroxy or alkoxy group leads to 3-halo-1-hydroxy- or 3-halo-1-alkoxydistannoxanes having the oxygen-bridged structure (Y = OH or OR in 1).



1a–j, R = Bu

a, X = Cl, Y = Cl; **b**, X = Cl, Y = OH; **c**, X = Cl, Y = OPh; **d**, X = Br, Y = Br; **e**, X = Br, Y = OH; **f**, X = Br, Y = OPh; **g**, X = NCS, Y = NCS; **h**, X = NCS, Y = OH; **i**, X = NCS, Y = OPh; **j**, X = NCS, Y = OMe

In contrast to the extensive structural studies, few have been reported on their reactions or synthetic applications. One such example is the distannoxane-catalyzed urethane formation discovered by Yokoo et al. in 1967, who have found that some of 1 are 100 times more active than tin catalysts usually employed such as dibutyltin dilaurate.[4]

In the course of our program on synthetic applications of organotin templates, we perceived that this unusual catalytic activity should be ascribed to the unique structure of 1 and started detailed investigations on the catalytic mechanism which should help delineate the reactivity features of 1.

There have appeared a number of proposals on the catalytic mechanism of organotin catalysts other than distannoxanes. Many authors have claimed that the ternary (tin–alcohol–isocyanate) complex is responsible for activation of the alcohol–isocyanate reaction.[5] Frisch and his co-workers have proposed the reaction between each reactant that is complexed with separate metals.[6] Davies and his co-workers have suggested the intermediacy of tin alkoxides which add to the isocyanate giving stannylcarbamates.[7] More recently, ionic intermediates such as $[Bu_2SnOCOC_{11}H_{23}]^{+}$[8] and $[Bu_2Sn(OAc)_2OMe]^{-}$[9] have been proposed as active species.

The present study stemmed from the expectation that the unique dimeric structure of distannoxanes should give rise to reactivities heretofore unknown, but characteristic of these compounds. Consequently, detailed investigation of the catalytic activity of various types of distannoxanes

---

[1] Organotin Templates in Organic Reactions. 6.

[2] Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.

[3] Yano, T.; Nakashima, K.; Otera, J.; Okawara, R. *Organometallics* **1985**, *4*, 1501 and references cited therein.

[4] Yokoo, M.; Ogura, J.; Kanzawa, T. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 57.

[5] (a) Britain, J. W.; Gemeinhardt, P. G. *J. Appl. Polym. Sci.* **1960**, *4*, 207. (b) Smith, H. A. *Ibid.* **1963**, *7*, 85. (c) Robins, J. *Ibid.* **1965**, *9*, 821. (d) Entelis, S. G.; Nesterov, O. V. *Kinet. Katal.* **1966**, *7*, 464.

[6] Reegen, S. L.; Frisch, K. C. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2883.

[7] Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 5238.

[8] Borkent, G. *Advances in Urethane Science and Technology* Frisch, K. C., Reegen, S. L., Eds.; Technomic: Westport, CT, 1974; Vol. 3, p 1.

[9] van der Weij, F. W. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 381.

0276-7333/86/2305-1167$01.50/0