Synthesis of 1-Phosphacycloalkene P–M(CO)$_5$ Complexes (M = Cr, W) by Intramolecular Phospha-Wittig Reactions

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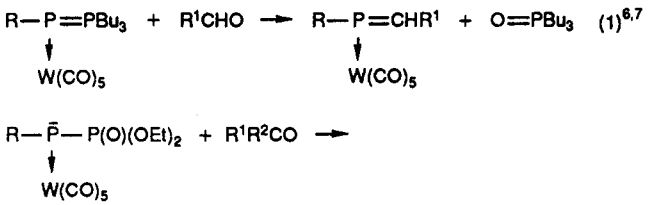
Intramolecular phospha-Wittig reactions have been used to prepare 1-phosphacyclopentene and 1-phosphacyclohexene complexes with M = Cr(CO)$_5$ or W(CO)$_5$. These complexes are unstable when the P=C double bond is substituted by a phenyl and isolable with a methyl substituent. In this last case, a slow dimerization occurs via a P—H + P=C intermolecular addition after partial isomerization of the 1-phosphacycloalkene into the corresponding secondary vinylphosphine complex. Intramolecular phospha-Wittig reactions fail for the synthesis of 1-phosphacyclopropene and 1-phosphacyclobutene complexes.

As in the case of cycloalkenes, the cyclic structure of 1-phosphacycloalkenes can give rise to interesting modifications of the reactivity of the double bond and can yield useful information on the stereochemistry of its reactions. If we restrict ourselves to the monounsaturated species, only a few such compounds are known. Noteworthy among them are a 2*H*-phosphirene and a 1-phosphacyclopentene both prepared by Regitz.[1] A Dewar-phosphinine has also been described by Regitz[2] and incorporates a 1-phosphacyclobutene ring. All these compounds[3] are heavily substituted in order to improve their stability. We have already noticed[4] that the complexation of phosphorus by tungsten pentacarbonyl improves the stability of the P=C double bond and allows to work with a lighter substitution scheme. Thus, we felt that it would be interesting to investigate the synthesis of 1-phosphacycloalkene P–M(CO)$_5$ complexes (M = W and other similar metals).

Results and Discussion

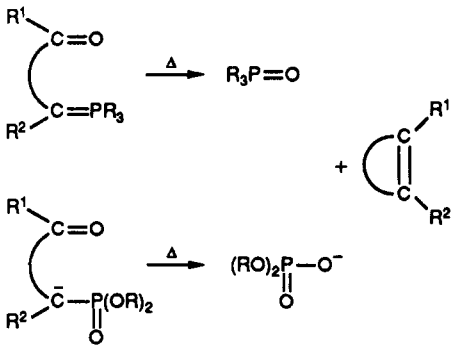
The intramolecular Wittig reaction is a well-known route to cycloalkenes[5] (Scheme I). One of the possible approaches was thus to devise an intramolecular phospha-Wittig synthesis of 1-phosphacycloalkene P–M(CO)$_5$ complexes. The two versions of the phospha-Wittig reaction are depicted in eqs 1 and 2 with tungsten as the metal.



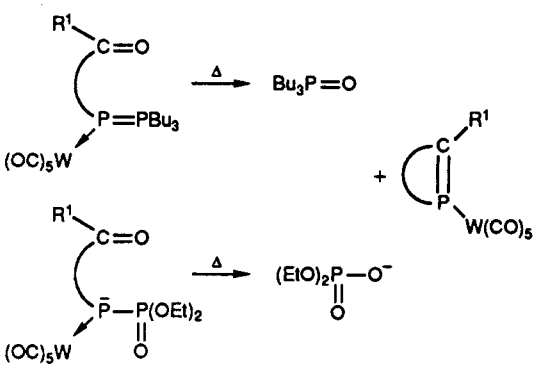
The problem was to incorporate a carbonyl functionality into the R substituent of the phospha-Wittig reagents in order to perform the cyclization (Scheme II). In our first attempts, we selected the 7-phosphanorbornadiene approach.[6] (Scheme III). Thus, two 7-(4-oxoalkyl)-7-phosphanorbornadiene complexes **4a,b** were synthesized as depicted in eq 3 from the readily available anionic phospholyl complex 1.[9]

The reaction of phosphanorbornadiene complex **4b** with tributylphosphine proceeded smoothly and produced the phospha-Wittig reagent,[6] which spontaneously cyclized to give the expected phosphacycloalkene complex **5b**. The formation of **5b** could be monitored by ^{31}P NMR analysis of the reaction mixture [$\delta(^{31}P)$(**5b**) + 181 ppm in THF], but **5b** is unstable and we were obliged to trap it by methanol. Only one isomer of the adduct **6b** was obtained

Scheme I. Synthesis of Cycloalkenes by Intramolecular Wittig or Wittig–Horner Reactions



Scheme II. Synthesis of 1-Phosphacycloalkene Complexes by Intramolecular "Phospha-Wittig" Reactions



(1) Wagner, O.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1257.
(2) Fink, J.; Rösch, W.; Vogelbacher, U.-J.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 280.
(3) Most of the 1-phosphacycloalkenes known today have been synthesized from phosphaalkynes. As such, they are mentioned in two recent reviews by Regitz on the chemistry of phosphaalkynes: Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484; *Chem. Rev.* **1990**, *90*, 191.
(4) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382.
(5) Becker, K. B. *Tetrahedron* **1980**, *36*, 1717.
(6) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407.
(7) Le Floch, P.; Mathey, F. *Synlett* **1990**, 171.
(8) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.
(9) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.

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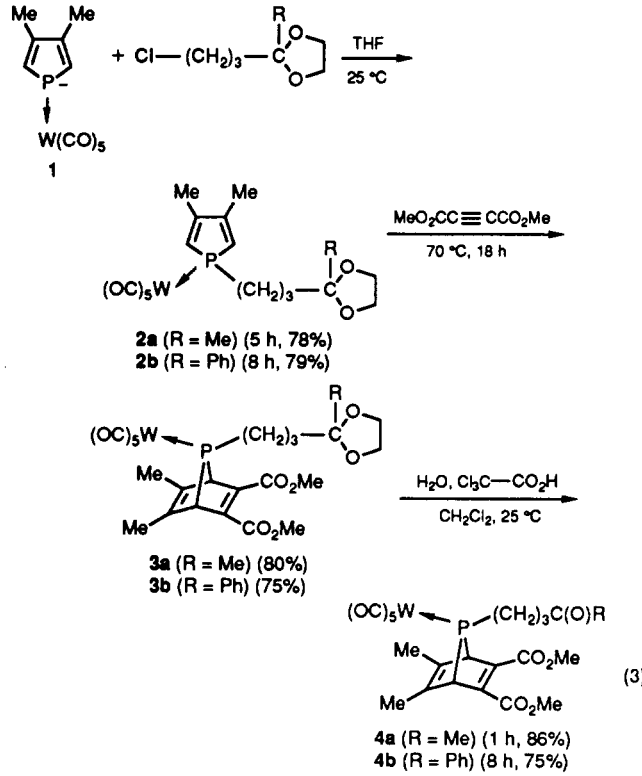
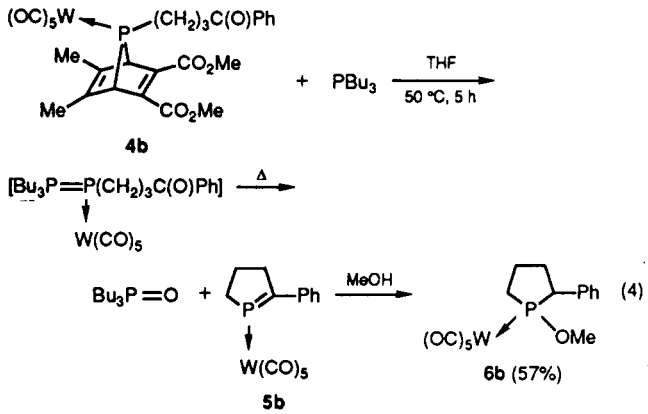
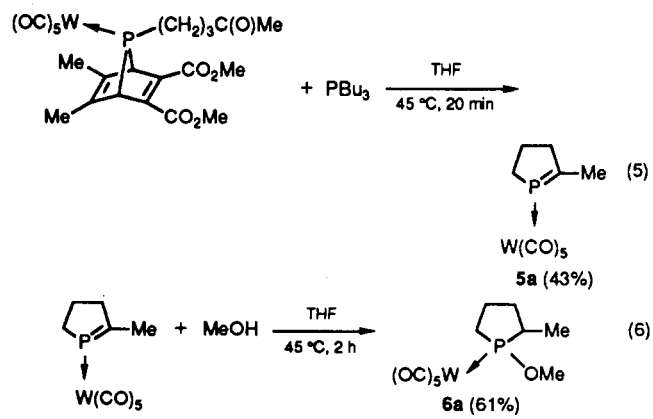


in fair yield, but its stereochemistry is unknown (eq 4).

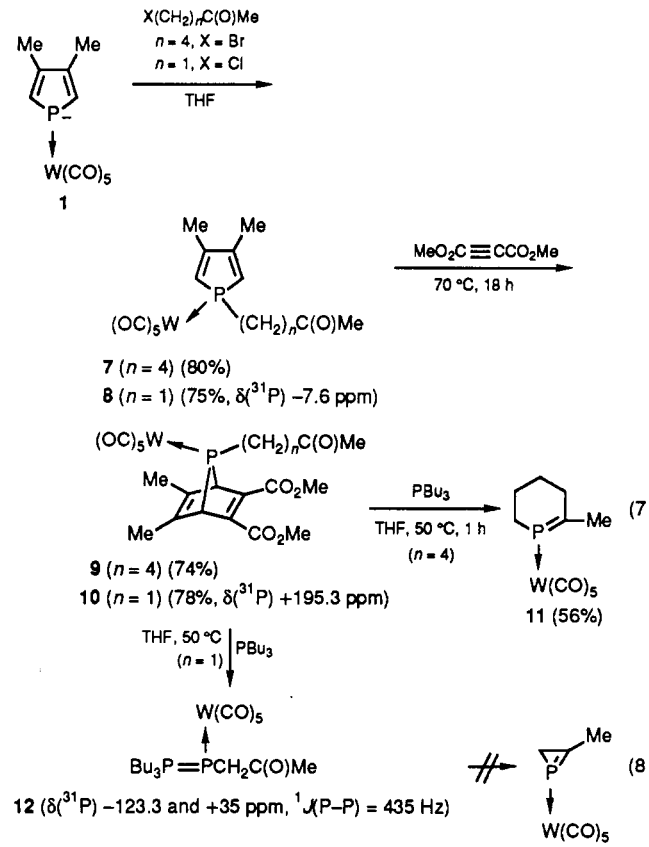


The reaction of phosphanorbornadiene complex **4a** with tributylphosphine proceeded similarly, but in that case, the phosphacycloalkene complex **5a** is stable and could be isolated as such in reasonable yield (eq 5).



Complex **5a** shows the expected ^{31}P resonance at low fields [$\delta(^{31}P)$(**5a**) +180 ppm]. The sp^2 carbon resonates at +194 ppm with a characteristic strong coupling with phosphorus [$^1J(^{13}C-^{31}P)$ = 49.5 Hz]. The difference of stability between the two phosphaalkene complexes **5a** and **5b** is surprising on a purely steric ground. The difference of polarity of the P=C bond between the two cases probably is a part of the explanation. Besides, a strong σ(C—H)/π(P=C) hyperconjugative interaction unlikely provides some additional stability to the methylated π-bond. Upon standing in the reaction mixture, **5a** slowly dimerizes to give a new product with a P–P bond [$\delta(^{31}P)$ +24.5 and +35.5 ppm in THF, ^1J(P–P) = 200 Hz], which has not been fully characterized. We will discuss this dimerization more in depth in the next paragraph. When the reaction of **4a** with PBu_3 is carried out in the presence of methanol, the methanol adduct **6a** is obtained as a mixture of two isomers (eq 6).

As a logical next step, we investigated the synthesis of 1-phosphacyclohexene and we attempted the synthesis of 1-phosphacyclopropene (2*H*-phosphirene[1]) complexes. A similar chemistry led to the expected products in the first case (eq 7).

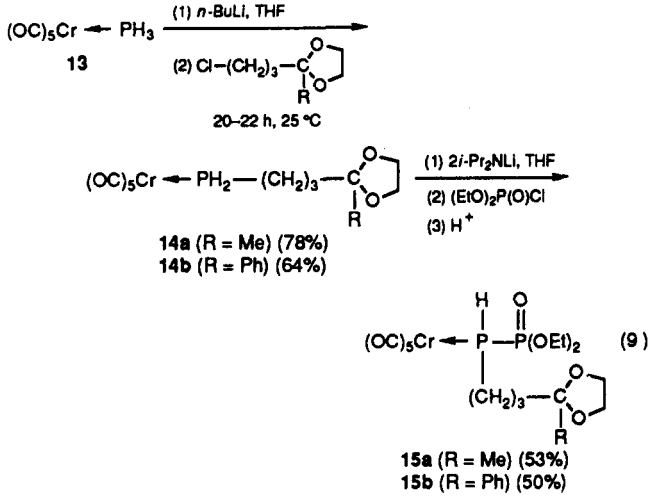


In the second case, the reaction was only monitored by ^{31}P NMR spectroscopy. In such a way, we could detect the formation of the phosphoranylidenephosphine complex **12** (eq 8), but it decomposes upon heating to give a complicated mixture of products.

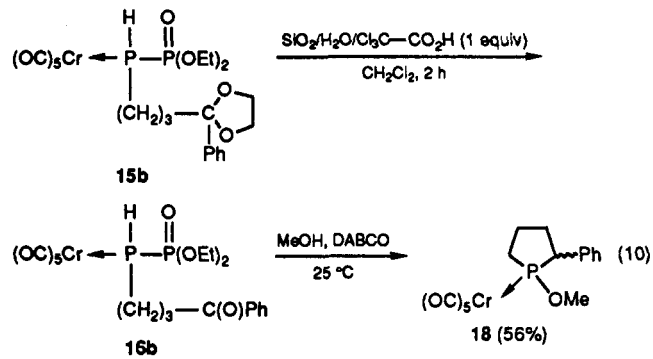
We also investigated the synthetic potential of the phosphorylphosphine approach[4,8] (eq 2). In that case, we decided to work in the chromium series because the anionic chromium pentacarbonyl complexes proved to be more stable than the corresponding tungsten complexes. Our starting product was the PH_3 complex **13**, which was easily obtained by reduction of the PCl_3 complex by $LiAlH_4$.[8] Complex **13** was first converted into the masked secondary (4-oxoalkyl)(phosphoryl)phosphine complexes **15a,b** (eq 9).

The unmasking of the keto groups of complexes **15a,b**[10] leads to unstable products **16a,b** (P—H and C=O func-

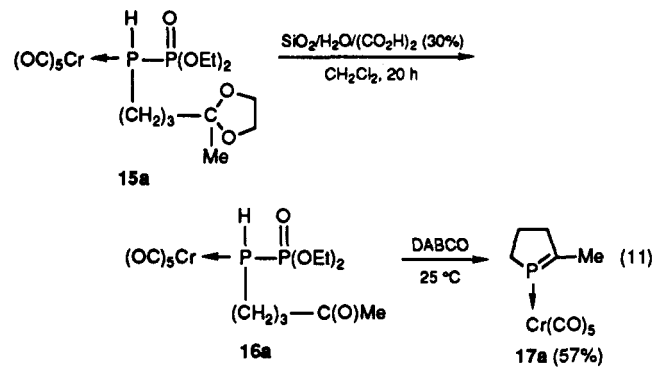
(10) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.



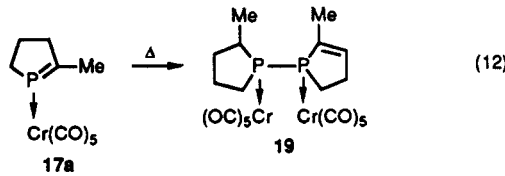
tionalities are not compatible), which are treated in situ by 1,4-diazabicyclo[2.2.2]octane to give the expected phosphacycloalkene complexes **17a,b**. As with tungsten, when R = Ph, the unsaturated heterocycle **17b** is unstable. It was allowed to react with methanol to give 18 as a mixture of two separable isomers (eq 10).



On the contrary, when R = Me, the 1-phosphacyclopentene complex **17a** is stable (eq 11). As in the case of

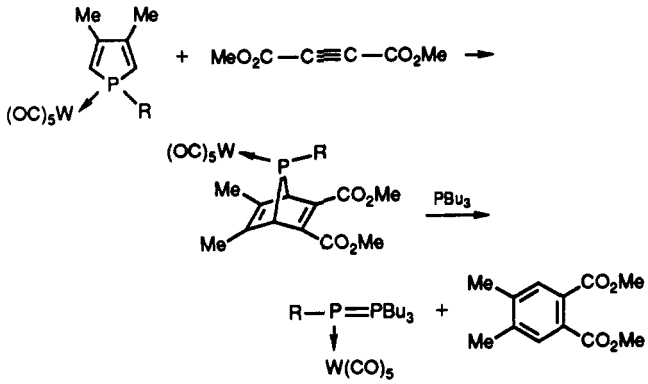


phosphaalkene complex **5a**, **17a** tends to dimerize when kept in concentrated solution (eq 12). The dimeric

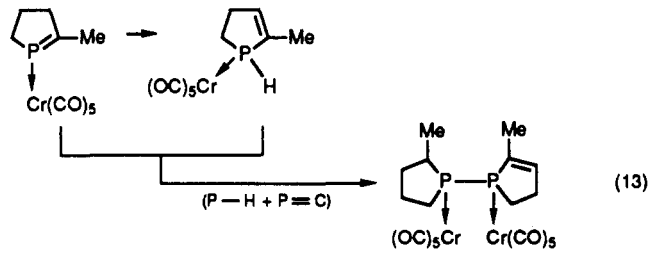


structure of **19** was established by its mass spectrum [EI, 70 eV: m/z 584 (M^+, 15%), 444 ($M^+ - 5CO$, 42%), 304 ($M^+ - 10CO$, 44%), 252 ($M^+ - 10CO - Cr$, 88%), 246 (100%) 200 ($M^+ - 10CO - 2Cr$, 28%)]. The ^{31}P NMR spectrum indicated the presence of a P–P bond AB system: $\delta(A)$ =

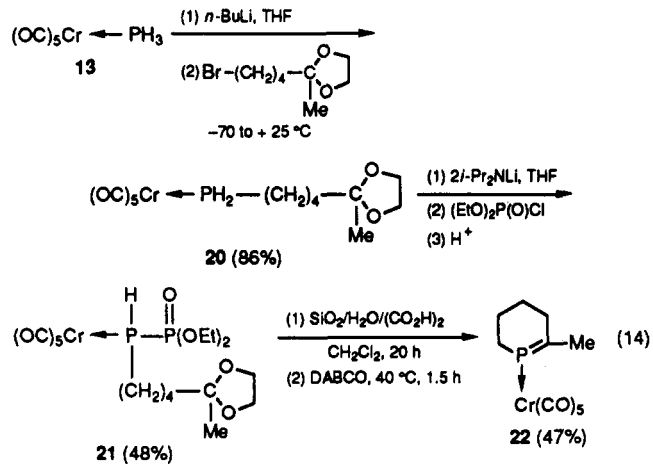
Scheme III. Synthesis of "Phospha-Wittig" Reagents via the 7-Phosphanorbornadiene Approach



78.7 ppm, $\delta(B)$ = 63.9 ppm in CH_2Cl_2, $^1J(P-P)$ = 224.6 Hz. The ^1H and ^{13}C NMR spectra showed one =C—*Me*, one *Me*—CH, one ethylenic H, and two ethylenic carbons. We have already shown[8] that phosphaalkene complexes tend to isomerize into secondary vinylphosphine complexes when phosphaallylic protons are available. The probable mechanism of this dimerization is depicted in eq 13. A similar dimerization was described for a 2*H*-phosphole complex.[9]

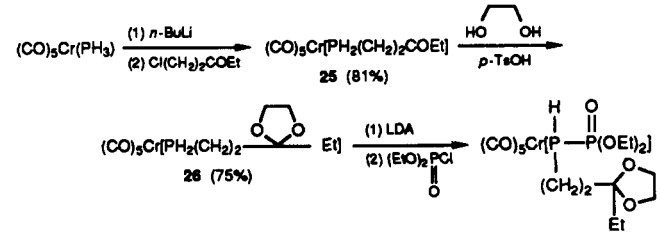


We were also able to synthesize a stable 1-phosphacyclohexane complex via the same approach (eq 14). On the

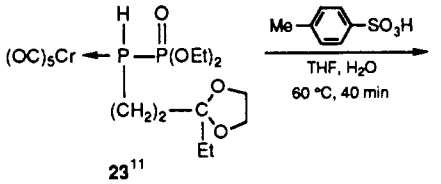


contrary, the synthesis of a four-membered ring was unsuccessful (eq 15). The keto derivative **24** is stable, and

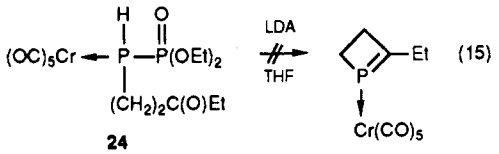
(11) Complex **23** was prepared as follows:



the cyclization does not take place even with LDA as the base.



23[11]



(15)

24

In spite of the failures observed in the synthesis of three- and four-membered rings,[12] this work demonstrates the flexibility of the phospha-Wittig reactions. Obviously, the substitution scheme can be adapted to solve a great variety of synthetic problems.

Experimental Section

NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C and a Bruker WP 80 SY spectrometer operating at 32.44 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif-sur-Yvette, France. Silica gel (70–230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers. The acetals are prepared by the reaction of parent carbonyl compounds with ethylene glycol and *p*-toluenesulfonic acid in benzene.

[2-Methyl-2-[3-(3,4-dimethylphospholyl)propyl]-1,3-dioxolane]pentacarbonyltungsten (2a). 2-Methyl-2-(3-chloropropyl)-1,3-dioxolane (2×10^{-2} mol) was added at 25 °C to a solution of (3,4-dimethylphospholyllithium)pentacarbonyltungsten complex (2×10^{-2} mol) in 50 mL of THF. After 5 h of stirring, the solvent was evaporated and the brown residue was chromatographed on silica gel with hexane/Et_2O (4/1) as eluent to give **2a**: yield 8.8 g (1.56×10^{-2} mol) (78%); yellow solid; mp 75 °C; ^{31}P NMR (CD_2Cl_2) δ 5.74 ($^1J(^{31}P-^{183}W)$ = 207.52); ^{1}H NMR (CD_2Cl_2) δ 1.23 (s, 3 H, CH_3), 1.3–2.1 (m, 6 H, CH_2), 2.14 (s, 6 H, CH_3), 3.9 (m, 4 H, OCH_2), 6.31 (d, ^2J(H-P) = 36.58, =C—H); ^{13}C NMR (CD_2Cl_2) δ 17.33 (d, ^3J(C-P) = 11.1, CH_3), 21.05 (s), 23.9 (s), 30.41 (d, ^1J(C-P) = 24.6, P-CH_2), 40.41 (d, ^2J(C-P) = 11.9, CH_2), 64.97 (s, OCH_2), 109.78 (s, O-*C*-O), 129.0 (d, ^1J(C-P) = 41.32, P—CH=), 151.44 (d, ^2J(C-P) = 7.9, P—CH=*C*), 196.79 (d, ^2J(C-P) = 7, CO cis), 200.02 (d, ^2J(C-P) = 17.12, CO trans); mass spectrum (^{184}W) *m/z* 564 (M, 30), 424 (M - 5CO, 26), 407 (424 - CH_3 - 2H, 100). Anal. Calcd for $C_{18}H_{21}O_7PW$: C, 38.32; H, 3.75. Found: C, 38.41, H, 3.79.

[2-Phenyl-2-[3-(3,4-dimethylphospholyl)propyl]-1,3-dioxolane]pentacarbonyltungsten (2b). The procedure is the same as for **2a** with 2-phenyl-2-(3-chloropropyl)-1,3-dioxolane (2×10^{-2} mol) replacing 2-methyl-2-(3-chloropropyl)-1,3-dioxolane. After 8 h of stirring and evaporation of the solvent, the residue was chromatographed with hexane/Et_2O (4/1) as eluent to give **2b**: yield 8.89 g (1.42×10^{-2} mol, 71%); yellow oil; ^{31}P NMR (CD_2Cl_2) δ 5.97 ($^1J(^{31}P-^{183}W)$ = 210.0); ^{1}H NMR (CD_2Cl_2) δ 1.3–2.0 (m, 6 H), 2.09 (s, 6 H, CH_3), 3.6–4.1 (m, 4 H, OCH_2), 6.25 (d, 2 H, ^2J(H-P) = 36.7, =C—H), 7.2–7.5 (m, 5 H, C_6H_5); ^{13}C NMR (CD_2Cl_2) δ 17.2 (d, ^3J(C-P) = 10.9, CH_3), 20.66 (s, CH_2), 30.1 (d, ^1J(C-P) = 24.5, CH_2-P), 41.6 (d, ^2J(C-P) = 11.6, CH_2), 64.85 (s, OCH_2), 110.24 (s, O-*C*-O), 125.98 (s, CH (C_6H_5)), 128.15 (s, CH (C_6H_5), 128.36 (s, CH (C_6H_5), 128.98 (d, ^1J(C-P) = 41.3, =CH), 142.85 (s, C (C_6H_5)), 151.4 (d, ^2J(C-P) = 8.3, =*C*—CH_3), 196.8 (d, ^2J(C-P) = 6.4, CO cis), 200.06 (d, ^2J(C-P) = 17.4, CO trans); mass spectrum (^{184}W) *m/z* 626 (M, 30), 542 (M - 3CO, 23), 486 (M - 5CO, 17), 407 (486 - C_6H_5 - 2H, 100).

[Methyl 4-(3,4-dimethylphospholyl)butyl ketone]pentacarbonyltungsten (7). 6-Bromo-2-hexanone (2×10^{-2} mol) was added at −78 °C to a solution of (3,4-dimethylphospholyllithium)pentacarbonyltungsten complex (2×10^{-2} mol) in 50 mL of THF. After 15 min, the mixture was warmed slowly to 25 °C and the solvent was evaporated. The yellow residue was chromatographed with hexane/Et_2O (5/1) as eluent to give **7**: yield 8.54 g (1.6×10^{-2} mol, 80%); yellow oil; ^{31}P NMR ($CDCl_3$) δ 2.43 ($^1J(^{31}P-^{183}W)$ = 207.5); ^{1}H NMR ($CDCl_3$) δ 1.2–1.5 (m, 2 H, CH_2), 1.5–1.7 (m, 2 H, CH_2), 1.8–2.0 (m, 2 H, CH_2), 2.1 (s, 3 H, $COCH_3$), 2.15 (s, 6 H, CH_3), 2.4 (t, 2 H, CH_2), 6.25 (d, 2 H, ^{2}J(H-P) = 36, =C—H); ^{13}C NMR ($CDCl_3$) δ 17.3 (d, ^3J(C-P) = 10.0, CH_3), 24.77 (d, ^2J(C-P) = 13.0, CH_2), 25.49 (s), 28.94 (d, ^1J(C-P) = 24.7, PCH_2), 30.08 (s), 42.94 (s, C(O)CH_2), 128.76 (d, ^1J(C-P) = 41.3, =C—H), 151.0 (d, ^2J(C-P) = 7.5, =*C*—), 196.32 (d, ^2J(C-P) = 7, CO cis), 199.34 (d, ^2J(C-P) = 17.6, CO trans), 208.22 (s, CO); mass spectrum (^{184}W) *m/z* 534 (M, 19), 506 (M - CO, 17), 478 (m - 2CO, 30), 450 (M - 3CO, 9), 422 (M - 4*CO*, 6), 394 (M - 5CO, 100). Anal. Calcd for $C_{17}H_{19}O_6PW$: C, 38.22; H, 3.58. Found: C, 38.75; H, 3.52.

Synthesis of (7-Phosphanorbornadiene)pentacarbonyltungsten Complexes 3a, 3b, and 9. Complexes **2a**, **2b**, and **7** (1.5×10^{-2} mol) and DMAD (3.75×10^{-2} mol) were heated without solvent at 70 °C for 18 h. The crude mixtures were then chromatographed first with hexane/CH_2Cl_2 (1/1) to remove traces of DMAD and then with Et_2O/hexane (4/1) as eluent.

3a: yield 8.47 g (1.2×10^{-2} mol, 80%); yellow solid; mp 80 °C; ^{31}P NMR ($CDCl_3$) δ 215.88 ($^1J(^{31}P-^{183}W)$ = 234.37); ^{1}H NMR (CD_2Cl_2) δ 1.20 (s, 3 H, CH_3), 1.5–1.8 (m, 4 H, CH_2), 1.95 (d, 6 H, ^4J(H-P) = 1.2, CH_3), 2.1–2.4 (m, 2 H, CH_2), 3.6 (d, 2 H, ^2J(H-P) = 2.8, CH), 3.79 (s, 6 H, OCH_3), 3.88 (m, 4 H, OCH_2); ^{13}C NMR (CD_2Cl_2) δ 16 (s, CH_3), 20 (s), 23.9 (s), 35.78 (s), 40.2 (d, ^2J(C-P) = 11, CH_2), 52.68 (s, OCH_3), 59.24 (d, ^1J(C-P) = 19.6, P-CH), 64.98 (s, OCH_2), 109.64 (s, O-*C*-O), 139.0 (d, ^2J(C-P) = 15.9, =*C*—Me), 145.64 (d, ^2J(C-P) = 4.4, =*C*—CO_2Me), 165.45 (s, *C*O_2Me), 196.7 (d, ^2J(C-P) = 6.3, CO *cis*), 198.5 (d, ^2J(C-P) = 24.9, CO *trans*); mass spectrum (^{184}W) *m/z* 705 (M - 1, 6), 484 ((CO)$_5$W$PC_7H_{13}O_2$, 38), 456 (484 - CO, 100), 428 (484 - 2CO, 32), 395 (100), 344 (484 - 5CO, 93). Anal. Calcd for $C_{24}H_{27}O_{11}PW$: C, 40.81; H, 3.85. Found: C, 40.97; H, 3.59.

3b: yield 8.64 g (1.12×10^{-2} mol, 75%); yellow oil; ^{31}P NMR (CD_2Cl_2) δ 217.75 ($^1J(^{31}P-^{183}W)$ = 234.37); ^{1}H NMR (CD_2Cl_2) δ 1.5–2.3 (m, 6 H, CH_2), 1.93 (s, 6 H, CH_3), 3.56 (d, 2 H, ^2J(H-P) = 2.47, C-H), 3.74 (m, 6 H, OCH_3), 4.0 (m, 6 H, OCH_2); ^{13}C NMR (CD_2Cl_2) δ 16.0 (s, CH_3), 19.0 (s, CH_2), 35.6 (s, P-CH_2), 41.57 (d, ^2J(C-P) = 9.2, CH_2), 52.6 (s, OCH_3), 59.2 (d, ^1J(C-P) = 19.6, C-P), 64.9 (s, OCH_2), 110.12 (s, O-*C*-O), 126.00, 128.20, 128.46 (s, C_6H_5), 139.1 (d, ^2J(C-P) = 15.7, =*C*—CH_3), 143.0 (s, C ipso C_6H_5), 145.62 (d, ^2J(C-P) = 4.3, O_2C—*C*=), 165.34 (s, *C*O_2CH_3), 196.64 (d, ^2J(C-P) = 6.5, CO cis), 198.5 (d, ^2J(C-P) = 23.7, CO trans); mass spectrum (^{184}W) *m/z* 546 ((CO)$_5$W$PC_{12}H_{15}O_2$, 4), 518 (M - CO, 13), 462 (546 - 3CO, 100). Anal. Calcd for $C_{29}H_{29}O_{11}PW$: C, 45.33; H, 3.8. Found: C, 46.77; H, 4.04.

9: yield 7.5 g (1.11×10^{-2} mol, 74%); yellow oil; ^{31}P NMR ($CDCl_3$) δ 214.38 ($^1J(^{31}P-^{183}W)$ = 234.37; ^{1}H NMR ($CDCl_3$) δ 1.2–1.7 (m, 4 H, CH_2), 1.88 (s, 6 H, CH_3), 2.05 (s, 3 H, CH_3), 2.1–2.3 (m, 2 H, CH_2), 2.4 (t, 2 H, C(O)CH_2), 3.5 (d, 2 H, ^2J(H-P) = 2.7, CH), 3.75 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 15.81 (s, =*C*—CH_3), 24.17 (s), 24.43 (s, CH_2), 29.68 (s), 34.97 (s, CH_2), 42.48 (s, $COCH_2$), 52.4 (s, OCH_3), 58.67 (d, ^1J(C-P) = 19.5, CH), 138.35 (d, ^2J(C-P) = 15.6, =*C*—CH_3), 145.05 (d, ^2J(C-P) = 4.2, =*C*—COO), 164.96 (s, COO), 195.97 (d, ^2J(C-P) = 6.8, CO cis), 197.56 (d, ^2J(C-P) = 25.3 Hz, CO trans), 207.69 (s, $COCH_3$); mass spectrum (^{184}W) *m/z* 677 (M, 6), 455 ((CO)$_5$W$P(CH_2)_4C(O)CH_3$, 75), 427 (455 - CO, 9), 399 (455 - 2CO, 38), 371 (455 - 3CO, 38), 341 (355 - 4CO - 2H, 100). Anal. Calcd for $C_{23}H_{25}O_{10}PW$: C, 40.83; H, 3.72. Found: C, 41.46; H, 3.72.

Synthesis of (7-Phosphanorbornadiene)pentacarbonyltungsten Complexes 4a and 4b. Complex **3a** or **3b** (1×10^{-2} mol) was added at 25 °C to a solution of H_2O (2.22×10^{-2} mol)

(12) Similarly, the intramolecular Wittig reaction fails for the synthesis of cyclopropenes and cyclobutenes; see ref 5. The cyclic strain associated with the three- and four-membered rings is supposed to prevent the formation of the oxaphosphetane intermediate.

and trichloroacetic acid (2×10^{-2} mol) in 20 mL of CH_2Cl_2. After 1 h for **3a** and 5 h for **3b**, the reaction mixture was washed with H_2O (3×15 mL) and the organic phase was dried on magnesium sulfate. After filtration and evaporation of the solvent, the yellow residue was chromatographed with Et_2O as eluent to give **4a**: yield 5.69 g (8.6×10^{-3} mol, 86%); yellow solid; mp 90 °C; ^{31}P NMR ($CDCl_3$) δ 213.77 ($^1J(^{31}P-^{183}W)$ = 234.37); ^1H NMR ($CDCl_3$) δ 1.6–1.9 (m, 2 H, CH_2), 1.95 (s, 6 H, CH_3), 2.12 (s, 3 H, CH_3), 2.2 (m, 2 H, CH_2), 2.53 (t, ^3J(H–H) = 7.0, 2 H, CH_2CO), 3.57 (d, 2 H, ^2J(H–P) = 2.6, C–H), 3.82 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 16.0 (s, CH_3), 19.1 (s, CH_3), 29.76 (s, CH_2), 34.88 (s, CH_2), 44.01 (d, ^2J(C–P) = 11.1, PCH_2CH_2), 52.63 (s, OCH_3), 58.94 (d, ^1J(C–P) = 19.48, P–CH), 138.59 (d, ^2J(C–P) = 15.65, =*C*—CH_3), 145.26 (d, ^2J(C–P) = 4.15, =*C*—CO_2), 165.24 (s, CO_2CH_3), 196.12 (d, ^2J(C–P) = 6.28, CO cis), 197.6 (d, ^2J(C–P) = 25.48, CO trans), 207.31 (s, CO); mass spectrum (^{184}W) *m/z* 634 (M – CO, 11), 522 (m – 5CO, 4), 440 ($(CO)_5WPC_5H_9O$, 100). Anal. Calcd for $C_{22}H_{23}O_{10}PW$: C, 39.90; H, 3.50. Found: C, 39.98; H, 3.52.

4b: yield 5.43 g (7.5×10^{-3} mol, 75%); yellow oil; ^{31}P NMR ($CDCl_3$) δ 213.9 ($^1J(^{31}P-^{183}W)$ = 234.37); ^1H NMR ($CDCl_3$) δ 1.93 (s, 6 H, CH_3), 1.8–2.0 (m, 2 H, CH_2), 2.2–2.5 (m, 2 H, CH_2), 3.0 (t, 2 H, ^3J(H–H) = 6.9, CO–CH_2), 3.59 (d, 2 H, ^2J(C–P) = 2.4, CH), 3.76 (s, 6 H, OCH_3), 7.3–7.6 (m, 3 H, C_6H_5), 7.9 (m, 2 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 15.76 (s, CH_3), 19.36 (s, CH_2), 34.77 (s, P–CH_2), 38.8 (d, ^2J(C–P) = 11, CH_2), 52.31 (s, OCH_3), 58.72 (d, ^1J(C–P) = 19.6, C–H), 127.8 (s, CH (C_6H_5)), 128.41 (s, CH (C_6H_5)), 132.9 (s, CH (C_6H_5)), 136.5 (s, C(C_6H_5)), 138.4 (d, ^2J(C–P) = 16, =*C*—CH_3), 145.0 (d, ^2J(C–P) = 4.1, =*C*—CO_2), 164.9 (s, COO), 195.95 (d, ^2J(C–P) = 6.7, CO cis), 197.4 (d, ^2J(C–P) = 26, CO trans), 198.07 (s, COPh); mass spectrum (^{184}W) *m/z* 502 (M – 222, 23), 446 (502 – 2CO, 57), 418 (502 – 3CO, 42), 390 (502 – 4CO, 93), 362 (502 – 5CO, 100).

Synthesis of [2-Methyl-1-phosphacyclopentene)pentacarbonyltungsten Complex 5a. Complex **4a** (3.31 g, 5×10^{-3} mol) and tributylphosphine (1.21 g, 6×10^{-3} mol) were heated in 5 mL of THF at 45 °C for 20 min. After evaporation of the solvent, the residue was quickly chromtographed with pentane as eluent to give **5a**: yield 0.9 g (2.15×10^{-3} mol, 43%); white solid; mp 90 °C; ^{31}P NMR (CD_2Cl_2) δ 180.21 ($^1J(^{31}P-^{183}W)$ = 244.14); ^1H NMR ($CDCl_3$) δ 1.2–1.8 (m); ^{13}C NMR (CD_2Cl_2) δ 21.0 (d, ^2J(C–P) = 12.9, CH_3), 29.44 (s, CH_2), 36.76 (d, J(C–P) = 11.5, CH_2), 46.11 (s, CH_2), 194.0 (d, ^1J(C–P) = 49.54, C=P), 196.65 (d, ^2J(C–P) = 9.4, CO cis), 201.45 (d, ^2J(C–P) = 26.96, CO trans); mass spectrum (^{184}W) *m/z* 424 (M, 30), 396 (M – CO, 13), 368 (M – 3CO, 30), 335 (100).

[1-(Methoxy)-2-methylphospholane]pentacarbonyltungsten Complex 6a. Complex **4a** (5×10^{-3} mol), tributylphosphine (6×10^{-3} mol), and methanol (5×10^{-2} mol) were heated in 5 mL of THF at 45 °C for 2 h. After evaporation of the solvent, the residue was quickly chromatographed with hexane/CH_2Cl_2 as eluent to give **6a**: yield 1.39 g (3.05×10^{-3} mol, 61%); colorless oil; ^{31}P NMR ($CDCl_3$) δ 158.98 ($^1J(^{31}P-^{183}W)$ = 258.78) (major isomer, 60%), [144.53 ($^1J(^{31}P-^{183}W)$ = 253.9) (minor isomer, 40%)]; ^1H NMR ($CDCl_3$) δ 1.0–2.5 (m), 1.25 (dd, ^3J(H–P) = 19.4, ^3J(H–H) = 7.7, $CHCH_3$), [1.34 (dd, ^3J(H–P) = 15.3, ^3J(H–H) = 6.8, $CHCH_3$) (minor isomer)], 3.45 (d, 3 H, ^3J(H–P) = 12.6, OCH_3) [3.49 (d, 3 H, ^3J(H–P) = 13.9, OCH_3) (minor isomer)]; ^{13}C NMR ($CDCl_3$) δ [12.0 (s, CH_3)], 17.5 (d, ^2J(C–P) = 12.0, CH_3), 25.03 (s, CH_2), [25.31 (s, CH_2)], [34.56 (s, CH_2)], 34.74 (d, ^2J(C–P) = 3.2, CH_2), 36.91 (d, ^1J(C–P) = 26.1, P–CH_2), [37.54, (d, ^1J(C–P) = 23.8, P–CH_2)], 41.95 (d, ^1J(C–P) = 22.2, P–CH), [47.29 (d, ^1J(C–P) = 31.8, P–CH)], 53.36 (s, OCH_3), [55.03 (s, OCH_3)], 196.58 (d, ^2J(C–P) = 7.7, CO cis), 199.0 (d, ^2J(C–P) = 34.2, CO trans); mass spectrum (^{184}W) *m/z* 456 (M, 47), 428 (M – CO, 36), 400 (M – 2CO, 32), 372 (M – 3CO, 83), 369 (M – 3CO – 3H, 100). Anal. Calcd for $C_{11}H_{13}O_6PW$: C, 28.97; H, 2.87. Found: C, 30.74; H, 2.88.

[1-(Methoxy)-2-phenylphospholane]pentacarbonyltungsten Complex 6b. Complex **4b** (5×10^{-3} mol), tributylphosphine (6×10^{-3} mol), and ethanol (5×10^{-2} mol) were heated in 5 mL of THF at 50 °C for 5 h. After evaporation of the solvent, the residue was chromatographed with hexane/CH_2Cl_2 (4/1) as eluent to give **6b**: yield 1.45 g (2.8×10^{-3} mol, 56%); yellow oil; ^{31}P NMR ($CDCl_3$) δ 160.18 ($^1J(^{31}P-^{183}W)$ = 273.43; ^1H NMR ($CDCl_3$) δ 2.0–2.8 (m, 6 H), 3.59 (m, CHPh), 3.60 (d, ^3J(H–P) = 12.5, OCH_3), 7.2–7.5 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 26.15 (s, CH_2), 32.91 (d, J(C–P) = 6.9, CH_2), 37.91 (d, J(C–P) = 24.1, CH_2), 53.77 (d, J(C–P) = 3.9), 55.44 (d, J(C–P) = 17.15), 127.37–129.12 (m, CH (C_6H_5)), 139.4 (d, ^2J(C–P) = 6, C ipso), 195.87 (d, ^2J(C–P) = 7.53, CO cis), 198.9 (d, ^2J(C–P) = 26.75, CO trans); mass spectrum (^{184}W) *m/z* 518 (M, 28), 490 (M – CO, 13), 434 (M – 4CO, 100). Anal. Calcd for $C_{16}H_{15}O_6PW$: C, 37.09; H, 2.92. Found: C, 37.76; H, 3.0.

Synthesis of [2-Methyl-1-phosphacyclohexene]pentacarbonyltungsten Complex 11. Complex **9** (5×10^{-3} mol) and tributylphosphine (6×10^{-3} mol) were heated in 5 mL of THF at 50 °C for 1 h. After evaporation of the solvent, the residue was quickly chromatographed with pentane as eluent to give **11**: yield 1.22 g (2.8×10^{-3} mol, 56%); colorless solid; mp 95 °C; ^{31}P NMR ($CDCl_3$) δ 161.77 ($^1J(^{31}P-^{183}W)$ = 246.58); ^1H NMR ($CDCl_3$) δ 1.6–2.6 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 23.41 (d, J(C–P) = 7.9), 24.67 (d, J(C–P) = 9), 26.55 (d, J(C–P) = 15.5), 31.94 (d, J(C–P) = 8), 38.55 (d, J(C–P) = 11.2), 183.83 (d, ^1J(C–P) = 42.2, C=P), 195.27 (d, ^2J(C–P) = 9.5, CO cis), 199.69 (d, ^2J(C–P) = 27.4, CO trans); mass spectrum (^{184}W) *m/z* 438 (m, 66), 410 (M – CO, 23). Anal. Calcd for $C_{11}H_{11}O_5PW$: C, 30.16; H, 2.52. Found: C, 30.32; H, 2.54.

General Procedure for the Synthesis of the (Alkylphosphane)pentacarbonylchromium Complexes 14a, 14b, and 20. *n*-BuLi (6.3 mL, 1.6 M solution in hexane) was added at –78 °C to a solution of complex **13** (2.2 g, 10 mmol) in THF. The reaction mixture was warmed slightly, and the corresponding halide (10 mmol) was added. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After hydrolysis, evaporation of the solvent, and extraction in ether, the final product was purified by chromatography on a silica gel column with hexane/ether (96/4) as eluent.

[2-Methyl-2-(3-phosphinopropyl)-1,3-dioxolane]pentacarbonylchromium (14a). The reaction mixture was stirred for 22 h at room temperature. **14a**: yield 2.8 g (78%); colorless, low-melting solid; ^{31}P NMR (hexane) δ –45.2; ^1H NMR (C_6D_6) δ 1.20 (s, CH_3), 3.22 (dt, ^1J(H–P) = 327.2, ^3J(H–H) = 6.9, PH_2), 3.48 (s, OCH_2); IR (decalin) ν(CO) 2070 (m), 1948 (vs) cm^{-1}; mass spectrum *m/z* 354 (m, 55), 214 (M – 5CO, 100).

[2-Phenyl-2-(3-phosphinopropyl)-1,3-dioxolane]pentacarbonylchromium (14b). The reaction mixture was stirred for 22 h at room temperature. **14b**: yield 2.7 g (64%); colorless solid; mp 80 °C (pentane); ^{31}P NMR (hexane) δ –46.3; ^1H NMR (C_6D_6) δ 0.9 (m, CH_2), 1.3 (m, CH_2), 1.7 (m, CH_2), 3.13 (dt, ^1J(H–P) = 327.7, ^3J(H–H) = 7.4, PH_2), 3.3–3.6 (m, OCH_2); IR (decalin) ν(CO) 2070 (m), 1948 (vs) cm^{-1}; mass spectrum *m/z* 416 (M, 34), 276 (M – 5CO, 100). Anal. Calcd for $C_{17}H_{17}O_7PCr$: C, 49.05; H, 4.12. Found: C, 49.57; H, 3.94.

[2-Methyl-2-(4-phosphinobutyl)-1,3-dioxolane]pentacarbonylchromium (20). The reaction between $(CO)_5CrPH_2Li$ and 2-methyl-2-(4-bromobutyl)dioxolane takes place between –70 °C and room temperature. **20**: yield 3.2 g (86%); low-melting solid; ^{31}P NMR (THF) δ –48.4; ^1H NMR (C_6D_6) δ 1.27 (s, CH_3), 3.28 (dt, ^1J(H–P) = 326.0, ^3J(H–H) = 12.7, PH_2), 3.53 (s, OCH_2); IR (decalin) ν(CO) 2070 (m), 1945 (vs) cm^{-1}; mass spectrum *m/z* 368 (M, 47), 228 (M – 5CO, 100). Anal. Calcd for $C_{13}H_{17}O_7PCr$: C, 42.40; H, 4.65. Found: C, 42.43; H, 4.57.

General Procedure for the Synthesis of the (Phosphorylphosphine)pentacarbonylchromium Complexes 15a, 15b, and 21. To a solution of 10 mmol of lithium diisopropylamide (LDA) in THF at –78 °C was added a THF solution of 5 mmol of the (alkylphosphane)pentacarbonylchromium complex (**14a, 14b, 20**). After 10 min, diethyl chlorophosphate (5.5 mmol) was added at –78 °C. The mixture was warmed to 0 °C and hydrolyzed with aqueous hydrochloric acid (pH < 7). After extraction with ether, the crude product was purified by column chromatography with hexane/dichloromethane (1/1) as eluent.

15a: yield 1.3 g (53%); colorless oil; ^{31}P NMR (ether) δ 25.4 (*AB*, $^1J_{AB}$ = 61.0, P(O)(OEt)$_2$), –21.5 (*AB*, PH); ^1H NMR (C_6D_6) δ 1.00 (t, ^3J(H–H) = 7.0, CH_2CH_3), 1.24 (s, C–CH_3), 3.50 (m, OCH_2), 3.9 (m, OCH_2), 4.12 (dt, ^1J(H–P) = 318.1, PH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum *m/z* 490 (M, 10), 350 (M – 5CO, 100).

15b: yield 1.8 g (64%); colorless oil; ^{31}P NMR (pentane) δ 23.3 (*AB*, $^1J_{AB}$ = 58.6, P(O)(OEt)$_2$), –19.7 (*AB*, PH); ^1H NMR (C_6D_6) δ 0.98 (t, ^3J(H–H) = 7.0, CH_3), 0.99 (t, ^3J(H–H) = 7.0, CH_3), 1.9 (m, 6 H, CH_2), 3.3–3.9 (m, 8 H, OCH_2), 4.05 (dt, ^1J(H–P) = 319.6,

PH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 552 (M, 5), 412 (M – 5CO, 100).

21: yield 1.2 g (48%); colorless oil; ^{31}P NMR (C_6D_6) δ 23.4 (*AB*, $^1J_{AB}$ = 61.0, P(O)(OEt)$_2$), –20.9 (*AB*, PH); ^1H NMR (C_6D_6) δ 0.98 (t, ^3J(H–H) = 7.1, CH_2CH_3), 1.00 (t, ^1J(H–H) = 7.1, CH_2CH_3), 1.25 (s, C–CH_3), 3.51 (s, OCH_2CH_2O), 3.88 (m, OCH_2CH_3), 4.16 (dt, ^1J(H–P) = 318.6, ^3J(H–H) = 5.9, PH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 504 (M, 10), 364 (M – 5CO, 100). Anal. Calcd for $C_{17}H_{26}O_{10}P_2Cr$: C, 40.49; H, 5.20. Found: C, 40.19; H, 5.45.

Synthesis of the 1-Phosphacycloalkene Complexes 17a and 22. Water (0.15 mL) was added with continuous magnetic stirring to a suspension of silica gel (1.5 g, silica gel 60, Merck, 70–230 mesh) in dichloromethane. After a few minutes, the acetal **15a** (2 mmol) and oxalic acid (60 mg) were added and stirring was continued at room temperature for 20 h. Sodium carbonate was added to neutralize the mixture. The solid phase was separated by filtration. Drying with $MgSO_4$ and evaporation of the solvent gave crude **16a**. DABCO (2 mmol) was added to a THF solution of **16a**. The reaction was complete in a few minutes. Complex **17a** was purified by chromatography with pentane.

The same procedure was used for the synthesis of **22** from **21**. The cyclization reaction in the presence of DABCO was complete after 1.5 h at 40 °C.

17a: yield 0.33 g (57%); pale yellow solid; mp < 50 °C; ^{31}P NMR (C_6D_6) δ 224.3; ^1H NMR (C_6D_6) δ 1.85 (d, ^3J(H–P) = 26.7, CH_3); ^{13}C NMR (C_6D_6) δ 18.54 (d, ^2J(C–P) = 12.1, CH_3), 26.45 (s, CH_2), 33.76 (d, J(C–P) = 6.0 Hz, CH_2), 44.29 (s, CH_2), 194.29 (d, ^1J(C–P) = 42.8, P=C), 215.48 (d, ^2J(C–P) = 18.1, cis CO), 221.54 (trans CO); IR (decalin) ν(CO) 2070 (m), 1960 (vs) cm^{-1}; mass spectrum m/z 292 (M, 26), 152 (M – 5CO, 100). Anal. Calcd for $C_{10}H_9PO_5Cr$: C, 41.11; H, 3.11. Found: C, 41.20; H, 3.19.

22: yield 0.29 g (47%); pale yellow oil; ^{31}P NMR (pentane) δ 214.1; ^1H NMR (C_6D_6) δ 1.55 (d, ^3J(H–P) = 28.8, CH_3); ^{13}C NMR (C_6D_6) δ 23.0 (d, J(C–P) = 8.1), 24.48 (d, J(C–P) = 8.6), 25.40 (d, J(C–P) = 14.6), 30.62 (s), 38.99 (d, J(C–P) = 12.1), 187.26 (d, ^1J(C–P) = 35.2, P=C), 215.98 (d, ^2J(C–P) = 18.2, cis CO), 221.96 (trans CO); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 306 (M, 26), 166 (M – 5CO, 100). Anal. Calcd for $C_{11}H_{11}O_5PCr$: C, 43.15; H, 3.62. Found: C, 41.28; H, 3.60.

Synthesis and Methanol-Trapping Reaction of the Phosphacyclopentene Complex 17b. Water (0.15 mL) was added to a stirred suspension of silica gel (1.5 g) in dichloromethane. Trichloroacetic acid (0.33 g, 2 mmol) and the acetal **15b** (2 mmol) were added, and the mixture was stirred at room temperature for 2 h. Neutralization with sodium carbonate, filtration of the solid phase, and drying with $MgSO_4$ gave crude **16b**. DABCO (2 mmol) was added to a THF/methanol (1/1) solution of **16b**. The reaction was complete in about 10 min. The two isomers of compound **18** were obtained separately after chromatography with hexane/ether (99/1) as eluent. Total yield: 0.43 g (56%). Isomer ratio: 85/15.

18 (minor isomer): colorless solid; mp < 50 °C, ^{31}P NMR (ether) δ 190.1; ^1H NMR (C_6D_6) δ 2.79 (m, CH (Ph)), 2.77 (d, ^3J(H–P) = 12.4, OCH_3); ^{13}C NMR (C_6D_6) δ 24.55 (s, CH_2), 33.67 (s, CH_2), 37.55 (d, J(C–P) = 21.6, CH_2), 54.18 (s), 57.84 (d, J(C–P) = 17.61), 216.9 (d, ^2J(C–P) = 14.6, cis CO); IR (decalin) ν(CO) 2070 (m), 1960 (s), 1940 (vs) cm^{-1}; mass spectrum m/z 386 (M, 12), 246 (M – 5CO, 100).

18 (major isomer): colorless oil; ^{31}P NMR (hexane/ether) δ 207.2; ^1H NMR (C_6D_6) δ 3.01 (d, ^3J(H–P) = 11.8, OCH_3), 3.1 (m, CH (Ph)); ^{13}C NMR (C_6D_6) δ 25.47 (s, CH_2), 32.81 (d, J(C–P) = 6.5, CH_2), 35.76 (d, J(C–P) = 19.6, CH_2), 52.34 (d, J(C–P) = 6.5), 54.64 (d, J(C–P) = 12.1), 216.31 (d, ^2J(C–P) = 15.1, cis CO), 221.2 (d, ^2J(C–P) = 6.0, trans CO); IR (decalin) ν(CO) 2065 (m), 1955 (s), 1940 (vs) cm^{-1}. Anal. Calcd for $C_{16}H_{15}O_6PCr$: C, 49.75; H, 3.91. Found: C, 49.75; H, 3.91.

Dimerization of the 1-Phosphacyclopentene Complex 17a to Compound 19. When kept in concentrated solution, complex **17a** dimerizes slowly to complex **19**. **19** was separated from the remaining **17a** by column chromatography with hexane/ether (90/10) as eluent.

19: colorless solid; mp 179 °C dec; ^{31}P NMR (CH_2Cl_2) δ 78.75 (*AB*, $^1J_{AB}$ = 224.6), 63.92 (*AB*); ^1H NMR ($CDCl_3$) δ 1.39 (dd, ^3J(H–P) = 17.2, ^3J(H–H) = 6.8, CHCH_3), 2.08 (d, ^3J(H–P) = 10.3, =C–CH_3), 6.25 (d, ^3J(H–P) = 27.6, =CH); ^{13}C NMR ($CDCl_3$) δ 16.79 (d, J(C–P) = 15.5), 17.54 (d, J(C–P) = 9.1), 26.14 (s), 30.31 (dd, J(C–P) = 22.4, 8.8), 32.65 (dd, J(C–P) = 18.3, 6.1), 33.30 (s), 37.27 (d, J(C–P) = 6.5), 38.88 (d, J(C–P) = 9.6), 135.75 (d, J(C–P) = 15.1, C=C), 140.61 (dd, J(C–P) = 12.2, 3.1, C=C); IR (CH_2Cl_2) ν(CO) 2070 (m), 2060 (m), 1950 (vs), 1940 (sh) cm^{-1}; mass spectrum m/z 584 (M, 15), 444 (M – 5CO, 47), 304 (M – 10CO, 45), 253 ((CO)$_5$Cr(PC$_5$H$_{10}$), 100). Anal. Calcd for $C_{20}H_{18}O_{10}P_2Cr$: C, 41.11; H, 3.11. Found: C, 40.86; H, 3.25.

Notes

Solid-State Structure of the Bis(allyl)rhodium Chloride Dimer

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Summary: ^{13}C NMR analysis of the solid, labeled bis(allyl)rhodium chloride dimer suggested a structure simpler than that reported previously as determined by X-ray crystallographic analysis. Reexamination of the solid-state structure of this compound showed it to be consistent with the simpler, NMR-determined structure.

In conjunction with studies of oxide-bound organorhodium complexes, we prepared the ^{13}C-labeled (allyl)rhodium chloride dimer, **1**, and examined its ^{13}C NMR spectrum in the solid state. Complex **1** was prepared from [(OC)$_2$RhCl]$_2$ and [1-^{13}C]allyl chloride. The ^{13}C NMR spectrum of **1** was obtained by using a JEOL GX 270 instrument operating at 67.9 MHz.[2] It consisted simply of two resonances of equal intensity at δ 77.2 and 45.2 and was similar to that for the material recorded in solution [δ 76.5 (J_{Rh-C} = 6.8 Hz) and 44.5 (J_{Rh-C} = 11.9 Hz)]. That only two signals were observed suggested a simple substitution geometry about the Rh, inconsistent with the reported structure[1] proposing some double-bond localization for the allyl ligands and noting unequal rhodium–

(1) McPartlin, M.; Mason, R. *Chem. Commun.* **1967**, 16.

(2) Conditions for this experiment were as follows: cross-polarization mixing time 1.5 ms; field strength for Hartman–Hahn match 50 kHz; ν_{rot} 5400 Hz; 100 transients.

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