state (or states) which, on the basis of the similar amounts of **4** and **5** formed in the CBrCl$_3$ experiment, undergo relatively nonselective cleavage of the Re–CH$_3$ and Re–C(O)CH$_3$ bonds. In the presence of CBrCl$_3$, the radicals resulting from this cleavage are trapped.[16]   Without CBrCl$_3$ in solution, the CpRe(CO)$_2$R· (R = Me, C(O)Me) can go on to product CpRe(CO)$_3$ either by an associative (17e–19e) or a dissociative mechanism of substitution of R· by CO. The CH$_3$· radicals produced are carbonylated, and the acetyl radicals can then either combine to form 2,3-butanedione or, in the presence of sufficient concentrations of CCl$_4$, react to form acetyl chloride; CCl$_4$ does not transfer chlorine rapidly enough (k = 8.2 M^{-1} s^{-1} at 7 °C)[12] to compete with carbonylation of the methyl radicals. This mechanism also accounts for the statistical distribution of isotopes in the reaction of **2** with ^{13}CO; acetyl radicals are known to undergo rapid interchange of acyl groups with 1,2-diketones.[17]

In summary, we have found that the cyclopentadienyl rhenium complexes discussed here undergo thermal and photochemical decomposition by different mechanisms; the latter process involves M–C bond homolysis, leading to methyl and acetyl radicals. The methyl radicals react competitively with CO and CBrCl$_3$; CCl$_4$ reacts more slowly and scavenges only the acetyl radical product of CH$_3$· carbonylation. It seems possible that some other organometallic "double carbonylation" reactions may take place by similar nonchain radical mechanisms;[18] in addition, our results suggest that CBrCl$_3$ is substantially more useful than CCl$_4$ as a diagnostic reagent for organic and organometallic radical intermediates.[19]

(16) Many instances are known in which photolysis of metal alkyl complexes leads to metal and alkyl radicals that can be trapped (e.g., by CCl$_4$ or spin traps); there is considerably less evidence for generation of acyl radicals in acyl metal complex irradiations. See, for example, ref 19 and: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: San Francisco, 1979. (b) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 766. (c) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* 1976, 14, 345. (d) Hudson, A.; Lappert, M. F.; Lednor, P. W.; MacQuitty, J. J.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* 1981, 2159.
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(18) Booth, G.; Chatt, J. *J. Chem. Soc. A* 1966, 634. Bauld, N. L. *Tetrahedron Lett.* 1963, 27, 1841. Ryand, M.; Kwang-Myeong, S.; Sawa, Y.; Tsutsumi, S. *J. Organomet. Chem.* 1966, 5, 305. Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1981, 54, 2161. Ozawa, F.; Yamamoto, A. *Chem. Lett.* 1981, 289. Nudelman, N. S.; Outumuro, P. *J. Org. Chem.* 1982, 47, 4347. Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. I, p 166. Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Books: Mill Valley, CA, 1980; p 490.
(19) CCl$_4$ has been used extensively to trap organometallic radicals, and bimolecular rate constants, k_T, of halogen abstraction by organometallic radicals from CX$_4$, CHX$_3$, CH$_2$X$_2$, and C$_6$H$_5$CH$_2$X (X = Cl or Br) have been estimated[19e] or more recently, directly measured.[19a–d] The ordering of increasing k_T roughly corresponds to a decrease in the C–X bond dissociation energy,[19b] supporting our observation that CCl$_3$Br is more efficient than CCl$_4$ at trapping metal radicals. (a) Lee, K.-W.; Hanckel, J. M.; Brown, T. L. *J. Am. Chem. Soc.* 1986, 108, 2266. (b) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* 1985, 4, 42 and references therein. (c) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* 1986, 25, 1852. (d) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* 1982, 104, 1842. (e) Laine, R. M.; Ford, P. C. *Inorg. Chem.* 1977, 16, 388. (f) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* 1983, 105, 5934.

Synthesis and Protonation Reactions of Trimethylphosphine-Substituted Carbyne Complexes of Molybdenum and Tungsten. The Tungsten Alkylidene Complexes [(W≡CHR)Cl$_2$(CO)(PMe$_3$)$_2$] as Precursors for Carbyne Complexes Containing Weakly Coordinated Ligands

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Summary: Efficient procedures for the synthesis of the tungsten carbyne complexes [(W≡CR)Cl(CO)(PMe$_3$)$_3$] (**2**, R = C$_6$H$_5$, C$_6$H$_4$CH$_3$-4) and [(M≡CPh)Br(PMe$_3$)$_4$] (**3**, M = W, and **5**, M = Mo) are described. Reaction of complex **3** with HBr gives the hydrido complex [(W≡CPh)Br$_2$(H)(PMe$_3$)$_3$]. Reaction of complexes **2** with HCl gives the tungsten alkylidene complexes [(W≡CHR)Cl$_2$(CO)(PMe$_3$)$_2$] (**7**) that can be deprotonated to give coordinatively labile anionic tungsten carbyne complexes [(W≡CR)Cl$_2$(CO)(PMe$_3$)$_2$]$^-$. Dehydrochlorination of **7** in the presence of ligands provides substituted tungsten carbyne complexes [(W≡CR)Cl(CO)(PMe$_3$)$_2$L] (L = pyridine, P-(OMe)$_3$, CNCMe$_3$). The crystal structure of the benzylidene complex [(W≡CHPh)Cl$_2$(CO)(PMe$_3$)$_2$] is reported.

Bis(donor ligand)-substituted carbyne complexes[1] of the group 6 transition metals have become easily accessible through the recent development of simple synthetic procedures.[2]   The bis(pyridine)-substituted complexes [(M≡CR)X(CO)$_2$(py$_2$)] (X = Cl, Br; py = pyridine; M = Cr, Mo, W; R = alkyl, aryl) are particularly useful systems since they combine increased thermal stability—compared to the tetracarbonylmetal carbyne complexes [(M≡CR)-X(CO)$_4$]—and a high degree of reactivity—due to coordinative lability of the two pyridine ligands. The lability of the pyridine ligands is essential in the synthesis of stable tungsten alkene carbyne complexes such as [(W≡CPh)-Cl(maleic anhydride)(CO)(py)$_2$].[4]   On the other hand, reaction of [(W≡CPh)Cl(CO)$_2$(py)$_2$] with alkynes leads to alkyne polymerization without detectable metal alkyne carbyne complexes as intermediates.[5]   Our interest in this latter type of metal complex led us to develop more strongly stabilized metal carbyne complexes containing only one weakly coordinated ligand. Availability of such

(1) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* 1977, 110, 805–815.
(2) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* 1985, 4, 608–610.
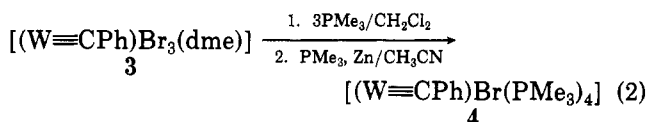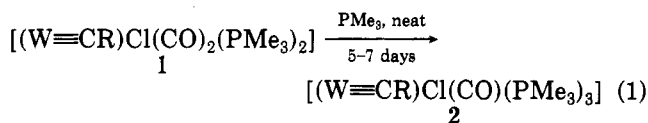(3) Fischer, E. O.; Kreis, G. *Chem. Ber.* 1976, 109, 1673–1683.
(4) Mayr, A.; Dorries, A. M.; McDermott, G. A. *J. Am. Chem. Soc.* 1985, 107, 7775–7776.
(5) Unpublished observations.

compounds, of course, would also be of general synthetic interest.

Treatment of the complexes [(W≡CR)Cl(CO)$_2$(PMe$_3$)$_2$]^2 (1a, R = C$_6$H$_5$; 1b, R = C$_6$H$_4$CH$_3$-4) with neat trimethylphosphine for 1 week at room temperature provides the tris(trimethylphosphine)-substituted complexes [(W≡CR)Cl(CO)(PMe$_3$)$_3$] (2a, R = C$_6$H$_5$; 2b, R = C$_6$H$_4$-4-CH$_3$).^{6} The reaction proceeds via as yet unidentified intermediates. After removal of PMe$_3$ in vacuo and recrystallization from ether, 2a and 2b are obtained as red and yellow crystals, respectively, in up to 92% yield. Substitution of the last carbonyl ligand has not been observed.^{7} The carbonyl-free complex [(W≡CPh)Br(PMe$_3$)$_4$]^8 (4) is accessible, however, in a reductive procedure from [(W≡CPh)Br$_3$(dme)]^9 (3, dme = dimethyoxethane). Complex

$$[(W≡CR)Cl(CO)_2(PMe_3)_2] \xrightarrow[\text{5-7 days}]{\text{PMe}_3, \text{ neat}} $$
$$\textbf{1}$$
$$[(W≡CR)Cl(CO)(PMe_3)_3] \quad (1)$$
$$\textbf{2}$$

$$[(W≡CPh)Br_3(dme)] \xrightarrow[\text{2. PMe}_3, \text{ Zn/CH}_3\text{CN}]{\text{1. 3PMe}_3\text{/CH}_2\text{Cl}_2} $$
$$\textbf{3}$$
$$[(W≡CPh)Br(PMe_3)_4] \quad (2)$$
$$\textbf{4}$$

3 is first allowed to react with trimethylphosphine in CH$_2$Cl$_2$ to give an intermediate, formulated as [(W≡CPh)Br$_3$(PMe$_3$)$_3$], which is reduced with zinc in acetonitrile in the presence of trimethylphosphine. The reduction step is analogous to the synthesis of [(W≡CCMe$_3$)Cl(PMe$_3$)$_4$] by sodium amalgam reduction of [(W≡CCMe$_3$)Cl$_3$-(PMe$_3$)$_3$].^{10} After removal of acetonitrile, 4 is extracted with diethyl ether. The ether is then slowly removed to leave air-sensitive deep purple crystals of 4 (61%) that are moderately thermally stable. Analytically pure crystals are obtained by recrystallization from diethyl ether. Complex 4 gives a well-resolved ^{1}H NMR spectrum,^{8} but the ^{13}C and ^{31}P NMR resonances are very broad even at low temperatures. The molybdenum analogue [(Mo≡CPh)Br(PMe$_3$)$_4$]^{11} (5) was prepared analogously in 69% yield by zinc reduction of [(Mo≡CPh)Br$_3$(PMe$_3$)$_3$]^{12} (6), in acetonitrile in the presence of PMe$_3$. Compound 6 is very air-sensitive and thermally labile. Related complexes [(Mo≡CSiMe$_3$)Br(PR$_3$)$_4$] have previously been prepared by reaction of the dinuclear alkylidene complexes [Mo$_2$-(CHSiMe$_3$)$_2$Br$_2$(PR$_3$)$_4$] with the corresponding phosphines.^{13}
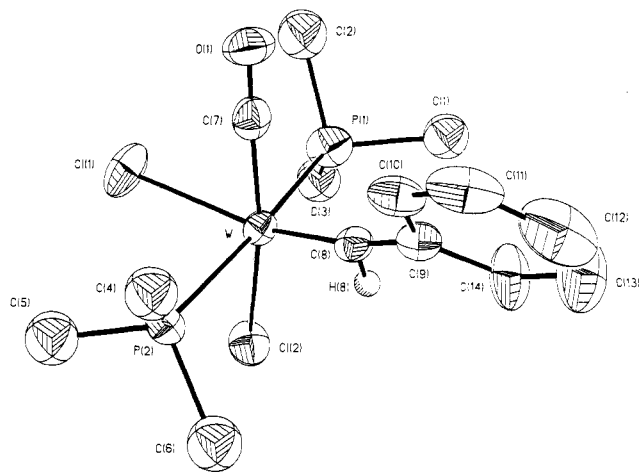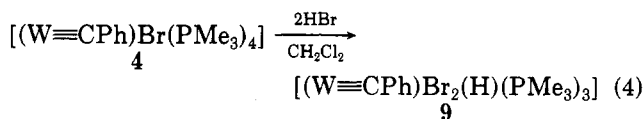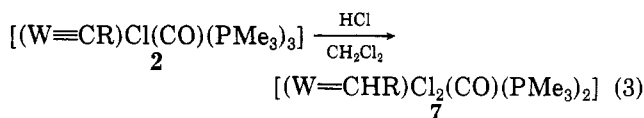

Figure 1. Molecular structure of [(W=CHPh)Cl$_2$(CO)(PMe$_3$)$_2$] (7a). Bond distances (Å) and angles (deg): W–C(8), 1.860 (7); W–H(8), 1.884; W–C(7), 1.963 (9); W–Cl(1), 2.444 (2); W–Cl(2), 2.480 (2); W–P(1), 2.511 (3); W–P(2), 2.496 (3); Cl(1)–W–C(8), 154.5 (2); Cl(2)–W–C(7), 168.9 (2); P(1)–W–P(2), 171.3 (1); W–C(8)–C(9), 164.6 (6); W–C(8)–H(8), 74.6; dihedral angle C(7)–W–C(8)–C(9), 24(3).

Protonation of the carbonyl-containing compounds 2 in CH$_2$Cl$_2$ with excess aqueous concentrated HCl at room temperature gives the tungsten alkylidene complexes [(W=CHR)Cl$_2$(CO)(PMe$_3$)$_2$] (7a, R = C$_6$H$_5$; 7b, R = C$_6$H$_4$-4-CH$_3$).^{14} The products are obtained in pure form

$$[(W≡CR)Cl(CO)(PMe_3)_3] \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{HCl}} $$
$$\textbf{2}$$
$$[(W=CHR)Cl_2(CO)(PMe_3)_2] \quad (3)$$
$$\textbf{7}$$

$$[(W≡CPh)Br(PMe_3)_4] \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{2HBr}} $$
$$\textbf{4}$$
$$[(W≡CPh)Br_2(H)(PMe_3)_3] \quad (4)$$
$$\textbf{9}$$

simply by drying the organic phase over anhydrous MgSO$_4$ and removal of the solvent. Crystalline samples are obtained from CH$_2$Cl$_2$/pentane. The molecular structure of 7a was determined by X-ray crystallography^{15} and is shown in Figure 1. The neopentylidene analogue [(W=

(6) **2a**: mp 106 °C; IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1896; ^{13}C NMR (ppm, CDCl$_3$) 261 (t, J_{PC} = 10.8 Hz, J_{CW} = 201.1 Hz, CPh), 227.5 (dt, $^2J_{PC,trans}$ = 43.5 Hz, $^2J_{PC,cis}$ = 6.7 Hz, J_{CW} = 154.4 Hz, CO); ^{31}P NMR (ppm, CDCl$_3$) -23.12 (d, $^2J_{PP}$ = 21.8 Hz, J_{PW} = 269.3 Hz), -26.54 (t, $^2J_{PP}$ = 21.8 Hz, J_{PW} = 219.4 Hz, PMe$_3$). Anal. Calcd for C$_{17}$H$_{32}$ClOP$_3$W: C, 36.16; H, 5.71. Found: C, 36.31; H, 5.81. **2b**: mp 100 °C; IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1893; ^{13}C NMR (ppm, CDCl$_3$) 261.9 (t, $^2J_{PC}$ = 10.8 Hz, CTol), 227.8 (dt, $^2J_{PC,trans}$ = 42.8 Hz, $J_{PC,cis}$ = 7.22 Hz, CO); ^{31}P NMR (ppm, CDCl$_3$) -23.03 (d, $^2J_{PP}$ = 25.9 Hz, J_{PW} = 268.2 Hz), -26.52 (t, J_{PP} = 22.0 Hz, J_{PW} = 219.8 Hz, PMe$_3$).

(7) Substitution of the last carbonyl ligand in **2a** by PMe$_3$, however, has been achieved photochemically. Cameron, R. E. Ph.D. Thesis, Princeton University, 1986.

(8) **4**: ^{1}H NMR (ppm, acetone-d_6) 7.01–7.08 (m, 5 H, Ph), 1.68 (pseudotriplet, 36 H, PMe$_3$); MS (m/e, ^{184}W, ^{79}Br) 656. Anal. Calcd for C$_{19}$H$_{41}$BrP$_4$W: C, 34.73; H, 6.29; Br, 12.16; P, 18.85. Found: C, 34.72; H, 6.43; Br, 12.18; P, 18.36.

(9) Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 548–549.

(10) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322–6329.

(11) **5**: ^{1}H NMR (acetone-d_6) δ 7.14 (m, br, 2 H, H$_o$-Ph), 7.05 (m, br, 3 H, H$_{m,p}$-Ph), 1.54 (s, br, 36 H, PMe$_3$); ^{13}C{^{1}H} NMR (acetone-d_6) δ 265 (CPh); ^{31}P{^{1}H} NMR (acetone-d_6) δ -5.54 (s, br, PMe$_3$).

(12) **6**: ^{1}H NMR (CDCl$_3$) δ 7.41–7.51 (m, 5 H, Ph), 1.81 (s, br, 27 H, PMe$_3$; ^{13}C{^{1}H} NMR (CDCl$_3$), -60 °C) δ 387 (q, $^2J_{CP}$ = 56.2 Hz, CPh); ^{31}P{^{1}H} NMR (CDCl$_3$, -60 °C) δ 57.37 (s, PMe$_3$).

(13) Ahmed, K. J.; Chisholm, M. H.; Huffman, J. C. *Organometallics* **1985**, *4*, 1168–1174.

(14) **7a**: mp 124 °C; IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1939; ^{1}H NMR (ppm, CDCl$_3$) 7.32 (m, 5 H, Ph), 1.67 (t, 18 H, P(CH$_3$)$_3$), -1.21 (t, 1 H, J_{PH} = 2.8 Hz, CHPh); ^{13}C NMR (ppm, CDCl$_3$) 233.5 (J_{CW} = 143.6 Hz, CO), 221.4 (J_{CW} = 78.9 Hz, J_{CH} = 82.3 Hz, CHPh). Anal. Calcd for C$_{14}$H$_{24}$Cl$_2$OP$_2$W: C, 32.03; H, 4.61. Found: C, 32.15; H, 4.81. **7b**: mp 130 °C dec; IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1938; ^{1}H NMR (ppm, CDCl$_3$) 7.15 (m, 4 H, C$_6$H$_4$), 2.37 (s, 3 H, CH$_3$), 1.65 (t, 18 H, P(CH$_3$)$_3$), -1.32 (t, 1 H, J_{PH} = 2.7 Hz, CHPh). Anal. Calcd for C$_{15}$H$_{26}$Cl$_2$OP$_2$W: C, 33.42; H, 4.86. Found: C, 33.17; H, 5.06.

(15) C$_{14}$H$_{24}$Cl$_2$OP$_2$W: fw = 525.1 g, monoclinic, $P2_1/n$, a = 8.420 (2) Å, b = 24.536 (8) Å, c = 9.719 (2) Å, β = 104.90 (2)°, V = 1940.3 (9) Å^3, Z = 4, ρ_{calcd} = 1.80 g cm^{-3}, μ(Mo Kα) = 67.3 cm^{-1}. All intensity measurements were made at low temperature (-93 ± 3 °C) by using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation and variable-rate ω scans. Of the 3414 unique reflections measured (3° ≤ 2θ ≤ 50°, ±h,+k,+l), 2837 were observed [|F$_o$| ≥ 3σ(F$_o$)]. Absorption corrections were applied on the basis of azimuthal scans of reflections with χ = 90° ± 20°, maximum transmission = 0.67, and minimum transmisstion = 0.34. The structure was solved by conventional heavy-atom techniques and refined by blocked-cascade least squares. Both methyl groups were disordered, each with two conformations, and they were refined with isotropic temperature factors; all other non-hydrogen atoms were refined with anisotropic temperature factors. The phenyl hydrogens and H(8) were located on difference Fourier maps. The phenyl hydrogens were subsequently idealized with C–H = 0.96 Å and CCH = 120°; H(8) was held fixed, and B(H) = 1.2B(C). Final cycle of blocked-cascade least-squares refinement: maximum and average shift/error = 0.010 and 0.001, respectively; maximum and minimum peaks in difference Fourier = 0.84 and -0.80 e/Å^3; R = 0.035 and R$_w$ = 0.035.

CHCMe$_3$)Cl$_2$(CO)(PMe$_3$)$_2$] (**8**) was previously prepared by Schrock[16] in the reaction between [(W=CHCMe$_3$)Cl$_3$-(H)(PMe$_3$)$_2$] and CO, and its structure was determined by Churchill.[16,17] Compounds **7** and **8** contain highly distorted alkylidene ligands due to interaction of the formal 16-electron metal centers with the alkylidene C–H bonds. In **7a**, C(8) and H(8) are almost equidistant from the metal, the W–C(8)–C(9) angle is 164.6 (6)°, and the W–C(8)–H(8) angle is 74.6°. The ^{1}H NMR signal of the alkylidene hydrogen atom is found at high field, -1.21 ppm (J_{HP} = 2.8 Hz). The neopentylidene ligand in **8** is slightly more distorted (W=C—C, 168.7 (3)°; W=C—H, 72.2 (20)°) than the benzylidene ligand in **7a**, indicating more electron transfer to tungsten by the neopentylidene ligand. Congruously, the carbonyl absorption is lower in **8** (1935 cm^{-1}) than in **7a** (1939 cm^{-1}), and the CH coupling constant in **8** (73 Hz) is smaller than in **7a** (82 Hz). Protonation of the carbonyl-free tungsten carbyne complex **4** with 2 equiv of HBr gas at -78 °C in CH$_2$Cl$_2$ followed by warming to 0 °C provides the hydrido tungsten carbyne complex [(W≡CPh)Br$_2$(H)(PMe$_3$)$_3$][18] (**9**) in 95% yield after recrystallization from THF/pentane. Analogues of **9**, [(W≡CR)Cl$_2$(H)(PMe$_3$)$_3$] (R = H, CMe$_3$), have been prepared previously.[10,16]

Schrock reported dehydrochlorination of the tungsten alkylidene complex [(W=CHCMe$_3$)Cl$_3$(H)(PMe$_3$)$_3$] in the presence of suitable ligands.[16] These results led us to consider dehydrohalogenation of **7** and **9** as possible pathways to substituted tungsten alkylidyne complexes. Reactions between the tungsten hydride complex **9** and bases did not lead to conclusive results; however, deprotonation of the activated C–H bond in **7** is possible even with only moderately strong bases. Addition of 1 equiv of 1-pyrrolidino-1-cyclopentene to **7a** at -78 °C in CH$_2$Cl$_2$ affords the thermally labile anionic tungsten carbyne complex [(CH$_2$)$_4$C=N(CH$_2$)$_4$][(W≡CPh)(Cl)$_2$(CO)-(PMe$_3$)$_2$] (**10**).[19] When a solution of **10** is warmed in the presence of pyridine, the complex [(W≡CPh)Cl(CO)-(py)(PMe$_3$)$_2$][20] (**11**) is obtained. Dehydrochlorination of

$$[(W≡CHPh)Cl_2(CO)(PMe_3)_2] \xrightarrow[\text{2. L}]{\text{1. base}}$$
$$\mathbf{7}$$

$$[(W≡CPh)Cl(CO)L(PMe_3)_2] \quad (5)$$
$$\mathbf{11}, L = py$$
$$\mathbf{12}, L = P(OMe)_3$$
$$\mathbf{13}, L = CNCMe_3$$
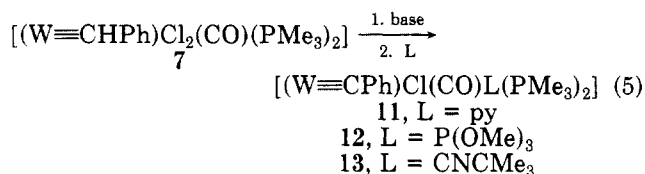
7a by *n*-butyllithium in THF at -78 °C followed by addition of P(OMe)$_3$ or Me$_3$CNC and warming to room temperature gives the substituted derivatives [(W≡CPh)Cl-(CO)L(PMe$_3$)$_2$] (**12**, L = P(OMe)$_3$; **13**, L = CNCMe$_3$).[20] All of these complexes contain a trans arrangement of the trimethylphosphine ligands as indicated by the presence of virtual triplets for the P(CH$_3$)$_3$ resonances in the ^{1}H NMR spectra. Reactions of **7a** with alkynes in the presence of 1,8-bis(dimethylamino)naphthalene generate labile products, which are postulated to be tungsten alkyne carbyne complexes of the type [(W≡CPh)Cl(alkyne)-(CO)(PMe$_3$)$_2$].[21] Thus, the activated tungsten alkylidene complexes [(W=CHR)Cl(CO)(PMe$_3$)$_2$] are useful equivalents of tungsten carbyne complexes containing a single lightly coordinated ligand.

(16) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739–1740.

(17) Churchill, M. W.; Wassermann, H. *J. Inorg. Chem.* **1983**, *22*, 1574–1578.

(18) **9**: ^{1}H NMR (acetone-d_6) δ 7.19–7.25 (m, 2 H, H$_o$-Ph), 7.11–7.15 (m, 3 H, H$_{m,p}$-Ph), 4.23 (q, 1 H, $^2J_{PH}$ = 69.35 Hz, J_{WH} = 20.43 Hz, W–H), 1.86 (d, 27 H, $^2J_{PH}$ = 9.08 Hz, P(CH$_3$)$_3$; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, -60 °C) δ 269.5 (m, CPh); P{^{1}H} NMR (acetone-d_6) δ -18.89 (s, br, PMe$_3$).

(19) **10**: ^{13}C NMR (ppm, CD$_2$Cl$_2$, -60 °C) 256.3 (t, $^2J_{CP}$ = 11.7 Hz, J_{CW} = 194 Hz, CPh), 245.1 (s, J_{CW} = 180 Hz, CO); ^{31}P NMR (ppm, CD$_2$Cl$_2$, -60 °C) -12.63 (J_{PW} = 288 Hz, PMe$_3$); IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1833.

(20) **11**: IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1870; ^{13}C NMR (ppm, CDCl$_3$) 255.6 (J_{CW} = 201.1 Hz, CPh), 238.8 (J_{CW} = 172.4 Hz, CO); ^{1}H NMR (ppm, CDCl$_3$) 1.40 (t, 18 H, P(CH$_3$)$_3$). Anal. Calcd for C$_{19}$H$_{28}$ClONP$_2$W: C, 40.20; H, 4.97. Found: C, 39.98; H, 5.02. **12**: IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1916; ^{1}H NMR (ppm, CDCl$_3$) 7.13 (m, 5 H, C$_6$H$_5$), 3.73 (d, 9 H, J_{PH} = 11.1 Hz, P(OCH$_3$)$_3$), 1.70 (t, 18 H, P(CH$_3$)$_3$). **13**: IR (cm^{-1}, CH$_2$Cl$_2$) ν_{CO} 1909; ^{1}H NMR (ppm, CDCl$_3$) 7.12–7.0 (m, 5 H, Ph), 1.67 (t, 18 H, P(CH$_3$)$_3$), 1.59 (s, 9 H, (CH$_3$)$_3$CNC).

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Book Reviews

Infrared and Raman Spectra of Inorganic and Coordination Compounds. 4th edition. By K. Nakamoto. Wiley, New York. 1986. ix + 484 pages. $55.00.

The book was written to present fundamental theories of vibrational spectroscopy in a condensed form and to illustrate their applications to inorganic, coordination, and organometallic compounds. Compared to the previous editions, the list of references has been updated and purged, and a new section, on bioinorganic compounds, has been included.

The theoretical part features summaries of standard topics, such as normal coordinates and their symmetry, band intensities and selection rules, group theory, with site group and factor group analysis, resonance Raman, band assignments, and others. Some of the sections may be too condensed to be fully comprehensible for the uninitiated reader, but a large list of source references provides an effective basis for extended studies.

In the main body of the text more than 2000 quotations include numerous review articles and reference books. The utility of vibrational spectroscopy in making inferences concerning molecular structure and bonding is illustrated with typical examples, covering the most important classes of compounds in the indicated areas. Many drawings of molecular structures, reproductions of characteristic IR and Raman spectra, and tables of vibrational frequencies and band assignments highlight the text and contribute to the clarity of the presentation.

For a book of this kind, this reviewer finds that the index is rather limited. With approximately 500 entries, many valuable details of interest are hidden in the text, and expanded listings of formulae and keywords would have greatly enhanced the effectiveness of the otherwise carefully prepared material. Nevertheless, graduate students as well as established spectroscopists and synthetic chemists in this field will find this a useful addition to their library.

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