Organometallics **2004,** *23,* 5903−5906

Bi- and Tetranuclear Tricarbido Complexes: $\mu,\sigma{:}\sigma'$ and $\mu,\sigma{:}\sigma'{:}\pi_{\perp}$ Coordination of Bridging C_3 Ligands

Rian D. Dewhurst, Anthony F. Hill,* and Anthony C. Willis

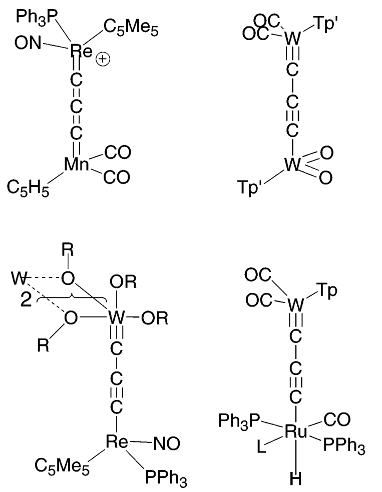
Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory 0200, Australia

Received August 26, 2004

*Summary: Fluoride-mediated desilylation of the propargylidyne [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz)$_3$}] (**1**; pz = pyrazol-1-yl) in the presence of [RhCl(CO)(PPh$_3$)$_2$] provides the bimetallic complex [Rh(C≡CC≡W(CO)$_2${HB(pz)$_3$})(CO)(PPh$_3$)$_2$] (**2b**), which reacts with iodine to give [Rh(C≡CC≡W(CO)$_2${HB(pz)$_3$})I$_2$(CO)(PPh$_3$)$_2$] (**3**) and with [Fe$_2$(CO)$_9$] to provide [RhFe$_2$(μ-C$_3$W(CO)$_2${HB(pz)$_3$})(CO)$_{10}$(PPh$_3$)] (**4**), a rare example of a tricarbido ligand incorporated within a cluster framework.*

Bimetallics spanned by linear chains of carbon atoms $L_nMC_xM'L_n$ have received considerable attention in recent times.[1] One impetus driving this research effort is the supposition that such C_x chains will provide molecular wires for electronic communication between metals. For the far more common situation where x is an even number, although the bonding description is primarily that of a localized $L_nM(C{\equiv}C)_yM'L_n$ ($x = 2y$) polyyne, there is mounting evidence for a degree of delocalization along the chain. The situation where x is an odd number ($x = 2y + 1$) presents a greater synthetic challenge, and this is reflected by the comparative scarcity of such compounds. Tricarbido ($x = 3$) ligands spanning two metals were until recently limited to the archetypes provided by Gladysz[2] and Templeton (Chart 1).[3] With a view to developing a more general route to tricarbido complexes, we have considered propargylidyne complexes[4−6] as possible sources of the C_3 unit. Thus, fluoride-mediated protodesilylation of a range of silylpropargylidynes $L_nM{\equiv}CC{\equiv}CSiMe_3$ in the presence of various ruthenium complexes provided convenient access to complexes of the form $L_nM{\equiv}CC{\equiv}C{-}Ru^{II}L_5$ (M = Mo, W).[7] Extending this approach to the reaction of [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz)$_3$}] (**1**) with Vaska's complex [IrCl(CO)(PPh$_3$)$_2$] provided the first bis(tricarbido) complex, [IrH(C$_3$W(CO)$_2${HB(pz)$_3$})$_2$(CO)(PPh$_3$)$_2$],[8] presumably via oxidative addition of [W(≡CC≡CH)(CO)$_2${HB(pz)$_3$}] to the putative intermediate [Ir(C$_3$W(CO)$_2${HB(pz)$_3$})(CO)(PPh$_3$)$_2$] (**2a**; Scheme 1). Working on the assumption that in general rhodium(I) is less prone to oxidative addition than iridium(I), we have now investigated the corresponding chemistry arising from [RhCl(CO)(PPh$_3$)$_2$]. This indeed results in the isolation of the coordinatively unsaturated bimetallic complex [Rh(C$_3$W(CO)$_2${HB(pz)$_3$})(CO)(PPh$_3$)$_2$] (**2b**), a compound that could be subsequently deployed in oxidative addition (I$_2$) or cluster construction (with [Fe$_2$(CO)$_9$]), the latter providing a novel tricarbido-ligated cluster.

Chart 1. Dimetallic Tricarbido Complexes[2,3,7]



Treating a dichloromethane solution of [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz)$_3$}] (**1**)[6] with [Bu$_4$N]F ("TBAF") in the presence of [RhCl(CO)(PPh$_3$)$_2$] leads over 2 days to the formation of a tan complex formulated as [Rh(C$_3$W(CO)$_2${HB(pz)$_3$})(CO)(PPh$_3$)$_2$] (**2b**).[9a] In the absence of crystallographic confirmation, the formulation of **2b** rests at present on spectroscopic and elemental microanalytical data in addition to reactivity (vide infra). Notably, the infrared spectrum measured in CH$_2$Cl$_2$ includes bands at 1997, 1979, 1945, and 1872 cm^{-1}, assigned to ν(C≡C), ν(WCO), ν(RhCO), and ν(WCO), respectively. The frequency of the absorption due to the rhodium carbonyl is consistent with rhodium(I) and may be compared with that found for [Rh(C≡CPh)(CO)(PPh$_3$)$_2$] (ν(CO) 1958 cm^{-1}).[10a] The interpretation of ^{13}C{^{1}H} NMR data for the tricarbido bridge is compromised by low solubility and the prevalence of phenyl and pyrazolyl resonances in the region where those for C_β

---

* To whom correspondence should be addressed. E-mail: a.hill@rsc.anu.edu.au.

(1) For a review of L_nMC_xR and $L_nMC_xML_n$ complexes, respectively, see: (a) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2002**, *48*, 71. (b) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179.

(2) (a) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824. (b) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 11071. (c) Deminski, R.; Szafert, S.; Haquette, P.; Lis, T.; Gladysz, J. A. *Organometallics* **1999**, *18*, 5438.

(3) Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418.

(4) Fischer, E. O.; Kalder, H. J.; Koehler, F. H. *J. Organomet. Chem.* **1974**, *81*, C23.

(5) Hart, I. J.; Hill, A. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2261.

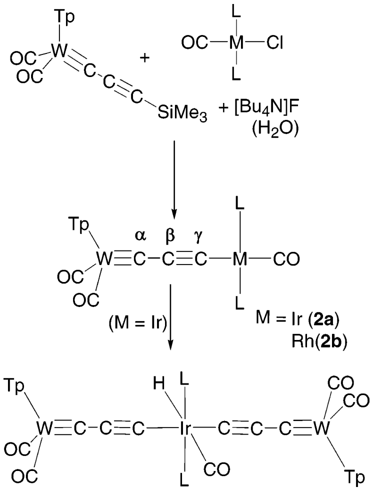
(6) (a) Schwenzer, B.; Schleu, J.; Burzlaff, N.; Karl, C.; Fischer, H. *J. Organomet. Chem.* **2002**, *641*, 134. (b) Schwenzer, B.; Fischer, H. *J. Organomet. Chem.* **2003**, *667*, 16.

(7) Dewhurst, R. D.; Hill, A. F.; Smith, M. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 476.

(8) Dewhurst, R. D.; Hill, A. F.; Willis, A. C. *Organometallics* **2004**, *23*, 1646.

10.1021/om0401152 CCC: $27.50
Publication on Web 11/10/2004

Scheme 1. Synthesis of Mono- and Bis(tricarbido) Complexes[a]



[a] Abbreviations: Tp = HB(pz)$_3$; L = PPh$_3$.

and C_γ (see Scheme 1 for designations) might be anticipated. Thus, while the alkylidyne resonance (C_α) is unambiguously located at δ 258.3, the doublet resonance at δ 128.8 is cautiously assigned to C_β and that for C_γ remains unidentified (a triplet is observed at δ 133.3; however, coupling to rhodium is not resolved). Remaining spectroscopic data are consistent with a *trans*-Rh(PPh$_3$)$_2$ arrangement. Specifically, the C^1-(PC$_6$H$_5$) ^{13}C resonance appears as a virtual triplet, while the $^{31}P\{^1H\}$ spectrum comprises one doublet resonance (δ 32.1, $^1J_{PRh}$ = 109 Hz).

Previous examples of bimetallic tricarbido complexes have involved 18-valence-electron and, in general, substitution-inert end-capping metal centers. The coordinative unsaturation of **2b**, however, offers a site of potential reactivity at the rhodium center. The reaction of **2b** with iodine results in a simple oxidative addition reaction to provide modest yields of the rhodium(III) complex [Rh(C$_3$W(CO)$_2${HB(pz)$_3$})I$_2$(CO)(PPh$_3$)$_2$] (**3**).[9b] The spectroscopic data for **3** are unremarkable, other than to note the expected increase in $\nu_{(CO)}$ for the rhodium(III)-bound carbonyl ligand (2029 cm^{-1}), consistent with oxidation of the metal center. The complex was crystallographically characterized, and the results of this study are summarized in Figure 1, which depicts the molecular geometry. The complex comprises octahedrally coordinated tungsten and rhodium centers linked by an essentially linear tricarbido ligand. Bond lengths along the WC$_3$Rh spine point toward a localized W$\equiv$CC$\equiv$C−Rh valence bond description, in keeping with the effective atomic number requirements of the two metal centers. Thus, the W1−C1 separation of 1.816(7) Å is well within norms for tungsten alkylidynes,[15a,b] and the C1−C2 (1.41(1) Å) and C2−C3 (1.21(1) Å) separations are consistent with $C_{sp}-C_{sp}$ single and triple bonds, respectively. The angles at C1, C2, and C3 (174.2(6), 176.8(8) and 178.4(6)°, respectively) are all very close to linear. There is a noticeable bending of the iodide ligands away from the Rh−C3 bond (I1−Rh−C3 (=93.45(3)°) + I2−Rh−C3 (=100.31(2)°) = 193.76°; I1−Rh−I2 = 166.23(3)°), which is accompanied by a modest bending of the phosphines toward the C$_3$ ligand (P1−Rh−C3 (=87.29(19)°) + P2−Rh−C3 (85.79(19)°) = 173.08°; P1−Rh−P2 = 172.31(6)°).

Given its structural features, the complex **3** might best be thought of as simply an exotic alkynyl complex of rhodium(III). Accordingly, an analogy between the precursor **2b** and the complex [Rh(C$\equiv$CPh)(CO)(PPh$_3$)$_2$][9] would seem appropriate. Little chemistry has been reported for this complex, other than its various syntheses[9−11] and its reactions with tetracyanoethene[12] and [Fe$_2$(CO)$_9$].[13] This latter reaction provides access to

---

[9] Compound **2b**: a suspension of [W($\equiv$CC$\equiv$CSiMe$_3$)(CO)$_2${HB(pz)$_3$}][6a] (100 mg, 0.178 mmol) and [RhCl(CO)(PPh$_3$)$_2$] (111 mg, 0.160 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with [Bu$_4$N]F (0.36 mL) and stirred for 2 days. Addition of ethanol and slow concentration provided a tan solid. Yield: 157 mg (83%). IR (Nujol): 2000 (ν(C$\equiv$C)), 1979 (ν(WCO)), 1941 (ν(RhCO)), 1866 (ν(WCO)) cm^{-1}. IR (CH$_2$Cl$_2$): 1997 (ν(C$\equiv$C)), 1979 (ν(WCO)), 1945 (ν(RhCO)), 1872 (ν(WCO)) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 7.71−7.37 (m × 2, 30 H, C$_6$H$_5$), 7.60, 7.56, 7.53 (m × 3, 6 H, $H^{3,5}$(pz)), 6.09 (m, 3H, H^4(pz)) ppm. $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$, 25 °C): 258.3 (C$\equiv$W), 227.3 (WCO), 145.0 (2C), 143.8 (1C) (C^5(pz)), 135.3 (vt, $^1J_{CP}$ = 38.2, C^1(C$_6$H$_5$)), 134.8 ($C^{2,6}$(C$_6$H$_5$)), 133.3 (t, C$\equiv$*C*Rh, $^2J_{CP}$ = 22.6, $^1J_{RhC}$ not resolved), 130.5 (C^3(pz)), 130.4 (C^4-(C$_6$H$_5$)), 128.8 (d, *C*$\equiv$CRh, $^2J_{RhC}$ = 11.6 Hz), 128.4 ($C^{3,5}$(C$_6$H$_5$)), 105.7 (3C) (C^4(pz)) ppm. $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 25 °C): 32.1 (d, $^1J_{PRh}$ = 109 Hz) ppm. ESI-MS: *m/z* 1144 [M]$^+$, 1116 [M − CO]$^+$, 882 [M − PPh$_3$]$^+$. Anal. Found: C, 52.08; H, 3.44; N, 6.80. Calcd for $C_{51}H_{40}BN_6O_3P_2RhW\cdot 0.5CH_2Cl_2$: C, 52.12; H, 3.48; N, 7.08. Compound **3**: a solution of **2b** (100 mg, 0.087 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with I$_2$ (24 mg, 0.096 mmol) and stirred overnight. The solution was reduced in volume and chromatographed on silica gel (CH$_2$Cl$_2$/petroleum ether, 40:60), providing a dark orange band. Crystallization from CH$_2$Cl$_2$/petroleum ether afforded a brown microcrystalline product. Yield: 37 mg (30%). IR (Nujol): 2102 (ν(Rh−C$\equiv$C)), 2029 (ν(Rh−CO)), 1959, 1881 (ν(W−CO)) cm^{-1}. IR (CH$_2$Cl$_2$): 2101 (ν(Rh−C$\equiv$C)), 2023 (ν(Rh−CO)), 1965, 1882 (ν(W−CO)) cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ 8.21 (m, 18 H, $H^{3,4,5}$-(C$_6$H$_5$)), 7.75 (d, 2 H, $^3J_{HH}$ = 1.5 Hz, H^3(pz)), 7.65 (d, 2 H, $^3J_{HH}$ = 2.5 Hz, H^5(pz)), 7.62 (d, 1 H, $^3J_{HH}$ = 1.0 Hz, H^3(pz)), 7.57 (d, 1 H, $^3J_{HH}$ = 2.5 Hz, H^5(pz)), 7.34 (m, 12 H, $H^{2,6}$(C$_6$H$_5$)), 6.15 (t, 2 H, $^3J_{HH}$ = 2.0 Hz, H^4(pz)), 6.11 (unresolved t, 1 H, H^4(pz)) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 256.7 (C$\equiv$W), 226.2 (W−CO), 145.2 (2 C), 143.7 (1 C) (C^5-(pz)), 135.0 (vt, $^1J_{PC}$ = 25.4 Hz, C^1(C$_6$H$_5$)), 134.7 (2 C) (C^3(pz)), 134.4 ($C^{2,6}$(C$_6$H$_5$)), 130.5 (C^4(C$_6$H$_5$)), 127.9 ($C^{3,5}$(C$_6$H$_5$)), 105.6 (2 C), 105.5 (1 C) (C^4(pz)) ppm; one resonance for the C^3(pz) carbon atoms is obscured by the $C^{1+2,6}$(C$_6$H$_5$) signals, and the signals for RhC$\equiv$C were not unequivocally identified. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 1.4 (d, $^1J_{P-Rh}$ = 82 Hz) ppm. ESI-MS: *m/z* 1440 [M + MeCN]$^+$, 1243 [M − CO − I]$^+$. Anal. Found: C, 44.18; H, 3.24; N, 5.93. Calcd for $C_{51}H_{40}BI_2N_6O_3P_2RhW$: C, 43.81; H, 2.88; N, 6.01. Crystal data for **3**·4CHCl$_3$: $C_{51}H_{40}BI_2N_6O_3P_2RhW\cdot 4CHCl_3$, M_r = 1875.75, triclinic, $P\bar{1}$ (No. 2), a = 13.2772(3) Å, b = 15.7757(3) Å, c = 17.1240(3) Å, α = 86.453(1)°, β = 74.519(1)°, γ = 74.725(1)°, V = 3334.36(12) Å^3, Z = 2, ρ_{calcd} = 1.868 g cm^{-3}, μ(Mo Kα) = 3.472 mm^{-1}, T = 150 K, orange plate, 11 811 independent measured reflections ($2\theta \le 50°$), R1 = 0.037, wR2 = 0.041 for 7523 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 749 parameters, CCDC 232409; Compound **4**: a suspension of [{(Tp)(CO)$_2$W}CCC{Rh(CO)(PPh$_3$)$_2$}] (100 mg, 0.087 mmol) and [Fe$_2$(CO)$_9$] (70 mg, 0.192 mmol) in thf (20 mL) was stirred overnight, during which time the orange [Fe$_2$(CO)$_9$] dissolved. The solution was reduced in volume and chromatographed on silica (CH$_2$Cl$_2$/petroleum ether, 20:80). An orange band was collected, which was dried in vacuo to give an orange powder. Yield: 54 mg (52%). IR (Nujol): 2068, 2041, 2019, 2006, 1981, 1972, 1895, 1882 cm^{-1}. IR (CH$_2$Cl$_2$): 2069, 2042, 2019 (ν({Fe$_2$Rh}−CO)) 1982, 1899 (ν(W−CO)) cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.66−7.15 (m, 21 H, C$_6$H$_5$ plus $H^{3,5}$(pz)), 6.15 (t, 3 H, $^3J_{HH}$ = 2 Hz, H^4(pz)) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 254.6 (C$\equiv$W), 224.4 (W−CO), 211.9 (Fe−CO), 185.2 (RhCO), 145.2 (1C), 144.0 (2C) (C^5-(pz)), 135.5 (1C), 135.2 (2C) (C^3(pz)), 134.0 (d, $^1J_{PC}$ = 34.2 Hz, C^1(C$_6$H$_5$)), 133.5 (d, $^2J_{PC}$ = 12.2 Hz, $C^{2,6}$(C$_6$H$_5$)), 130.3 (C^4(C$_6$H$_5$)), 128.4 (d, $^3J_{PC}$ = 9.7 Hz, $C^{3,5}$(C$_6$H$_5$)), 105.9 (3C) (C^4(pz)) ppm. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 25 °C): 15.5 (d, $^1J_{PRh}$ = 127 Hz) ppm. ESI-MS: *m/z* 1184 [M]$^+$, 1105 [M − 3CO]$^+$, 1022 [M − 6CO]$^+$. Anal. Found: C, 44.10; H, 3.13; N, 6.50. Calcd for $(C_{40}H_{25}BFe_2N_6O_{10}PRhW)\cdot 1.5C_5H_{12}$: C, 43.95; H, 3.34; N, 6.47 (pentane confirmed by ^{1}H NMR integration). Crystal data for **4**·1.5CHCl$_3$: $C_{40}H_{25}BFe_2N_6O_{10}PRhW\cdot 1.5CHCl_3$, M_r = 1368.97, monoclinic, $C2/c$, a = 30.6623(2) Å, b = 12.4475(1) Å, c = 26.8170(2) Å, β = 102.5002(3)°, V = 9992.59(13) Å^3, Z = 8, ρ_{calcd} = 1.820 g cm^{-3}, μ(Mo Kα) = 3.521 mm^{-1}, T = 200 K, brown plate, 11 474 independent measured reflections ($2\theta \le 55°$), R1 = 0.028, wR2 = 0.032 for 6047 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 609 parameters, CCDC 232410.

[10] (a) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202. (b) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. *J. Organomet. Chem.* **1972**, *34*, C37.

[11] Bruce, M. I.; Humphrey, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955.

[12] Choi, J.-C.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *17*, 3044.

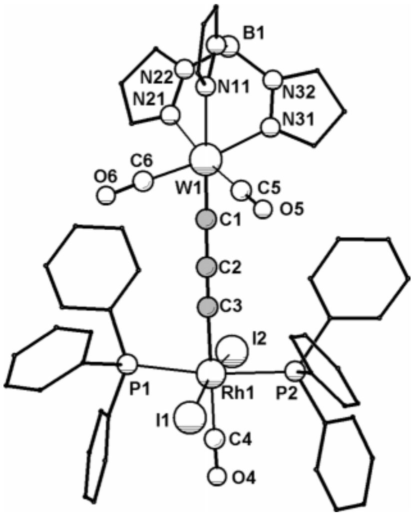
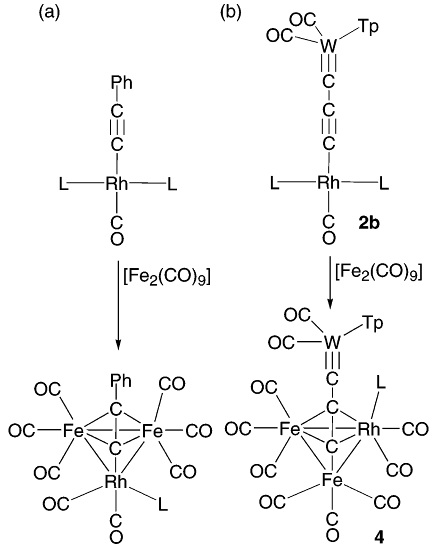


Figure 1. Molecular geometry of **3** (hydrogen atoms omitted; phenyl and pyrazolyl rings simplified). Selected bond distances (Å) and angles (deg): W1−C1 = 1.816(7), I1−Rh1 = 2.6833(7), I2−Rh1 = 2.7093(7), Rh1−C3 = 2.005(8), Rh1−C4 = 1.956(8), C1−C2 = 1.41(1), C2−C3 = 1.21(1); I1−Rh1−I2 = 166.23(3), P1−Rh1−P2 = 172.32(6), I1−Rh1−C3 = 93.45(19), I2−Rh1−C3 = 100.31(19), P1−Rh1−C3 = 87.29(19), P2−Rh1−C3 = 85.79(19), W1−C1−C2 = 174.2(6), C1−C2−C3 = 176.8(8), Rh1−C3−C2 = 178.4(6).

Scheme 2. Reactions of $[Fe_2(CO)_9]$ with $[Rh(C{\equiv}CR)(CO)L_2]$[a]



[a] Abbreviations: L = PPh_3; Tp = $HB(pz)_3$. Legend: (a) R = Ph;[14] (b) R = $C{\equiv}W(CO)_2\{HB(pz)_3\}$.

the trinuclear cluster $[Fe_2Rh(\mu\text{-}C{\equiv}CPh)(CO)_8(PPh_3)]$ (Scheme 2). Although not structurally characterized at the time, the formulation rested convincingly on structural data for the iridium analogue. This has prompted us to investigate the reaction of **2b** with $[Fe_2(CO)_9]$ as a potential route to clusters bearing the tricarbido ligand. A slow reaction was found to ensue at room temperature (thf) to provide after chromatography a modest yield (52%) of a compound formulated as the tetranuclear complex $[Fe_2Rh(\mu\text{-}C_3W(CO)_2\{HB(pz)_3\})(CO)_8(PPh_3)]$ (**4**).[9c] Although the complex was ultimately characterized crystallographically (Figure 2), its nature also followed in part from spectroscopic data. The appearance of a $^{13}C\{^1H\}$ resonance at δ 254.6 in the NMR spectrum indicated that the tungsten alkylidyne linkage remained intact rather than becoming involved within the cluster. Only single resonances were observed for the tungsten- (δ 224.4) and iron-bound carbonyls (δ 211.9), suggesting fluxionality in the latter. That the single phosphine is bound to rhodium rather than iron was indicated by the appearance of a doublet resonance in the $^{31}P\{^1H\}$ NMR spectrum (δ 15.5, $^1J_{PRh}$ = 127 Hz).

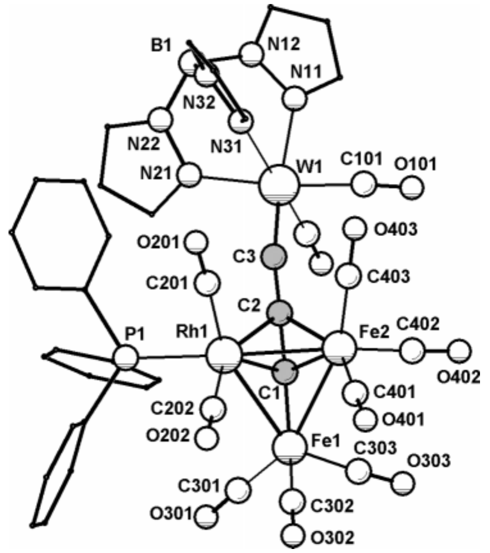


Figure 2. Molecular geometry of **4** (hydrogen atoms omitted; phenyl and pyrazolyl rings simplified). Selected bond distances (Å) and angles (deg): W1−C3 = 1.826(6), Rh1−Fe1 = 2.7214(8), Rh1−Fe2 = 2.5525(8), Rh1−C1 = 2.163(5), Rh1−C2 = 2.230(5), Fe1−Fe2 = 2.623(1), Fe1−C1 = 1.800(5), Fe2−C1 = 2.021(5), Fe2−C2 = 2.144(5), C1−C2 = 1.322(7), C2−C3 = 1.407(7); Fe1−Rh1−Fe2 = 59.54(2), Rh1−Fe1−Fe2 = 57.02(2), Rh1−Fe1−C1 = 52.48(15), Fe2−Fe1−C1 = 50.26(16), Rh1−Fe2−Fe1 = 63.43(2), Rh1−Fe2−C1 = 54.99(14), Fe1−Fe2−C1 = 43.24(15), Rh1−Fe2−C2 = 55.87(13), Rh1−C1−Fe1 = 86.2(2), Rh1−C1−Fe2 = 75.10(17), Rh1−C1−C2 = 75.3(3), Fe1−C1−C2 = 157.5(4).

The geometry of the WC_3RhFe_2 assembly does not follow unambiguously from spectroscopic data; however, the molecular structure in a crystal of a chloroform solvate was determined crystallographically (Figure 2).[9c] In addition to confirming that the WC_3 unit remains intact, the most notable feature is that it traverses one Rh1−Fe2 bond (2.553(1) Å) which is contracted relative to the remaining Rh1−Fe1 bond (2.721(1) Å). Nevertheless, the C1−C2 bond remains comparatively short (1.322(7) Å) compared to the "single" C2−C3 bond (1.408(7) Å), while the alkylidyne linkage (W1−C3 = 1.825(6) Å) remains within norms for octahedral tungsten carbyne complexes.[15] It is of interest that the

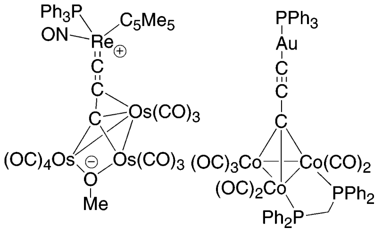
---

[13] Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *235*, 105.

[14] Bruce, M. I.; Koutsantonis, G. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *407*, 391.

[15] For general reviews of the chemistry of alkylidyne complexes see: (a) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (b) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (d) Mayr, A.; Ahn, S. *Adv. Transition Met. Coord. Chem.* **1996**, *1*, 1. (e) *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; NATO ASI Series C392; Kluwer: Dordrecht, The Netherlands, 1992.

Chart 2. Polymetallic Tricarbido Complexes[16,17]



ground-state geometry for **4** is distinct from that of [$IrFe_2(\mu\text{-}C{\equiv}CPh)(CO)_8(PPh_3)$],[14] in which the Ir−C σ-bond is retained with the alkynyl group traversing the Fe−Fe bond.

Concluding Remarks. The isolation of **2b** is noteworthy, given that previous examples of tricarbido complexes involved 18-electron precise metal centers at either end of the C_3 chain. In contrast, **2b** has a coordinatively unsaturated metal end cap capable of entering into both redox and cluster-building reactions. Its isolation also adds support to the inferred intermediacy of **2a** in the formation of [$IrH(C_3W(CO)_2\{HB(pz)_3\})_2(CO)(PPh_3)_2$]. The cluster **4** joins the compounds [$Os_3\{\mu_3\text{-}\eta^2\text{-}CC{=}C{=}Re(NO)(PPh_3)(\eta\text{-}C_5Me_5)\}(\mu\text{-}OMe)(CO)_{10}$][16] and [$Co_3(\mu_3\text{-}CC{\equiv}CAuPPh_3)(\mu\text{-}dppm)(CO)_7$][17] (Chart 2) in providing a new alternative mode for coordination of the tricarbido fragment to a cluster framework, the distinction being that for **4** the C_3 unit was constructed prior to incorporation in a cluster (bridge-assisted cluster synthesis).

Supporting Information Available: Full details of the crystal structure determinations of **3** (CCDC 232409) and **4** (CCDC 232410), including positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0401152

---

(16) Falloon, S. B.; Szafert, S.; Arif, A. M.; Gladysz, J. *Chem. Eur. J.* **1998**, *4*, 1033.

(17) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. Unpublished work referred to in ref 1.