

The spectroscopic properties of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CH}_2\text{Ph})^5$ indicate that it retains the molecular structure shown in Figure 1 in solution. A notable feature of its ^1H NMR spectrum in C_6D_6 is the high-field position of the AB doublet due to the diastereotopic methylene protons of the CH_2SiMe_3 ligand. This feature is undoubtedly a manifestation of the shielding provided by the still-extant ring current of the benzyl's phenyl ring.¹¹

The propensity to attach benzyl ligands in a η^2 manner appears to be a general property of this class of compounds since a variety of $\text{Cp}'\text{M}(\text{NO})\text{X}(\eta^2\text{-CH}_2\text{Ph})$ complexes ($\text{Cp}' = \text{Cp}, \text{Cp}^*$; $\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{alkyl, halide}$) display this structural feature.^{4,12} Indeed, a closer examination of similar structures exhibited by d^0 and d^{0f^n} metal benzyl complexes¹³ may well reveal that their $\text{M-CH}_2\text{Ph}$ interactions should also be formulated as in B.

Representation B above reflects primarily a valence-bond description of the $\text{Mo-CH}_2\text{Ph}$ bonding in $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CH}_2\text{Ph})$. It does not, however, provide a rationale for why the benzyl ligand in this compound does not coordinate in a η^3 fashion to the metal center¹⁴ and undergo the characteristic $\sigma\text{-}\pi$ electronic distortion found for the η^3 -allyl ligands in the related $\text{CpMo}(\text{NO})(\eta^3\text{-allyl})\text{X}$ compounds.¹⁵ Perhaps a detailed molecular orbital description of the bonding in $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CH}_2\text{Ph})$ or a related complex can provide the requisite insights.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and J.T. and a postgraduate scholarship to N.H.D.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CH}_2\text{Ph})$ (3 pages); a table of structure factors (22 pages). Ordering information is given on any current masthead page.

(12) Legzdins, P.; Phillips, E. C. Manuscript in preparation.

(13) That benzyl ligands can attach to metal centers in a η^2 fashion has been noted previously by other workers (cf.: Jordan, R. F.; LaPointe, R. E.; Bajur, C. S.; Echols, S. F.; Willett, R. J. *Am. Chem. Soc.* **1987**, *109*, 4111 and references cited therein). However, we are the first to invoke that these ligands then provide three electrons to the metal centers in the manner represented by resonance hybrid B.

(14) There does not appear to be a steric encumbrance to such a coordination mode.

(15) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268 and references cited therein.

Dimetallostannylene-Transition-Metal Complexes

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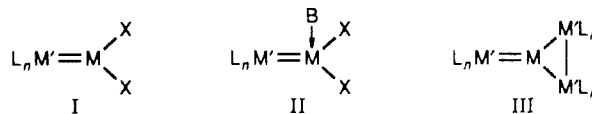
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Summary: The crystalline complex $[\{\text{Fe}(\text{CO})_3(\mu\text{-CO})\}(\text{SnFp}_2)]_2\text{-}(O, \text{Sn})$ (**1**), $[\{\text{Cr}(\text{CO})_4(\mu\text{-CO})\}(\text{SnFp}_2)]_2\text{-}(O, \text{Sn})$ (**2**), and $[\text{Fe}(\text{CO})_4\{\text{SnFp}_2(\text{Py})\}]$ (**3**) [$\text{Fp} = \text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$] have been prepared; X-ray data on **1** and **2** show them to be centrosymmetric dimers by virtue of two isocarbonyl-tin bonds.

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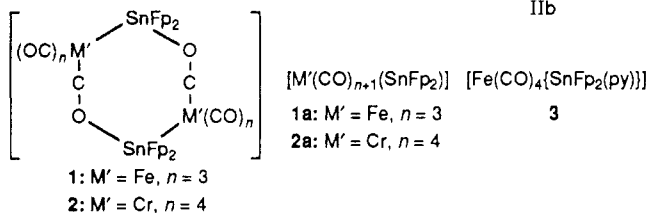
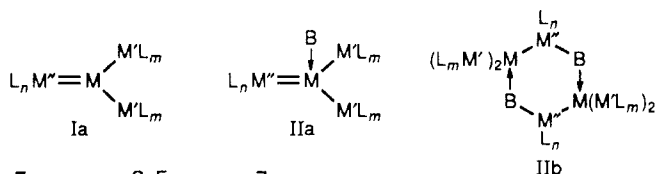
Heavy group 14 metal carbene analogues MX_2 or related neutral Lewis base (B) adducts $\text{MX}_2(\text{B})$ have an extensive transition-metal (M' or M'') coordination chemistry as terminal ligands, forming complex I or II ($L_n, L_m =$ the sum of all the ligands at M' or M'').¹ In I and II, X has gen-



erally been a monoanionic C-, N-, O-, P-, or S-centered ligand or a halide. Rarely has X been a transition-metal-centered group, and then the derived complexes invariably had structure III, in which the main-group metal

M is part of an $\text{M}'\text{MM}'$ ring: $[\text{W}(\text{CO})_5\{\text{M}(\text{W}_2(\text{CO})_{10})\}]$ ($\text{M} = \text{Ge}, \text{Sn}$),^{2a} $[\text{W}(\text{CO})_5\{\text{Sn}(\text{THF})(\text{W}_2(\text{CO})_{10})\}]$,^{2b} or $[\text{Mn}(\text{Cp})(\text{CO})_2\{\text{M}(\text{Mn}(\text{Cp})(\text{CO})_2)_2\}]$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5, \eta\text{-C}_5\text{H}_4\text{Me}$, $\text{M} = \text{Ge};^{2c,d}$ $\text{Cp} = \eta\text{-C}_5\text{H}_4\text{Me}$, $\text{M} = \text{Sn};^{2e}$ $\text{Cp} = \eta\text{-C}_5\text{H}_5$, $\text{M} = \text{Pb}^{2f}$).

We now report two members of a new class of complex, the acyclic dimetallostannylenes (**1a**): $[\text{Fe}(\text{CO})_4\{\text{SnFp}_2\}]$ (**1a**) and $[\text{Cr}(\text{CO})_5\{\text{SnFp}_2\}]$ (**2a**; $\text{Fp} = [\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$).



Complexes **1a** and **2a** are dimers **1** and **2** in the crystalline state, by virtue of two isocarbonyl-tin bonds, $\text{M}'\text{CO}^+\text{-SnFp}_2$. Their thermal stability is surprising, as facile reductive elimination of Fp_2 was expected.³ The complexes $[\text{Fe}(\text{CO})_4\{\text{SnFp}_2(\text{Py})\}]$ (**3**), $[\{\text{Fe}(\text{CO})_3(\mu\text{-CO})\}(\text{SnFp}_2)]_2\text{-}(O, \text{Sn})$ (**1**) and $[\{\text{Cr}(\text{CO})_4(\mu\text{-CO})\}(\text{SnFp}_2)]_2\text{-}(O, \text{Sn})$ (**2**) are representative of two further new classes IIa and IIb: **2** is the first mixed dimetallostannylene-metal complex (i.e., $\text{M}' \neq \text{M}''$).

The dimetallostannylene complexes **1** and **2** were obtained by alternative alkali-metal chloride eliminations, (i) $[\text{M}'(\text{CO})_{n+1}]^{2-}/\text{SnCl}_2\text{Fp}_2$ or (ii) (for $\text{M}' = \text{Cr}$) $[\text{Cr}(\text{CO})_5\{\text{SnCl}_2(\text{THF})\}]/2 \text{KFp}$, yielding ca. 50% yields of red crystalline **1**⁴ and **2**,⁵ respectively (slow crystallization from

(1) Petz, W. *Chem. Rev.* **1986**, *86*, 1019. Lappert, M. F. *Silicon, Germanium, Tin, Lead Compd.* **1986**, *9*, 129.

(2) (a) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O.; Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 331. (b) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428. (c) Melzer, D.; Weiss, E. *J. Organomet. Chem.* **1984**, *263*, 67. (d) Gäde, W.; Weiss, E. *J. Organomet. Chem.* **1981**, *213*, 451. (e) Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (f) Kneuper, H.-J.; Herdweck, E.; Herrmann, W. *J. Am. Chem. Soc.* **1987**, *109*, 2508.

(3) Low-coordinate lead(II) complexes $\text{M}'\text{X}_2$ featuring $[\text{MoCp}(\text{CO})_3]^-$ σ -substituents (X) are very sensitive to elimination of the Mo-Mo-bonded dimer with concomitant deposition of metallic lead; cf.: Hitchcock, P. B.; Lappert, M. F.; Michalczuk, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2635.

(4) $[\{\text{Fe}(\text{CO})_3(\mu\text{-CO})\}(\text{SnFp}_2)]_2\text{-}(O, \text{Sn})$ (**1**). IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 2948, 2025, 2016, 2001, 1984, 1966, 1952, 1930, 1894; $\nu(\text{CO}\rightarrow\text{Sn})$ 1824. Anal. Calcd for $\text{C}_{36}\text{H}_{20}\text{Fe}_6\text{O}_{16}\text{Sn}_2$: C, 33.7; H, 1.58. Found: C, 33.6; H, 1.61. Crystal data for **1**: monoclinic, space group $P2_1/n$, $a = 11.041$ (5) Å, $b = 12.588$ (5) Å, $c = 15.029$ (8) Å, $\beta = 99.91$ (4)°, $V = 2057.5$ Å³, $Z = 2$, $D_c = 2.07$ g cm^{-3} , $F(000) = 1240$ (monochromated Mo K α radiation, $\lambda = 0.71069$ Å, $\mu = 33.2$ cm^{-1}). Refinement of 3069 reflections with $|F^2| > \sigma(F^2)$ converged with final residuals $R = 0.032$ and $R' = 0.043$.

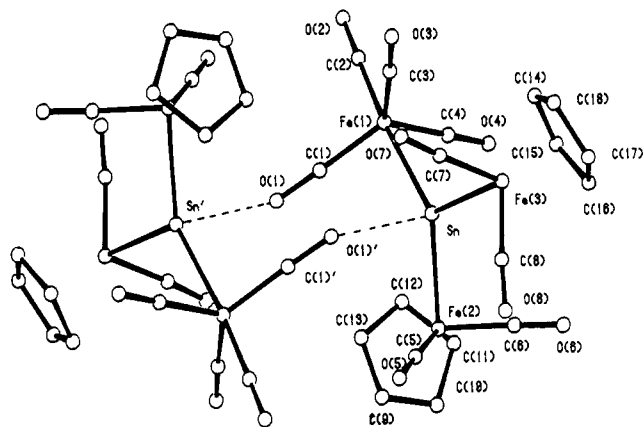


Figure 1. Ball-and-stick drawing of $[\{\text{Fe}(\text{CO})_3(\mu\text{-CO})\}(\text{SnFp}_2)_2(\text{O},\text{Sn})]$ (1). Selected bond distances (Å): Sn-Fe(1) = 2.527 (1); Sn-Fe(2) = 2.538 (1); Sn-Fe(3) = 2.548 (1); Sn-O(1)' = 2.781 (3); Fe(1)-C(1) = 1.757 (4); C(1)-O(1) = 1.152 (5). Selected bond angles (deg): Fe(1)-Sn-Fe(2) = 122.91 (2); Fe(1)-Sn-Fe(3) = 117.00 (2); Fe(2)-Sn-Fe(3) = 117.29 (2); O(1)'-Sn-Fe(1) = 94.93 (7); Sn-O(1)'-C(1)' = 135.7 (3); Fe(1)-C(1)-O(1) = 178.2 (4).

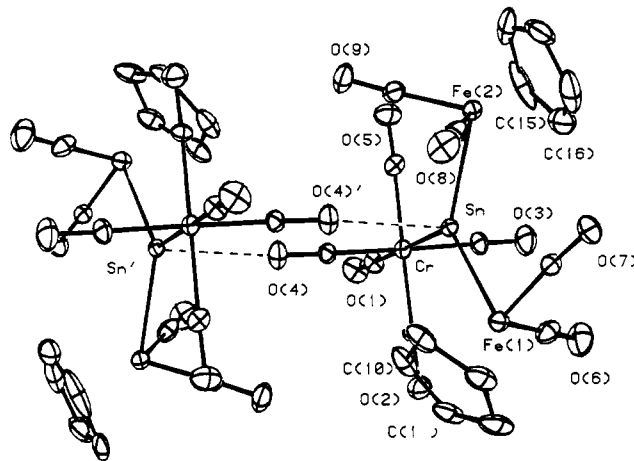


Figure 2. ORTEP drawing of $[\{\text{Cr}(\text{CO})_4(\mu\text{-CO})\}(\text{SnFp}_2)_2(\text{PhMe})(\text{O},\text{Sn})]$ (2) (toluene solvate not shown). Selected bond distances (Å): Sn-Cr = 2.624 (1); Sn-Fe(1) = 2.570 (1); Sn-Fe(2) = 2.550 (2); Sn-O(4)' = 2.976 (7); Cr-C(4) = 1.862 (9); C(4)-O(4) = 1.166 (12). Selected bond angles (deg): Cr-Sn-Fe(1) = 121.81 (5); Cr-Sn-Fe(2) = 121.46 (4); Fe(1)-Sn-Fe(2) = 115.74 (4); O(4)'-Sn-Cr = 98.5 (1); Sn-O(4)'-C(4)' = 169.4 (7); Cr-C(4)-O(4) = 176.9 (6).

saturated toluene solutions). Reaction i was effective for the iron complex 1, but the competing Sn(II)/M'(-II) redox pathway appeared to dominate in the chromium system, as $[\{\text{FeCp}(\text{CO})_2\}_2]$ (Fp_2) was the major organometallic product. The monomers $[\text{M}''(\text{CO})_{n+1}(\text{SnFp}_2)]$ (**1a**⁶ and **2a**⁷) were only stable in noncoordinating solvents, reassociating upon solvent removal. Dissolving 1 in tetrahydrofuran yielded $[\text{Fe}(\text{CO})_4(\text{SnFp}_2(\text{B}))]$ (B = THF),⁸ which reconverted into the dimer under vacuum. The related pyridine complex (B = py, **3**) was isolated in the crystalline state.⁹

A distinguishing feature of both the crystalline stannylenes **1** and **2** was a low-frequency IR (Nujol) CO stretching mode (1, 1824 cm^{-1} ; 2, 1865 cm^{-1}). This is inconsistent with $[\text{Fe}(\text{CO})_4(\text{L})]$ or $[\text{Cr}(\text{CO})_5(\text{L})]$ models (cf. data on L = phosphine, phosphite, etc.) and led to the notion that there might be an interaction between the divalent tin moiety and coordinated CO. This was verified by X-ray data; crystalline **1** and **2** (as the toluene solvate) (Figures 1 and 2) are isocarbonyl-bridged dimers such that

one *cis*-M''(CO)_n-based CO group from each $[\text{M}''(\text{CO})_n(\text{SnFp}_2)]$ unit is joined to the other $[\text{M}''(\text{CO})_n(\text{SnFp}_2)]$ unit via an O-Sn linkage, resulting in an eight-membered

Sn-O-C-M''-Sn-O-C-M'' ring. The ability of carbonyl oxygen to function as a Lewis donor toward a tin(II) acceptor is to our knowledge without precedent but may have generality among group 14 metal(II) centers bearing nonchelating transition-metal σ -substituents. In support, we note that in the crystalline *free* heavy group 14 metal dimetallo carbene complex $[\text{M}(\text{M}'\text{L}_n)_2]$, $[\text{Pb}\{\text{Mo}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\mu\text{-CO})\}\{\text{Mo}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_3\}_2(\text{O},\text{Pb})]$, there is such a bond, $\text{MoCO}^+-\text{Pb}^-$.³

The long and variable Sn-O distances in **1** (2.781 (3) Å) and **2** (2.976 (7) Å) imply that these bonds are weak. In contrast to bimetallic isocarbonylmetal complexes involving harder acceptors such as Mg(II), Al(III), La(III), Yb(III), and Zr(IV),¹⁰ the isocarbonyl M''C-O and M''-C bond lengths in **1** or **2** do not differ significantly from the terminal C-O and M''-C distances; we conclude that in the latter the (stannoxycarbyne)metal resonances contributor $\text{M}''\equiv\text{COSn}$ is relatively unimportant. The stronger Sn-O bonds in the Fe complex **1** than in the Cr analogue **2** probably reflect the superior π -back-bonding $\text{L}_n\text{M}''\text{-CO}$ of the d^8 Fe(0) center (four CO's competing for d_{π} M'' electrons) versus the d^6 Cr(0) center (with its five CO's).

The cyclic trimetallostannylenes(germylenes) complexes III^{2a,c,d} contain one short and two long transition-metal (M')-group 14 metal (M) distances (differences of ca. 0.1 Å), and this has been interpreted as evidence for main-group-metal-transition-metal $p_{\pi}\text{-}d_{\pi}$ bonding, i.e., a $>\text{M}=\text{M}'\text{L}_n$ resonance contributor. As the three Fe-Sn distances in **1** are almost identical, such π -bonding may be less significant for **1**. Further support for this view comes from a comparison of (i) the Fe-Sn bond lengths in **1** and $[\text{Fe}(\text{CO})_4(\text{Sn}(\text{OAr})_2)]$ (Ar = $\text{C}_6\text{H}_3\text{Bu}'_2\text{-2,6}$, ca. 0.12 Å shorter)¹¹ and (ii) the Cr-Sn bond lengths in **2** and $[\text{Cr}(\text{CO})_5(\text{SnR}_2)]$ (R = $\text{CH}(\text{SiMe}_3)_2$, ca. 0.06 Å shorter).¹²

(5) $[\{\text{Cr}(\text{CO})_4(\mu\text{-CO})\}(\text{SnFp}_2)_2(\text{PhMe})(\text{O},\text{Sn})]$ (2). IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 2037, 1990, 1978, 1962, 1949, 1931, 1916; $\nu(\text{CO}\rightarrow\text{Sn})$ 1866. Anal. Calcd for $\text{C}_{38}\text{H}_{20}\text{Cr}_2\text{Fe}_4\text{O}_{18}\text{Sn}_2\text{C}_7\text{H}_8$: C, 38.0; H, 1.98. Found: C, 37.4; H, 1.73. Crystal data for 2: triclinic, space group $P1$, $a = 9.070$ (5) Å, $b = 10.538$ (2) Å, $c = 14.306$ (4) Å, $\alpha = 104.39$ (2)°, $\beta = 96.57$ (3)°, $\gamma = 108.17$ (3)°, $V = 1235.6$ Å³, $Z = 1$, $D_c = 1.91$ g cm^{-3} , $F(000) = 694$ (monochromated Mo K α radiation, $\lambda = 0.71069$ Å, $\mu = 26.2$ cm^{-1}). Refinement of 2250 reflections with $|F^2| > \sigma(F^2)$ converged with final residuals $R = 0.044$ and $R' = 0.053$.

(6) Data for $[\text{Fe}(\text{CO})_4(\text{SnFp}_2)]$ (**1a**). IR (toluene, cm^{-1}): $\nu(\text{CO})$ 2055, 2024, 1989, 1945, 1915, 1890 (sh). ¹H NMR (C_6D_6 , δ): 4.21 (s, Cp). ¹³C NMR (C_7D_8 , δ): 215.0 (Fe(CO)₄), 211.1 (FeCp(CO)₂), 83.9 (Cp). ¹¹⁹Sn NMR (C_7D_8 , δ): 724.4. Molecular weight determination (cryoscopy in C_6H_6): found, 600; monomer requires 640.

(7) $[\text{Cr}(\text{CO})_5(\text{SnFp}_2)]$ (**2a**). IR (toluene, cm^{-1}): $\nu(\text{CO})$ 2037, 2021, 1986, 1941, 1918. ¹H NMR (CD_2Cl_2 , δ): 7.21 (br s, PhMe), 4.94 (s, Cp), 2.35 (s, PhMe). ¹³C NMR (CD_2Cl_2 , δ): 230.9 (trans-CrCO); 219.0 (FeCO, ²J_{Sn-C} = 62.6 Hz); 211.2 (cis-CrCO, ²J_{Sn-C} = 62.6 Hz); 138.3, 129.3, 128.5, 125.6 (PhMe); 84.0 (Cp); 21.5 (PhMe).

(8) Data for $[\text{Fe}(\text{CO})_4(\text{SnFp}_2(\text{THF}))]$. IR (THF, cm^{-1}): $\nu(\text{CO})$ 2053, 2016, 1981, 1929, 1909, 1884, 1867. ¹H NMR ($\text{C}_6\text{D}_6\text{O}$, δ): 4.25 (s, Cp). ¹³C NMR ($\text{C}_7\text{D}_8\text{O}$, δ): 217.7 (FeCp(CO)₂), 214.3 (Fe(CO)₄), 85.0 (Cp). ¹¹⁹Sn NMR ($\text{C}_7\text{D}_8\text{O}$, δ): 887.8.

(9) Data for $[\text{Fe}(\text{CO})_4(\text{SnFp}_2(\text{py}))]$ (**3**). IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 2004, 1976, 1956, 1935, 1915, 1885, 1871; $\nu(\text{C}=\text{N})$ 1601. ¹H NMR (C_7D_8 , δ): 7.0 (br m, py), 4.39 (s, Cp). ¹³C NMR (C_7D_8 , δ): 217.8 (FeCp(CO)₂), 214.5 (Fe(CO)₄), 149.8 (br s, NCHCCHCCHC), other pyridine ¹³C resonances obscured by solvent, 84.3 (Cp). Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{Fe}_3\text{NO}_8\text{Sn}$: C, 38.4; H, 2.11; N, 1.95. Found: C, 35.4; H, 2.26; N, 2.09 (black residues obtained after ignition of samples may indicate formation of carbide species). X-ray data will be published later.

(10) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Sartain, W. J.; Selegue, J. P. *Organometallics* **1984**, *3*, 1922. (c) Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. *Inorg. Chem.* **1985**, *24*, 1389.

(11) Hitchcock, P. B.; Lappert, M. F.; Thomas, S. A.; Thorne, A. J.; Carty, A. J.; Taylor, N. J. *J. Organomet. Chem.* **1986**, *315*, 27.

Together with the almost planar arrangement of the SnFe_3 (1) or SnFe_2Cr (2) core, we conclude that the zwitterionic resonance contributor $(\text{OC})_n(\mu\text{-CO})\text{M}^{\prime\prime-+}\text{SnFp}_2$ predominates, which (i) accounts for the Lewis acidity of the Sn(II) center and (ii) identifies $\text{M}^{\prime\prime}\text{-CO}$ rather than $\text{Fe}(\text{Cp})\text{-CO}$ as the more basic carbonyl.

Acknowledgment. M.J.M. thanks the U.S. National Science Foundation for a grant.

Supplementary Material Available: Details of the data collection for 1, tables of isotropic and anisotropic thermal parameters, fractional atomic coordinates, and bond distances and angles for 1 and 2, an ORTEP drawing of 1, and a diagram of the disordered toluene molecule in 2 (14 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

(12) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* 1976, 2275.

Reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_2\text{W}\equiv\text{WCl}_2(\eta^5\text{-C}_5\text{H}_4\text{R})]$ (R = Me, Prⁱ) with Alkynes: X-ray Crystal Structures of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{W}_2\text{Cl}_4(\mu\text{-C}_4\text{Me}_4)]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{W}_2\text{Cl}_2(\text{O})(\mu\text{-C}_4\text{Me}_4)]$

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Summary: The dimers $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{W}_2\text{Cl}_4]$ (**1a**, R = Prⁱ; **1b**, R = Me) react with an excess of but-2-yne (C_2Me_2) to give the flyover bridge compounds *cis*- $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{W}_2\text{Cl}_4(\mu\text{-C}_4\text{Me}_4)]$ (**2a,b**), which undergo thermal rearrangement in solution or in the solid state to the isomeric *trans* species (**3a,b**). The X-ray crystal structure of **3b** reveals a planar bridging $\mu\text{-C}_4\text{Me}_4$ group that lies symmetrically perpendicular to the W-W (2.9295 (7) Å) bond. Hydrolysis of **2** or **3** gives the monooxidtungsten derivatives *trans*- $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{W}_2\text{Cl}_2(\text{O})(\mu\text{-C}_4\text{Me}_4)]$ (**4a,b**).

Examples of "flyover bridge" compounds, in which a coupled dialkyne fragment (C_4R_4) bridges a dimetal center, are plentiful in the chemical literature.¹ A common feature of even the symmetrically substituted derivatives of this class (e.g., $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_4\text{Ph}_4)]^{1h,2}$) is that the $\mu\text{-C}_4\text{R}_4$ fragment exhibits a pronounced "lean" toward one metal atom. These structures may be formally described as a metallacyclopentadiene fragment that is η^4 -bound to the

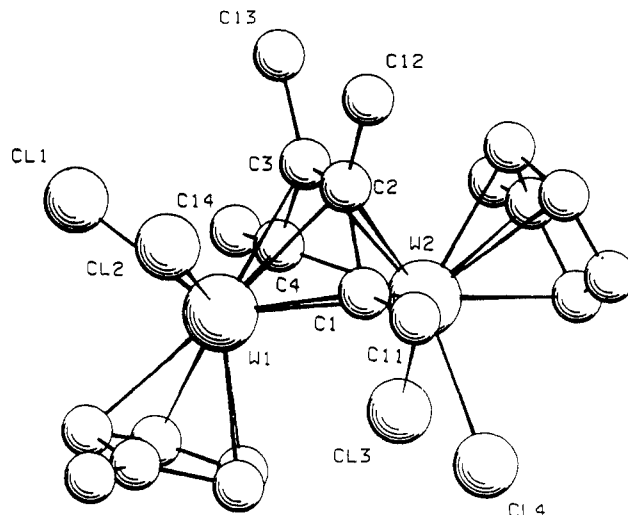


Figure 1. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{W}_2\text{Cl}_4(\mu\text{-C}_4\text{Me}_4)]$ (**3b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: W(1)-W(2) = 2.9295 (7), W(1)-Cl(1) = 2.486 (3), W(1)-Cl(2) = 2.474 (4), W(2)-Cl(3) = 2.481 (1), W(2)-Cl(4) = 2.471 (4), W(1)-C(1) = 2.11 (1), W(2)-C(1) = 2.11 (1), W(1)-C(2) = 2.39 (1), W(2)-C(2) = 2.38 (2), W(1)-C(3) = 2.36 (2), W(2)-C(3) = 2.38 (1), W(1)-C(4) = 2.10 (2), W(2)-C(4) = 2.10 (1), C(1)-C(2) = 1.46 (2), C(2)-C(3) = 1.44 (2), C(3)-C(4) = 1.43 (2), C(1)-C(11) = 1.52 (2), C(2)-C(12) = 1.50 (2), C(3)-C(13) = 1.51 (2), C(4)-C(14) = 1.53 (2), W(1)-Cp_{cent}(1) = 1.99, W(2)-Cp_{cent}(2) = 2.06; Cl(1)-W(1)-Cl(2) = 77.7 (2), Cl(3)-W(2)-Cl(4) = 78.6 (1), Cl(1)-W(1)-W(2) = 125.7 (1), Cl(2)-W(1)-W(2) = 125.4 (1), C(2)-C(1)-C(11) = 121.3 (13), C(3)-C(4)-C(14) = 121.6 (16), C(1)-C(2)-C(11) = 121.9 (15), C(4)-C(3)-C(13) = 122.2 (16), C(2)-C(3)-C(13) = 117.2 (13), C(3)-C(2)-C(12) = 119.4 (15), W(1)-C(1)-W(2) = 88.0 (5), W(1)-C(4)-W(2) = 88.4 (6); \angle (least-squares plane C(1)-C(4))-(plane containing W(1) and W(2)) = 89.8. Cp_{cent}(1) and Cp_{cent}(2) refer to the calculated $\eta^5\text{-C}_5\text{H}_4\text{Me}$ ring centroids for W(1) and W(2), respectively.

second metal atom.³ We recently described the synthesis and crystal structure of $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{W}_2\text{Cl}_4]$ (**1a**, R = Prⁱ), in which the unsupported $\text{W}\equiv\text{W}$ triple bond undergoes reversible addition of dihydrogen.⁴ Here we report reactions of **1a** (R = Prⁱ) and **1b** (R = Me) with alkynes.

When a toluene solution of $[(\eta^5\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{W}_2\text{Cl}_4]$ (**1a**) was treated with an excess of but-2-yne at room temperature over 12 h, the purple microcrystalline product **2a**, analyzed as $[(\eta^5\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{W}_2\text{Cl}_4(\text{C}_2\text{Me}_2)_2]$, was obtained in ca. 60% yield.⁵ The ¹H NMR spectrum of **2a** showed signals assignable to a $\eta^5\text{-C}_5\text{H}_4\text{Pr}^i$ moiety and two further singlets at δ 3.53 and 1.75. The ¹³C NMR spectrum showed, in addition to signals characteristic of an $\eta^5\text{-C}_5\text{H}_4\text{Pr}^i$ ring, two quartets at δ 33.3 and 15.8 assignable to methyl group carbon atoms and two additional singlets assignable to quaternary carbon atoms at δ 188.3 and 101.3. The compound **2a** isomerizes in THF solution at room temperature over 2 days to give the orange compound **3a** of identical empirical formula in quantitative yield. The NMR spectra of **3a** were very similar to those for **2a** but now showed two spectroscopically inequivalent $\eta^5\text{-C}_5\text{H}_4\text{Pr}^i$ ligands. Single

(3) The solid-state structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})(\mu\text{-C}_4\text{Ph}_4)]$ differs slightly from this general description. The terminal carbon atoms of the $\mu\text{-C}_4\text{Ph}_4$ fragment were equidistant from both Cr atoms, but the internal (bridgehead) carbon atoms bond much more strongly to the Cr atom that does not bear the CO ligand: (a) Bradley, J. S. *J. Organomet. Chem.* 1978, 150, C(1). (b) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1982, 173.

(4) Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* 1989, 732.

(5) Satisfactory elemental analyses (C, H \pm 0.3%; Cl \pm 0.4%) have been obtained for all the new compounds in this work.

(1) For examples and leading references see: (a) Curtis, D. M. *Polyhedron* 1987, 6, 759. (b) Winter, M. J. *Adv. Organomet. Chem.* 1989, 29, 101. (c) Burho, W. A.; Chisholm, M. H. *Adv. Organomet. Chem.* 1987, 27, 311. (d) Fehllhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 545-555. (e) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 5, pp 192-209. (f) Veldman, M. E. E.; Van der Waal, H. R.; Veenstra, S. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* 1980, 197, 59. (g) Bateman, L. R.; Maitlis, P. M.; Dahl, L. F. *J. Am. Chem. Soc.* 1969, 91, 7292. (h) Riley, P. E.; Davis, R. E. *Acta Crystallogr.* 1975, B31, 2928.

(2) (a) The deviation of sawhorse $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_4\text{H}_4)]$ from ideal C_{2v} symmetry has been attributed to a second-order Jahn-Teller distortion; Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* 1978, 17, 126. (b) Thermal racemization of the optically active species $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_4\text{H}(\text{OH})_2\text{R})]$ is thought to proceed via a symmetrical C_{2v} transition state: Case, R.; Jones, E. R. H.; Schwartz, N. V.; Whiting, M. C. *Proc. Chem. Soc. (London)* 1969, 256.