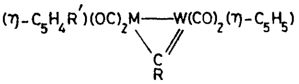
Tungsten Complexes with Bridging Alkylidyne Ligands: *X*-Ray Crystal Structure of $[(\eta\text{-}Me_6C_6)(OC)_2\overline{Cr(\mu\text{-}CC_6H_4Me\text{-}4)W}(CO)_2(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$

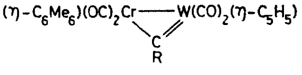
By MICHAEL J. CHETCUTI, MICHAEL GREEN, JOHN C. JEFFERY, F. GORDON A. STONE, and AUDREY A. WILSON
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary The alkylidyne tungsten complex $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ reacts with low-valent compounds of chromium, manganese, rhenium, cobalt, and rhodium to afford heteronuclear dimetalla complexes with a bridging $CC_6H_4Me\text{-}4$ ligand; the molecular structure of $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$ is established by a single-crystal *X*-ray diffraction study.

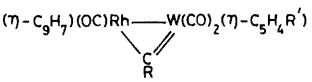
ALKYNES often form complexes with low-valent metal compounds. Herein we establish a similar reactivity pattern for $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$, demonstrating experimentally the isolobal relationship between the CR and $W(CO)_2(\eta\text{-}C_5H_5)$ groups,[1] and providing a versatile synthetic route to heteronuclear dimetal compounds.



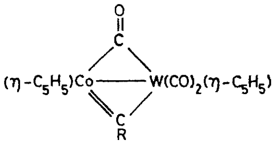
(1) M = Mn, R′ = Me
(2) M = Re, R′ = H



(3)



(4)
a, R′ = H
b, R′ = SiMe₃



(5)

R = $C_6H_4Me\text{-}4$

U.v. irradiation of $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ in tetrahydrofuran under nitrogen, followed by addition of $[W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$)[2] affords, after chromatography, deep violet crystals (60% yield) of complex (**1**) {ν_{CO}(methyl cyclohexane) 1 957s, 1 913s, 1 877s, and 1 865(sh) cm^{-1}; n.m.r. ($CDCl_3$): ^1H, τ 2·66 [$(AB)_2$ quartet, 4H, C_6H_4Me, J(AB) 8 Hz], 4·61 (s, 5H, C_5H_5), 5·54 (m, br, 4H, C_5H_4Me), 7·68 (s, 3H, C_6H_4Me), and 8·18 (s, 3H, C_5H_4Me); ^{13}C ($CDCl_3$, ^1H-decoupled) δ 395·5 [μ-*C*, J(WC) 129 Hz] p.p.m.} Compound (**2**) was similarly prepared from $[Re(CO)_3(\eta\text{-}C_5H_5)]$ as black crystals, and the ^{13}C n.m.r. spectrum revealed the carbyne carbon resonance at δ 344 [J(WC) 123 Hz] p.p.m.

U.v. irradiation of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ in tetrahydrofuran under argon, followed by addition of $[W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)]$ gave, following chromatography, deep green crystals of compound (**3**) {$\nu_{CO}(CH_2Cl_2)$ 1 921s, 1 861s, and 1 837s cm^{-1}; n.m.r.: ^1H ($CDCl_3$), τ 2·75[$(AB)_2$ quartet, 4H, C_6H_4Me, J(AB) 8 Hz], 4·75 (s, 5H, C_5H_5), 7·69 (s, 3H, C_6H_4Me), and 7·99 (s, 18H, C_6Me_6); $^{13}C(CD_2Cl_2)$, δ 431 (μ-C), 249, 245, 237, and 222 (CO) p.p.m.} An *X*-ray diffraction study was carried out on (**3**) to establish the structure of the molecule.†

Crystal data: (**3**), $C_{29}H_{30}CrO_4W\cdot CH_2Cl_2$, *M* 678·1, monoclinic, space group $P2_1/c$, $a = 9{\cdot}680(4)$, $b = 16{\cdot}595(4)$, $c = 18{\cdot}151(5)$ Å, $\beta = 93{\cdot}16(3)°$, $U = 2\,911(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}74$, $D_c = 1{\cdot}74$ g cm^{-3}, $F(000) = 1\,504$, μ(Mo-K_α) = 46·2 cm^{-1}. Current *R* 0·041(*R'* 0·043) for 4 653 absorption-corrected intensities [295 K, $2\theta \leqslant 55°$, $F \geqslant 5\sigma(F)$, Syntex $P3_m$ diffractometer, Mo-K_α (λ = 0·710 69 Å)].

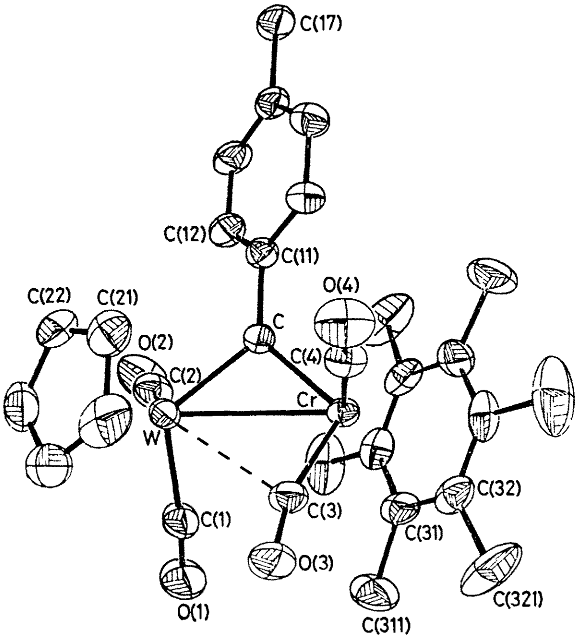


FIGURE. The molecular structure of complex (**3**). Bond lengths: Cr–W 2·941(1), C–Cr 1·928(6), C–W 2·025(6), Cr–C(3) 1·840(6), C(3)–O(3) 1·17(1), W–C(3) 2·69(1) Å. Angles: Cr·C·W 96·1(3), C·W·Cr 40·7(2), C·Cr·W 43·2(2), Cr·C(3)·O(3) 163(1)°.

The molecular structure (Figure) shows a Cr–W bond [2·941(1) Å] bridged by the CC_6H_4Me-4 ligand. The C–W distance [2·025(6) Å] is longer than the W–C(carbyne) distance [1·82(2) Å] in [$W{\equiv}CC_6H_4Me$-4$(CO)_2(\eta$-$C_5H_5)$],[2] and similar to that [2·14(2) Å] in the carbene complex [$W{=}CPh_2(CO)_5$].[3] Based on covalent radii a W=C bond would be *ca.* 1·91 Å.[4] It is thus apparent that the C–W separation in (**3**) corresponds to a double bond as might be expected in order for the tungsten atom to acquire an 18-electron configuration. Electron density at the tungsten evidently results[5] in the presence of the semi-bridging carbonyl [$\angle$ Cr·C(3)·O(3) 163(1)°], so that there is electron delocalization among the atoms Cr, C, W, and C(3). Indeed, the μ-C–Cr distance [1·928(6) Å] is little different from that found [2·04(3) Å] in [$Cr{=}C(OMe)Ph(CO)_5$].[6]

Indenyldicarbonylrhodium reacts at room temperature with light petroleum solutions of the compounds [$W{\equiv}CR(CO)_2(\eta$-$C_5H_4R')$] (R' = H or $SiMe_3$) to give (70—90%) the dark brown microcrystalline complexes (**4a**) {[$\nu_{CO}(CH_2Cl_2)$ 1 985m, 1 917s, and 1 837m cm^{-1}; ^{13}C n.m.r. ($CDCl_3$), δ 312 [d, μ-*C*, *J*(RhC) 30 Hz], 226, 223 (W*C*O), and 189 [d, Rh*C*O, *J*(RhC) 88] p.p.m.} and (**4b**) {ν_{CO}-(hexane), 1 985m, 1 925s, and 1 855m cm^{-1}; n.m.r. ($CDCl_3$): ^{1}H, τ 2·7—3·4 (m, 8H, C_6H_4Me-4 and 4-H—7-H of C_9H_7), 4·2—4·8 (m, 7H, $C_5H_4SiMe_3$ and 1-H—3-H of C_9H_7), 7·9 (s, 3H, Me-4), and 9·86 (s, 9H, $SiMe_3$); ^{13}C, δ 312 [d, μ-*C*, *J*(RhC), 29 Hz, *J*(WC) 149], 228 [W*C*O, *J*(WC) 195], 224 [W*C*O, *J*(WC) 171], and 190 [d, Rh*C*O, *J*(RhC) 88] p.p.m.}

Cyclopentadienyldicarbonylcobalt and [$W{\equiv}CR(CO)_2$-$(\eta$-$C_5H_5)$] after u.v. irradiation in tetrahydrofuran afforded dark brown crystals of (**5**) {^{13}C n.m.r.: δ 332 [μ-*C*, *J*(WC) 144 Hz], 227·2 [W*C*O, *J*(WC) 198], 226·7 [W*C*O, *J*(WC) 215], and 199·5 (Co*C*O) p.p.m.}; the i.r. spectrum (methylcyclohexane) of which showed terminal CO bands at 1 973s and 1 917s cm^{-1}, and a bridging CO absorption at 1 774m cm^{-1}.

The synthesis of complexes (**1**)—(**5**), and the earlier preparation of [$PtW(\mu$-CC_6H_4Me-4$)(CO)_2(PMe_2Ph)_2$-$(\eta$-$C_5H_5)$],[4] demonstrate the ubiquitous nature of complexes having dimetallacyclopropene rings, the reactivity of which merits attention.

We thank the S.R.C. for support, and the Commonwealth Scholarship Commission for a scholarship (M. J. C.).

(*Received, 9th July* 1980; *Com.* 748.)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
[2] E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrick, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.
[3] C. P. Casey, T. J. Burkhardt, C. A. Bunnel, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1977, **99**, 2127.
[4] T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609.
[5] F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1.
[6] O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1968, 642.