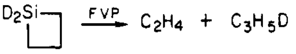
migration of H (D) in **4** (**22**) is demanded in the formation of propene.



22

At this time we are at a loss to explain the formation of ethylene observed by Ring[13b] in the decomposition of propylsilylene (**18**). The derived rates of ethylene formation make it impossible for **4** to enter the kinetic scheme. Furthermore, we can find neither ethylene nor silacyclobutane **17** in the products from **20**. Thus, further study is clearly warranted (and is in progress) before the complete picture of the deceptively simple decomposition of hydridosilacyclobutanes can be viewed.

Acknowledgment. The Iowa state group gratefully acknowledges the National Science Foundation, and the Leicester group acknowledges SERC for support of this work.

Registry No. 4, 287-29-6; 17, 765-33-3.

Coordination and Scission of Alkynes on a Ditungsten–Diiridium Framework. The Crystal Structure of $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph)$

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Summary: The reaction between $Cp_2W_2Ir_2(CO)_{10}$ and C_2Ph_2 produces $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ (by cleavage of a W–W bond) and $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ (by cleavage of a W–Ir bond); these processes apparently operate independently and appear to be general for disubstituted acetylenes. The species $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, studied by X-ray diffraction, crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.253$ (9) Å, $b = 15.629$ (4) Å, $c = 18.731$ (4) Å, $\beta = 96.86$ (4)°, $V = 4143$ (3) Å^3, and $Z = 4$. Convergence was achieved with $R_F = 8.5\%$ for all 4887 data and $R_F = 5.8\%$ for those 3395 data greater than 3σ. The metal core defines a fused triangulated rhombus with a dihedral angle of 170.33° about the common Ir(1)–W(1) edge. The μ_3-CPh ligand lies above the Ir(1)–W(1)–W(2) triangle. A $\mu_3\text{-}C_3Ph_3$ ligand lies above the Ir(1)–W(1)–Ir(2) triangle (i.e., on the same side of the cluster as the μ_3-CPh ligand); it participates in a η^3-allyl linkage to Ir(2) and is σ bonded to Ir(1) and W(1).

Previously we reported the syntheses and structures of $CpWIr_3(CO)_{11}$ and $Cp_2W_2Ir_2(CO)_{10}$ together with the use of these compounds as precursors to alumina-supported bimetallic particles.[1] In order to develop an understanding of the way in which the compounds might interact with the support, we have explored aspects of their reactivity in solution. Herein we report the results of treating $Cp_2W_2Ir_2(CO)_{10}$ with alkynes, including the crystal structure of one product that provides evidence for C≡C bond scission and redistribution of alkylidyne units.

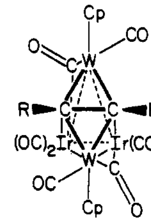
Table I. Yields (%) of Products from Reaction of $Cp_2W_2Ir_2(CO)_{10}$ with Alkynes

alkyne	$Cp_2W_2Ir_2(CO)_8$-(alkyne)	$Cp_2W_2Ir_2(CO)_6$-(alkyne)$_2$
C_2Ph_2	34	16
$C_2(p\text{-tol})_2$	55	trace
$C_2(CF_3)_2$	92	trace
$C_2Ph(CO_2Et)$	29	trace
$C_2(CO_2Et)_2$	58	none observed[a]
C_2PhMe	48	none observed[a]

[a] In these cases minor amounts of brown compounds containing *seven* carbonyl groups (MS) are obtained. These products have not been structurally characterized.

$Cp_2W_2Ir_2(CO)_{10}$ and C_2Ph_2 were heated in refluxing CH_2Cl_2 until all starting material was consumed (3 h). After preparative TLC and crystallization, green $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ and dark green "$Cp_2W_2Ir_2(CO)_6(C_2Ph_2)_2$" were isolated in 34% and 16% yields, respectively. The formulas of the products were determined by FAB mass spectroscopy and confirmed by additional spectroscopic and physical data.[2] Treatment of isolated $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ with C_2Ph_2 in refluxing CH_2Cl_2 did not form any of the minor product. Similar treatment of $Cp_2W_2Ir_2(CO)_{10}$ with other alkynes gave generally analogous results, with $Cp_2W_2Ir_2(CO)_8$(alkyne) the dominant product in all cases (see Table I).

The ^1H and ^{13}C NMR data show that the general structure of $Cp_2W_2Ir_2(CO)_8(C_2RR')$ is a "butterfly" complex, a closo octahedron derived from inserting the alkyne into a W–W bond of the W_2Ir_2 framework (see I). Rapid terminal-to-bridging and bridging-to-terminal rearrangement of the carbonyls bound to tungsten is indicated by the observation of only one averaged ^{13}C NMR signal for these carbonyls in $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$ even at −70 °C. In the case of an unsymmetrical alkyne, however, operation of this process does not fully average the carbonyl environments; two averaged W–CO signals and four averaged Ir–CO signals are seen for $Cp_2W_2Ir_2(CO)_8(C_2PhMe)$ even



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[1] (a) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *J. Am. Soc.* **1981**, *103*, 7383. (b) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1981**, *20*, 4112. (c) Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1359.

[2] $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$: ^1H NMR ($CDCl_3$) δ 6.9 (10 H, m, Ph), 4.60 (10 H, s, Cp); ^{13}C NMR (CD_2Cl_2, −70 °C) δ 225.4 (4 C, $J_{WC} = 171$ Hz), 173.2 (2 C), 173.0 (2 C); IR (CCl_4, ν_{CO}) 2104 (w), 2074 (s), 2047 (s), 2023 (w), 2007 (m), 1821 (m, br), 1769 cm^{-1} (w, br); MS (FAB), m/z 1284 (M$^+$), 1284 − 28X, X = 1–8. Anal. Calcd for $C_{32}H_{20}O_8W_2Ir_2$: C, 29.92; H, 1.57. Found: C, 29.91; H, 1.57. $Cp_2W_2Ir_2(CO)_6(C_2Ph_2)_2$: ^1H NMR ($CDCl_3$) δ 6.8–6.3 (20 H, m, br, Ph), 5.22 (5 H, s, Cp), 5.16 (5 H, s, Cp); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 243.4, 239.4, 214.1, 205.3, 169.2, 167.6; IR (CCl_4, ν_{CO}) 2055 (vs), 2031 (w), 2011 (s), 1989 (m), 1929 (m), 1801 cm^{-1} (m, br); MS (FAB), m/z 1406 (M$^+$), 1406 − 28X, X = 1–6.

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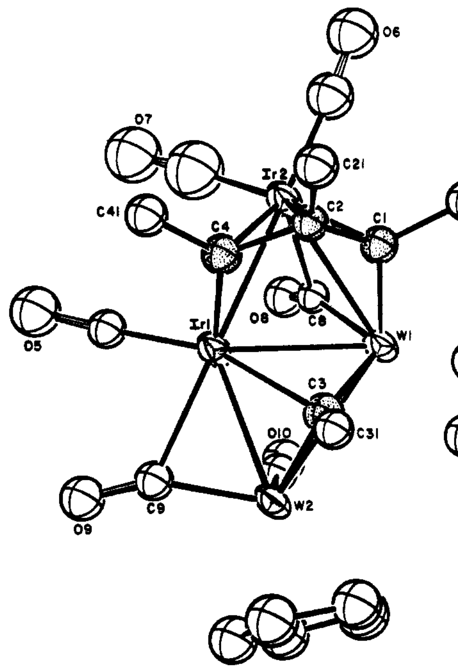

Figure 1. ORTEP-II diagram of the core of the $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ molecule. Phenyl groups (whose ipso carbons are C(11), C(21), C(31), C(41)) are omitted for clarity. Distances of interest (in Å) are as follows: (a) metal–metal bond lengths, W(1)–W(2) = 3.080 (1), W(1)–Ir(1) = 2.723 (2), W(1)–Ir(2) = 2.852 (2), Ir(1)–Ir(2) = 2.720 (1), W(2)–Ir(1) = 2.665 (2); (b) metal–$(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ ligand distances, W(1)–C(1) = 2.231 (24), Ir(2)–C(1) = 2.233 (25), Ir(2)–C(2) = 2.296 (25), Ir(2)–C(4) = 2.302 (26), Ir(1)–C(4) = 2.069 (24); (c) metal–$(\mu_3\text{-}CPh)$ ligand distances, W(1)–C(3) = 2.012 (29), W(2)–C(3) = 2.081 (27), Ir(1)–C(3) = 2.180 (28).

at room temperature.[3] A similar rearrangement process has been observed for related homometallic butterfly complexes.[4]

The NMR data obtained for "$Cp_2W_2Ir_2(CO)_6(C_2Ph_2)_2$" do not define a unique structure, so an X-ray diffraction study has been performed.[5] The results (see Figure 1) show that the molecule contains an almost flat W_2Ir_2 core, consisting of two triangles fused at the W(1)–Ir(1) edge (dihedral angle W(1)–Ir(1)–W(2)/W(1)–Ir(1)–Ir(2) = 170.33°). A $\mu_3\text{-}\eta^3$-1,3-dimetalla-allyl (C_3Ph_3) moiety is π bonded to Ir(2) and σ bonded to Ir(1) and W(1). On the same face of the tetrametallic core, a μ_3-CPh moiety bridges Ir(1), W(1), and W(2). Ir(1) is linked to one terminal carbonyl, whereas Ir(2) has two. Each tungsten atom is attached to an $\eta^5\text{-}C_5H_5$ ring and to a semibridging carbonyl having a signficant interaction with an adjacent iridium atom (W(2)–[C(9)–O(9)]···Ir(1), α = 0.24;[6] W(1)–[C(8)–O(8)]···Ir(2), α = 0.13[6]). Atom W(2) also bears a terminal carbonyl ligand. The carbonyl ^{13}C NMR spectrum is consistent with this structure.

Overall the tetrametallic core is associated with 60 valence electrons, rather than the 62 expected for a (5M–M) triangulated rhombus.

The formation of $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^2\text{-}C_3Ph_3)$ involves the scission of one C–C triple bond and the condensation of one of the resulting alkylidyne moieties with a second alkyne. Each of these reactions has recently been observed separately in other systems.[7,8] Most interesting is the fact that a W–Ir bond is cleaved in forming $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$ whereas a W–W bond is cleaved in forming $Cp_2W_2Ir_2(CO)_8(C_2Ph_2)$. These processes occur independently, with the initial reaction apparently determining the final products. [Vahrenkamp[9] has recently observed that H_2 and C_2Ph_2 react at different sites in $Ru_2Co_2(CO)_{13}$.]

Finally, the reactions of alkynes with $Cp_2W_2Ir_2(CO)_{10}$ occur under much milder conditions and proceed more cleanly than analogous reactions with the isoelectronic $Ir_4(CO)_{12}$.[10]

Preliminary work has shown that similar reactions occur also with $CpW(CO)_2(CTol)$; however, the products are not yet fully defined.

Acknowledgment. This work was supported at the University of Illinois by National Science Foundation Grant DMR 80-20250 (to J.R.S.) and at SUNY-Buffalo by Grant CHE 80-23448 (to M.R.C.). Instruments supported by the Grants NSF CHE 79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

Registry No. I (R = R′ = Ph), 91687-09-1; I (R = r′ = *p*-tol), 91687-10-4; I (R = R′ = CF_3), 91687-11-5; I (R = Ph, R′ = CO_2Et), 91687-12-6; I (R = R′ = CO_2Et), 91687-13-7; I (R = Ph, R′ = Me), 91687-14-8; $Cp_2W_2Ir_2(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)$, 91687-15-9; $Cp_2W_2Ir_2(CO)_{10}$, 80398-82-9; $CpW(CO)_2(Ctol)$, 60260-15-3; C_2Ph_2, 501-65-5; $C_2(p\text{-}tol)_2$, 2789-88-0; $C_2(CF_3)_2$, 692-50-2; $C_2Ph(CO_2Et)$, 2216-94-6; $C_2(CO_2Et)_2$, 762-21-0; C_2PhMe, 673-32-5.

Supplementary Material Available: Tables of final positional parameters for non-hydrogen atoms, anisotropic thermal parameters, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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[3] $Cp_2W_2Ir_2(CO)_8(C_2PhMe)$: ^{13}C NMR (CD_2Cl_2, 20 °C) δ 222.6 (2 C, *J*(WC) = 171 Hz), 221.7 (2 C, *J*(WC) = 170 Hz), 176.2 (1 C), 175.3 (1 C), 174.5 (1 C), 171.6 (1 C).

[4] Stuntz, G. F.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 2596.

[5] This complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 14.2534 (88) Å, b = 15.6285 (39) Å, c = 18.7311 (36) Å, β = 96.860 (38)°, V = 4142.7 (29) Å^3, and Z = 4. Diffraction data for 2θ = 4.5–45.0° (Mo Kα) were collected on a Syntex $P2_1$ diffractometer and were corrected for absorption and a linear decay (to 72% initial intensity). The structure was solved by direct methods (MULTAN 76) and refined to R_F = 8.5% for 237 parameters against 4887 data (R_F = 5.8% for those 3395 data with $|F_o| > 3.0\sigma(|F_o|)$).

[6] $\alpha = (d_1 - d_2)/d_1$, where d_1 is the "short" M–CO distance and d_2 is the "long" M–CO distance. See: Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

[7] Alkyne scission: (a) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619 (and references therein). (b) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

[8] Alkylidyne–alkyne coupling: Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151 (and references therein).

[9] Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 183.

[10] Heveldt, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 340.

Hydrogen Bonding in Organometallic Ligands and Possible Implications for CO/H_2 Chemistry. First Carbonylation of an Isolable Metal α-Hydroxyalkyl Complex

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Summary: The metallacyclic α-hydroxyalkyl complex $(CO)_4\overline{MnNH_2CHR_1CHR_2CHO}H$ (**2c**, $R_1 = R_2 = -(CH_2)_4-$) carbonylates (−3 ± 1 °C, 250–360 psi of CO) to an acyl

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