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Reversible Scission of Coordinated Acetylide Ligand: Characterization and Reactivity Studies of WRu_4 and WRu_5 Carbide−Alkylidyne Clusters

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The chemistry of carbido metal cluster compounds has developed in recent years to constitute a distinct research domain.[1] It has been established from the many carbide clusters synthesized from their group 8 precursors that the interstitial carbides can be derived either by the disproportionation of the carbon monoxide ligand[2] or by the scission of the coordinated isocyanide ligands.[3] The oxidative decarbonation of the acetylide ligand in the acetylide complexes $[Cp(CO)_2MC_2Ph][Co_2(CO)_6]$ (M = Fe, Ru)[4] and the C−C bond cleavage of the phosphinoalkyne ligand in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ illustrate the potential of the acetylide ligands in exhibiting similar reaction patterns, as they are isoelectronic to both CO and isocyanide ligands.[5] In the oxidative decarbonation reaction, the acetylide ligand expels the α-carbon atom to produce the alkylidyne clusters $CpMCo_2(CO)_7(\mu_3\text{-}CPh)$ irreversibly. The mechanistic details of the C−C bond cleavage of the phosphinoalkyne ligand are also not well understood due to the complex side reactions. In this paper, we report the first observation of a reversible carbide formation from an acetylide cluster and thus verify the conformity between ligated acetylides and carbide−alkylidynes.[6]

The acetylide cluster $CpWRu_2(CO)_8(C_2Ph)$ (**1**), in which the acetylide ligand adopts two μ_3-η^2-coordination modes in solution, was prepared by condensation of $CpW(CO)_3(C_2Ph)$ and $Ru_3(CO)_{12}$ in refluxing toluene.[7] Two new higher nuclearity cluster compounds were formed when **1** was treated with $Ru_3(CO)_{12}$ in refluxing heptane for 17 h (Scheme 1). These products were identified as pentanuclear $CpWRu_4(\mu_5\text{-}C)(CO)_{12}(\mu\text{-}CPh)$ (**2**, 68%)[8] and hexanuclear carbido cluster $CpWRu_5(\mu_6\text{-}C)(CO)_{14}(\mu\text{-}CPh)$ (**3**, 19%).[9] Both compounds were characterized by spectroscopic as well as single-crystal X-ray diffraction studies.

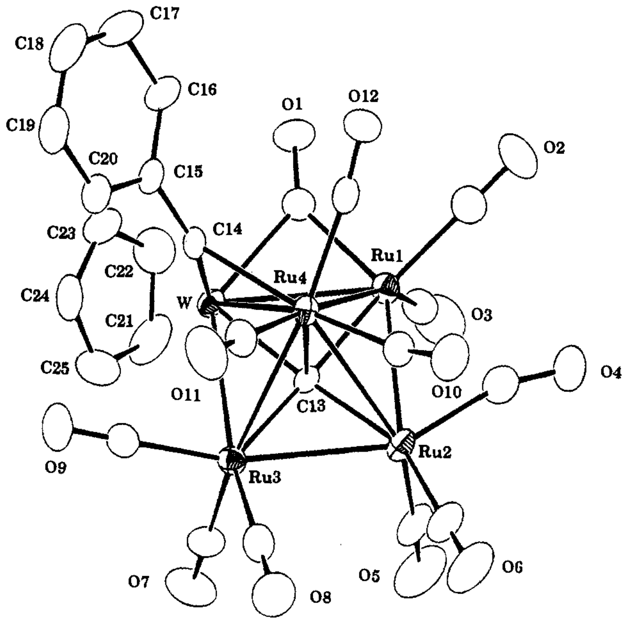
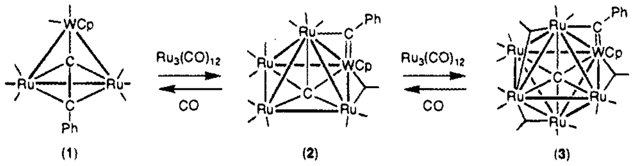


Figure 1. Molecular structure of **2** and the atomic numbering scheme. Selected bond lengths (Å): W(1)−Ru(1) = 2.881(1), W(1)−Ru(3) = 2.914(1), W(1)−Ru(4) = 2.863(1), Ru(1)−Ru(2) = 2.820(1), Ru(1)−Ru(4) = 2.856(1), Ru(2)−Ru(3) = 2.801(1), Ru(2)−Ru(4) = 2.880(1), Ru(3)−Ru(4) = 2.794(1), W(1)−C(13) = 2.053(6), Ru(1)−C(13) = 2.029(6), Ru(2)−C(13) = 1.992(6), Ru(3)−C(13) = 2.031(6), Ru(4)−C(13) = 2.190(6), W(1)−C(1) = 2.215(6), Ru(1)−C(1) = 2.006(6), W(1)−C(14) = 1.871(6), and Ru(4)−C(14) = 2.291(6).

Scheme 1.



Compound **2** contains two crystallographically distinct molecules in the asymmetric crystal unit.[10] Both molecules are structurally similar, and an ORTEP diagram of one of these molecules is shown in Figure 1. The metal framework of **2** is best described as a WRu_4 square pyramidal arrangement with one Ru atom occupying the apical site. The carbide atom is located at a position slightly below the WRu_3 plane (0.177(6) Å). The asymmetric phenylalkylidyne ligand spans the W−Ru(4) edge and the unique bridging CO lies on an adjacent basal W−Ru edge. The resulting core arrangement resembles that of many reported Ru_5 square pyramidal carbido cluster compounds.[11] In agreement with the solid-state structure, the ^{13}C NMR signals of the carbide and the alkylidyne signals resonate

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[8] Selected data for **2**. IR (C_6H_{12}): ν(CO) 2076 (m), 2039 (vs), 2025 (s), 2008 (m), 1982 (w), 1975 (w), 1962 (vw), 1788 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, room temperature): δ 7.29 (t, 2H, $J_{H-H} = 7.4$ Hz), 7.21 (t, 1H, $J_{H-H} = 7.4$ Hz), 6.79 (d, 2H, $J_{H-H} = 7.4$ Hz), 5.78 (s, 5H). ^{13}C NMR (CD_2Cl_2, room temperature): δ 424.0 (μ_5-C, $J_{C-W} = 88$ Hz), 302.3 (μ-*C*Ph, $J_{C-W} = 156$ Hz), 159.1 (*i*-C_6H_5), 128.7 (2C, *o*-C_6H_5), 128.0 (*p*-C_6H_5), 121.8 (2C, *m*-C_6H_5), 97.2 (C_5H_5). Anal. Calcd for $C_{25}H_{10}O_{12}Ru_4W_1$: C, 27.54; H, 0.92; O, 17.61. Found: C, 27.42; H, 0.96; O, 17.71.

[9] Selected data for **3**. IR (C_6H_{12}): δ(CO) 2075 (s), 2034 (vs), 1982 (m, br), 1894 (w, br), 1849 (vw, br), 1784 (m, br) cm^{-1}. ^1H NMR ($CDCl_3$, room temperature): δ 7.35 (t, 2H, $J_{H-H} = 7.4$ Hz), 7.26 (t, 1H, $J_{H-H} = 7.4$ Hz), 6.68 (d, 2H, $J_{H-H} = 7.4$ Hz), 5.53 (s, 5H). ^{13}C NMR ($CDCl_3$, room temperature): δ 425.1 (μ_6-C), 335.9 (μ-*C*Ph), 163.7 (*i*-C_6H_5), 129.5 (2C, *o*-C_6H_5), 128.7 (*p*-C_6H_5), 120.4 (2C, *m*-C_6H_5), 93.7 (C_5H_5). Anal. Calcd for $C_{27}H_{10}O_{14}Ru_5W_1$: C, 25.99; H, 0.81. Found: C, 25.98; H, 0.90.

[10] Crystal data for **2**: $C_{25}H_{10}O_{12}Ru_4W_1$, MW = 1090.47, triclinic space group $P\bar{1}$, $a = 12.855(3)$ Å, $b = 13.603(4)$ Å, $c = 16.748(3)$ Å, $\alpha = 79.00(2)°$, $\beta = 85.91(2)°$, $\gamma = 89.48(3)°$, $V = 2867(1)$ Å^3, $Z = 4$, $d_{calcd} = 2.526$ g/cm^3, $F(000) = 2024$, μ(Mo Kα) = 61.66 mm^{-1}, $R_F = 0.025$, and $R_w = 0.026$.

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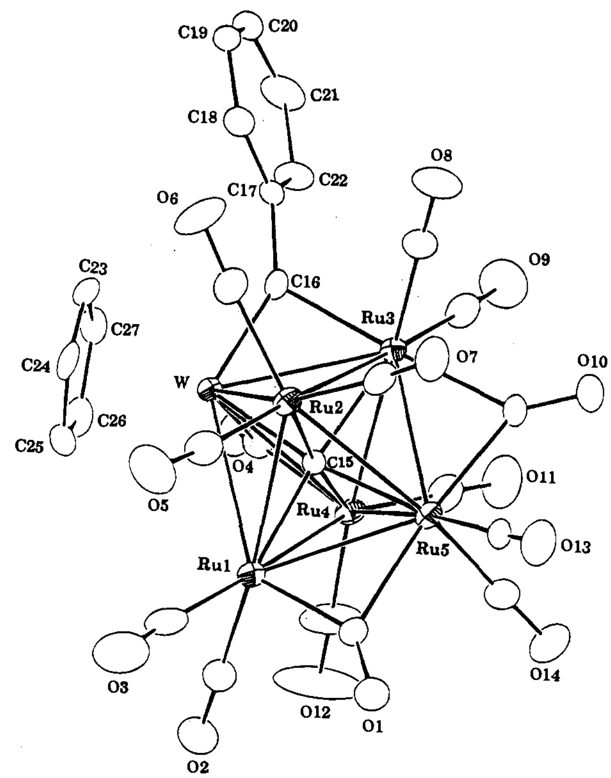

Figure 2. Molecular structure of **3** and the atomic numbering scheme. Selected bond lengths (Å): W−Ru(1) = 3.229(1), W−Ru(2) = 2.943(1), W−Ru(3) = 2.856(1), W−Ru(4) = 2.921(1), Ru(1)−Ru(2) = 2.925(1), Ru(1)−Ru(4) = 2.988(1), Ru(1)−Ru(5) = 2.817(1), Ru(2)−Ru(3) = 2.819(1), Ru(2)−Ru(5) = 2.877(1), Ru(3)−Ru(4) = 2.896(1), Ru(3)−Ru(5) = 2.839(1), Ru(4)−Ru(5) = 2.936(1), W−C(15) = 2.080(5), Ru(1)−C(15) = 2.037(5), Ru(2)−C(15) = 2.066(5), Ru(3)−C(15) = 2.106(5), Ru(4)−C(15) = 2.025(5), Ru(5)−C(15) = 2.103(5), W−C(16) = 1.893(5), and Ru(3)−C(16) = 2.176(5).

at δ 424.0 (J_{C-W} = 88 Hz) and 302.3 (J_{C-W} = 156 Hz). In addition, seven CO signals were observed at δ 231.1 (br), 209.2, 200.7, 195.9 (br), 192.7 (br), 191.4, and 190.1 (br) with relative intensities 2:2:2:1:2:2:1 in the ^{13}C NMR spectrum recorded at −50 °C.[12] This indicated a rapid exchange of the carbonyl group C(1)O(1) with one of the three terminal CO ligands on Ru(3) to produce a time-averaged C_s symmetry in solution. The hexanuclear compound **3** possesses a slightly distorted octahedral WRu_5 core with three edge-bridging CO ligands and one alkylidyne ligand on a W−Ru edge (Figure 2).[13] A few ruthenium octahedral carbido clusters with 86 valence electrons are reported,[14] but none possess an unsymmetrical alkylidyne on the ligand sphere.

Complex **2** is an intermediate en route to **3**, as the latter can be obtained in 60% yield by heating **2** with $Ru_3(CO)_{12}$ in refluxing toluene (Scheme 1). Furthermore, thermolysis of a 1:1:2 mixture of **1**, $Cp^*WRu_2(CO)_8(C_2Tol)$, and $Ru_3(CO)_{12}$ in toluene (10 h) afforded the four carbido cluster compounds **2**, **3**, and the Cp* derivatives $Cp^*WRu_4(\mu_5\text{-}C)(CO)_{12}(\mu\text{-}CTol)$ and $Cp^*WRu_5(\mu_6\text{-}C)(CO)_{14}(\mu\text{-}CTol)$. These four compounds were separated by thin-layer chromatography. Subsequent ^1H NMR analyses of these compounds provided conclusive evidence for no exchange of the μ-CR groups between the different carbido clusters. This clearly demonstrates that the formation of the carbido clusters involves no scrambling of the W metal fragment and the alkylidyne unit. On the basis of the above crossover experiment and the chemistry developed for the butterfly WOs_3 acetylide clusters,[15] we propose that the transformations **1** → **2** → **3** involve the prior formation of a hypothetical acetylide complex $CpWRu_3(CO)_{11}(C_2Ph)$, followed by cleavage of the C−C bond to afford **2** and **3** by the addition of $Ru(CO)_n$ fragments. The W atom appears to play an important role, since the resulting alkylidyne ligand in **2** ends up coordinated to the W atom. Furthermore, the related W−Os and W−Ru clusters facilitate the C−C bond scission of alkyne moieties.[16]

The reaction sequence can be reversed to regenerate the acetylide cluster **1**. Treatment of **3** with pressurized CO (14 atm) in toluene at 78 °C afforded **1** in 94% yield. Also, carbonylation of **2** under similar conditions produced **1** (Scheme 1). It is quite interesting to note that the degradation of **3** does not stop at the stage of the pentanuclear **2** and proceeds to the regeneration of the C−C linkage in **1**. This reactivity pattern is in sharp contrast to the relative inertness of the parent carbido cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}$, stable even under 80 atm of CO at 90 °C.[17] Attempts to isolate other carbide−alkylidyne intermediates are currently in progress.

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Supplementary Material Available: Variable-temperature ^{13}C NMR spectra of **2** and tables of crystal data, bond distances and angles, calculated positions of hydrogen atoms, and anisotropic thermal parameters for **2** and **3** (19 pages); listings of structure factors (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] The variable-temperature ^{13}C NMR spectra of **2** are presented in the supplementary material.

[13] Crystal data for **3**: $C_{27}H_{10}O_{14}Ru_5W_1$, MW = 1247.57, monoclinic space group $P2_1/c$, a = 17.381(3) Å, b = 10.030(5) Å, c = 17.907(1) Å, β = 97.74(1)°, V = 3093(1) Å^3, Z = 4, d_{calcd} = 2.679 g/cm^3, $F(000)$ = 2312, μ(Mo Kα) = 61.88 mm^{-1}, R_F = 0.023, and R_w = 0.022.

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