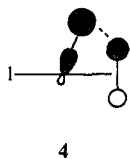
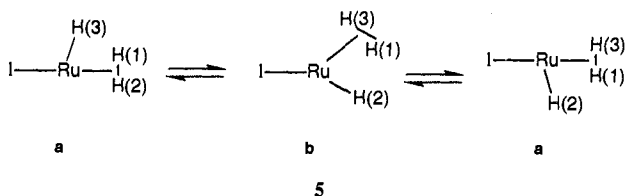


H₂ remains preferentially in the same plane as the Ru-H(3) bond with a small rotational barrier of 3 kcal/mol. Remarkably the interaction between the metal d orbitals and σ_{HH}^* is similar for the in-plane and out-of-plane orientation of H₂. The preference for a coplanar arrangement can be traced to a cis interaction between the Ru-H σ bond and the σ_{HH}^* orbital (4). This interaction is also responsible for the fact that the Ru-H is bent toward the H₂ ligand. As has been previously shown in an Fe(II)-H/H₂ complex,^{4a} this interaction creates a nascent bond between the hydride and the closest H center of H₂. This nascent bond should facilitate the exchange process between the hydrogens.



A possible path for exchanging the H centers is shown in 5 (perpendicular phosphine ligands removed for clarity). The transition structure between two equivalent square pyramids (5a) is a distorted trigonal bipyramid with an acute angle between H₂ and H and the I ligand trans to it (5b). Such a structure, which is calculated to be very close in energy to the minimum and which has even been observed as a stable structure in the case of an Ru(II) and two Ir(III) complexes (with R and H at the acute angle),^{13,14} should facilitate the exchange process by favoring the proximity between H and H₂.



Compound 2 is unusual for several reasons. Firstly, it is the first well-characterized 16-electron dihydrogen derivative, which demonstrates that electron saturation is not a necessary condition for the stabilization of coordinated H₂; there is no evidence for an agostic interaction between the cyclohexyl group and the metal. Secondly, the molecule adopts an octahedral type structure with a vacant coordination site. The dihydrogen molecule lies in the I-Ru-H(3) plane and not along the P(1)-Ru-P(2) axis, which is shown to be a manifestation of the cis interaction. Finally the H(1)-H(2) distance (1.03 (7) Å) is one of the longest reported so far in nonclassical H₂ complexes,¹⁵ whereas the H(1)-H(3) distance (1.66 (6) Å) is short, a structure that should facilitate hydride/dihydrogen exchange.

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Supplementary Material Available: Experimental data of the X-ray diffraction study of compound 2 including full experimental details and tables of atomic coordinates and thermal parameters (8 pages); table of observed and calculated structure factors for 2 (27 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $[\{\text{Ru}(\text{CO})_2(\text{Cp})\}_2(\mu\text{-C}\equiv\text{C})]$: An Ethynediyl Complex Formed during Tungsten-Catalyzed Alkyne Metathesis

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Metal complexes with all-carbon ligands provide interesting models for the carbide fragments formed as reactive intermediates during carbon monoxide and acetylene conversion reactions on heterogeneous catalyst surfaces.¹ There are several bicarbide clusters which fall into two classes, those with encapsulated C₂ ligands² and those with two separate C₁ ligands.³ Generally, the carbide ligands tend to be unreactive because they are "buried" in the clusters. Complexes with C₂ ligands bonded to only two or three metals are quite rare.^{4,5} We are interested in using metal ethynediyls (L_nMC≡CML_n) as an approach to reactive metal bicarbide complexes.

We previously reported that the stoichiometric reaction of $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\text{Cp})]$ with $[\text{W}(\equiv\text{C}Et)(\text{OCMe}_3)_3]$ leads to the μ -carbide complex $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$ by alkyne metathesis, with elimination of MeC≡CET.⁶ While optimizing this procedure, we realized that the direct reaction of $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\text{Cp})]$ with $[\text{W}_2(\text{OCMe}_3)_6]$ should be equally capable of forming the carbide complex, since the initial reaction of these complexes should give equimolar amounts of $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$ and $[\text{W}(\equiv\text{CMe})(\text{OCMe}_3)_3]$, ultimately leading to only $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$ by loss of volatile MeC≡CMe (Scheme I). Although this is the case in toluene solvent, carrying out the reaction in isoctane solution leads to the formation of a yellow precipitate of $[\{\text{Ru}(\text{CO})_2(\text{Cp})\}_2(\mu\text{-C}\equiv\text{C})]$ (1) in 52% yield.⁷ The compounds remaining in solution (NMR) are $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$, $[\text{W}(\equiv\text{CMe})(\text{OCMe}_3)_3]$,

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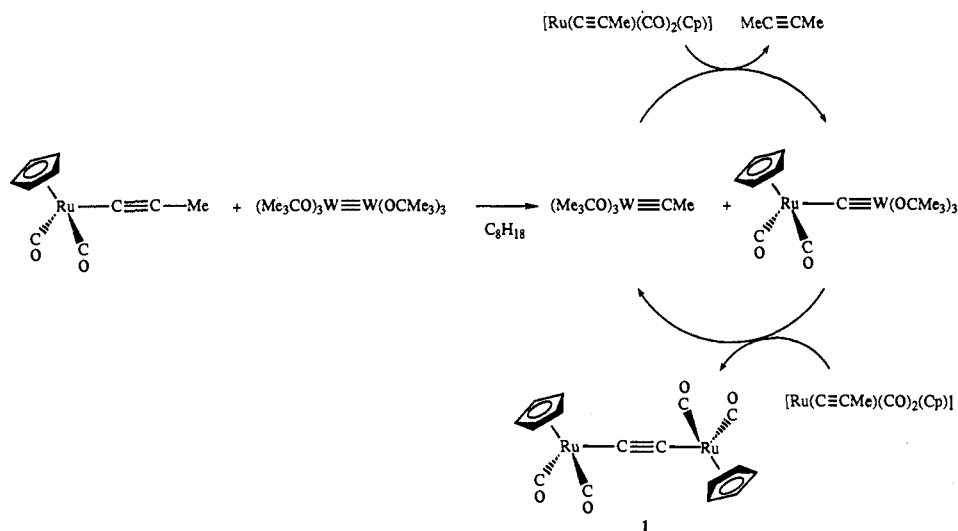
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(6) Latesky, S. L.; Selegue, J. P. *J. Am. Chem. Soc.* 1987, 109, 4731-4733. (7) A mixture of $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\text{Cp})]$ (187 mg, 0.716 mmol) and $[\text{W}_2(\text{OCMe}_3)_6]$ (20 mg, 0.025 mmol) in isoctane (30 mL) was stirred at ambient temperature for 2 h. The pale yellow precipitate was collected on a glass frit to give 1 (90 mg). The filtrate was further stirred for 12 h to give a second crop of 1 (20 mg, total yield 66%). A stoichiometric reaction of $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\text{Cp})]$ (450 mg, 1.72 mmol) and $[\text{W}_2(\text{OCMe}_3)_6]$ (693 mg, 0.86 mmol) in isoctane (50 mL) gave a precipitate of 1 (211 mg, 52%) in addition to $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$ (365 mg, 33%) which was recovered from the solution.

Scheme 1



and a small amount of $[\{\text{Ru}(\text{CO})_2(\text{Cp})\}_2(\mu\text{-C}\equiv\text{C})]$. A catalytic amount of $[\text{W}_2(\text{OCMe}_3)_6]$ (3 mol %) leads more slowly to a precipitate of **1** in 66% yield, with ca. 9 turnovers per W. In support of the mechanism proposed in Scheme 1, $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\text{Cp})]$ reacts with $[(\text{Cp})(\text{CO})_2\text{RuC}\equiv\text{W}(\text{OCMe}_3)_3]$ in isooctane to give a precipitate of **1** (60% yield) and 1 equiv of $[\text{W}(\equiv\text{CMe})(\text{OCMe}_3)_3]$, which remains in solution. Physical properties of **1**, in particular a ^{13}C NMR singlet resonance at 74.7 ppm, are consistent with the ethynediyl formulation.⁸ The appearance of four $\nu(\text{CO})$ absorptions in the infrared spectrum suggests that both syn and anti isomers are present in solution at room temperature. Compound **1** has no infrared-active carbon-carbon triple bond stretch.

The structure of **1** was confirmed by an X-ray diffraction study (Figure 1).⁹ The Ru1-C1-C2-Ru2 chain is linear, with Ru-C distances of 2.05 (1) and 2.04 (1) Å and a C1-C2 distance of 1.19 (1) Å, consistent with the localized canonical form $\text{Ru}-\text{C}\equiv\text{C}-\text{Ru}$. The cyclopentadienyl ligands are oriented anti to one another in the solid-state structure of **1**. Overall $[\text{Ru}(\text{CO})_2(\text{Cp})]$ geometries are similar to related structures.¹⁰⁻¹³

This preparation of an ethynediyl complex by using metal-catalyzed alkyne metathesis is unprecedented, although alkyne metathesis products were formed in reactions of $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PMe}_2\text{Ph})_2]$ with $[\text{W}_2(\text{OCMe}_3)_6]$ or $[\text{W}_2(\text{OCHMe}_2)_6(\text{py})_2]$.^{4c} Conceptually simpler attempts to prepare ethynediyls by reactions of C_2^{2-} salts with metal complexes are rarely successful,^{5f,h} apparently due to redox side reactions.¹⁴ Deprotonations of cationic μ -ethynyl complexes^{5a-c} and reactions of $\text{ClC}\equiv\text{CCl}$ with $[\text{M}(\text{CO})_3(\text{Cp})]^-$ ($\text{M} = \text{Cr}, \text{W}$)^{5g} have led to ethynediyls in a few cases.

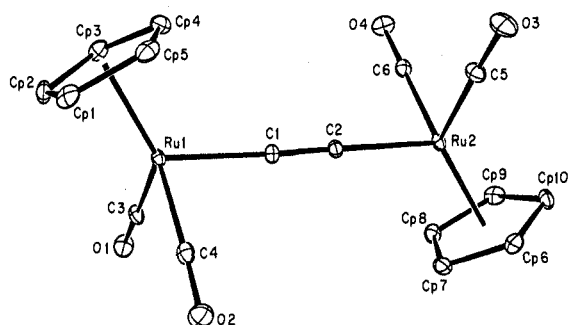


Figure 1. Plot of the structure of **1** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ru1-C4 1.87 (1), Ru1-C3 1.88 (1), Ru1-C1 2.05 (1), Ru2-C6 1.84 (1), Ru2-C5 1.86 (1), Ru2-C2 2.04 (1), C1-C2 1.19 (1); C4-Ru1-C3 90.7 (5), C4-Ru1-C1 86.6 (4), C3-Ru1-C1 90.5 (4), C6-Ru2-C5 90.1 (5), C6-Ru2-C2 88.1 (5), C5-Ru2-C2 88.4 (4), C2-C1-Ru1 178.1 (9), C1-C2-Ru2 179.6 (9).

Except for a report of the structure, protonation, and redox behavior of $[\{\text{Re}(\text{CO})_5\}_2(\mu\text{-C}\equiv\text{C})]$,^{5e} very little is known about the chemical properties of ethynediyls. In the cyclic voltammogram of **1**, two irreversible electrochemical oxidation waves are observed at 308 and 834 mV,¹⁵ consistent with oxidation at the ethynediyl bridge as suggested for $[\{\text{Re}(\text{CO})_5\}_2(\mu\text{-C}\equiv\text{C})]$. The ethynediyl bridge of **1** is quite reactive. For example, **1** reacts with $[\text{Fe}_2(\text{CO})_9]$ in THF at room temperature to give $[\text{Ru}_2\text{Fe}_2(\text{C}_2)(\text{CO})_9(\text{Cp})_2]$, which is currently under investigation.

Acknowledgment. We are grateful to the U.S. Department of Energy (DE-FG05-85ER13432), the Kentucky EPSCoR program (NSF Grant RII-8610671), and the Ashland Oil Foundation for financial support, to the University of Kentucky Major Research Instrumentation Bond Program for equipment, and to Johnson-Matthey, Inc., for a loan of ruthenium trichloride.

Supplementary Material Available: Complete experimental and spectroscopic details for compound **1** and listings of crystal structure data, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes (9 pages); listing of experimental and calculated structure factors for **1** (15 pages). Ordering information is given on any current masthead page.

(8) Properties of **1**: mp 148 °C dec; ^1H NMR (200 MHz, C_6D_6) δ_{H} 4.63 (s, Cp); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ_{C} 74.7 (s, $\text{C}\equiv\text{C}$), 88.0 (s, Cp), 199.8 (s, CO); IR ($\nu(\text{CO})$, toluene) 2048 (m), 2031 (s), 2024 (sh), 1980 (s). Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{O}_4\text{Ru}$: C, 41.03; H, 2.15. Found: C, 41.05; H, 2.15.

(9) Crystal data for **1**: yellow needle, CAD4 diffractometer, Mo K α radiation, 3003 unique reflections, 2337 with $(F_o)^2 \geq 3\sigma(F_o)^2$ for refinement, $P1$, $Z = 2$, $\rho_{\text{calcd}} = 2.008 \text{ g}\cdot\text{cm}^{-3}$, $a = 9.786$ (3) Å, $b = 13.822$ (2) Å, $c = 5.915$ (2) Å, $\alpha = 102.11$ (2)°, $\beta = 97.96$ (2)°, $\gamma = 87.81$ (2)°, $V = 774.7$ (3) Å³, $\mu = 19.255 \text{ cm}^{-1}$, no absorption or extinction corrections, solved by using Patterson, DIRDIF,¹⁶ and difference Fourier methods, H atoms idealized, non-hydrogen atoms refined with anisotropic thermal parameters to $R = 5.9\%$, $R_w = 7.8\%$ with 199 variables.

(10) $[\text{Ru}(\text{CO})_2(\text{Cp})]$ structures: R = $\text{CH}_2\text{Ru}(\text{CO})_2(\text{Cp})$, $d(\text{Ru}-\text{C}) = 2.18$ Å;¹¹ R = $\text{COC}_{10}\text{H}_{13}$, $d(\text{Ru}-\text{C}) = 2.090$ (6) Å;¹² R = CONH_2 , $d(\text{Ru}-\text{C}) = 2.084$ (7) Å;¹³ R = $\text{C}\equiv\text{W}(\text{OCMe}_3)_3$, $d(\text{Ru}-\text{C}) = 2.09$ (2) Å.⁵

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