

Notes

Oxidative Substitution of $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$ with Disubstituted Alkynes: Facile Formation and Reduction of $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{RR}')$

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Summary: Oxidation of the decaruthenium carbonyl cluster $[\text{Z}]_2[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]$ (**1**) ($\text{Z}^+ = \text{PPN}^+, \text{Et}_4\text{N}^+$) with $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ (2 equiv) at room temperature in the presence of disubstituted alkynes forms the neutral derivatives $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{RR}')$ (**2**, $\text{R}, \text{R}' = \text{Ph}_2$; **3**, $\text{R}, \text{R}' = \text{Tol}_2$; **4**, $\text{R}, \text{R}' = \text{Ph}, \text{Me}$). Compounds **2–4** are readily reduced with methanolic hydroxide to produce the previously known $[\text{Ru}_{10}\text{C}_2(\text{CO})_{22}(\text{C}_2\text{Ph}_2)]^{2-}$ (**5**) and its analogs.

Introduction

The decaruthenium cluster anion $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$ (**1**) has a structure that can be viewed as two Ru_6C octahedra sharing a common edge.¹ Essentially the same framework structure is adopted by both $\text{Rh}_{10}\text{C}_2(\text{CO})_{18}\{\text{AuPPh}_3\}_4$ and $\text{Rh}_{10}\text{C}_2(\text{CO})_{18}\{\text{AuPPh}_3\}_4$.² Related decanuclear clusters include $[\text{Ni}_{10}(\mu_8\text{-C}_2)(\text{CO})_{16}]^{2-}$, which is described as having a dicarbide unit encapsulated by two capped trigonal prisms fused at a square face,³ $[\text{M}_{10}(\mu_6\text{-C})(\text{CO})_{24}]^{2-}$ ($\text{M} = \text{Os},^4 \text{Ru}$),⁵ which have tetracapped octahedral structures, and the rhodium clusters $[\text{Rh}_{10}(\mu_8\text{-E})(\text{CO})_{22}]^{n-}$ ($\text{E}^{n-} = \text{S}^{2-},^6 \text{P}^{3-},^7$ and As^{3-} –⁸), which display bicapped square antiprisms of the metal atoms.⁹

Compound **1** is reluctant to undergo substitution, but at 125 °C it reacts with diphenylacetylene to form $[\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)]^{2-}$.¹⁰ In this derivative, the basic biocuboctahedral framework is maintained, but it is folded at the fused edge, forming a bond between two apical Ru atoms, and the alkyne ligand bridges this new Ru–Ru bond. Unfortunately, despite the fact that this

substitution reaction is quite clean (and reversible under CO), the high temperature required is generally unfavorable to the preparation of less stable derivatives.

Activation by oxidation is a promising alternative to thermal activation for achieving substitution in higher nuclearity clusters.^{11,12} Such oxidative substitution reactions have been exploited for the parent octahedral cluster $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$, which gives substituted, neutral products with two-, four-, and even six-electron donor ligands.^{13,14} With alkynes, the resultant derivatives $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{C}_2\text{R}_2)$ have the alkyne ligands coordinated in typical face-bridging (μ_3, η^2) positions.^{14b} Here, we report that oxidative substitution of **1** with diphenylacetylene and related alkynes, using ferricenium ion for activation, provides neutral alkyne derivatives, such as $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)$ (**2**). Interestingly, however, the alkyne ligand in **2** is not face-bonded but displays the same edge-bridging coordination mode found previously in $[\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)]^{2-}$ (**5**). Furthermore, the neutral cluster **2** is reduced readily with hydroxide ion to give dianion **5**. The transformations involving **1**, **2**, and **5** are summarized in Scheme 1.

Experimental Section

General Procedures. Dichloromethane was distilled from CaH_2 and stored over 4 Å molecular sieves under nitrogen. Hexanes and diethyl ether were distilled from Na/benzophenone under nitrogen. The alkynes and salts ($[\text{NET}_4]\text{Cl}$ and $[\text{PPN}]\text{Cl}$) were purchased from Aldrich Chemical and were used as received. The alumina (Brockman, activity I, Aldrich) was degassed for 24 h under vacuum and deactivated with water (5% w/w). The starting materials $[\text{Z}]_2[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{1a}$ and $[\text{Cp}_2\text{Fe}][\text{BF}_4]^{15}$ were prepared by literature procedures. Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier transform spectrometer. A General Electric QE-300 spectrometer was used to obtain the ¹H and ¹³C NMR spectra. The staff of the facilities maintained by the School of Chemical Sciences provided elemental analyses and negative ion FAB mass spectra.

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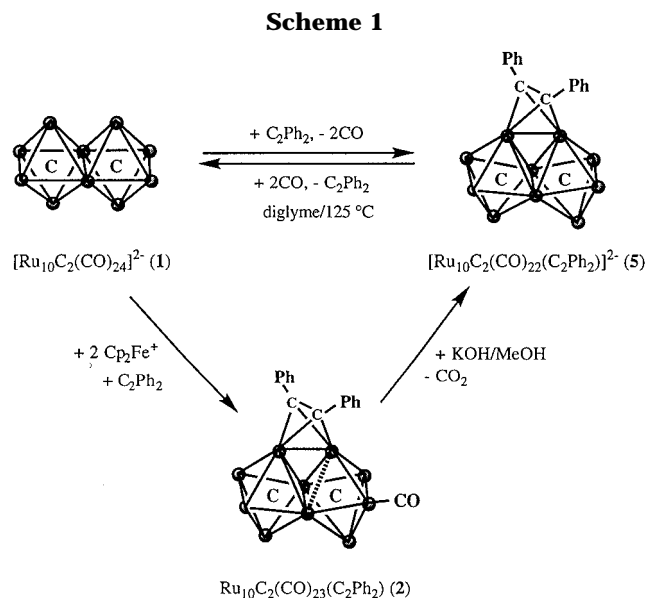
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Synthesis of $Ru_{10}C_2(CO)_{23}(C_2Ph_2)$ (2). A solution of $[PPN]_2[Ru_{10}C_2(CO)_{24}]$ (30.0 mg, 0.0108 mmol) and C_2Ph_2 (23.7 mg, 0.133 mmol) in 15 mL of CH_2Cl_2 was prepared in a 50 mL flask under N_2 . From a pressure-equalizing dropping funnel, a solution of $[Cp_2Fe][BF_4]$ (9.2 mg, 0.034 mmol) in 10 mL of CH_2Cl_2 was added dropwise over 10 min. The resulting solution was stirred for 1.5 h at room temperature and then filtered via cannula, leaving a small amount of dark precipitate. The solvent was removed under vacuum, and the residue was washed with three 5 mL portions of a 1:1 MeOH/ H_2O mixture. The residue was dissolved in CH_2Cl_2 , and this solution was layered with hexane. Dark crystals formed at $-20^\circ C$ (13.0 mg, 0.0067 mmol, 62%). Anal. Calcd for $C_{39}H_{10}O_{23}Ru_{10} \cdot CH_2Cl_2$: C, 24.74; H, 0.62. Found: C, 23.95; H, 0.69. FAB-MS: m/z 1837 ($M^- - CO$), 1687 ($M^- - C_2Ph_2$). IR (ν_{CO} , CH_2Cl_2): 2094 (w), 2076 (m, sh), 2066 (s, sh), 2057 (vs), 2049 (s, sh), 2031 (m, sh), 1978 (br), 1849 (br), 1825 (br) cm^{-1} .

Synthesis of $Ru_{10}C_2(CO)_{23}(C_2Tol_2)$ (3). A solution of $[PPN]_2[Ru_{10}C_2(CO)_{24}]$ (28.0 mg, 0.0101 mmol) and C_2Tol_2 (20.0 mg, 0.097 mmol) in 20 mL of CH_2Cl_2 was prepared in a 50 mL three-necked flask under N_2 . $[Cp_2Fe][BF_4]$ (10.0 mg, 0.037 mmol) was added to the solution as a solid, resulting in the change of the solution color from purple to dark red brown. The solution was stirred for 5 min and then filtered through a short silica gel column (2 cm height). The solvent was removed under vacuum, and the residue was washed with hexane (ca. 50 mL total) in order to remove ferrocene. The product was crystallized from CH_2Cl_2 /hexane at $-20^\circ C$ as thin needles (11.9 mg, 0.0063 mmol, 62%). Anal. Calcd for $C_{41}H_{14}O_{23}Ru_{10}$: C, 26.12; H, 0.75. Found: C, 26.00; H, 0.96. FAB-MS: m/z 1893 (M^-), 1865 ($M^- - CO$), 1687 ($M^- - C_2Tol_2$). IR (ν_{CO} , CH_2Cl_2): 2094 (w), 2076 (m, sh), 2066 (s, sh), 2056 (vs), 2047 (sh, s), 2030 (m), 1845 (br), 1826 (br) cm^{-1} . 1H NMR ($CDCl_3$): δ 7.32 (d, 2 H, $J = 8$ Hz), 7.28 (d, d, 2 H, $J = 8$ Hz), 2.42 (s, 3 H). ^{13}C NMR (75 MHz, $-95^\circ C$): δ 235.7 (s, 1 C), 234.9 (s, 1 C), 226.4 (s, 1 C), 216.5 (s, 1 C), 201.3 (s, 1 C), 200.0 (s, 3 C), 197.9 (s, 1 C), 197.3 (s, 2 C), 196.3 (s, 1 C), 195.0 (s, 1 C), 194.5 (s, 2 C), 192.2 (s, 1 C), 191.6 (s, 1 C), 191.2 (s, 1 C), 189.7 (s, 1 C), 188.2 (s, 2 C), 187.8 (s, 1 C), 185.7 (s, 1 C).

Synthesis of $Ru_{10}C_2(CO)_{23}(C_2PhMe)$ (4). In a 50 mL flask a mixture of 26.5 mg (0.0095 mmol) $[PPN]_2[Ru_{10}C_2(CO)_{24}]$ and 50 μL (0.40 mmol) of 1-phenyl-1-propyne was dissolved in 15 mL of CH_2Cl_2 under N_2 . A solution of $[Cp_2Fe][BF_4]$ (11.1 mg, 0.0407 mmol) in 15 mL of CH_2Cl_2 was added from a dropping funnel over 10 min. The resulting mixture was stirred for 1 h and then filtered. The solution volume was reduced by half under vacuum, and then an equal volume of hexane was added. The flask was held at $-20^\circ C$ to precipitate

Table 1. Summary of Crystallographic Data for $[Ru_{10}C_2(CO)_{23}(C_2Ph_2)] \cdot CH_2Cl_2$

formula	$C_{40}H_{12}Cl_2O_{23}Ru_{10}$	D_{calc} ($g\ cm^{-3}$)	2.555
fw	1942.10	μ (Mo $K\alpha$) (mm^{-1})	3.087
space group	$P2_1/c$	λ (Mo $K\alpha$) (\AA)	0.71069
temp (K)	299(2)	$F(000)$	3640
a (\AA)	11.934(4)	θ range (deg)	1.67–22.50
b (\AA)	17.337(7)	no. of reflns coll'd	6983
c (\AA)	24.515(8)	no. of indep reflns	6607
β (deg)	95.396(7)	R_{int}	0.0943
V (\AA^3)	5050(3)	$R1 [I > 2\sigma(I)]$	0.0539
Z	4	wR2	0.1073

the product. The filtrate was decanted, and the precipitate was washed first with hexane (2 \times 5 mL) and then with methanol (4 \times 3 mL). The residue was finally dried under vacuum (yield 12.7 mg, 0.0071 mmol, 75%). Anal. Calcd for $C_{34}H_8O_{23}Ru_{10}$: C, 22.63; H, 0.45. Found: C, 23.20; H, 0.73. FAB-MS: m/z 1803 (M^-), 1775 ($M^- - CO$), 1687 ($M^- - C_2MePh$). IR (ν_{CO} , CH_2Cl_2): 2095 (w), 2070 (m, sh), 2054 (s), 2047 (s), 2032 (m, sh), 1826 (br) cm^{-1} . 1H NMR ($CDCl_3$): δ 7.46 (m, 5 H), 3.05 (s, 3 H).

Reduction of 2 to 5. To a solution of $Ru_{10}C_2(CO)_{23}(C_2Ph_2)$ (17.4 mg, 0.0093 mmol) in methanol (10 mL) was added 2.0 mL of a 0.030 M KOH/MeOH solution (0.060 mmol). The solution was stirred for 12 h, at which point the IR spectrum indicated that all of the $Ru_{10}C_2(CO)_{23}(C_2Ph_2)$ had been consumed. An excess of $[NEt_4]Cl$ (40.0 mg, 0.190 mmol) was added to the reaction mixture, and the solvent was removed under vacuum. The residue was placed on a column of neutral alumina, and compound 5 was eluted as a red-purple band with dichloromethane. The product was recrystallized from CH_2Cl_2 /Et $_2$ O (yield 14.5 mg, 0.0069 mmol, 74%) and identified by its IR spectrum.¹⁰

Reduction of 3 to 6. To a methanol solution (5 mL) of $Ru_{10}C_2(CO)_{23}(C_2Tol_2)$ (10.2 mg, 0.0054 mmol) was added 1.0 mL of a 0.030 M KOH/MeOH solution (0.030 mmol), and the reaction mixture was stirred at room temperature for 21 h. An excess of $[PPN]Cl$ (95.6 mg, 0.167 mmol) was added, and the solvent was removed under vacuum. The residue was washed with H_2O (4 \times 5 mL) and then dissolved in dichloromethane; the solution was filtered, and the product was precipitated with diethyl ether. The filtrate was decanted, and the precipitate was dried under vacuum (yield 13.6 mg, 86%). FAB-MS: m/z 2403 ($M - PPN^-$). IR (ν_{CO} , CH_2Cl_2): 2040 (w), 2003 (s), 1999 (s), 1983 (sh, m) cm^{-1} . 1H NMR (CD_2Cl_2): δ 7.65 (m, 24 H), 7.45 (m, 36 H), 7.14 (d, 2 H, $J = 8$ Hz), 7.07 (d, 2 H, $J = 8$ Hz), 2.31 (s, 3 H).

Reduction of 4 to 7. The procedure was analogous to that for 5 above. A light purple band of 7 was eluted from the alumina column with acetone, and the product was identified by its spectroscopic properties. FAB-MS: m/z 1895 ($M - NET_4^-$). IR (ν_{CO} , CH_2Cl_2): 2042 (w), 2005 (s, sh), 1997 (vs), 1920 (w, br) cm^{-1} . 1H NMR ($CDCl_3$): δ 7.37 (m, 5 H), 3.51 (q, 8 H, $J = 7.2$ Hz), 2.83 (s, 3 H), 1.40 (tt, 12 H, $J = 7.5, 1.8$ Hz).

Structure Determination of 2. A crystal suitable for X-ray diffraction was obtained from the slow evaporation of a CH_2Cl_2 solution of 2. Crystallographic details are given in Table 1. Data were reduced using step-scan profile analysis¹⁶ and corrected for absorption.¹⁷ The structure was solved by direct methods;¹⁸ correct positions for Ru atoms were deduced from an E -map. Partial structure expansion revealed positions for the remaining non-H atoms, including disordered positions for carbonyl atoms 1C and a disordered solvate molecule. Successful convergence of the least-squares refinement (SHELXL-93)¹⁹ was indicated by the maximum shift/error for

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the last cycle. The highest peak in the final difference Fourier map was in the vicinity of the disordered solvate molecule.

Results and Discussion

Synthesis and Spectroscopic Characterization.

The neutral cluster compounds $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{RR}')$ ($\text{R} = \text{R}' = \text{Ph}_2$, **2**; $\text{R} = \text{R}' = \text{ToI}_2$, **3**; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, **4**), are synthesized at room temperature from **1** and the appropriate alkyne by using slightly more than 2 equiv of $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ as an oxidant (see Scheme 1). The reaction proceeds rapidly, finishing in about 1 h. Treatment of the neutral species **2–4** with hydroxide in a methanol solution reduces the clusters to give the corresponding dianions **5–7**; salts have been isolated with both $[\text{NEt}_4]^+$ and $[\text{PPN}]^+$ as counteranions. The reaction presumably proceeds by nucleophilic attack of OH^- on a CO ligand, followed by H β -elimination to give CO_2 and a proton that is transferred to the basic medium. It is interesting to note that the neutral compounds **2–4** decompose on alumina, whereas the corresponding anions **5–7** elute easily from the column with dichloromethane or acetone. Salts of the $[\text{PPN}]^+$ counterion tend to elute more rapidly than those of $[\text{NEt}_4]^+$.

Negative ion FAB mass spectra have generally been very useful in identifying these large cluster compounds, although a molecular ion was not observed for **2**. The FAB mass spectra of compounds **2–7** show successive loss of CO and alkyne, indicating that the Ru_{10} structure framework is quite stable.

The IR spectra of **2**, **3**, and **4** are virtually identical; all show five CO bands in the terminal region between 2100 and 1900 cm^{-1} , and they also contain broad bands in the region from 1826 to 1849 cm^{-1} , indicating bridging carbonyls. A larger number of CO bands observed in the spectra of **2–4** compared with the spectra of **5–7** is consistent with the significantly less symmetrical structure of **2** compared with **5** (see below). The frequency of the strongest CO band shifts from 2057 cm^{-1} for the neutral compounds to 1997 cm^{-1} for the dianionic clusters. Substitution of the R groups on the alkyne has little effect on the CO frequencies in either case.

Crystal Structure of 2. An ORTEP drawing of $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)$ is shown in Figure 1, and metal–metal bond distances are given in Table 2. The structure of **2** is qualitatively similar to that of **5**¹⁰ but notably less symmetrical. As for **5**, the original biotetrahedral framework of **1**¹ is folded along the shared axis in **2** as a strong interaction forms between the two apical atoms Ru4 and Ru5 (2.738(2) Å) that are bridged by the alkyne ligand. The corresponding distance for Ru4–Ru5 in **5** is 2.711(1) Å. There is also a concomitant significant lengthening of the distance between Ru1 and Ru8 (3.892(2) vs 3.823(1) Å in **5**). The hinge angle at the Ru9–Ru10 vector is 160°, similar to that found in **5**¹⁰, but there is also a slight twist of the octahedral subunits, giving torsion angles Ru3–Ru2–Ru9–Ru10 = 5.17(6)° and Ru6–Ru7–Ru9–Ru10 = –0.52(7)°. The average Ru–C(carbide) distance is, however, essentially unchanged at 2.07 Å from that of 2.06 Å in **5** and 2.07 Å in **1**.

Comparing categories of average metal–metal distances in the structures of **2** and **5** (for **2** and **5**, respectively (Å) (i) CO-bridged apical–equatorial, 2.786,

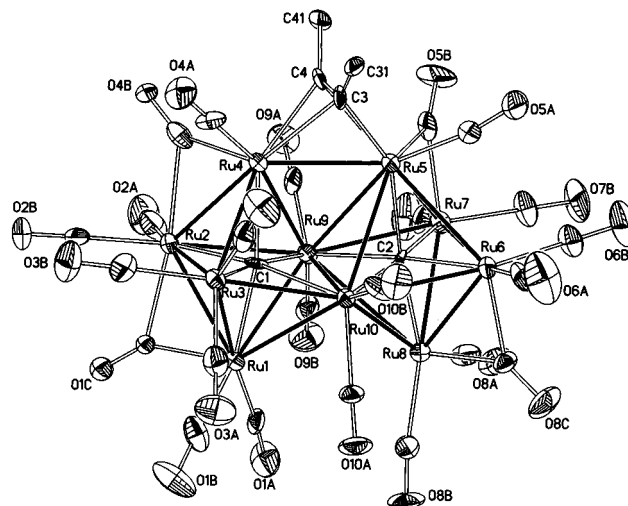


Figure 1. ORTEP drawing of $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)$ (**2**) (35% thermal ellipsoids). Phenyl groups are removed for clarity, except ipso carbons C31 and C41.

Table 2. Metal–Metal Distances (Å) for $\text{Ru}_{10}\text{C}_2(\text{CO})_{23}(\text{C}_2\text{Ph}_2)$ (2**)**

Apical–Equatorial (CO Bridged)			
Ru1–Ru2	2.770(2)	Ru2–Ru4	2.817(2)
Ru5–Ru7	2.800(2)	Ru6–Ru8	2.756(2)
Apical–Equatorial (Nonbridged)			
Ru1–Ru3	2.926(2)	Ru3–Ru4	2.879(2)
Ru5–Ru6	2.909(2)	Ru7–Ru8	2.896(2)
Apical–Hinge			
Ru1–Ru9	2.907(2)	Ru8–Ru9	3.076(3)
Ru4–Ru9	3.026(2)	Ru5–Ru9	2.959(2)
Ru8–Ru10	2.903(2)	Ru1–Ru10	2.921(2)
Ru5–Ru10	3.038(2)	Ru4–Ru10	3.292(2)
Hinge–Hinge			
Ru9–Ru10			2.787(2)
Equatorial–Hinge			
Ru2–Ru9	2.927(2)	Ru3–Ru10	2.847(2)
Ru6–Ru10	2.965(2)	Ru7–Ru9	2.884(2)
Equatorial–Equatorial			
Ru2–Ru3	3.041(2)	Ru6–Ru7	3.009(2)
Apical–Apical			
Ru4–Ru5	2.738(2)	Ru1–Ru8	3.892(2)

2.783; (ii) nonbridged apical–equatorial, 2.903, 2.907; (iii) apical–hinge, 3.015, 2.995; (iv) hinge–hinge, 2.787, 2.765; (v) equatorial–hinge, 2.906, 2.912; (vi) equatorial–equatorial, 3.025, 3.004) does not reveal any systematic structural distortions. However, one apical–hinge distance in **2** ($\text{Ru4–Ru10} = 3.292(2)$ Å) is significantly longer (by 0.216 Å) than any other such distance in the structure. The octahedral subunit containing this vector also evidences the larger torsion angle. An analogous distance in the structure of **5** also was relatively lengthened (3.125(1) Å), but not to the same extent as in **2**.

A second unique feature in the structure of **2** is the unsymmetrical distribution of the bridging carbonyls. The structures of both **1** and **5** contain four bridging CO's, two on each of their octahedral subunits, placed symmetrically around the cluster framework to give a C_2 rotation axis. Compound **2** also contains four bridging carbonyl ligands; however, CO1C, CO4B, and CO5B are oriented toward one side of the cluster while CO8C is oriented to the opposite side, thereby decreasing the symmetry to C_1 .

The alkyne carbon distance C3–C4 is 1.32(3) Å in **2** compared to 1.30(2) Å in **5**, and the alkyne angles of C4–C3–C31 and C3–C4–C41 in **2** are bent significantly to 138(2)° and 137(2)°, respectively, similar to those in **5** (139(1)° for each).

Solution NMR studies of Ru₁₀C₂(CO)₂₃(C₂Tol₂). Variable-temperature ¹H and ¹³C NMR studies of **3** were performed to probe its structure and dynamic behavior in solution. At –95 °C, the ¹H NMR spectrum of **3** exhibits two broad singlets for the two methyl groups on the ditolylacetylene ligand (δ 2.38, 2.28, $\Delta\nu$ = 30 Hz). These two signals coalesce to one signal upon raising the temperature to –85 °C (ΔG^\ddagger = 9.3 kcal/mol). This phenomenon is possible only with significant carbonyl scrambling and simultaneous metal framework flexing that leads to the generation of an effective mirror plane bisecting the alkyne C–C bond. At –95 °C, the ¹³C NMR spectrum of **3** shows 4 singlets in the bridging carbonyl region and 14 singlets in the terminal carbonyl region. This pattern, especially the four distinct bridging carbonyl signals, is consistent with the solid state structure. Upon raising the temperature to –80 °C, the bridging carbonyl signals and some terminal carbonyl

signals broaden, indicating the onset of selective exchange. At 20 °C, only two broad signals are observed, indicating facile, global carbonyl scrambling.

Summary. Oxidation of [Ru₁₀C₂(CO)₂₄]²⁻ with ferrocenium ion provides a quick, low-temperature route for alkyne substitution, with the formation of the neutral Ru₁₀C₂(CO)₂₃(C₂RR') derivatives. Reduction of the neutral species with OH⁻ generates the corresponding dianionic derivatives. These procedures offer the prospect of preparing other derivatives of the Ru₁₀C₂ core involving various two- and four-electron donors.

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Supporting Information Available: Tables of positional parameters, bond distances, bond angles, and anisotropic thermal parameters for the structural analysis of [Ru₁₀C₂(CO)₂₃(C₂Ph₂)]·CH₂Cl₂ (13 pages). Ordering information is given on any current masthead page.

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