ORGANOMETALLICS

Oxidation of (alkylidyne)triruthenium clusters. Spectroscopic characterization of the cation radicals [H3Ru3(CX)(CO)9-nLn]+ (X = OMe, L = PPh3, n = 2, 3; X = OMe, L = AsPh3, n = 3; X = SEt, NMeCH2Ph, L = PPh3, n = 3) and the decomposition products [H3Ru3(CO)7L3]+

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Oxidation of (Alkylidyne)triruthenium Clusters. Spectroscopic Characterization of the Cation Radicals $[H_3Ru_3(CX)(CO)_{9-n}L_n]^+$ (X = OMe, L = PPh_3, $n = 2, 3$; X = OMe, L = $AsPh_3$, $n = 3$; X = SEt, $NMeCH_2Ph$, L = PPh_3, $n = 3$) and the Decomposition Products $[H_3Ru_3(CO)_7L_3]^+$

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Summary: Chemical or electrochemical oxidation of $[H_3Ru_3(CX)(CO)_{9-n}L_n]$ (X = OMe, L = PPh_3, $n = 2, 3$; X = OMe, L = $AsPh_3$, $n = 3$; X = SEt, NMeBz, L = PPh_3, $n = 3$) reversibly forms the corresponding cation radical $[H_3Ru_3(CX)(CO)_{9-n}L_n]^+$. Decomposition of $[H_3Ru_3(COMe)(CO)_6L_3]^+$ generates $[H_3Ru_3(CO)_7L_3]^+$. The complexes $[H_3Ru_3(CX)(CO)_{9-n}L_n]^+$ were characterized by ^1H NMR and EPR spectroscopies. The complexes $[H_3Ru_3(CO)_7L_3]^+$ were characterized by ^1H and ^{31}P NMR spectroscopies and by comparison of the spectra with those of $[H_3Os_3(CO)_{10-n}L_n]^+$ (L = PPh_3, $n = 0, 1$).

Electrochemical activation has become an important technique in organometallic chemistry, as odd-electron intermediates have been identified in a number of fundamental reactions, including ligand substitution and oxidative addition.[1] Odd-electron species derived from tetra- and trimetallic alkylidynes have been of interest for some time.[2] We present here the new class of cation-radical clusters $[H_3Ru_3(CX)(CO)_{9-n}L_n]^+$ and a new example of electrochemical activation of a methylidyne ligand, in which O–CH_3 bond cleavage from the moderately stable radical cations $[H_3Ru_3(COMe)(CO)_6L_3]^+$ forms the new complexes $[H_3Ru_3(CO)_7L_3]^+$.

One-electron oxidation of $H_3Ru_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ (X = OMe, L = PPh_3, $n = 3$, **1a**; X = OMe, L = PPh_3, $n = 2$, **1b**; X = OMe, L = $AsPh_3$, $n = 3$, **1c**; X = SEt, L = PPh_3, $n = 3$, **1d**; X = NMeBz, L = PPh_3, $n = 3$, **1e**)[3] in dichloromethane solution can be achieved by chemical or electrochemical methods. Cyclic voltammograms of these clusters exhibit in each case two one-electron-oxidation waves, the first of which is quasi-reversible and the second irreversible (e.g. **1a** and **1e**, Figure 1).[4] The cyclic voltammograms of the mono- and unsubstituted analogues each display only a single, irreversible anodic wave. A single one-electron oxidation of **1a–e** can also be achieved with the chemical oxidants $AgSO_3CF_3$, $[FeCp_2][PF_6]$, and $[Fe(o\text{-}phen)_3][ClO_4]_3$, in each instance causing the yellow solution to immediately become dark green, attributed to

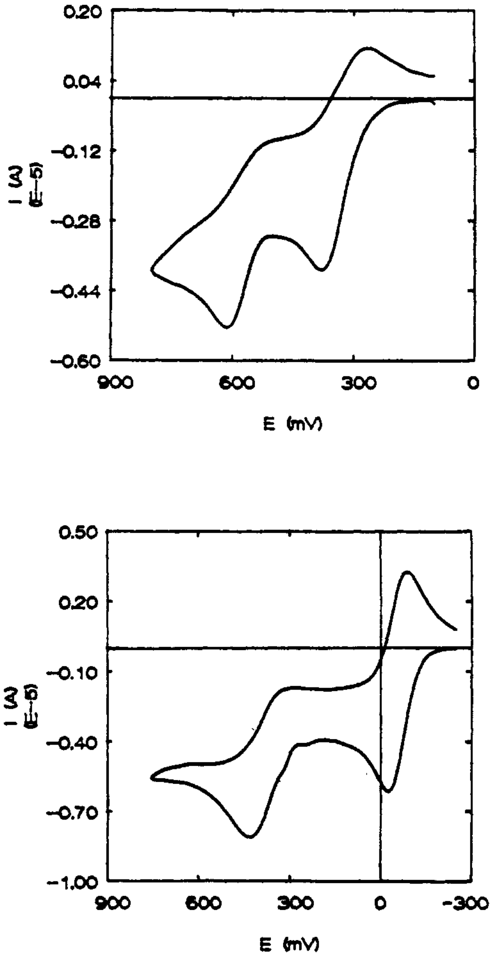

Figure 1. Cyclic voltammograms of $H_3Ru_3(COMe)(CO)_6(PPh_3)_3$ (**1a**; upper) and $H_3Ru_3(CNMeCH_2Ph)(CO)_6(PPh_3)_3$ (**1e**; lower) (0.1 M NBu_4BF_4 in dichloromethane, 100 mV/s). Potentials are referenced to the SCE.

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[3] These compounds were prepared by ligand substitution on the parent carbonyls according to procedures published previously for other $H_3Ru_3(CX)(CO)_{9-n}L_n$ clusters: (a) Rahman, Z. A.; Beanan, L. R.; Bavaro, L. M.; Modi, S. P.; Keister, J. B.; Churchill, M. R. *J. Organomet. Chem.* **1984**, *263*, 75. (b) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219. (c) Churchill, M. R.; Ziller, J. W.; Dalton, D. M.; Keister, J. B. *Organometallics* **1987**, *6*, 806.

[4] **1a**: IR (CH_2Cl_2) 2035 s, 2009 vs, 1959 m cm^{-1}; $(E_{p,a} + E_{p,c})/2 = 0.31$ V ($\Delta E_p = 117$ mV, $i_{p,c}/i_{p,a} = 0.77$), $E_{p,a} = 0.60$ V. **1b**: $(E_{p,a} + E_{p,c})/2 = 0.51$ V ($\Delta E_p = 70$ mV, $i_{p,c}/i_{p,a} = 0.88$), $E_{p,a} = 0.77$ V. **1c**: $(E_{p,a} + E_{p,c})/2 = 0.45$ V ($\Delta E_p = 86$ mV, $i_{p,c}/i_{p,a} = 0.84$), $E_{p,a} = 0.68$ V. **1d**: IR (CH_2Cl_2) 2036 s, 2013 vs, 1962 m cm^{-1}; $(E_{p,a} + E_{p,c})/2 = 0.35$ V ($\Delta E_p = 77$ mV, $i_{p,c}/i_{p,a} = 0.78$), $E_{p,a} = 0.81$ V. **1e**: IR (CH_2Cl_2) 2030 vs, 2002 s, 1953 m cm^{-1}; $(E_{p,a} + E_{p,c}/2 = -0.06$ V ($\Delta E_p = 61$ mV, $i_{p,c}/i_{p,a} = 0.97$), $E_{p,a} = 0.35$ V. Cyclic voltammetry data were recorded in dichloromethane solution (0.1 M NBu_4BF_4) at 100 mV/s and referenced to SCE ($(E_{p,a} + E_{p,c})/2$ for ferrocene is 0.53 V under the same conditions).

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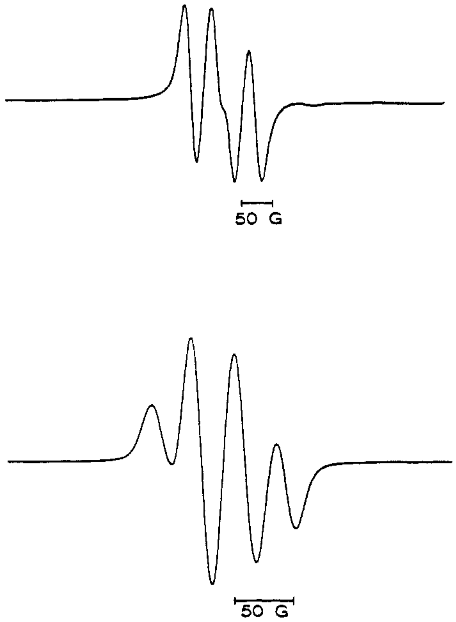
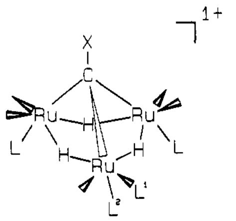


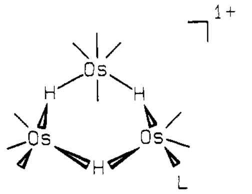
Figure 2. EPR spectra of $[H_3Ru_3(COMe)(CO)_6(PPh_3)_3]^+$ (**2a**; upper) and $[H_3Ru_3(CNMeCH_2Ph)(CO)_6(PPh_3)_3]^+$ (**2e**; lower) in dichloromethane solution at 25 °C.

the formation of the corresponding cation radicals **2a**–e. The cyclic voltammogram of **2a** is identical with that of **1a**, indicating that **2a** is the product of the first electrochemical oxidation, and chemical reduction of **2a** regenerates **1a** (99% conversion). The ^1H NMR spectrum of **2a** displays broad resonances for hydrides and a methyl group (integration vs an internal standard gives a yield for **2a** of 86% from **1a**), consistent with its formulation as a paramagnetic product.[5] EPR spectra were obtained for **2a**, **2b**, **2d**, and **2e**.[5] The EPR spectrum of **2e** consists of a quartet with coupling to three equivalent ^{31}P nuclei (Figure 2), and the spectrum of **2b** shows coupling to two equivalent ^{31}P nuclei. However, the EPR spectrum of **2a** displays a strong four-line absorption, indicative of hyperfine coupling to two inequivalent ^{31}P nuclei (Figure 2). Since **1a–e** have equivalent, axial EPh_3 ligands, a structural rearrangement must have occurred during the formation of **2a**. We propose structure I (**2a**,**d**, L = L^1 = PPh_3, L^2 = CO; **2c**, L = L^1 = $AsPh_3$, L^2 = CO; **2b**, L^1 = L^2 = CO, L = $AsPh_3$; **2e**, L = L^2 = PPh_3, L^1 = CO) having the same basic cluster geometry as **1a–e**, but with isomerization of an EPh_3 ligand from an axial to an equatorial coordination site for **2a**, **2c**, and **2d**. This proposal is consistent with the similarity between the IR spectra in the carbonyl region for **1e** and **2e** (the spectrum of the latter shifted to higher frequency, as expected for its positive charge) and the dissimilarities between the IR spectra of **1a** and **2a** and of **1d** and **2d**.[4,5] This structure accounts for the coupling of the unpaired electron to only two of the three inequivalent ^{31}P nuclei for **2a**, since the SOMO of $[H_3Ru_3(CX)(CO)_9]^+$, by analogy to $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$,[6] is expected to be largely Ru–C bonding in character, localized primarily trans to the axial coordination sites. Electron-transfer-induced ligand isomerization has precedent in the chemistry of monometallic complexes.[7]

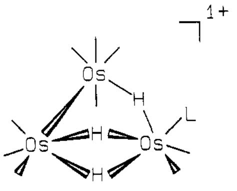


I

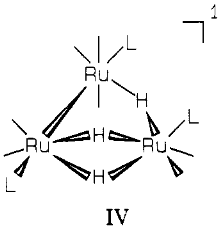
The cation radicals decompose upon standing in solution, with the times required for decomposition at room temperature varying from minutes (**2c**) to hours (**2e**). Products from **2b**, **2d**, and **2e** have not been characterized. Decompositions of solutions of **2a** or **2c** produce red solutions whose ^1H and ^{31}P NMR spectra indicate the presence of diamagnetic products **3**, containing three inequivalent hydrides and inequivalent ligands L, in addition to variable quantities of **1a** or **1c**.[8] In no case is there a resonance that can be attributed to a methyl group associated with **3**, and we have been unable to identify an organic product derived from this substituent. The probable formula is therefore $[H_3Ru_3(CO)_7L_3]^+$ (**3a**, L = PPh_3; **3c**, L = $AsPh_3$), heretofore unknown. Consistent with this proposal, the ^1H NMR spectra of **3a** and **3c** are notably similar to those of $[H_3Os_3(CO)_{10-n}(PPh_3)_n]^+$ (n = 0 (**4a**), 1 (**4b**)), previously prepared by protonation of the unsaturated clusters $H_2Os_3(CO)_{10-n}(PPh_3)_n$ (n = 0 (**5a**), 1 (**5b**)).[9] In accordance with this assignment, oxidation of $H_3Os_3(COMe)(CO)_8(PPh_3)$ with Ag^+ produces a fleeting green color before the solution turns bright yellow, and the ^1H NMR spectrum of the yellow solution shows the presence of **4b**. The identity of **4b** was confirmed by deprotonation with NEt_3 and isolation of the neutral product **5b** (34% isolated yield). The structure of **4b**, which was previously proposed by Johnson, Lewis, and co-workers, is II, based upon ^1H NMR spectra. However, we propose the alternative structure III, based upon the low symmetry of the ^{13}C NMR spectra (inconsistent with II) and the large ^1H–^{31}P coupling constant, which indicates a trans rela-



II



III



IV

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(5) **2a**: ^1H NMR ($CDCl_3$) 4.1 (v br) and –15.1 (v br) ppm; ^{31}P NMR ($CDCl_3$) 20.9 (v br) ppm; EPR (CH_2Cl_2, 25 °C) g = 2.08 (dd), $A_1(^{31}P)$ = 40.4 G, $A_2(^{31}P)$ = 59.8 G; IR (CH_2Cl_2) 2088 w, 2067 m, 2029 s, 2018 vs, 1975 w cm^{-1}. **2b**: ^1H NMR ($CDCl_3$) 3.9 (v br, 3 H), –15.8 (v br, 1 H), –16.4 (v br, 2 H) ppm; EPR (CH_2Cl_2, 25 °C): g = 2.08 (t), $A(^{31}P)$ = 51.1 G. **2d**: EPR (CH_2Cl_2, 25 °C): g = 2.06 (dd), $A(^{31}P)$ = 34.8, 48.2 G; IR (CH_2Cl_2) 2087 w, 2070 s, 2029 sh, 2021 vs, 1975 w cm^{-1}. **2e**: EPR (CH_2Cl_2, 25 °C) g = 2.06 (q), $A(^{31}P)$ = 36.3 G; IR (CH_2Cl_2) 2057 s, 2036 vs, 1953 s cm^{-1}. EPR spectra were recorded on an IBM/Bruker X-band ER-200 SRC spectrometer with a microwave power of 20 mW.

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(8) **3a**: ^1H NMR ($CDCl_3$) –11.13 (br s, 1 H), –11.56 (d, 1 H, J_{PH} = 48 Hz), –12.35 (br s, 1 H) ppm; ^{31}P NMR ($CDCl_3$) 29.4 (s, 1 P), 33.7 (s, 1 P), 40.7 (d, 1 P, J_{PH} = 48 Hz) ppm. **3c**: ^1H NMR ($CDCl_3$) –11.02 (dd, 1 H_A), –12.56 (dd, 1 H_B), –12.66 (dd, 1 H_C) ppm, J_{AB} = J_{BC} = J_{AC} = 2.5 Hz.

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tionship between one of the hydrides and the PPh_3 ligand.[10] By analogy, the structure adopted by **3a,c** is IV.

Complete characterization of **3a,c** is hampered by the instability of these compounds. Decomposition of **2a,c** frequently produces some **1a,c** in addition to **3a,c**, but addition of excess Ag^+ does not produce **3a,c** in higher yield. In one experiment decomposition of **2a** produced **1a** and **3a** in 30 and 42% yields, respectively, based upon the initial quantity of **1a**. Treatment of **3** with triethylamine or methanol does not give neutral products analogous to **5a** and **5b**. In fact, ruthenium analogues to **5a** and **5b** appear to be unstable. The new cations **3a,c** therefore cannot be prepared by the route used for **4a,b**.

The chemistry of the cation radicals **2a–e** is currently under investigation. In addition to $O-CH_3$ bond cleavage, the reactivity for ligand substitution, hydride transfer to unsaturated hydrocarbons, and reductive elimination of C–H or H–H bonds may differ significantly from the reactivity of the diamagnetic precursors, thus providing an excellent opportunity to explore the enhanced reactivity of odd-electron cluster species.

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[10] **4a**: ^1H NMR ($CDCl_3$) −12.33 (d, 2 H_A), −14.49 (t, 1 H_B) ppm, J_{AB} = 1.4 Hz; ^{13}C NMR ($CDCl_3$) 161.8 (s, 2 C), 164.4 (s, 1 C), 166.8 (s, 1 C), 170.1 (s, 1 C), 170.2 (s, 1 C), 170.5 (s, 2 C), 172.0 (s, 2 C) ppm. **4b**: ^1H NMR ($CDCl_3$) −11.89 (d, 1 H, J_{PH} = 7.3 Hz), −12.03 (d, 1 H, J_{PH} = 30.5 Hz), −13.78 (d, 1 H, J_{PH} = 9.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) 165.4 (s, 1 C), 165.7 (d, 1 C, J_{PC} = 8.6 Hz), 166.1 (s, 1 C), 168.0 (d, 1 C, J_{PC} = 9.6 Hz), 170.6 (s, 1 C), 170.7 (s, 1 C), 171.2 (s, 1 C), 173.6 (s, 1 C), 175.0 (d, 1 C, J_{PC} = 8.6 Hz) ppm; ^{31}P NMR ($CDCl_3$) 9.53 ppm.

Rapid and Efficient Procedures for the Synthesis of Monocyclopentadienyl Complexes of Hafnium and Zirconium

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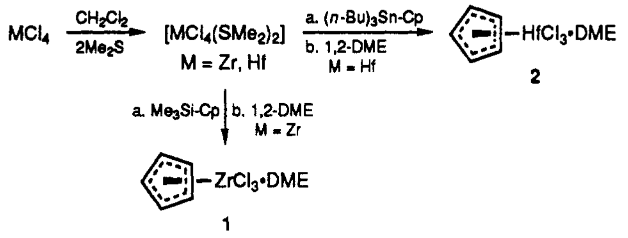
Summary: Bis(dimethyl sulfide) complexes of zirconium(IV) chloride and hafnium(IV) chloride have been found to undergo facile substitution reactions with 1-(trimethylsilyl)cyclopenta-2,4-diene and 1-(tri-*n*-butylstannyl)cyclopenta-2,4-diene, respectively, to afford the corresponding (η^5-cyclopentadienyl)trichlorozirconium and -hafnium complexes in good to excellent yield.

Monocyclopentadienyl complexes of hafnium and zirconium possess reactivity profiles that differ considerably from those of their bis-η^5-C_5H_5 counterparts. It is, therefore, not surprising that these complexes have assumed an increasingly important role in synthetic[2] and mechanistic[3] endeavors. Despite the intensifying interest in these compounds, practical routes for their preparation in pure form remain very few in number. At the present time, the most widely utilized procedure for the synthesis of $CpZrCl_3$ involves the free-radical chlorination of zirconocene dichloride.[4] This method is somewhat exacting and can on occasion give varying amounts of $ZrCl_4$ as a consequence of over-chlorination.[5] The preparation of $CpHfCl_3$ via the chlorination of Cp_2HfCl_2 has not been reported. However, the expense of Cp_2HfCl_2 would likely categorize such an approach as an act of desperation. The published synthesis of the hafnium derivative is nevertheless laborious. It involves the treatment of a 10% excess of $HfCl_4$ with 0.5 equiv of Cp_2Mg and subsequent purification by multiple recrystallizations to furnish the bis(tetrahydrofuran) complex $CpHfCl_3 \cdot 2THF$ free of $HfCl_4$ and Cp_2HfCl_2 in a maximum of 25% yield.[6] In this paper, we report a direct, one-step procedure that is suitable for the preparation of $CpZrCl_3$ and $CpHfCl_3$ as the corresponding 1,2-DME complexes in high yield.


Scheme I

Results and Discussion. As part of our continuing interest in the synthetic applications of the early transition elements, we required large quantities of *pure* $CpZrCl_3$ complexes. In 1980, Clark and co-workers reported that $CpTiCl_3$ could be synthesized in high yield via the reaction of $TiCl_4$ with 1-(trimethylsilyl)cyclopenta-2,4-diene (TMSCp).[7] It was therefore, at first, quite surprising that $CpZrCl_3$ and $CpHfCl_3$ had not been prepared by analogous procedures. In an effort to explore this possibility, several attempts were made to effect the direct cyclopentadienylation of commercial $ZrCl_4$ in CH_2Cl_2 with TMSCp. Unfortunately, under these *heterogeneous* reaction conditions, partial polymerization of the TMSCp was found to occur with concomitant formation of Cp_2ZrCl_2 as well as intractable side products. Attempts to utilize soluble complexes of the type $ZrCl_4 \cdot 2OR_2$ formed by the treatment of $ZrCl_4$ with various ethers (e.g., Et_2O, $(i\text{-}Pr)_2O$, and $PhOCH_3$ (2 equiv/equiv of Zr)) in the above process gave no appreciable reaction.

In sharp contrast to these discouraging results, simple exposure of TMSCp (1 equiv) to the homogeneous complex prepared in situ by the treatment of $ZrCl_4$ *with* $(CH_3)_2S$ *(2 equiv,* CH_2Cl_2*, 0 °C) led to the formation of* $CpZrCl_3 \cdot 2SMe_2$ *in excellent yield after several minutes.*

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[1] Fellow of the Alfred P. Sloan Foundation 1989–1991.

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