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Efficient synthesis, redox characteristics, and electronic structure of a tetravalent tris(cyclopentadienyl)cerium alkoxide complex

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and no enhancement at δ 3.78. Irradiation at δ 6.30 resulted in a 3.5% enhancement at δ 3.62 and no enhancement at δ 3.78. Irradiation at δ 3.62 resulted in a 4.3% enhancement at δ 6.52 and no enhancement at δ 6.30. Irradiation at δ 3.78 resulted in a 1.3% enhancement at δ 6.52 and less than 0.5% enhancement at δ 6.30.

Reaction of [(2-Furyl)methoxycarbene]pentacarbonylchromium (7) with 1-Hexyne: Acetylative Workup.[6b] The reaction of complex 7 and 1-hexyne was carried out according to the procedure described above for the reaction of 7 and 3-hexyne and required 20 h at 85 °C to go to completion in THF. After the reaction was complete, 2 equiv of acetic anhydride and a catalytic amount (~0.05 equiv) of sodium acetate was added to the reaction mixture which was then degassed by the freeze–thaw method (two cycles) and then heated at 85 °C for an additional 6 h. The reaction mixture was opened to air and stripped of volatiles and the resultant residue taken up in ether and filtered through Celite. After removal of the ether the residue was quickly chromatographed through silica gel, which had been pretreated with triethylamine, by elution with hexanes, which had been previously degassed be purging with argon, to give a 29% yield the furan **68**. Elution with 10% ethyl acetate in hexanes gave a 60% yield of acetylated benzofuran **67**. The following spectral data were collected for the benzofuran **67**: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, *J* = 7.4 Hz, $\mathrm{CH_2C}H_3$), 1.37 (sext, 2 H, *J* = 7.6 Hz, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.58 (pent, 2 H, *J* = 7.7 Hz, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 2.38 (s, 3 H, -$\mathrm{CO_2C}H_3$), 2.57 (br t, 2 H, *J* = 7.7 Hz, -$\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 4.00 (s, 3 H, $\mathrm{ArOC}H_3$), 6.56 (d, 1 H, *J* = 2.4 Hz, 3-C*H*), 6.64 (s, 1 H, 6-C*H*), 7.56 (d, 1 H, *J* = 2.5 Hz, 2-C*H*); IR ($CHCl_3$) 1750 s, 1650 m, 1480 s, 1365 m, 1340 m, 1150 m, 1055 m, 915 w, 870 w, 830 w; colorless prisms from benzene/hexanes; mp 52–52.5 °C; yield 60%. The following data were collected for the furan **68**: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H, *J* = 7.1 Hz, $\mathrm{CH_2C}H_3$), 1.43 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.58 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 2.44 (br t, 2 H, *J* = 6.6 Hz, $\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 3.81 (s, 3 H, $\mathrm{ArOC}H_3$), 6.56 (dd, 1 H, *J* = 1.6, 3.4 Hz, 4′-C*H*), 6.70 (br d, 1 H, *J* = 2.1 Hz, 4-C*H*), 7.23 (d, 1 H, *J* = 3.5 Hz, 3′-C*H*), 7.61 (br t, 1 H, *J* = 1.5 Hz, 5′-C*H*); colorless oil; yield 29%.

Reaction of Oxygen-Labeled [(2-Furyl)([^{17,18}O]methoxy)carbene]pentacarbonylchromium (7†) with Methyl 4-Pentynoate (8) in THF. This reaction was conducted in THF solution, in a manner identical with that described for the reaction of **7** with **8**, and provided the oxygen-labeled furan **11**†: ^{17}O NMR ($CDCl_3$, H_2O standard) δ 24.7; ^{13}C NMR ($CDCl_3$), doubled peaks due to ^{18}O chemical shift perturbation, δ 60.093, 60.065 (2-$\mathrm{CH^{18}OC}H_3$), 155.846, 155.833 (2-$\mathrm{C}H^{18}\mathrm{OCH_3}$). The ^{17}O NMR and mass spectra of **11**† can be found in the supplementary material.

Reaction of Carbon-Labeled [(2-Furyl)methoxycarbene]penta[^{13}C]carbonylchromium (7*) with Methyl 4-Pentynoate (8) in THF. This reaction was conducted in THF solution, in a manner identical with that described for the reaction of **7** with **8**, and provided the carbon-labeled furan **11***: ^{13}C NMR, 15-fold enhancement of ^{13}C at δ 155.8 (2-$\mathrm{C}HOCH_3$).

Acknowledgment. This work was supported by a grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8517103). We thank the Dow Chemical Co. for a predoctoral fellowship (J.S. M.). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Research Center (CA 14599).

Registry No. 7, 34741-93-0; **7**$^+$, 115731-27-6; **7***, 115731-28-7; **8**, 21565-82-2; **9**, 115678-85-8; **9a**, 115678-86-9; **11**, 115678-87-0; **11**$^+$, 115678-99-4; **11***, 115679-00-0; **12-Z**, 115678-88-1; **12-E**, 115678-90-5; **13**, 115731-29-8; **16-Z**, 115705-09-4; **17**, 115678-89-2; **23**, 29160-36-9; **25-Z**, 115678-94-9; **25-E**, 98748-82-4; **41**, 115678-95-0; **42**, 115678-96-1; **43-Z**, 115678-97-2; **43-E**, 115678-98-3; **48**, 5390-04-5; **49-Z**, 115678-92-7; **49-E**, 115678-93-8; **50**, 115678-91-6; **51-Z**, 115705-08-3; **67**, 99107-57-0; **68**, 115705-10-7; $Cr(CO)_6$, 13007-92-6; [^{18}O]-MeOH, 5770-05-8; ^{13}CO, 1641-69-6; EtC≡CEt, 928-49-4; HC≡C-*n*-Bu, 693-02-7; 2-furyllithium, 2786-02-9; [tetramethylammonium][(2-furyl)oxidocarbene]pentacarbonylchromium, 33594-68-2; [lithium][(2-furyl)oxidocarbene]pentacarbonylchromium, 64655-84-1.

Supplementary Material Available: ^{17}O NMR and mass spectra for compound **11**† and NOE difference spectra for compounds **12-Z** (4 pages). Ordering information is given on any current masthead page.

Efficient Synthesis, Redox Characteristics, and Electronic Structure of a Tetravalent Tris(cyclopentadienyl)cerium Alkoxide Complex

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The complex $Cp_3Ce(O\text{-}i\text{-}Pr)$ ($Cp = \eta^5\text{-}C_5H_5$) can be efficiently prepared from cerium tetrakis(isopropoxide) and Me_3SnCp. It is shown to be a genuine Ce(IV) complex by ^{1}H/^{13}C NMR, elemental analysis, and cyclic voltammetry/controlled potential coulometry in $Bu_4N^+BF_4^-$/THF. The latter data indicate that $Cp_3Ce(O\text{-}i\text{-}Pr)$ is a relatively strong oxidizing agent ($E_{1/2}$ = +0.32 vs SSCE) and that one-electron reduction is both electrochemically and chemically reversible. Electronic structure calculations at the nonrelativistic Xα–DVM level suggest nonnegligible Ce–Cp f orbital covalency and yield transition state ionization energies in good agreement with He I/He II photoelectron spectra. There are substantial differences in redox properties and metal–ligand bonding between $Cp_3Ce(O\text{-}i\text{-}Pr)$ and the other known tetravalent cerium organometallic complex $Ce(C_8H_8)_2$.

Although recent results demonstrate that organolanthanides[2] can be prepared via efficient and rational approaches in a variety of low formal oxidation states (<+3),[2–6] the chemistry of well-characterized organo-

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lanthanides in high formal oxidation states (>+3)[7] remains sparse. Streitwieser et al.[8] recently confirmed the earlier synthesis/formulation by Cesca et al.[7] of the unusual sandwich complex $Ce(COT)_2$ (COT = η^8-C_8H_8) and provided evidence for significant Ce(IV)–COT bond covalency as well as for considerable stabilization of the +4 oxidation state. These results raise the question of whether the COT ligand is unique or whether other ligand arrays can also stabilize tetravalent organocerium complexes, and if so, how the properties of these complexes compare with those of $Ce(COT)_2$. We report here a reexamination of the complex $Cp_3Ce(O\text{-}i\text{-}Pr)$ (Cp = η^5-C_5H_5) also reported by Cesca et al.[7] and prepared by them in minute yields (eq 1). We describe an efficient synthetic route to such

$$Ce(O\text{-}i\text{-}Pr)_4{\cdot}i\text{-}PrOH + 2MgCp_2 \rightarrow Cp_3Ce(O\text{-}i\text{-}Pr) + 2\,Mg(O\text{-}i\text{-}Pr)_2 + CpH \quad (1)$$

4% yield

compounds, an electrochemical investigation of redox properties, and correlated He I/He II photoelectron spectroscopic, first-principle Xα–DVM studies of the electronic structure. It will be seen that there are striking differences in redox characteristics and bonding between $Cp_3Ce(O\text{-}i\text{-}Pr)$ and $Ce(C_8H_8)_2$.

Experimental Section

Materials and Methods. Air-sensitive compounds were handled with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line, in Schlenk-type glassware interfaced to a high vacuum (10^{-5} Torr) system, or under a dinitrogen atmosphere in a Vacuum Atmospheres glovebox with an efficient recirculator. Argon (Matheson, prepurified) and dinitrogen (Liquid Air Corp., high purity), were purified by passage through sequential columns of MnO and Davidson 4A molecular sieves.[9]

Toluene, pentane, and THF were distilled from Na/K/benzophenone under dinitrogen and were condensed and stored in vacuo on the vacuum line in bulbs containing a small amount of $(Cp_2TiCl)_2ZnCl_2$,[10] or Cp'_2UCl_2 as an O_2/H_2O indicator. THF for electrochemical experiments was additionally distilled from Na/K and freeze–pump–thawed immediately prior to use. The reagents $Ce(O\text{-}i\text{-}Pr)_4{\cdot}i\text{-}PrOH$[11] and Me_3SnCp[12] were prepared by the literature procedures. Tetra-*n*-butylammonium fluoroborate ($TBABF_4$) was obtained from Southwestern Analytical Chemical, Austin, TX. It was recrystallized three times from acetone/ether and dried in vacuo.

Table I. NMR Spectral Data[a] for $(C_5H_5)_3Ce[O\text{-}i\text{-}CH(CH_3)_2]$

^1H (270 MHz, toluene-d_8)
6.16 (1 H, hep, C*H*), 5.55 (15 H, s, C_5H_5), 1.82 (6 H, d, CH_3)
^{13}C (67.8 MHz, toluene-d_8)
122.1 (d, $^1J_{^{13}C-H}$ 167 Hz, CH), 81.81 (d, $^1J_{^{13}C-H}$ = 140 Hz, C_5H_5), 28.57 (q, $^1J_{^{13}C-H}$ = 124 Hz, CH_3)

[a] Chemical shifts in ppm. [b] Abbreviations: s, singlet; d, doublet, q, quartet, hep, heptet.

Physical and Analytical Methods. Proton and carbon NMR spectra were recorded on a JEOL FX-270 (FT, ^1H 270 MHz, ^{13}C 67.80 MHz) spectrometer. Chemical shifts were recorded versus internal solvent signals and are reported relative to internal TMS.

Electrochemical measurements were performed with a PAR Model 273 potentiostat/galvanostat which was interfaced to a Zenith ZF-158 (XT-type) personal computer and used locally developed software. Experiments were carried out in vacuum-tight three-compartment cells with all connections made through ground-glass joints. All studies were performed in the three-electrode configuration using a platinum gauze auxiliary electrode and a silver wire quasi-reference (AgRE) electrode. Controlled potential coulometry (CPC) studies utilized a large area platinum gauze working electrode (ca. 8 cm^2), while cyclic voltammetry was performed with a Pt disk working electrode sealed in soft glass. The potential of the AgRE was referenced back to the SSCE potential by using the ferrocene/ferrocenium couple as an external standard. All potentials are reported vs the SSCE potential. Solutions were prepared on a high vacuum line by vacuum transferring the solvent (THF) directly into the electrochemical cell containing the supporting electrolyte ($TBABF_4$) and a known amount of compound. After transfer, the cell was backfilled with a positive pressure of argon.

PE spectra were recorded on a Perkin-Elmer PS18 spectrometer modified by the inclusion of a hollow cathode discharge source giving a high output of the He II radiation (Helectros Development Corp.). The spectra were accumulated in the "multiple-scan mode" with the aid of an IBM PC AT computer directly interfaced to the spectrometer. The energy scale of consecutive scans was locked to the reference values of the Ar $^2P_{3/2}$ and He($1s^{-1}$) self-ionization lines.

Elemental analyses were performed by Dornis und Kolbe Mikroanalytiches Laboratorium, Mülheim, West Germany.

Improved Synthesis of $Cp_3Ce(O\text{-}i\text{-}Pr)$. Cerium(IV) isopropoxide ($Ce(O\text{-}i\text{-}Pr)_4$, 0.259 g, 0.715 mmol) was dissolved in 15 mL of toluene and 2.90 mL (2.69 mmol) of a 0.928 M solution of Me_3SnCp in toluene was added by syringe. The resulting mixture was heated at 65 °C for 24 h, during which time the color changed from pale yellow to a deep brown. The mixture was then cooled to room temperature and filtered, and the volatile components were removed from the filtrate under high vacuum. Recrystallization of the residual solids from a minimum volume (ca. 2 mL) of pentane by slow cooling to −78 °C afforded 0.194 g (69% yield) of black, microcrystalline product. The product can also be purified by sublimation at 70 °C (10^{-5} Torr); however, this results in loss of product and is not necessary for purification.

Anal. Calcd for $C_{18}H_{22}CeO$: Ce, 54.80; H, 5.62. Found: C, 54.82; H, 5.68.

^1H and ^{13}C NMR data (Table I) are in good agreement with the proposed formulation. Literature[7] ^1H data (solvent unspecified) appear to be similar.

Computational

Nonrelativistic Xα–DVM (discrete variational method) electronic structure calculations were carried out on a VAX 11/750 minicomputer. The molecular electron density was approximated with an s-wave expansion (overlapping spherical functions on every center) in calculating the potential, and the SCF equations were converged by a self-consistent charge (SCC) procedure.[13] This approach has previously been shown to give satisfactory results

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Table II. Xα–DVM Electronic Structural Results and Photoelectron Spectroscopic Data for Cp_3CeOMe[a]

MO	ground state (eV)	TSIE (eV)	IE (exptl)[b] (eV)	composition (%)							predominant character
				Ce							
				s	p	d	f	Cp_3	O	CH_3	
20a″	5.20	7.31	7.41 (*a*)	0	0	2	25	66	6	1	π-Cp
26a′	5.32	7.32	7.76 (*b*)	0	1	0	6	83	8	2	π-Cp
19a″	5.40	7.43		0	0	0	21	79	0	0	π-Cp
25a′	5.38	7.49		0	0	2	15	77	5	1	π-Cp
18a″	6.13	8.26	8.47 (*c*)	0	0	5	4	62	23	6	π
24a′	6.37	8.59		0	0	4	3	41	43	9	O(2p)
17a″	6.57	8.81	9.41 (d)	0	0	10	3	38	40	9	O(2p)
23a′	6.67	8.92		0	0	7	2	69	18	4	π
22a′	8.25	10.67		0	0	1	0	99	0	0	σ-onset, Cp

[a] Calculations performed on Cp_3CeOMe; spectra recorded on $Cp_3Ce(O\text{-}i\text{-}Pr)$. [b] Labels refer to spectral features in Figures 2 and 3.

for f-element complexes.[14] Details of the computational procedures have been given elsewhere.[13b,15] Slater transition-state ionization energies (TSIE's)[16] were evaluated for each MO reported in Table II. The actual calculation was performed on Cp_3CeOMe, with metrical parameters extrapolated from ionic radii and data for other appropriate Cp_3MX complexes.[1d,17,18] The Ce–O–CH_3 angle was taken to be 154°.[19]

Results and Discussion

Synthesis, Characterization, and Redox Properties. Attempts were made to prepare $Cp_3Ce(O\text{-}i\text{-}Pr)$ from $Ce(O\text{-}i\text{-}Pr)_4$ by using a variety of cyclopentadienylating agents. As monitored by ^1H NMR, both TlCp and $MgCp_2$ give extensive reduction at room temperature to paramagnetic Ce(III) complexes, while no reaction is observed with Me_3SiCp in THF up to reflux temperatures. However, the mild cyclopentadienylating reagents R_3SnCp (R = Me, *n*-Bu)[20] give essentially quantitative yields of the desired product (eq 2) as monitored by NMR. The R =

$$\mathrm{Ce(O\text{-}}i\mathrm{\text{-}Pr)_4} + 3\mathrm{R_3SnCp} \xrightarrow[\text{toluene}]{65\ ^\circ\mathrm{C}} \mathrm{Cp_3Ce(O\text{-}}i\mathrm{\text{-}Pr)} + 3\mathrm{R_3Sn(O\text{-}}i\mathrm{\text{-}Pr)} \quad (2)$$

$$\mathrm{R} = \mathrm{CH_3},\ 69\%\ \text{isolated yield}$$
$$\mathrm{R} = n\text{-Bu},\ 20\%\ \text{isolated yield}$$

CH_3 reagent is preferred since the greater volatility of $Me_3Sn(O\text{-}i\text{-}Pr)$ facilitates workup. The high solubility of $Cp_3Ce(O\text{-}i\text{-}Pr)$ necessitates recrystallization from small amounts of pentane at low temperatures and results in lower isolated yields. Alternatively, the product can be sublimed at 70 °C (10^{-5} Torr) with some loss of material. ^1H and ^{13}C NMR data for $Cp_3Ce(O\text{-}i\text{-}Pr)$ are set out in Table I and are in excellent accord with the proposed structure. The chemical shifts and narrow line widths[21] are in accord with a diamagnetic Ce(IV) formulation. Further studies indicate that the approach of eq 2 is also successful with $Me_3Sn(C_5H_4Me)$.[22]

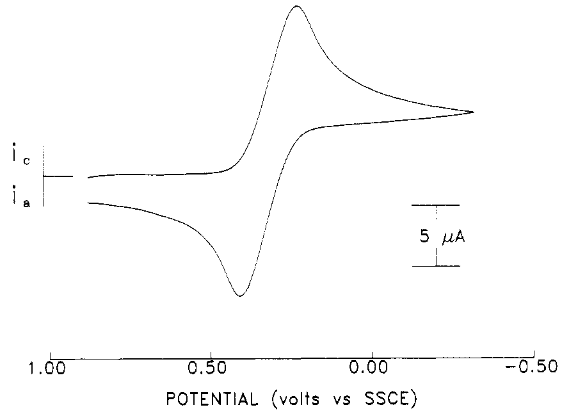

Figure 1. Cyclic voltammogram of $Cp_3Ce(O\text{-}i\text{-}Pr)$ as a solution in THF/0.25 M $TBABF_4$. Scan speed: 50 mV/s.

A typical cyclic voltammogram of $Cp_3Ce(O\text{-}i\text{-}Pr)$ is shown in Figure 1. The data are in agreement with a reversible, one-electron process (ΔE_p = 175 mV; ΔE_p(ferrocene) = 195 mV under the same conditions) having $E_{1/2}$ = +0.32 V vs SSCE. Conclusive proof of chemical reversibility is provided by coulometric experiments. Controlled potential coulometry of measured quantities of $Cp_3Ce(O\text{-}i\text{-}Pr)$ at −0.50 V confirms that reduction is a one-electron process. Furthermore, after the solution was left standing 1 h at room temperature, subsequent oxidation of this solution at +0.60 V yields 99% of the coulombs passed during reduction. A cyclic voltammogram of this oxidized solution is identical with that recorded prior to reduction and reoxidation. Hence, reversibility (eq 3) obtains on the time scale of at least 1 h.

$$\mathrm{Cp_3Ce(O\text{-}}i\mathrm{\text{-}Pr)} + e^- \rightleftharpoons \mathrm{Cp_3Ce(O\text{-}}i\mathrm{\text{-}Pr)^-} \quad (3)$$

The present $E_{1/2}$ value of +0.32 V indicates that $Cp_3Ce(O\text{-}i\text{-}Pr)$ is a relatively strong oxidizing agent—stronger than TCNQ (+0.13 V vs SSCE) and comparable to $FeCp_2^+$ (+0.31 V vs SSCE) in nonaqueous solution. In contrast, the reported $E_{1/2}$ value for $Ce(COT)_2$ in THF/$TBABF_4$ is −1.52 V vs SSCE,[8] demonstrating dramatically

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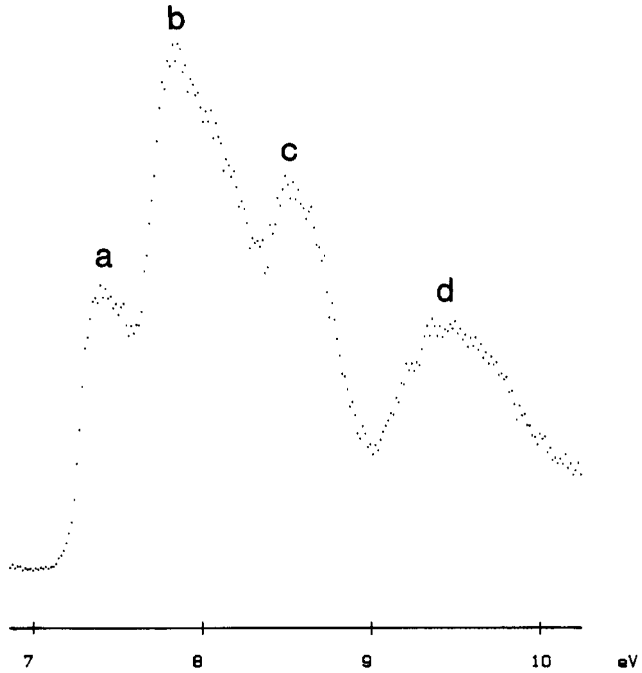

Figure 2. He I photoelectron spectrum of $\mathrm{Cp_3Ce}$(O-*i*-Pr) in the 6.8–10.2 eV ionization energy region. The band labels refer to Table II.

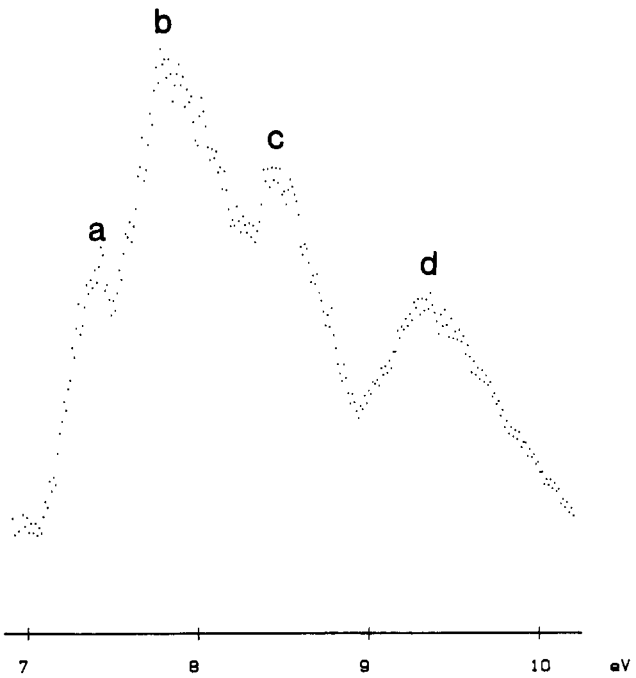

Figure 3. He II photoelectron spectrum of $\mathrm{Cp_3Ce}$(O-*i*-Pr) in the 6.8–10.2 eV ionization energy region. The band labels refer to Table II.

greater stabilization of the Ce(IV) oxidation state in the latter compound.

Electronic Structure Calculations and PE Spectra. Qualitatively, the frontier orbitals of $\mathrm{Cp_3MX}$ systems[15,23] can be readily generated in a localized bond model from the π MO's of three $\mathrm{Cp^-}$ anions (the individual e_1'' MO's will be the greatest contributors[24]) yielding an a_2, 2e, a_1 set, as well as σ and O(2p) lone pairs on OMe. Under idealized C_{3v} symmetry, the oxygen lone pairs are degenerate and are expected to be considerably below the Cp-based MO's in energy.[19a,25] The lower symmetry resulting from bending of the Ce–O–C vector is expected to break the degeneracy and slightly mix these orbitals with the π Cp set. Judging from results on other f-element $\mathrm{Cp_3MX}$ systems, the effect will not be large.[14,24a,25]

In Table II are set out the results of the Xα–DVM calculations on $\mathrm{Cp_3CeOMe}$ for the nine outermost MO's. It can be seen that the MO's can basically be grouped into three sets, depending upon their dominant compositions: (i) π-based Cp-derived MO's (20a″, 26a′, 19a″, 25a′, 18a″, and 23a′),[27] (ii)O(2p)-derived lone pair orbitals (24a′, 17a″), and (iii) lower energy inner π- and σ-ligand orbitals which are not significantly involved in metal–ligand bonding (22a′ and lower). It can also be seen in Table II that there is nonnegligible mixing with/covalency involving metal f orbitals, especially in the case of the Cp-derived 20a″, 19a″, and 25a′ MO's. In several other MO's, there are smaller, comparable contributions from both 5d and 4f orbitals.

He I and He I photoelectron spectra of $\mathrm{Cp_3CeOMe}$ are presented in Figures 2 and 3, respectively. Data are set out in Table II. The He I spectrum closely resembles that of other $\mathrm{Cp_3MX}$ compounds[15,23b,25a] of various metals, with four bands (ca. 1:3:2:2 intensity rates) in the IE region below 10.5 eV. From Table II it can be seen that there is excellent agreement between the experimental IE values and those calculated within the transition-state formalism.[15,16] Thus, assignment of the spectrum is straightforward, with band a assignable to ionization from the 20a″ MO, band envelope b to ionization from 26a′, 19a″, and 25a′, band envelope c to ionization from 18a″ and 24a′, and band envelope d to ionization from the remaining 17a″ and 23a′ MO's. Ionization of the 22a′ MO is obscured by the onset of a number of strongly overlapped transitions above 10 eV. Upon switching to He II radiation, no major changes in relative band intensities are observed (typical of trivalent cyclopentadienyl lanthanide PE spectra[24a]). This behavior is in marked contrast to that of 5f $\mathrm{Cp_3UOEt}$[28] and may reflect greater Cp and O(2p) character in the ionized $\mathrm{Cp_3Ce}$(O-*i*-Pr) MO's (less metal–ligand covalency). It is also noteworthy that the He I → He II changes in the $\mathrm{Cp_3Ce}$(O-*i*-Pr) spectrum are qualitatively smaller than in the $\mathrm{Ce(COT)_2}$ spectrum.[8]

Conclusions

These results demonstrate that tetravalent cerium organometallic chemistry is not unique to cyclooctatetraene systems and that chemically efficient routes exist to other tetravalent systems ($\mathrm{Cp_3CeOR}$) which may be more functionalizable.[22] The present electrochemical data reveal very large $\mathrm{(COT)_2/Cp_3,OR}$ ligation influences on the Ce(IV)/Ce(III) couple—1.84 V. These differences likely reflect, among other factors, differences in metal–ligand bond covalency,[8,29] which is also suggested by differing He I →

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He II intensity responses in the photoelectron spectra. The $\mathrm{Cp_3CeOMe}$ electronic structure has been studied using the nonrelativistic $X\alpha$–DVM formalism, and the results are in good agreement with He I/He II photoelectron spectroscopic data. The calculations reveal some Ce–Cp f orbital bond covalency. Although it is well-known that nonrelativistic $X\alpha$ calculations tend to overestimate f orbital contributions to metal–ligand bonding (and to underestimate d orbital contributions),[29,30] this effect should be relatively minor for lanthanides, in contrast to actinides.[29b,c] In sum, the Ce(IV) ligation is rather different in these two organometallic compounds.

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Registry No. $\mathrm{Ce(O\text{-}}i\mathrm{\text{-}Pr)_4}$, 63007-83-0; $\mathrm{Me_3SnCp}$, 2726-34-3; $\mathrm{Cp_3Ce(O\text{-}}i\mathrm{\text{-}Pr)}$, 39452-86-3; $\mathrm{Cp_3CeOMe}$, 39452-83-0; $\mathrm{Bu_3SnCp}$, 94930-04-8; $\mathrm{Me_3Sn(O\text{-}}i\mathrm{\text{-}Pr)}$, 30955-89-6.

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Effects of Mixed-Metal Composition upon the Kinetics and Thermodynamics of Cluster Reactions. Preparation of $\mathrm{HRu_{3-\mathit{n}}Os_{\mathit{n}}(\mu\text{-}COMe)(CO)_{10}}$ and $\mathrm{H_3Ru_{3-\mathit{n}}Os_{\mathit{n}}(\mu_3\text{-}COMe)(CO)_9}$ (n = 1 or 2) and Their Relative Reactivities toward Ligand Substitution and Reductive Elimination of Hydrogen

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The new clusters $\mathrm{HRu_2Os(\mu\text{-}COMe)(CO)_{10}}$, $\mathrm{H_3Ru_2Os(\mu_3\text{-}COMe)(CO)_9}$, $\mathrm{HRuOs_2(\mu\text{-}COMe)(CO)_{10}}$, and $\mathrm{H_3RuOs_2(\mu_3\text{-}COMe)(CO)_9}$ have been synthesized and characterized by spectroscopic methods. Retention of the mixed-metal core during hydrogenation of $\mathrm{HM_2M'(\mu\text{-}COMe)(CO)_{10}}$ and carbonylation of $\mathrm{H_3M_2M'(\mu_3\text{-}COMe)(CO)_9}$ proves that cluster fragmentation does not occur during these reactions. Competition experiments were used to determine relative rates of hydrogenation of $\mathrm{HM_3(\mu\text{-}COMe)(CO)_{10}}$ to $\mathrm{H_3M_3(\mu_3\text{-}COMe)(CO)_9}$, attributed to the relative rates of CO dissociation, as $\mathrm{M_3 = Ru_3}$ (4500) > $\mathrm{Ru_2Os}$ (1100) > $\mathrm{RuOs_2}$ (220) ≫ $\mathrm{Os_3}$ (1) at 343 K. Direct measurements of the rate constants for carbonylation of $\mathrm{H_3M_3(\mu_3\text{-}COMe)(CO)_9}$ to $\mathrm{HM_3(\mu\text{-}COMe)(CO)_{10}}$ give relative rates: $\mathrm{M_3 = Ru_3}$ (210) > $\mathrm{Ru_2Os}$ (72) > $\mathrm{RuOs_2}$ (38) ≫ $\mathrm{Os_3}$ (1) at 353 K. The similarity of the rates of carbonylation for all clusters having at least one Ru atom, but a greatly reduced rate for the $\mathrm{Os_3}$ cluster, suggests that reductive elimination of dihydrogen occurs from a single metal atom in the transition state, even though the hydride ligands bridge two metal atoms in the ground state. Equilibrium constants for hydrogenation and for isomerization of $\mathrm{HM_2M'(\mu\text{-}COMe)(CO)_{10}}$ were used to obtain estimates of the Ru–H–Ru (408 kJ/mol) and Os–H–Os (425 kJ/mol) bond energies and for the differences in bond energies $\{E(\mathrm{RuHOs}) - E(\mathrm{RuOs})\}$ (299 kJ/mol), $\{E(\mathrm{Os_2(\mu\text{-}C)}) - E(\mathrm{Ru_2(\mu\text{-}C)})\}$ (42 kJ/mol), and $\{E(\mathrm{Os_2(\mu\text{-}C)}) - E(\mathrm{RuOs(\mu\text{-}C)})\}$ (24 kJ/mol), based upon the assumptions that $\{E(\mathrm{M_2(\mu\text{-}C)}) - E(\mathrm{M_3(\mu_3\text{-}C)})\} = 0$ (M = Ru or Os), $\{E(\mathrm{Os_3(\mu_3\text{-}C)}) - E(\mathrm{RuOs_2(\mu_3\text{-}C)})\} = (^1/_3)\{E(\mathrm{Os_3(\mu_3\text{-}C)}) - E(\mathrm{Ru_3(\mu_3\text{-}C)})\}$, and $\{E(\mathrm{Os_3(\mu_3\text{-}C)}) - E(\mathrm{Ru_2Os(\mu_3\text{-}C)})\} = (^2/_3)\{E(\mathrm{Os_3(\mu_3\text{-}C)}) - E(\mathrm{Ru_3(\mu_3\text{-}C)})\}$.

The reactivity of mixed-metal clusters has been of interest for many years.[2] One goal of research in this area has been to combine, in one molecule, metals having very different chemical properties and thus to induce unique chemical transformations. Another valuable property of mixed-metal clusters is that their lower symmetry allows an additional probe for cluster reactivity.

We have investigated the mechanisms of a number of reactions of the alkylidyne cluster series $\mathrm{HM_3(\mu\text{-}CX)(CO)_{10}}$ (M = Ru or Os; X = OMe or $\mathrm{NR_2}$) and $\mathrm{H_3M_3(\mu_3\text{-}CX)(CO)_9}$ (X = OMe, Cl, Br, $\mathrm{CO_2Me}$, SEt, Ph, H, or alkyl), including ligand substitution,[3] oxidative addition and reductive elimination of molecular hydrogen,[4] reductive elimination of C–H bonds,[5] hydrogen transfer to alkenes and alkynes,[6] and alkylidyne–alkyne coupling.[7] In several of these studies, important questions have remained, concerning the number of metal atoms involved in the mechanism, the site of reactivity, and the possible involvement of cluster fragmentation.

In an effort to answer these questions we have now prepared the mixed-metal alkylidynes $\mathrm{HRu_2Os(\mu\text{-}COMe)(CO)_{10}}$, $\mathrm{HRuOs_2(\mu\text{-}COMe)(CO)_{10}}$, $\mathrm{H_3Ru_2Os(\mu_3\text{-}}$

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