Organolanthanoids. 9. Electrochemical Reduction of Tris(cyclopentadienyl)samarium(III), -ytterbium(III), and -europium(III) Compounds in Tetrahydrofuran

A. M. Bond,*[1] G. B. Deacon,*[2] and R. H. Newnham[2]

Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria 3217, Australia, and the Chemistry Department, Monash University, Clayton, Victoria 3168, Australia

Received March 25, 1986

The cyclopentadienyl complexes $(C_5H_5)_3M$ (M = Sm, Yb, and Eu) and $(MeC_5H_4)_3Sm$ undergo chemically reversible electrochemical reduction in tetrahydrofuran at platinum, gold, and mercury electrodes under purified nitrogen to give $[(C_5H_5)_3M]^-$ species, $(C_5H_5)_3M + e^- \rightarrow [(C_5H_5)_3M]^-$. As required by this reaction, reversible electrochemical oxidation of $KSm(C_5H_5)_3$ to give $(C_5H_5)_3Sm$ has also been observed. The reversible half-wave potentials, $E^r_{1/2}$ (approximately equal to the standard redox potential $E°$), are considerably more negative than for reduction of M(III) to M(II) in water, indicating that both solvent and ligand terms are important in lanthanoid redox chemistry. The $E^r_{1/2}$ values show that thermodynamic stability of the divalent species toward oxidation falls in the sequence M = Eu > Yb > Sm. The kinetic reactivity with adventitious moisture and/or oxygen follows the thermodynamic sequence with $[(C_5H_5)_3Sm]^-$ being particularly sensitive to traces of water. Reaction of $(C_6F_5)_2Yb$ with cyclopentadiene and $(C_6F_5)_2Hg$ provides a new synthesis of $(C_5H_5)_3Yb$.

Although the most stable oxidation state of the lanthanoid elements is III,[3] oxidation state II is quite well-established and many of the dihalides are known.[4,5] Aqueous divalent chemistry is essentially restricted to europium, ytterbium, and samarium [$E°$(III/II) = -0.35, -1.10, and -1.50 V vs. SCE, respectively].[6] Reduction of other aqueous trivalent lanthanoids to the free metal in a one-[7-10] or two-step[11] process has been claimed under polarographic conditions at the dropping mercury electrode, but the reduction potentials are at variance with commonly accepted (e.g., ref 3) calculated thermodynamic $E°$ values[6] and ignore an earlier attribution that the polarographic waves include a contribution from the reduction of hydrolysis products[12] (see also ref 13). The exact mechanism of reduction of such complexes and the thermodynamic significance of some of the polarographic half-wave potentials, $E_{1/2}$, are therefore uncertain. Both Sm(II) and Yb(II) are readily oxidized by water,[3] but some stabilization can be effected by complexation with crown ethers.[8] Use of melts has enabled most lanthanoid(II) species to be observed.[14-17] By assuming that the difference in redox potentials between pairs of lanthanoid ions is similar in aqueous solution to that in melts, it has been possible to estimate $E°$(III/II) in water for lanthanoid ions in addition to europium, ytterberium, and samarium[16,17] which can be measured directly. These values agree with commonly accepted calculated thermodynamic $E°$ values[6] except for Tb and Gd. Propylene carbonate or dimethyl sulfone media prevented oxidation of Sm(II) and Yb(II) by the solvent, though the $E_{1/2}$ values are similar to those in water.[18,19] Little has been reported on the electrochemistry of organolanthanoids except an investigation of the oxidation of bis(pentamethylcyclopentadienyl)ytterbium(II)[17] and calculations of values for the europium and samarium analogues.[21] Reduction of the organoamidolanthanoid $Yb[N(SiMe_3)_2]_3$ has also been studied.[22] We now report the reduction of some tris(cyclopentadienyl)lanthanoids in tetrahydrofuran (THF) for the elements (Sm, Eu, Yb) which are known[23] to give lanthanoid(II) organometallics. The oxidative electrochemical behavior of $KSm(C_5H_5)_3$ has also been studied to assist in defining the exact nature of the electrode process. Additionally, the development of an electrochemical cell which can be attached to a vacuum line and simultaneously enables voltammetric measurements to be made at platinum, gold, and mercury electrodes is described. This and related procedures have been developed to ensure the integrity of data obtained on moisture- and oxygen-sensitive compounds. In future reports, detailed electrochemical studies concerning the reduction of other tris(cyclopentadienyl)lanthanoid(III) compounds, not so far known to exist in oxidation state (II), will be described.[24]

---

[1] Deakin University.

[2] Monash University.

[3] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th. ed; Wiley: New York, 1980; Chapter 23.

[4] Brown, D. *Halides of the Lanthanides and Actinides*; Wiley: London, 1968.

[5] Johnson, K. E.; Mackenzie, J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 43-48.

[6] Johnson, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1671-1675. For recent calculations, see: Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1985**, *89*, 3317-3319.

[7] Musikas, C.; Haine, R. G.; Peterson, J. R. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2935-2940.

[8] Yamana, H.; Mitsugashira, T.; Shiokawa, Y.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2615-2617.

[9] Estee, C. R.; Glockler, G. *J. Am. Chem. Soc.* **1948**, *70*, 1344-1347.

[10] Shiokawa, Y.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2910-2913.

[11] Khasgiwale, K. A.; Mehta, M. M.; Pappachan, A. L.; Sundaresan, M. *J. Electrochem. Soc. India* **1982**, *31*, 13-15.

[12] Lage, R. F.; Timmick, A. *Anal. Chem.* **1964**, *36*, 1258-1264.

[13] Bogaert, M.; Kiekens, P.; Temmerman, E. *Bull. Soc. Chim. Belg.* **1984**, *93*, 107-111.

[14] Schoebrechts, J. P.; Gilbert, B. P.; Duyckaerts, G. *J. Electroanal. Chem.* **1983**, *145*, 127-138.

[15] Schoebrechts, J. P.; Gilbert, B. P.; Duyckaerts, G. *J. Electroanal. Chem.* **1983**, *145*, 139-146.

[16] Mikheev, N. B. *Radiochim. Acta* **1983**, *32*, 69-80.

[17] Mikheev, N. B. *Inorg. Chim. Acta* **1984**, *94*, 241-248.

[18] Bulhoes, L. O. de S.; Rabockai, T. *Electrochim. Acta* **1982**, *27*, 1071-1073.

[19] Varlashkin, P. G.; Peterson, J. R. *J. Less-Common Met.* **1983**, *94*, 333-341.

[20] Gaughan, G. T. Ph.D. Thesis, University of Oregon, 1983.

[21] Watson, P. L., unpublished results in footnote 5 of: Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598-601.

[22] Bradley, D. C.; Ahmed, M. *Polyhedron* **1983**, *2*, 87-95.

[23] Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 21.

[24] Bond, A. M., Deacon, G. B., Newnham, R. H., unpublished results.

0276-7333/86/2305-2312$01.50/0

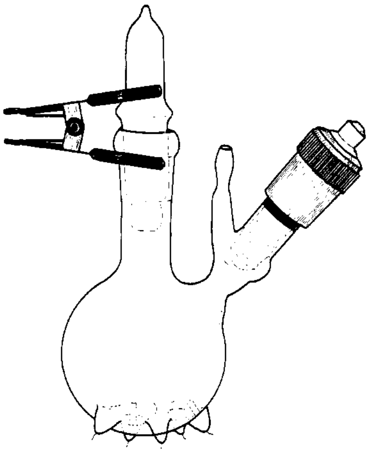

Figure 1. Schematic diagram of the multielectrode electrochemical cell which is attached to a vacuum nitrogen line.

Experimental Section

Electrochemistry. Electrochemical measurements were carried out with a Princeton Applied Research Model 174A Polarographic Analyser at 20 ± 1 °C. The cell (Figure 1) which can be connected to a vacuum line was fitted with a Teflon tap and a greaseless joint and had three platinum and two gold electrodes sealed through the glass, close together, and protruding approximately 0.5 cm into the cell. Platinum electrodes of several sizes (0.1 and 0.5 mm diameter wire, 1.5 × 0.1 mm plates) were examined. The smaller wire electrodes gave the most satisfactory results. Gold wire electrodes were approximately 0.5-mm diameter. One of the gold electrodes was coated with mercury before examination of each solution so that platinum, gold, and mercury working electrodes, a platinum quasi-reference electrode, and a platinum auxiliary electrode were available for use with each solution. The presence of multiple platinum electrodes enabled the working electrode to be changed from one to another if the electrochemical processes or other factors caused excessive poisoning of the electrode surface. While the actual measurements were made relative to a quasi-platinum reference electrode, reported data are relative to the $[(C_5H_5)_2Fe]^{+/0}$ redox couple, ferrocene being used in situ as an internal standard.[25] The presence of this compound did not interfere with the organolanthanoid electrochemical processes. Initial experiments with tris(cyclopentadienyl)samarium(III), using ferrocene as an external and an internal standard, showed that wave shapes and current values were unaffected by the presence of ferrocene. Additionally, there was no evidence for the appearance of the blue $[(C_5H_5)_2Fe]^+$ cation in any of the systems, as might be expected if the trivalent organolanthanoids were reduced by ferrocene. The reversible $E^r_{1/2}$ values indicate such reactions should not occur.

Spectroscopic Measurements. These were carried out as described previously.[26-28]

Reagents. Tetrabutylammonium perchlorate (G.F.S. Chemicals) and tetrabutylammonium hexafluorophosphate (Southwestern Chemicals) were ground to a fine power and dried at 140 °C for 4 h under vacuum. Ferrocene (PCR Research Chemicals) was sublimed before use. Bis(pentafluorophenyl)mercury(II),[29] tris(cyclopentadienyl)samarium(III),[28] tris(methylcyclopentadienyl)samarium(III),[28] and potassium tris(cyclopentadienyl)samarate(II)[30] were prepared and characterized as described elsewhere.[28-30] Tris(cyclopentadienyl)(tetrahydrofuran)europium(III) was prepared by a modification of a reported transmetalation method.[31] Solvents, nitrogen, and argon were purified as in earlier papers.[26-28]

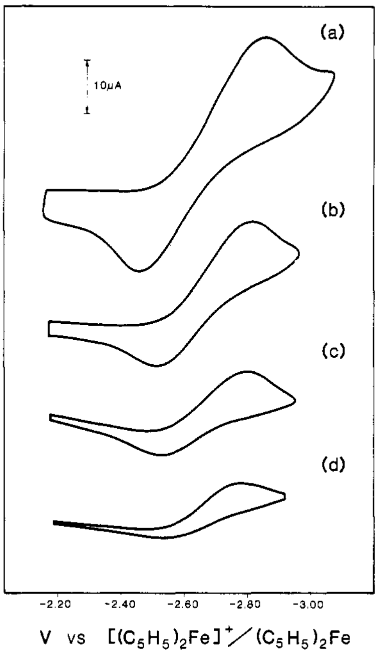

Figure 2. Cyclic voltammograms of $(C_5H_5)_3Sm$ in THF (Bu_4NClO_4, 0.1 M) at 20 ± 1 °C using a Pt electrode. Scan rates: (a) 500 mV s^{-1}; (b) 200 mV s^{-1}; (c) 100 mV s^{-1}; (d) 50 mV s^{-1}.

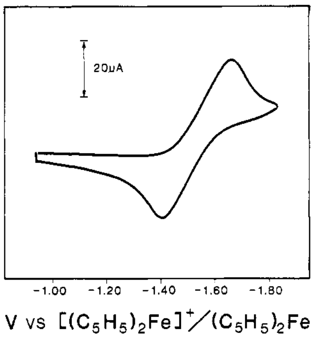

Figure 3. Cyclic voltammogram of $(C_5H_5)_3Eu$ in THF (Bu_4NClO_4, 0.1 M) at 20 ± 1 °C using a Pt electrode at a scan rate of 100 mV s^{-1}.

Tris(cyclopentadienyl)(tetrahydrofuran)ytterbium(III). Ytterbium powder[28] (2.49 mmol) and bis(pentafluorophenyl)mercury(II) (3.74 mmol) were stirred in tetrahydrofuran (20 mL) for 4 h after initiation of transmetalation under purified nitrogen.[26,27] Freshly cracked cyclopentadiene (10 mmol) was then added, and the suspension was stirred for 38 h, with a further addition of cyclopentadiene after 23 h being recommended to ensure completion of the reaction. The green reaction mixture was heated to reflux, filtered through a Celite pad, and reduced in volume to 5 mL under vacuum. After addition of hexane (5 mL) and cooling in ice, the green title compound crystallized and was filtered off under nitrogen, washed with hexane, and dried under vacuum (yield, 46%). The mass and visible/near-infrared spectra were in agreement with reported data.[32,33]

Handling Methods. All the organolanthanoids are air- and moisture-sensitive and were handled under purified argon or nitrogen in Vacuum Atmospheres HE43-2 or Monash/CSIRO recirculating dryboxes. The organolanthanoid, ferrocene, and the supporting electrolyte, tetrabutylammonium perchlorate or hexafluorophosphate, were added to the electrochemical cell in

---

(25) Gagne, R. R.; Koval, C. A.; Lisensky, B. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

(26) Deacon, G. B.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1977**, *135*, 103–114.

(27) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121–141.

(28) Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Aust. J. Chem.* **1984**, *37*, 517–525.

(29) Deacon, G. B.; Smith, R. N. M. *Russ. J. Org. Chem.* (*Engl. Transl.*) **1982**, 1584–1585.

(30) Deacon, G. B.; Pain, G. N.; Tuong, T. D. *Polyhedron* **1985**, *4*, 1149–1150.

(31) Suleimanov, G. Z.; Kurbanov, T. Kh.; Nuriev, Ya. A.; Rybakova, L. F.; Beletskaya, I. P. *Dokl. Chem.* **1982**, *265*, 254–258.

(32) Thomas, J. L.; Hayes, R. G. *J. Organomet. Chem.* **1970**, *23*, 487–489.

(33) Calderazzo, F.; Pappalardo, R.; Losi, S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 987–999.

Table I. Representative Cyclic Voltammetric Data for Reduction of $(C_5H_5)_3M$ (M = Sm, Yb, Eu), Reduction of $(MeC_5H_4)_3Sm$, and Oxidation of $[(C_5H_5)_3Sm]^-$ in Tetrahydrofuran (0.1 M Bu_4NClO_4) at 20 ± 1 °C[a]

compd	electrode	scan rate, mV/s	E_p^{red},[b] V[f]	E_p^{ox},[c] V[f]	ΔE_p,[d] V	$E^r_{1/2}$,[e] V[f]
$(C_5H_5)_3Sm$	Pt	500	-2.86	-2.46	0.40	-2.66
		200	-2.81	-2.51	0.30	$-2.66^{g,h}$
		200^{i}	-2.76^{i}	-2.50^{i}	0.26^{i}	-2.63^{i}
		100	-2.79	-2.51	0.28	$-2.65^{g,h}$
		50	-2.78	-2.53	0.25	$-2.66^{g,h}$
$[K(C_5H_5)_3Sm]^{j}$	Pt	200	-2.68	-2.52	0.18	-2.60
		50	-2.67	-2.51	0.16	-2.59
$(MeC_5H_4)_3Sm$	Pt	500	-2.80	-2.66	0.16	-2.73
		200	-2.80	-2.66	0.14	-2.73^{g}
	Hg	500	-2.81	-2.59	0.22	-2.70
		200	-2.75	-2.59	0.16	-2.67^{g}
		100	-2.74	-2.60	0.14	-2.67^{g}
	Au	500	-2.79	-2.61	0.18	-2.70
		200	-2.76	-2.64	0.12	-2.70^{g}
$(C_5H_5)_3Yb$	Pt	500	-2.05	-1.79	0.26	-1.92
		200	-2.08	-1.80	0.28	-1.94
	Hg	500	-2.15	-1.69	0.46	-1.92
		200	-2.10	-1.69	0.41	-1.90
$(C_5H_5)_3Eu$	Pt	200	-1.71	-1.39	0.32	-1.55
		100	-1.66	-1.40	0.26	-1.53
	Hg	500	-1.73	-1.35	0.38	-1.54
		200	-1.66	-1.42	0.24	-1.54

[a] Exact response observed for E_p^{ox}, E_p^{red}, and ΔE_p depends on concentration, electrode size and scan rate because of resistance effects. However, the calculated value of $E_{1/2}^{r}$ is essentially independent of all these parameters (see text). [b] E_p^{red} = reduction peak potential. [c] E_p^{ox} = oxidation peak potential. [d] ΔE_p = the modulus of the peak-to-peak separation. [e] $E_{1/2}^{r}$ = calculated reversible half-wave potential. [f] V vs. $[(C_5H_5)_2Fe]^{+/0}$. [g] Not chemically reversible at given scan rate, i.e., $[i_p^{red}/i_p^{ox}]$ not unity. [h] Became chemically reversible with predrying of the solvent by $(C_5H_5)_3Eu$. [i] 0.1 M Bu_4NPF_6 as the electrolyte. [j] Studied as an oxidation process. All other data are for reduction processes.

a drybox in amounts to give concentrations of (1–5) × 10^{-3} M for the first two compounds and 0.1 M for the electrolytes. This cell was then connected to a vacuum/nitrogen line. Purified tetrahydrofuran (10 mL) was added by syringe techniques under nitrogen in each case.

Results and Discussion

Results for the electrochemical reduction of $(C_5H_5)_3M$ (M = Sm, Eu, or Yb) and $(MeC_5H_4)_3$ Sm derivatives and for the oxidation of $KSm(C_5H_5)_3$ are summarized in Table I, and representative cyclic voltammograms are shown in Figures 2 and 3. The $E^r_{1/2}$ values are relative to the $[(C_5H_5)_2Fe]^{+/0}$ [$E°$ = 0.400 V vs. NHE][34] couple, ferrocene being used as an internal standard[25] and are approximately equal to the standard redox potential, $E°$.

Benedetti[35] has shown conclusively that uncompensated resistance (ohmic *iR* drop) strongly influences data for the reversible one-electron voltammetric oxidation of ferrocene in tetrahydrofuran. This was confirmed in the present work as peak-to-peak separations in cyclic voltammetric experiments were substantially greater than nernstian and were concentration-dependent. Consequently a strategy for minimizing the influence of *iR* drop on data was developed as follows. The ferrocene reference material was present in solution at an approximately equal concentration to that of $(C_5H_5)_3M$. The $E^r_{1/2}$ values for oxidation of ferrocene and reduction of $(C_5H_5)_3M$ were obtained by averaging the oxidation peak potential and the reduction peak potential in each case. The averaging process was assumed to approximately correct for the *iR* drop and for any influence of slow electron transfer which may be present. Furthermore, the differences between $E^r_{1/2}$ for reduction of $(C_5H_5)_3M$ and $E^r_{1/2}$ for oxidation of ferrocene calculated in the above manner can be considered to represent the thermodynamic $E^r_{1/2}$ value for reduction of $(C_5H_5)_3M$ relative to the $[(C_5H_5)_2Fe]^{+/0}$ redox couple. To obtain valid data the value of $E^r_{1/2}$ reported by this method had to be found to be essentially independent of electrode material (platinum, gold, or mercury), concentration, and scan rate as required for measurement of a thermodynamic parameter. Representative data in Table I show that this requirement was generally met at the ±20 mV level or better. The need to use relatively high concentrations of $(C_5H_5)_3M$ in the 5 × 10^{-3} M concentration range, to avoid problems with reaction with adventitious water present, enhances the problem of *iR* drop. All data obtained confirm that, as theoretically expected, the *iR* drop is greater at the larger area mercury electrode, at faster scan rates, and at higher concentrations but that the *iR* correction method proposed works acceptably well under all operating conditions used. Peak-to-peak separations, ΔE_p, for oxidation of ferrocene and reduction of $(C_5H_5)_3M$ were both in the range of 100–400 mV over the conditions examined. The nonunity of reduction and oxidation peak heights in some experiments (see later discussion) is consistent with a chemical reaction following charge transfer. However, this term leads to errors in $E^r_{1/2}$ less than the ±20 mV uncertainty associated with *iR* drop so a correction term for the chemical step was not included in any of the calculations of $E^r_{1/2}$ for reduction of $(C_5H_5)_3M$.

(a) Reduction of $(C_5H_5)_3Sm$. Cyclic voltammograms for the reduction of $(C_5H_5)_3Sm$ between -2.20 and -3.00 V vs. $[(C_5H_5)_2Fe]^{+/0}$ at a range of scan rates at a platinum electrode are shown in Figure 2. They are characterized by a well-defined reduction peak in the negative potential direction and an oxidation peak on the reverse scan. The peak to peak separation is a function of scan rate as is the ratio of reduction peak current, i_p^{red}, to oxidation peak current, i_p^{ox}. At 500 mV/s, i_p^{red}/i_p^{ox} is close to unity, but, at 50 mV/s, the oxidation peak is considerably attenuated in some experiments. This can be attributed to greater sensitivity to traces of air/moisture for the reduction product than for $(C_5H_5)_3Sm$. Consistent with this hypothesis, it was observed that deliberate brief exposure to the atmosphere causes the oxidation peak to disappear. Furthermore, when traces of water and/or oxygen in the tetrahydrofuran in the cell were scavenged by $(C_5H_5)_3Eu$

---

(34) Koepp, H. M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* **1960**, *64*, 483–491.

(35) Benedetti, A. V. *Ecletica Quim.* **1984**, *9*, 13–21; *Chem. Abstr.* **1986**, *104* 118340e.

prior to addition and electrochemical reduction of $(C_5H_5)_3Sm$, the voltammograms were fully reversible, $i_p^{red}/i_p^{ox} = 1.0 \pm 0.1$, at all scan rates (50, 100, 200, 500 mV/s). The size of the oxidation peak in cyclic voltammograms for reduction of aqueous Sm(III) is dependent on the scan rate[7] owing to the ready oxidation of Sm(II) by water.[3] Use of Bu_4NPF_6 electrolyte gave a similar voltammetric response to that for Bu_4NClO_4, suggesting that the electrolyte anions are essentially inert (see Table I). The observed reduction of $(C_5H_5)_3Sm$ (Figure 2 and Table I) is consistent with reaction 1

$$(C_5H_5)_3Sm(THF)_x + e^- \rightleftharpoons [(C_5H_5)_3Sm(THF)_y]^- + (x - y)THF \quad (1)$$

with an $E^r_{1/2}$ value of −2.66 V vs. $[(C_5H_5)_2Fe]^{+/0}$. Chemical reduction of $(C_5H_5)_3Sm$ with potassium has recently been shown to give $KSm(C_5H_5)_3$.[30] Although the compound has not been characterized crystallographically, the analytical composition and oxidation state II, from electronic spectroscopy, are clear. If the stoichiometries of the isolated $(C_5H_5)_3Sm(THF)$[28] and $KSm(C_5H_5)_3$[30] reflect solution solvation, $x = 1$ and $y = 0$. In subsequent equations solvent molecules are omitted for simplicity. The ion $[(C_5H_5)_3Sm]^-$ is isoelectronic with $(C_5H_5)_3Eu$ but is markedly less stable owing to its powerful reducing properties.

(b) Oxidation of $KSm(C_5H_5)_3$. The cyclic voltammogram exhibits a chemically reversible oxidation $[i_p^{ox}/i_p^{red} = 1.0 \pm 0.1]$ with a similar $E^r_{1/2}$ value to that observed for reduction of $(C_5H_5)_3Sm$. This confirms the identification of the reduction product as $[(C_5H_5)_3Sm]^-$ (eq 1). For $KSm(C_5H_5)_3$, $[i_p^{ox}/i_p^{red}]$ is independent of scan rate, in contrast with $(C_5H_5)_3Sm$. The samarium(II) substrate is extremely air- and moisture-sensitive, far more than $(C_5H_5)_3Sm$, and would scavenge any traces of oxygen or water from the system prior to the electrochemical measurements. In the reduction of $(C_5H_5)_3Sm$, the disparate reactivities of this compound and $[(C_5H_5)_3Sm]^-$ toward traces of oxygen and moisture give $[i_p^{red}/i_p^{ox}] > 1$ when slow scan speeds are used except under extremely dry conditions.

(c) Reduction of $(MeC_5H_4)_3Sm$. The electrochemical behavior of this compound is very similar to that of $(C_5H_5)_3Sm$ (Table I). Cyclic voltammetric studies on three different electrodes [Pt, Au, Hg; see Experimental Section and Figure 1 for the cell design] show that $E^r_{1/2}$ is independent of the electrode surface (Table I). The value of $E^r_{1/2}$ is marginally more negative than that of $(C_5H_5)_3Sm$, indicating that substitution by the electron-donating methyl group makes electron transfer to samarium slightly more difficult. A similar conclusion has been drawn from comparison of the electrochemical reduction of $(MeC_5H_4)_3UCl$ and $(C_5H_5)_3UCl$.[20]

(d) Reduction of $(C_5H_5)_3M$ (M = Eu or Yb). The cyclic voltammogram of $(C_5H_5)_3Eu$ is shown Figure 3. Tris(cyclopentadienyl)ytterbium(III) shows essentially similar behavior, but reduction occurs at more negative potentials. Both give extremely well-defined chemically reversible couples, $[i_p^{red}/i_p^{ox}] = 1.0 \pm 0.1$, and similar $E^r_{1/2}$ values are obtained on platinum and mercury electrodes for each compound. The electrode process can be attributed to reaction 2 (M = Eu or Yb), the products $[(C_5H_5)_3Eu]^-$ and $[(C_5H_5)_3Yb]^-$ being isoelectronic with $(C_5H_5)_3Gd$ and $(C_5H_5)_3Lu$, respectively. In an analogous reaction, electrochemical reduction of $((Me_3Si)_2N)_3Yb$ to $[((Me_3Si)_2N)_3Yb]^-$ has been reported.[22] The order of $E^r_{1/2}$ values, Eu > Yb > Sm, for $(C_5H_5)_3M$ derivatives (Table I) parallels the order for $E°[M(III)/M(II)]$ in aqueous solution, but the difference between ytterbium and europium is less marked than in aqueous solution. Even with allowance for the use of a $[(C_5H_5)_2Fe]^{+/0}$ standard (0.400 vs. NHE)[34] the resulting $(C_5H_5)_3M/[(C_5H_5)_3M]^-$ potentials [−2.33 (Sm), −1.52 (Yb), −1.15 (Eu)] are much more negative than the corresponding M(III)/M(II) redox potentials in aqueous solution. Differing solvent and ligand effects are operative in these different systems, and clearly both terms must be carefully considered. The importance of these terms is emphasised by noting that $E^r_{1/2}$ values for oxidation of the $[(C_5H_5)_2M^{II}(solvent)]^{+/0}$ system in acetonitrile are estimated to be −2.4, −1.78, and −1.22 V vs. $[(C_5H_5)_2Fe]^{+/0}$ for M(II) = Sm, Yb, and Eu, respectively.[21]

$$(C_5H_5)_3M + e^- \rightleftharpoons [(C_5H_5)_3M]^- \quad (2)$$

Brief exposure of the $(C_5H_5)_3M$ (M = Yb or Eu) solutions to air/moisture causes preferential disappearance of the oxidation peak, as is the case for $(C_5H_5)_3Sm$. The order of sensitivity to moisture is M = Sm > Yb > Eu and corresponds with the order of the electrode potentials. Both $(C_5H_5)_3Eu$ and $[(C_5H_5)_3Eu]^-$ are notably more stable to moisture than the other compounds, and the reduction wave for $(C_5H_5)_3Eu$ was still visible after 5 min exposure to air/moisture.

(e) General Remarks. Electrode potentials for reduction of $(C_5H_5)_3M$ (M = Sm, Yb, or Eu) and $(MeC_5H_4)_3Sm$ indicate that the thermodynamic redox stability of the divalent complexes $[(RC_5H_4)_3M]^-$ (R = H or Me) increases in the order M = Sm < Yb < Eu. The kinetic reactivity order for $[(RC_5H_4)_3M]^-$ (R = H or Me) decreases in the sequence M = Sm > Yb > Eu and parallels the thermodynamic instability order. The data obtained in this work are therefore in general agreement with existing data on lanthanide redox chemistry. However, the role of the solvent and ligands are clearly very important as shown in the present study, and their combined effect makes reduction substantially more difficult thermodynamically in tetrahydrofuran than in water.

(f) The Preparation of $(C_5H_5)_3Yb$. A new preparation of tris(cyclopentadienyl)ytterbium(III) has been introduced in the present work. Bis(pentafluorophenyl)ytterbium(II), prepared "in situ" from bis(pentafluorophenyl)mercury(II) and ytterbium metal,[26,27] reacts with cyclopentadiene in the presence of an appropriate amount of $(C_6F_5)_2Hg$ to give the trivalent cyclopentadienyl in satisfactory yield. The likely reaction sequence is (3)–(5). Reactions 3 and 4 have been independently observed in previous studies.[36,37] A reaction analogous to (5) may be a step in ligand-exchange syntheses of $(RC_6H_4)_3Sm$ (R = H or Me) from (pentafluorophenyl)samarium species and the appropriate cyclopentadiene[36] while the direction of (5) is consistent with the relative acidities of pentafluorobenzene and cyclopentadiene (see ref 36 and references therein). Initial oxidation of $(C_6F_5)_2Yb$ to $(C_6F_5)_3Yb$ by the excess of $(C_6F_5)_2Hg$ can probably be ruled out, as the characteristic orange color of $(C_6F_5)_2Yb$ was unaffected by the presence of the mercurial. Given the extreme simplicity of the preparation of the mercurial,[29] this route to tris(cyclopentadienyl)ytterbium(III) is certainly competitive with

$$(C_6F_5)_2Yb + 2C_5H_6 \rightarrow (C_5H_5)_2Yb + 2C_6F_5H \quad (3)$$

$$2(C_5H_5)_2Yb + (C_6F_5)_2Hg \rightarrow 2(C_5H_5)_2YbC_6F_5 + Hg \quad (4)$$

$$(C_5H_5)_2YbC_6F_5 + C_5H_6 \rightarrow (C_5H_5)_3Yb + C_6F_5H \quad (5)$$

---

(36) Deacon, G. B.; Newnham, R. H. *Aust. J. Chem.* **1985**, *38*, 1757–1765.

(37) Deacon, G. B.; Fallon, G. D.; Mackinnon, P. I.; Newnham, R. H.; Pain, G. N.; Tuong, T. D.; Wilkinson, D. L. *J. Organomet. Chem.* **1984**, *277*, C21–C24.

the best current route to this compound, viz., oxidative transmetalation between ytterbium metal and thallous cyclopentadienide.[28]

Acknowledgment. We gratefully acknowledge the financial support of the Australian Research Grants Scheme and thank Rare Earth Products, Liverpool, England, for a gift of REACTON metallic ytterbium and europium.

Registry No. $(C_5H_5)_3Sm$, 1298-55-1; $(C_5H_5)_3Yb$, 1295-20-1; $(C_5H_5)_3Eu$, 12216-04-5; $(MeC_5H_4)_3Sm$, 39470-14-9; $[K(C_5H_5)_3Sm]$, 100225-49-8; bis(pentafluorophenyl)mercury(II), 973-17-1; ytterbium, 7440-64-4; cyclopentadiene, 542-92-7.

A Theoretical Analysis of the Stepwise Reduction of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$ to $[(\eta\text{-}C_5H_5)Re(NO)(CH_3)(PPh_3)]$

Richard F. Fenske,* Maria Clelia Milletti, and Michael Arndt

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received January 27, 1986

The stepwise reduction of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$ to $[(\eta\text{-}C_5H_5)Re(NO)(CH_3)(PPh_3)]$ is investigated from a theoretical point of view. All the rhenium complexes involved in the reaction are found to have HOMOs and LUMOs that are similar in nature. The HOMOs are mainly metal d in character, while the LUMOs appear to be antibonding combinations of rhenium d orbitals and nitrosyl π^* orbitals. In the reaction sequence being studied proton attacks have the overall effect of lowering orbital energies, while reduction destabilizes most molecular orbitals. Also investigated is the site of nucleophilic and electrophilic attack, which is found to be the nitrosyl ligand for the nucleophile and the oxygen atom at the original carbonyl site for the electrophile.

Introduction

Lately, new interest in organometallic complexes has been generated by their possible use in the transformation of coal into various organic molecules;[1] specifically, they have been studied as homogeneous[2] or heterogeneous[3,4] catalysts in the reduction of CO.[5] Gladysz has considered a variety of pseudotetrahedral[6] organorhenium complexes, studying their role as catalysts[7] as well as their stereoisomerism, which is important in stereospecific reactions.[8–15] The chemistry involved in the synthesis and reactivity of these rhenium compounds is interesting from a theoretical point of view; the reactions studied present features that can be analyzed in a straightforward manner and at the same time reveal interesting aspects of the reactivity of organometallic compounds.

In a previous paper[16] one of these organorhenium complexes, $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$, and its reduction to the neutral formyl $[(\eta\text{-}C_5H_5)Re(NO)(CHO)(PPh_3)]$ have been analyzed in detail. The present work proposes to take that analysis further, following in a stepwise fashion the reaction that leads to the complete reduction of the formyl ligand to a methyl ligand.[7]

Experimentally,[7] Gladysz has shown that the reduction of the formyl complex to the methyl species can occur: (1) by addition of $BH_3{\cdot}THF$ to the formyl compound, (2) by the reaction of the carbonyl complex (which is the precursor to the formyl ligand) with $NaBH_4$ in THF/H_2O, and (3) by electrophile-induced disproportionation of the formyl complex by either CH_3SO_3F or CH_3CO_2H. In an excellent series of experimental studies, Gladysz demonstrated that all three reaction sequences are equivalent to a series of alternating nucleophilic and electrophilic attacks. This sequence of reactions can thus provide information as to how the energetics of the rhenium complex change upon gradual reduction and what the role of the alternating electrophilic attack is. In addition, previous work has shown that reduction of CO to CHO in the same rhenium complex occurs via the nitrosyl ligand, which is energetically more apt to form a coordinate-covalent bond with the attacking nucleophile.[16] In this paper it will be

---

[1] Pruett, R. L. *Science (Washington, D.C.)* **1981**, *211*, 11.

[2] Heinrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 77.

[3] Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

[4] Perkins, P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 3895.

[5] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[6] The adjective pseudotetrahedral is being used in order to be consistent with Gladysz's designation;[13] in actuality, the geometry of complexes of the type being considered here is more rigorously octahedral. Accordingly, the calculations have been carried out for geometries in which three of the ligands lie on the *x*, *y*, and *z* axes, while the Cp^- ring is centered on the C_3 axis of symmetry going through the origin (see Figure 1).

[7] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

[8] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

[9] Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782.

[10] Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879.

[11] Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

[12] Merrifield, J. H.; Fernandez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

[13] Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

[14] Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846.

[15] Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

[16] Fenske, R. F.; Milletti, M. C. *Organometallics* **1986**, *5*, 1243.