Inorg. Chem. **1985**, *24*, 4433–4435

muthal (Ψ) scans of five reflections ($00\bar{4}$; $00\bar{8}$; $0,0,\overline{12}$; $0,0,\overline{18}$; $0,0,\overline{22}$) at high χ angles (85.90°). Transmission factors were in the range 0.997–0.579. Structure factors were calculated in the usual way (*Lp* corrections applied, no extinction correction), and the standard deviations on the intensities were calculated in terms of statistics alone. Reflections having $|F_o| \geqslant 3\sigma|F_o|$ were considered as observed. The structure was solved by Patterson and Fourier methods[13] and refined by a block-diagonal least-squares procedure (the function minimized is $\sum w(|F_o| - {}^1/_2|F_c|)^2$) with weights obtained from a Cruickshank scheme.[14] The refined parameters included anisotropic thermal factors for Pt, Sn, Cl, and P atoms, isotropic for the others. During the final least-squares cycles the contribution of the hydrogen atoms in their calculated positions (C–H = 1.00 Å; B = 5.0 Å^2) was taken into account but not refined.[15]

Registry No. **4**, 99148-35-3; [PtCl(SnCl$_3$)(**1b**)(PEt$_3$)], 99148-37-5; [PtCl(SnCl$_3$)(**2**)(PEt$_3$)], 79453-27-3; [PtCl(SnCl$_3$)(**3**)(PEt$_3$)], 99148-36-4; *trans*-PtCl$_2$(C$_2$H$_4$)(*p*-ClC$_6$H$_4$^{15}NH$_2$), 99148-38-6; *trans*-PtCl$_2$(C$_2$H$_4$)(*p*-CH$_3$C$_6$H$_4$^{15}NH$_2$), 99148-39-7; *trans*-PtCl$_2$(C$_2$H$_4$)(*p*-ClC$_6$H$_4$^{15}N=C(CH$_3$)$_2$, 99148-40-0; *trans*-PtCl$_2$(C$_2$H$_4$)(*p*-CH$_3$C$_6$H$_4$^{15}N=C(CH$_3$)$_2$, 99148-41-1; [PtCl(SnCl$_3$)(PEt$_3$)]$_2$, 83719-68-0; ^{15}NH$_2$C$_6$H$_4$-*p*-Cl, 24176-54-3; Pt, 7440-06-4; Sn, 7440-31-5; Zeise's salt, 16405-35-9; *p*-toluidine, 106-49-0.

Supplementary Material Available: Tables of bond distances and angles, crystal data and intensity collection parameters, positional and thermal parameters, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(14) Cruickshank, D. W. J. In "Crystallographic Computing"; Ahmed F. R., Ed.; Munksgaard: Copenhagen, 1970.

(15) Scattering factors and the correction for the real part of the anomalous dispersion for Pt, P, Cl, and Sn atoms were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773.

(17) Canziani, F.; Garlaschelli, L.; Malatesta, M. C.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2395.

(18) Conzelmann, W.; Koola, J. D.; Kunze, U.; Strähle, J. *Inorg. Chim. Acta* **1984**, *89*, 147.

(19) Del Pra, A.; Zanotti, G.; Bombieri, G.; Ros, R. *Inorg. Chim. Acta* **1979**, *36*, 121.

(20) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 725.

(21) Porzio, W.; Musco, A.; Immirzi, A. *Inorg. Chem.* **1980**, *19*, 2537.

(22) Canziani, F.; Albinati, A.; Garlaschelli, L.; Malatesta, M. C. *J. Organomet. Chem.* **1978**, *146*, 197.

(23) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C. *Inorg. Chem.* **1975**, *14*, 2653.

(24) Elder, R. C.; Pesa, F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 268.

(25) Russell, D. R.; Tucker, P. A.; Wilson, S. *J. Organomet. Chem.* **1976**, *104*, 387.

(26) Colamarino, P.; Orioli, P. L. *J. Chem. Soc., Dalton Trans.* **1975**, 1656.

(27) Melanson, R.; Rochon, F. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 941.

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Reexamination of the Deuteration of Phenol Catalyzed by an Ortho-Metalated Ruthenium Complex

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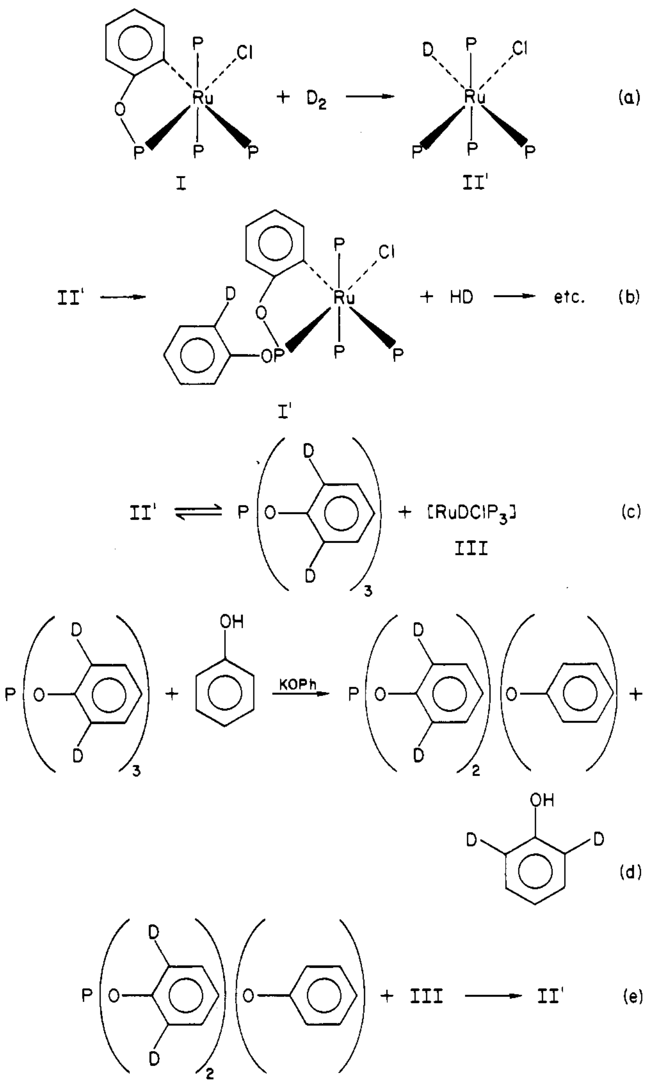
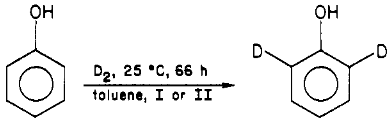
The synthesis of I was reported in 1969[1] (see Scheme I). Complex I reacted with H$_2$ to produce II (or II′ with D$_2$, see Scheme I), in which the ortho-metalated bond is broken.[1] The reaction of I with D$_2$ results in the deuterated analogue of II. In addition, all the ortho positions of the triphenyl phosphite ligands were deuterated.[1]

Scheme I



Complexes I and II were reported to catalyze the ortho deuteration of phenol with D$_2$, eq 1.[1]



(1)

While work in this laboratory confirmed that the reaction of D$_2$ with I resulted in selective ortho deuteration of the phosphite ligands on I, the reaction of eq 1 did not proceed as reported. Deuterium incorporation into phenol was found to be extremely slow when phenol was reacted with I and D$_2$. Phenol ortho deuteration with D$_2$ catalyzed by I was only accomplished by using a transesterification cocatalyst, the details of which reactions are presented here.

Experimental Section

The syntheses of ruthenium complexes[1] were carried out in an argon-filled Vacuum Atmospheres drybox or by utilizing standard Schlenk techniques. Toluene and THF were distilled from purple solutions of sodium benzophenone ketyl. Chloroform was vacuum-transferred from P$_4$O$_{10}$. Mass spectra of gas samples were recorded on a Varian MAT 731 instrument. GCMS were recorded by using a Varian 311A instrument. ^{13}C (20 MHz) and ^{31}P (32.203 MHz) NMR spectra were recorded on a Varian FT-80 NMR spectrometer.

Attempted Phenol Deuteration in Toluene (Eq 1). Run a. Phenol (0.0792 g, 0.84 mmol) and I (0.084 g, 0.061 mmol) were combined in 13 mL of toluene and placed in a 90-mL Fischer-Porter bottle under argon. The mixture was subjected to three freeze/degas/thaw cycles. D$_2$ was added (860 mm, 3.57 mmol) and the contents stirred at ambient temperature for 72 h. The noncondensable gases were analyzed by mass

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[1] Parshall, G. W.; Knoth, W. H.; Shunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990.

[2] Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

0020-1669/85/1324-4433$01.50/0

spectroscopy to obtain a H_2:HD:D_2 ratio of 2.2:19.4:78.4. The calculated ratio, assuming exchange only between D_2 and I, is H_2:HD:D_2 = 2.7:27.4:69.9. The calculated ratio, assuming both phenol and I took part in the exchange with D_2, is H_2:HD:D_2 = 26.6:38.6:44.8.

The solution from run a was reduced in volume by rotary evaporation. The toluene solvent from this reaction showed no deuterium incorporation. Phenol and $P(OPh)_3$ were then vacuum-transferred from the resulting oil. Analysis of the transferred material by GCMS showed phenol, C_6H_5OH (d_0 only), and $P(OPh)_3$ with the following *m/e* (%): 310 (4.8), 311 (18.6), 312 (30.1), 313 (26.2), 314 (13.1), 315 (6.9). GCMS analysis of $P(OPh)_3$ (natural abundance) showed the following *m/e* (%): 310 (61.6), 311 (26.3), 312 (8.1). 313 (2.8), 314 (1.1).

Run b. Phenol (0.326 g, 3.36 mmol) and I (0.327 g, 0.24 mmol), freshly prepared, free of trace phosphite, and from a different batch than in run a, were combined in 30 mL of benzene in a 250-mL Fischer-Porter bottle under argon. This bottle was charged with D_2 (16 psi, 9.78 mmol) and then stirred at ambient temperature for 144 h. The noncondensable gases were analyzed by mass spectroscopy to obtain a H_2:HD:D_2 ratio of 24.4:38.3:37.2. The calculated ratio, assuming exchange only between D_2 and I, is H_2:HD:D_2 = 4.8:34.3:60.9. The calculated ratio, assuming both I and phenol took part in the exchahge with D_2, is H_2:HD:D_2 = 14.8:47.2:38.0. The phenol and $P(OPh)_3$ from this reaction were analyzed by GCMS, which showed the following *m/e* (%): for phenol 94 (82.7), 95 (15.8), 96 (1.5); for $P(OPh)_3$ 310 (0.5), 311 (4.4), 312 (15.9), 313 (24.5), 314 (25.2), 315 (20.5), 316 (7.2), 317 (1.7). GCMS analysis of phenol showed the following *m/e* (%): 94 (91.2), 95 (7.8), 96.0 (1.0). The $^{13}C\{^1H\}$ NMR of the vacuum-transferred material from this run showed normal resonances for phenol, consistent with low deuterium incorporation. The phosphite resonances occur at δ 128.7 (s, para), 123.48 (s, para), and 121.15 (broad, ortho, reduced in intensity due to loss of NOE).

Reaction of 2,6-Dideuteriophenol with I and H_2. Complex I (0.018 g, 0.013 mmol) and phenol-2,6-d_2[3] (0.118 g, 1.23 mmol) were combined in 20 mL of toluene in a 250-mL Fischer-Porter bottle under argon. The bottle was charged with H_2 (14 psi, 9.0 mmol) and the contents stirred at ambient temperature for 66 h. Analysis of the phenol by GCMS showed no loss of the deuterium label from phenol.

Transesterification of $P(OPh)_3$ with *o*-Cresol. $P(OPh)_3$ (1.00 g, 3.22 mmol) and *o*-cresol (0.99 g, 9.17 mmol) were combined in 5 mL of toluene. NaH (0.07 g, 60% in mineral oil, 1.8 mmol) was added and the contents shaken for 5 min. GC analysis indicated a phenol to cresol ratio of 1.0:1.43. Cresol/phenol-containing phosphites were present, $P(OPh)_{3-n}(OC_6H_4CH_3)_n$: $n = 0$ (12.8%), $n = 1$ (38.0%), $n = 2$ (36.6%), $n = 3$ (12.6%). Sodium phenoxide/sodium cresoxide precipitates from toluene solution but not THF. The same ratio of phenol and phosphite products was obtained in THF solvent. The transesterification reaction was also demonstrated by using *o*-ethylphenol in place of *o*-cresol.

Phosphite Exchange with I. Complex I (0.257 g, 0.019 mmol) and $P(p\text{-}OC_6H_4CH_3)_3$ (0.020 g, 0.057 mmol) were combined in 2 mL of $CDCl_3$. Analyis by ^{31}P NMR showed the presence of free $P(OPh)_3$ and $P(p\text{-}OC_6H_4CH_3)_3$ in a ratio of 1.0:0.77. The calculated ratio for complete phosphite ligand exchange between I and tricresyl phosphite is 1.0:0.75. In addition, the resonances for I that are normally well resolved are broadened to complex multiplets also consistent with random exchange of phosphite ligands.

Synthesis of $[(p\text{-}CH_3C_6H_4O)_3P]_3(p\text{-}CH_3C_6H_4O)_2\overline{POC_6H_3CH_3Ru}Cl)$[5] (I′). Complex I′ was made in a fashion analogous to the preparation of I with the substitution of $P(OPh)_3$ by $P(p\text{-}OC_6H_4CH_3)_3$. $RuHCl(PPh_3)_3$[4] (1.05 g, 1.1 mmol) was suspended in 40 mL of degassed hexane. $P(p\text{-}OC_6H_4CH_3)_3$ (3.5 mL) was added and the mixture refluxed for 1 h. An oily white solid mass was purified by chromatography (30 × 1 cm) on Florisil by elution with hexane (125 mL), a 50:50 hexane:diethyl ether mixture (100 mL), and then with diethyl ether. The ether fraction contained I′, which was obtained as colorless crystals upon cooling; mp 191 °C. Anal. (Schwarzkopf Microanalytical Laboratory) Calcd for $C_{84}H_{83}ClP_4O_{12}Ru$: C, 65.33; H, 5.38; P, 8.04. Found: C, 65.59; H, 5.60; P, 7.83. ^{31}P NMR ($CDCl_3$): δ 153.2 (d of t, J = 43.4, 61.7 Hz), 121.3 (d of t, J = 43.6, 50.1 Hz), 113.6 (d of d, J = 61.7, 49.9 Hz); cf. for I δ 155.2 (d of t, J = 43, 61.5 Hz), 123.9 (d of t, J = 41.5, 50.5 Hz), 116.5 (d of d, J = 61.5, 49 Hz).

Phosphite Exchange with I′. Complex I′ (0.053 g, 0.034 mmol) and $P(OPh)_3$ (0.044 g, 0.14 mmol) were combined in 2 mL of $CDCl_3$. ^{31}P NMR analysis indicated $P(OPh)_3$ and $P(p\text{-}OC_6H_4CH_3)_3$ in a ratio of 0.64:1.0. The calculated ratio of complete phosphite ligand exchange between I′ and $P(OPh)_3$ is 1.03:1.0.

Table I. Percent Deuterium Incorporation in $P(OPh)_3$ from Eq 1

	run a[a]	run b[b]		run a[a]	run b[b]
d_0	5.9	0.6	d_4	10.0	25.0
d_1	21.7	5.3	d_5	5.7	19.2
d_2	31.6	18.5	d_6		4.1
d_3	25.1	26.1	d_7		0.7

[a] See Experimental Section for conditions. [b] Percent deuterium incorporation in phenol run b: d_0, 88.3; d_1, 10.0; d_2, 1.7.

Phenol Deuteration. I (0.076 g, 0.055 mmol), phenol (0.061 g, 0.65 mmol), and KOPh (0.068 g, 0.52 mmol) were combined in 10 mL of THF in a 90-mL Fischer-Porter bottle. The contents were degassed, pressurized with D_2 (30 psi, 7.1 mmol), and then stirred for 75 h at ambient temperature. Analysis by ^{13}C NMR after hydrolysis with 0.1 M HCl showed phenol with its ortho resonance reduced in intensity due to lowered NOE, consistent with ortho deuteration. EIMS and GCMS analysis confirmed the formation of phenol-d_2.

Control Experiment. Phenol (0.061 g, 0.65 mmol) and KOPh (0.061 g, 0.52 mmol) were combined in 10 mL of THF in a 90-mL Fischer-Porter bottle. The contents were degassed, pressurized with D_2 (30 psi, 7.1 mmol), and then stirred for 114 h at ambient temperature. Analysis by ^{13}C NMR after hydrolysis with 0.1 M HCl showed normal resonances for phenol (no deuterium incorporation). Analysis by GCMS confirmed this result.

Results and Discussion

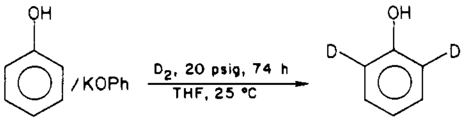
Reexamination of Equation 1. The product, phenol-2,6-d_2, of eq 1 was inferred by the previous workers from mass spectroscopy. The ratio H_2:HD:D_2 was measured, and this measurement suggested that phenol was dideuterated. In the present work, it was found that measurement of ratios of H_2:HD:D_2 was not a reliable method of establishing phenol deuteration. Essentially, no deuterium incorporation into phenol was observed under conditions in which the gas ratios suggested formation of deuterated phenol (the H_2:HD:D_2 ratios agreed with the ratios reported for this reaction). For instance, reaction 1 was run for 144 h. The H_2:HD:D_2 ratio was consistent with extensive ortho deuteration of I and phenol; however, Table I shows that there was only 11.7% deuterium incorporation into phenol. Table I shows that extensive deuterium incorporation into $P(OPh)_3$ took place. These results were confirmed by $^{13}C\{^1H\}$ NMR, which had normal resonances for phenol but which showed that the resonance for the ortho carbon of $P(OPh)_3$ at δ 121.15 is broadened and reduced in intensity due to lowered NOE.

When 2,6-dideuteriophenol was reacted with I and H_2 in toluene at 25 °C, no loss of deuterium label from phenol was detected by mass spectroscopy of the phenol. None of the solvents from these reactions was enriched in deuterium.

A mechanism for reaction 1 in terms of reversible loss of phosphite from Ru and transesterification of substituted and unsubstituted phenol with phosphite has recently been suggested.[2]

The transesterification reaction between triphenyl phosphite and phenol is not facile in toluene or THF at room temperature. However, a facile exchange occurred if NaH was added to a THF solution of *o*-cresol or *o*-ethylphenol and triphenyl phosphite.

Phenol ortho deuteration was accomplished by reacting phenol with D_2 in THF in the presence of I and KOPH (eq 2).



(2)

The presence of KOPh facilitates the exchange between phenol and triphenyl phosphite (eq 2). The amount of deuterium incorporation should be compared to that shown in Table I. This reaction represented catalytic ortho deuteration of phenol.

When I and *p*-cresol were combined in chloroform or THF, no cresol incorporation into the phosphites of I was noted. In addition, if I and $NaOC_6H_4CH_3$ were combined in THF, no phenol was observed. This observation is consistent with the fact that transesterification occurred only between *free* triphenyl phosphite

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[3] Tashiro, J.; Iwasaki, A.; Fukata, G. *J. Org. Chem.* **1978**, *43*, 196.

[4] Hallman, P. S.; McGarvey, B. P.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

[5] Compound I′ has been reported: Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 639.

and cresoxide but not *bound* triphenyl phosphite. When I and $P(OC_6H_4CH_3)_3$ were combined in $CDCl_3$, ^{31}P NMR and GC analysis showed that phosphite exchange was facile at room temperature.

The complete phenol deuteration reaction catalyzed by I is shown in Scheme I.

Steps a and b were shown previously[1] and are confirmed by the present work. Complete ortho deuteration of the triphenyl phosphite ligands of II was shown by mass spectroscopy and ^{13}C NMR. Facile exchange of triphenyl phosphite (the equilibrium of step c), was shown by ^{31}P NMR. Intermediate III is probably a five-coordinate Ru(II) complex for which there is ample precedence.[6] The transesterification reaction on free triphenyl phosphite was demonstrated by ^{31}P NMR and GCMS.

These results confirm that D_2 selectively deuterates the ortho positions on the triphenyl phosphite ligands of I. Catalytic deuteration of phenol was greatly accelerated only by the addition of a transesterification cocatalyst. This study represents the first example of catalysis via an ortho metalated complex.[2,7,8] Extension of this work to other insertable groups (other than D_2) is under study.

Acknowledgment. Hans Grade and Steve Dorn are acknowledged for their skilled mass spectroscopic analysis. Cindy Herderich is thanked for her help in preparation of the manuscript. George Parshall, Du Pont, is thanked for reading a preprint of the manuscript and for providing some helpful suggestions.

Registry No. I, 25839-18-3; I′, 99212-16-5; $RuHCl(PPh_3)_3$, 55102-19-7; $P(OPh)_3$, 101-02-0; $P(OPh)_2(O_6H_4CH_3)$, 99128-51-5; $P(OPh)(OC_6H_4CH_3)_2$, 99128-52-6; $P(OC_6H_4CH_3)_3$, 2622-08-4; KOPh, 100-67-4; D_2, 7782-39-0; $P(p\text{-}OC_6H_4CH_3)_3$, 620-42-8; *o*-cresol, 95-48-7; phenol-d_2, 64045-88-1; phenol, 108-95-2.

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(6) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Chapter 32.3.

(7) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.

(8) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.

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Electrochemical Studies of Cerium Chelate Complexes[†]

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Lanthanides tend to form trivalent ions except in cases where electronic configurations corresponding to a rare gas (Xe) or a half-filled or filled 4f subshell stabilize di- or tetravalent ions. Cerium is well-known for having a tetravalent ion with the Xe electron configuration, and the facile conversion of Ce(IV) to Ce(III) is the basis for numerous redox-related reactions. Although chelation often has dramatic effects on the redox potentials of transition-metal ions, there are no systematic studies of chelation effects on the redox potentials of lanthanides. Our results show that shifts in the redox potential of about 250 mV can be produced by using various substituted SALEN, *N*,*N*′-ethylenebis(salicylideneamine), ligands. Even greater changes in the Ce(III)/Ce(IV) couple can be produced by changing the chelating ligand.

Experimental Section

All chemicals were reagent grade and were used as received except for tetrabutylammonium perchlorate (TBAP), which was recrystallized from ethyl acetate and dried at 50 °C under vacuum. $Ce(DAPSC)_2(ClO_4)_3{\cdot}3H_2O$ was synthesized as described previously.[1]

Electrochemical cells were of the three-electrode type. The working electrode was a Corning No. 476060 platinum disk with area 0.357 cm^2 for cyclic voltammetry (CV) and platinum gauze for controlled-potential coulometry (CPC). The counter electrode was a spiral of platinum wire for CV and platinum gauze for CPC. The reference electrode was Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) against which all the potentials were measured. The potentials are reported vs. SCE to facilitate comparisons with literature values. Instrumentation was from Princeton Applied Research and has been described previously.[2] Spectrophotometric grade acetonitrile containing TBAP (0.1 M) was used as electrolyte for all measurements.

Analyses were performed by the University of Florida Microanalytical Services. Infrared spectra were recorded on a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer.

The complexes were synthesized by the addition of an ethanolic (200 proof) solution of ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, to an ethanolic solution of the ligand and triethylamine (a 1:2 mole ratio). The dianionic ligands used were SALEN (*N*,*N*′-ethylenebis(salicylideneamine)), 5-BrSALEN (*N*,*N*′-ethylenebis(5-bromosalicylideneamine)), 5-MeOSALEN, (*N*,*N*-ethylenebis(5-methoxysalicylideneamine)), and SALOPHEN, (*N*,*N*′-phenylenebis(salicylideneamine)). The $Ce(SALEN)_2$ complex can also be prepared from a cerium(III) perchlorate solution, salicylaldehyde, and ethylenediamine.

The precipitated complex was filtered, washed with ethanol and ether, and air-dried. Infrared spectra indicated the presence of ligand and the absence of nitrate. Satisfactory analyses were obtained on samples recrystallized from acetonitrile. Found (calcd) data are as follows. $Ce(SALEN)_2$: C, 57.07 (57.13); H, 4.03 (4.19); N, 8.16 (8.33). $Ce(5\text{-}BrSALEN)_2{\cdot}0.5H_2O$: C, 38.85 (38.54); H, 2.40 (2.53); N, 5.63 (5.62). $Ce(5\text{-}MeOSALEN)_2{\cdot}1.5H_2O$: C, 53.98 (53.75); H, 4.42 (4.64); N, 6.92 (7.37). $Ce(SALOPHEN)_2{\cdot}0.5H_2O$: C, 61.90 (62.09); H, 3.70 (3.26); N, 7.66 (7.24).

Results and Discussion

Synthesis. Cerium complexes of SALEN, both protonated and deprotonated, have been prepared previously by at least two groups.[3,4] We have found that the complexes with protonated SALEN can be prepared in near-quantitative yield with the addition of triethylamine to assist in proton removal. Several attempts to prepare $Ce(SALEN)_2$ without the addition of base did indeed lead to the desired product, but yields were exceedingly low and the product was impure. Infrared spectra suggest that the impurity was a complex containing protonated SALEN and nitrate, probably $Ce(H_2SALEN)_2(NO_3)_4{\cdot}H_2O$. The preparation of complexes with the substituted SALEN ligands proceeded readily in the presence of triethylamine. Thus, the method is a general one for the preparation of deprotonated SALEN complexes with cerium and may be applicable to other tetravalent metals and ligands as well.

Electrochemistry. The redox potential of cerium in a number of complexes was measured. Quasi-reversible charge-transfer processes were observed for $Ce(SALEN)_2$ and its derivatives and analogues, for $Ce(DAPSC)_2(ClO_4)_3{\cdot}3H_2O$,[1] and for an as yet uncharacterized complex with *o*-aminophenol. The cerium(III) complexes of 2,6-diacetylpyridine bis(acetylhydrazone) (DAPAH)[5] and 2,9-diformyl-1,10-phenanthroline disemicarbazone (PHENSC)[6] were examined, but we observed no oxidation wave for these complexes.

SALEN Derivatives. This is the first investigation of the electronic effects of a ligand on the redox potential of a lanthanide ion. Four Ce(IV) complexes with dinegative tetradentate ligands formed from salicylaldehyde and its derivatives and either ethylenediamine (SALEN) or *o*-phenylenediamine (SALOPHEN) were examined by using cyclic voltammetry. Figure 1 shows a typical cyclic voltammogram for $Ce(SALEN)_2$. Table I lists

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(1) Thomas, J. E.; Palenik, G. J. *Inorg. Chim. Acta* **1980**, *44*, L303.

(2) Wester, D. W.; Sullivan, J. C. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2919.

(3) Bullock, J. I.; Tajmir-Riahi, H.-A. *Inorg. Chim. Acta* **1980**, *38*, 141.

(4) Dutt, N. K.; Nag, K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2493.

(5) Palenik, R. C., private communication.

(6) Aghabozorg, H.; Palenik, R. C.; Palenik, G. J., unpublished results.

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