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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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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[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38.

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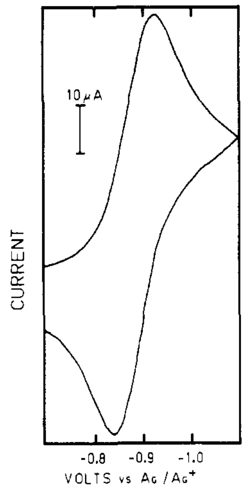

Figure 1. Cyclic voltammogram of Ce(SALEN)$_2$.

Table I. Electrochemical Data for SALEN Complexes

reaction	*E*, V vs. SCE	ref
$V(SALEN)^{2+} + e^- \rightarrow V(SALEN)^+$	-0.480	12
$VO(SALEN)^+ + e^- \rightarrow VO(SALEN)$	+0.380	12
$Mn(SALEN)^+ + e^- \rightarrow Mn(SALEN)$	-0.265	9
$Fe(SALEN)^+ + e^- \rightarrow Fe(SALEN)$	-0.622	13
$Co(SALEN) + e^- \rightarrow Co(SALEN)^-$	-1.15	14
$Co(SALEN)^+ + e^- \rightarrow Co(SALEN)$	+0.158	15
$Ni(SALEN) + e^- \rightarrow Ni(SALEN)^-$	-1.88	16
$Ni(SALEN)^{2+} + 2e^- \rightarrow Ni(SALEN)$	+1.03	17
$Cu(SALEN) + e^- \rightarrow Cu(SALEN)^-$	-1.21	18
$Ce(SALEN)_2 + e^- \rightarrow Ce(SALEN)_2^-$	-0.676	this work
$Ce(5\text{-}BrSALEN)_2 + e^- \rightarrow Ce(5\text{-}BrSALEN)_2^-$	-0.521	this work
$Ce(5\text{-}MeOSALEN)_2 + e^- \rightarrow Ce(5\text{-}MeOSALEN)_2^-$	-0.776	this work
$Ce(SALOPHEN)_2 + e^- \rightarrow Ce(SALOPHEN)_2^-$	-0.529	this work

formal potentials that were measured in acetonitrile using ferrocene (+0.076 V) as an internal standard. Charge-transfer rate constants, K_s, were calculated by the method of Nicholson[7] using diffusion coefficients and peak potential separations calculated from cyclic voltammograms from 100 to 5 mV/s. The rate constants ranged from 0.012 to 0.059, well within the range for quasi-reversible electron transfer. The number of electrons transferred was measured as 1.00 ± 0.02 by controlled-potential coulometry for the SALEN complex. Comparison of peak currents for the complexes and for ferrocene then was used as an indication that the charge-transfer processes for all the complexes involved one electron.

A variation of more than 250 mV, from -0.521 to -0.776 V, in the formal potential of the Ce(IV)-SALEN-type complexes was observed. This range is similar to that reported for studies involving the transition metals Mo and Mn with similar ligands.[8-11] The trend observed for the cerium complexes is that Ce(5-BrSALEN)$_2$ is reduced at a potential more positive than that for Ce(SALEN)$_2$, which in turn is reduced at a more positive potential than Ce(5-MeOSALEN)$_2$. This trend reflects the effect of the electron-withdrawing ability of the substituents on salicylaldehyde. A linear correlation between the Hammett σ_p parameters, a measure of electron-withdrawing ability, and redox potential is observed. Comparison of the different classes of ligand, SALEN (-0.676 V) vs. SALOPHEN (-0.529 V), also shows a shift of the formal potential. In the case of SALOPHEN, the negative charge on the donor oxygen atoms can be delocalized over the entire ligand. As a result, the Ce(IV) ion sees less electron density and is easier to reduce. Similar trends and arguments were given for the Mo and Mn complexes.

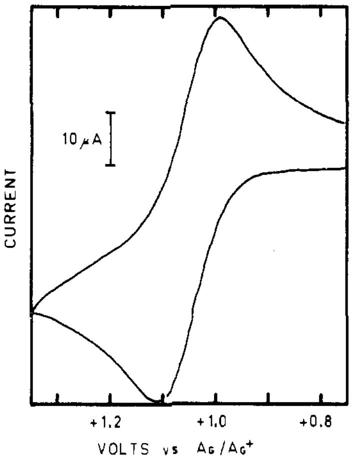

Figure 2. Cyclic voltammogram of Ce(DAPSC)$_2$(ClO$_4$)$_3$.

In the case of the lanthanides the metal ion orbitals are expected to interact very weakly with the ligand orbitals. However, the Ce(IV) ion should show stronger interactions than the usual +3 lanthanide ion. The fact that the shift in formal potentials is of the same magnitude as that found for Mo and Mn suggests that electron transfer involves orbitals that are predominantly ligand in character. Therefore, while substituent effects may be useful for fine tuning the redox potential of a Ce(IV) complex, major variations in the redox potential require a new class of ligands. A similar conclusion was reached for the transition metals Mo and Mn.

Relationship to Other SALEN Complexes. The planar, tetradentate, dinegative nature of SALEN makes it an attractive ligand for studies of transition-metal complexes where octahedral or square-planar geometry is quite common. Electrochemical studies of SALEN complexes with first-row transition metals have yielded the redox potentials listed in Table I. Inspection of Table I reveals that the reduction potential of Ce(SALEN)$_2$ most closely equals that of Fe(SALEN)$^+$. Thus, SALEN greatly stabilizes Ce(IV) as shownby the much more negative shift in reduction potential when compared to the aqueous system (Ce(IV)-(III), +1.20 V vs. SCE; Fe(III)-(II), +0.53 V vs. SCE).

Diacetylpyridine Derivatives and Other Complexes. The disemicarbazone of 2,6-diacetylpyridine, DAPSC, forms a complex with cerium(III) in which two pentadentate ligands surround the central metal.[1] The complex is electrochemically active, showing a quasi-reversible charge-transfer process at +1.049 V vs. Ag/Ag$^+$. A typical cyclic voltammogram appears in Figure 2. The charge-transfer rate constant is 2.9×10^{-3} cm/s. The formal potential for this complex is at a much more positive value than those for the SALEN complexes, a shift of almost 2 V. The reason for this shift may be connected with either the difficulty involved in electron-transfer oxidation from the enclosed Ce(III) ion or the inability of DAPSC to supply sufficient electron density to stabilize a Ce(IV) complex. With respect to the latter point, ligands such as DAPAH and PHENSC, which are even less electron donating than DAPSC, show no oxidation waves up to the limit of solvent decomposition. On the other hand, *o*-aminophenol, a very electron-rich ligand, forms a complex with Ce(IV) that is reduced in a quasi-reversible charge-transfer process

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at −1.251 V. This potential is even more negative than that for the SALEN complexes. Since this complex is as yet uncharacterized, further statements regarding the effect of the electron-donating ability of *o*-aminophenol are not possible at this time.

Registry No. Ce(SALEN)$_2$, 98839-38-4; Ce(SALEN)$_2^-$, 98839-41-9; Ce(5-BrSALEN)$_2$, 98839-39-5; Ce(5-BrSALEN)$_2^-$, 98839-42-0; Ce(5-MeOSALEN)$_2$, 98839-40-8; Ce(5-MeOSALEN)$_2^-$, 98839-43-1; Ce(SALOPHEN)$_2$, 88178-02-3; Ce(SALOPHEN)$_2^-$, 98839-44-2; Ce(DAPSC)$_2$(ClO$_4$)$_3$, 74841-15-9.

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Preparation of a Novel P–P-Bonded Diphosphine

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Both steric bulk and electronic donor/acceptor capability of tertiary phosphine ligands are known to exert quite drastic regiochemical and stereochemical consequences in reactions catalyzed by organometallic complexes. A balance of these steric and electronic factors is important, for example, in such reactions as the oxo or hydroformylation reaction. In general, phosphine ligands with a wide range of steric bulk are known.[3] The donor/acceptor nature of the phosphine is largely limited by the electronic properties of the organic groups bonded to phosphorus. However, there appear to be few or no examples of phosphines in which both the electronic and steric properties were designed and successfully incorporated into the ligand. Control of steric effects in phosphine ligands is well-known,[3] but electronic properties such as basicity are usually indirectly determined by the properties of the groups attached to the phosphorus atom, e.g., aryl vs. alkyl. Attempts to prepare a phosphine ligand with a strongly electron-withdrawing substituent and steric bulk similar to that of a strong donor ligand in which the phosphorus atom is an integral part of a bicyclic ring structure led instead to formation of a P–P-bonded diphosphine[4,5] by rather novel chemistry.

We developed a method to introduce alkyl groups based on quaternization of secondary phosphines with alkyl halides. While this route proved successful for prepn. of tertiary phosphines from alkyl bromides and halides, extension of the reaction to perfluoroalkyl iodides led to formation of P–P-bonded diphosphines by an unusual P–CF$_2$R cleavage reaction. In this note we discuss this unusual reaction and report some interesting synthetic chemistry of the bicyclic phosphine system. Results of cobalt-catalyzed oxo reactions using the diphosphine ligand are also reported.

Experimental Section

All reactions were conducted in a Vacuum Atmospheres Dri-Lab or with conventional vacuum and Schlenk techniques. Solvents were dried and deoxygenated over sodium/benzophenone ketyl. Routine reaction product analysis was obtained by VPC with a $^1/_8$ in. × 1 ft OV-101 column (temperature program: 100–240 °C at 10 °C/min, 4 min initial hold) with comparison to known compounds. Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 299 spectrophotometer. ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer at 32.203 MHz operating in the Fourier transform mode, and ^{1}H NMR spectra were obtained with the same instrument. Phosphorus spectra were measured with positive chemical shifts taken as downfield from phosphoric acid. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The bicyclic phosphines and diphosphines described in this paper are extremely air-sensitive, and when care is not taken in handling, air-oxidation products can be seen by VPC.

HPC_8H_{14}. This preparation is similar to that previously described.[7] Two isomers of HPC_8H_{14} are obtained, i.e., 9-phosphabicyclo[4.2.1]nonane and 9-phosphabicyclo[3.3.1]nonane. The synthesis uses phosphine, PH_3, which is highly flammable and toxic, and 1,5-cyclooctadiene, which has a nauseating odor. Appropriate precautions should be taken when handling multigram quantities of phosphine. Careful pressure checking of the autoclave prior to reaction, continual monitoring for phosphine gas, and an isolated, well-ventilated reaction area are highly recommended. The reaction was carried out in an evacuable autoclave system with pressure-release devices and exterior vents. Phosphine was condensed into the autoclave from weighing bombs by cooling with dry ice.

Degassed 1,5-cyclooctadiene (128 mL), hexane (64 mL), and a radical initiator, Vazo-64 (2,2′-azobis(2-methylpropionitrile)) (7.5 g) were charged into the autoclave, and following N_2 purge the phosphine (35 g) was added. The reactor was carefully heated to 77–80 °C for 5 h (above 80 °C, reaction rates were excessive). After cooling and purging with N_2, the viscous liquid products were drained into a large sublimation apparatus. Excess solvent was evaporated, and the solid white product was obtained by vacuum sublimation at 25 °C to a −78 °C cold finger; yield 73.2 g. IR: ν_{P-H}, 2266 cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): δ −49.5 (s), −55.7 (s) with respective relative intensities of 1:2 for the two isomers. ^{31}P NMR (undecoupled, C_6D_6): overlapping doublets of triplets, $^1J_{P-H}$ = 190 Hz, $^2J_{P-H}$ = 28 Hz. The gas chromatogram of HPC_8H_{14} showed two compounds in a 1:2 ratio corresponding to 1,4- and 1,5-addition of PH_3 to cyclooctadiene, in agreement with ref 7.

$C_6H_{13}PC_8H_{14}$. Quaternization. A solution of 15.0 g (0.106 mol) of HPC_8H_{14} and 17.43 g (0.106 mol) of hexyl bromide in 50 mL of octane was placed in a vacuum reaction bulb. The contents were degassed at −78 °C and then heated at 70 °C. A white solid formed, which after 6 days was collected by filtration, washed with octane, and dried under vacuum; yield 23.6 g, 72.7%. Anal. Calcd for $C_{14}H_{28}BrP$: C, 54.73; H, 9.18; Br, 26.01; P, 10.08. Found: C, 56.52; H, 9.45; Br, 24.64; P, 9.51. This is consistent with contamination by 2.6 wt % of the starting material $C_8H_{15}P$. IR: ν_{P-H}, 2310 cm^{-1}. ^{31}P{^{1}H} NMR (CD_3CN): two overlapping singlets, δ 264.8, 262.0 (ratio 1:0.28). ^{31}P NMR (undecoupled, CD_3CN): broad doublet, $^1J_{P-H}$ = 517 Hz.

Deprotonation. To a suspension of 39.1 g (0.128 mol) of the quaternary salt in 50 mL of toluene was added 6.13 g (0.128 mol) of 50% NaH/50% mineral oil dispersion (previously washed with hexane). Gas evolution occurred immediately. The reaction mixture was degassed at −78 °C with further periodic degassing over 4 days. The solid was then filtered, suspended in toluene, and treated again with NaH. Both toluene-soluble fractions were combined and filtered. VPC analysis showed the presence of a trace of HPC_8H_{14} and a major component presumed to be $C_6H_{13}PC_8H_{14}$, previously prepared by us according to another method.[7] Purification was achieved by vacuum distillation at ca. 15 mmHg. The fraction collected between 145 and 155 °C was retained; yield 10.2 g (92.6% pure by VPC), 32.6%. Only a trace of a second isomer was seen by VPC. ^{31}P{^{1}H} NMR (C_6D_6): δ −32.2 (s).

Reaction of HPC_8H_{14} with C_3F_7I. Quaternization. HPC_8H_{14} (9.38 g, 0.066 mol) and 20.0 g of C_3F_7I (0.068 mol) were allowed to react according to the procedure used for hexyl bromide. A white solid was obtained, which was washed with pentane and dried under vacuum; yield 17.36 g. Anal. Calcd for a 50% mixture of $C_{16}H_{29}IP_2$ and $C_{16}H_{28}I_2P_2$: C, 40.61; H, 6.07; P, 13.09. Found: C, 41.32; H, 6.48; P, 13.83; F, 1.08. Analyses of a replicate reaction showed variable amounts of fluorine from 1 to 6%. ^{31}P{^{1}H} NMR (CD_3CN): AB quartet, δ 239.9, J_{P-P} = 323 Hz; AB quartet, δ 220.9, J_{P-P} = 389 Hz; singlet, δ 297.5 (ratio 8.9:1.5:1). ^{31}P NMR (undecoupled, CD_3CN): singlet at δ 297.5 became a doublet, $^1J_{P-H}$ = 478 Hz. We were unable to obtain an acceptable IR spectrum.

Deprotonation. The salt from the quarternization reaction was deprotonated at room temperature according to the procedure used for the hexyl bromide reaction. The crude product was purified by three successive crystallizations from toluene cooled to −40 °C; yield 6.4 g (55% based on $C_{16}H_{28}P_2$). Anal. Calcd for $C_{16}H_{28}P_2$: C, 68.08; H, 9.99; P, 21.94. Found: C, 68.04; H, 9.97; P, 20.73; F, 0.02. ^{1}H NMR (C_6D_6): 1.86 (overlapping CH_2 and CH resonances). ^{31}P{^{1}H} NMR (C_6D_6) (Figure 1): δ −27.2 (AB quartet, J_{P-P} = 180 Hz), −48.0 (s).

Reaction of $P(C_8H_{14})^-$ Anion with Alkyl Halides. To a chilled (0 °C) solution of 7.1 mL of 2.5 M butyllithium (0.018 mol) in 30 mL of diethyl ether under argon was added dropwise a solution of 2.5 g (0.018 mol) of HPC_8H_{14} in ether. The solution turned pale yellow, and a white solid

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