350–220 nm. The solid salt is stable for months when stored at −15 °C, and at room temperature it is stable for at least a few days.

Potentiometric Measurements. At 25 °C normal titrations of aqueous solutions of *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$ with base (or acid) could be made. At 34.5 °C the equilibration reactions between the monools and the diol made such a procedure unreliable, and each pH measurement was made on freshly prepared solutions. Thermostated ca. 10^{-2} M solutions of *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$ in 1 M $NaClO_4$ and the appropriate amount of 0.1 M $HClO_4$, 0.9 M $NaClO_4$ or 0.1 M NaOH, 0.9 M $NaClO_4$ were prepared as quickly as possible. Reliable readings on the pH meter could be obtained about 30 s after the time of mixing. The measurements were continued over a period of 10 min, and the pH at the time of mixing was determined by linear extrapolation that typically showed $\Delta(pH)/\Delta(min) \approx 0.02$. The definition $pH = -\log [H^+]$ was employed throughout, and concentration pH standards were made in the salt medium in question. The parameters given in Table II were calculated from measurements at 25 and 34.5 °C.

Spectra and Treatment of Spectral Data. Pseudo-first-order rate constants, k_{obsd}, and activation parameters were calculated as described previously.[2,4-6] The k_{obsd} values were calculated from absorbances measured at two or three of the wavelengths: λ = 300, 250, and 240 nm.

In all kinetic runs the hydrogen ion concentration changed slightly. These changes were generally about 1–3%, although in experiments with low initial $[H^+]$ changes of up to 8% were calculated (eq 1 and 3). However, the error introduced by this variation is very small, since at low $[H^+]$ the dependence of k_{obsd} on $[H^+]$ is small. For each experiment, the hydrogen ion concentrations at t_0, $[H^+]_0$, and equilibrium, $[H^+]_\infty$, were calculated and the values $[H^+] = {}^1/_2([H^+]_0 + [H^+]_\infty)$ were then used in the subsequent calculations.

The calculations of K_1 were based on molar absorbances of solutions of pure diol, ϵ_D, pure monool, ϵ_M, and the equilibrium solution, ϵ_∞, measured at 10 wavelengths in the wavelength region λ = 240–280 nm and using the equation $K_1 = (\epsilon_D - \epsilon_\infty)K_{a1}/(\epsilon_\infty - \epsilon_M)([H^+] + K_{a1})$.

Using the values for K_{a1} determined potentiometrically (Table II), values of K_1 at 25 and 34.5 °C were then calculated from measurements made on solutions with $[HClO_4] = 10^{-3}$, 5×10^{-4}, and 10^{-4} M, respectively.

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Optical Resolution of "Weakly Chiral" P(OPh)(OC_6H_4-*p*-Cl)(OC_6H_4-*p*-Me)

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The first resolution of an enantiomeric phosphorus triester, namely P(OPh)(OC_6H_4-*p*-Cl)(OC_6H_4-*p*-Me) (**1**), is reported. Compound **1** is remarkably stable to substituent exchange when pure. The unusually distant seat of chirality from the phosphorus appears to have interesting consequences on some chirality-dependent phenomena at this atom.

Whereas enantiomers of PRR′R″ molecules tend to be stable to racemization via substituent exchange, those of the type RPhPER (E = S, O, NH),[2] PhP(OEt)($OZMe_3$) (Z = Si, Sn),[3] and MeP(OMe)(O-*i*-Pr)[4] are not. In view of the importance of a variety of chiral phosphorus compounds as ligands in transition-metal catalysts in asymmetric syntheses[5] and the potentially strong role of phosphorus chirality in the cyclophosphamide class of antitumor drugs[6] and in membrane phospholipids,[7] the separation of enantiomers of esters of the type P(OR)(OR′)(OR″)[8,9] is a worthy goal. Herein is reported for the first time the enantiomeric resolution of such a system, namely P(OPh)(OC_6H_4-*p*-Cl)(OC_6H_4-*p*-Me) (**1**).

Compound **1** is interesting in several respects. Although syntheses of compounds of the type P(OPh)(OAr′)(OAr″) have been reported before,[8] these procedures in our hands produced only mixtures of up to nine of the possible ten esters attainable by the exchange of OAr groups, as shown by ^{31}P NMR spectroscopy. As seen in reaction 1, the 51% yield of (±)-**1** formed

$$\mathrm{PhOPCl_2} \xrightarrow[\substack{\mathrm{HOC_6H_4\text{-}p\text{-}Cl}\\ 2\mathrm{NEt_3}}]{\mathrm{HOC_6H_4\text{-}p\text{-}Me}} \underset{(\pm)\text{-}\mathbf{1},\ 51\%}{\mathrm{P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)}} + \underset{28\%}{\mathrm{P(OPh)(OC_6H_4\text{-}p\text{-}Cl)_2}} + \underset{21\%}{\mathrm{P(OPh)(OC_6H_4\text{-}p\text{-}Me)_2}} \quad (1)$$

under the mild conditions employed here is approximately that expected from random attack of $PhOPCl_2$ by addition of a mixture of two phenols in the first step. Similar yields are obtained when (±)-**1** is made by treating *p*-$MeC_6H_4OPCl_2$ or *p*-Cl-$C_6H_4OPCl_2$ with an equimolar mixture of the other two phenols. By contrast, when sequential addition of the phenols in either order to $PhOPCl_2$ was carried out (as per literature reports[8]), ^{31}P NMR analysis indicated only 12–15% yields of (±)-**1** in the reaction mixture and correspondingly higher yields of the other two products shown in reaction 1. Interestingly, however, rapid flame distillation of such a mixture of esters brought the yield of (±)-**1** up to ca. 50%. It is interesting that sequential addition of the phenols to *cis*-$I_2Pt[P(OPh)Cl_2]_2$, which is presumably formed as an intermediate in the one-pot synthesis of *cis*-$Cl_2Pt(\mathbf{1})_2$ in reaction 2, does lead

$$\mathrm{PhOPCl_2} \xrightarrow[\substack{2.\ \mathrm{HOC_6H_4\text{-}p\text{-}Me}\\ 3.\ \mathrm{HOC_6H_4\text{-}p\text{-}Cl}}]{1.\ \textit{cis}\text{-}\mathrm{Cl_2Pt(NCPh)_2}} \textit{cis}\text{-}\mathrm{Cl_2Pt[(\pm)\text{-}1]_2} \quad (2)$$

to a 51% yield of this complex (as an *R,R*, an *R,S*, and an *S,S* mixture) in which **1** is coordinated. A second remarkable property of triester (±)-**1** is that it is quite stable when pure,[10] showing evidence of exchange in the ^{31}P NMR spectrum only after 3 days in $(CD_3)_2CO$ at room temperature. Even after a neat sample is heated for 1.5 h at 100 °C, 88% of (±)-**1** remains. Third, in the enantiomers (+)-**1** and (−)-**1** obtained via Scheme I, the seat of

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(2) Omelanczuk, J.; Mikolajcyk, M. *J. Am. Chem. Soc.* **1979**, *101*, 7292. Krawiecka, B.; Skrzypczynski, Z.; Michalski, J. *Phosphorus* **1973**, *3*, 177. Mikolajczyk, M.; Drabowicz, J.; Omelanczuk, J.; Fluck, E. *J. Chem. Soc., Chem. Commun.* **1975**, 382. Lakshmikantham, M. V.; Cava, M. P.; Garito, A. F. *J. Chem. Soc., Chem. Commun.* **1975**, 383. Horner, L.; Jordan, M. *Phosphorus Sulfur* **1980**, *8*, 235.

(3) Vande Berg, G. R.; Platenburg, D. H. J. M.; Benschop, H. P. *J. Chem. Soc., Chem. Commun.* **1971**, 606.

(4) Horner, L.; Balzer, W. D. *Tetrahedron Lett.* **1965**, 1157.

(5) See, for example: Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. Eliel, E. L., Otsuka, S., Eds. "Asymmetric Reactions and Processes in Chemistry"; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 185.

(6) For a recent review, see: Stec, W. J. *Organophosphorus Chem.* **1982**, *13*, 145.

(7) Tsai, M.-D.; Jiang, R.-T.; Bruzik, K. *J. Am. Chem. Soc.* **1983**, *105*, 2478.

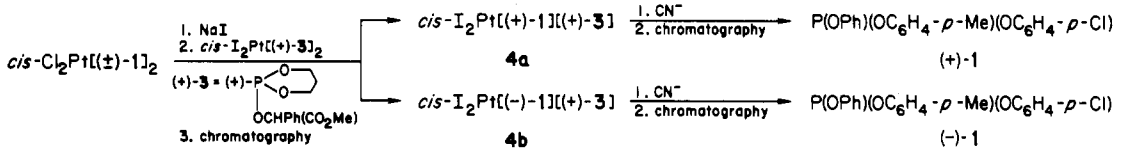
(8) Gerrard, W.; Hudson, H. R. In "Organophosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1973; Vol. 5, p 177 and references therein.

(9) After the present work was completed, a report appeared on the synthesis of racemic P(OMe)(O-*t*-Bu)(O-c-C_5H_9): Copper, D.; Trippett, S.; White, C. *J. Chem. Res., Synop.* **1983**, 234.

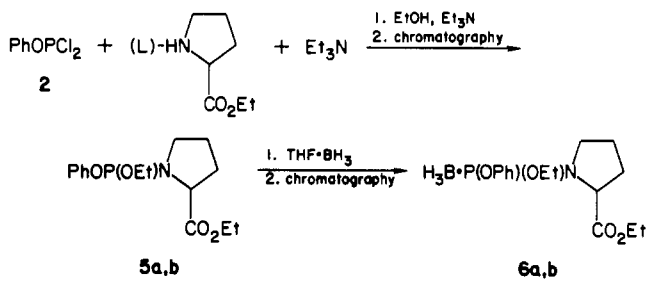
(10) Traces of R_3N or R_3NHCl accelerate exchange.

0020-1669/85/1324-2132$01.50/0

Scheme I



Scheme II



chirality is unusually distant from the chiral atom. This feature may be largely responsible for the failure of the corresponding phosphates[11] of (±)-**1** to exhibit ^{31}P or ^{1}H NMR chemical shift differences in the presence of chiral shift reagents that were sufficiently resolved to be useful in assessing the optical purity of the enantiomers of the parent compounds (±)-**1**. The enantiomers of (±)-**1** lose optical activity over a period of weeks at room temperature. Although no direct estimate of the optical purity for the enantiomers of **1** is available, the enantiomeric resolution of H(ClCH$_2$CH$_2$)NPOCH$_2$CH$_2$CH$_2$NCH$_2$CH$_2$Cl and of (ClCH$_2$CH$_2$)$_2$NPOCH$_2$CH$_2$CH$_2$NCH$_2$CH$_2$Cl by the route shown in Scheme I produced the corresponding enantiomers in 95% or better optical purity.[12] The relatively remote origin of chirality for phosphorus in **1** may also be related to the observation that the diastereomers **5a,b** in Scheme II could not be separated by a wide variety of techniques[13] (nor could the diastereomers of the borane adduct **6a,b**[14]), whereas the Pt(II) diastereomers **4a,b** in Scheme I were easily separated. Thus stereo differentiation of the diastereomers of **5a,b** and of **6a,b** may be weak if interaction of the chromatographic medium is primarily at phosphorus (or at the H$_3$B·P moiety in the case of **6a,b**). Coordination of the enantiomers of **1** to Pt(II) in **4a,b**, however, sterically congests the fourth position on phosphorus in **1** (as well as on the resolving ligand (+)-**3**, thereby perhaps forcing the separation medium to seek binding sites nearer to the sources of chirality lying close to the peripheries of these diastereomeric complexes.

Experimental Section

All solvents used were reagent grade or better and were dried according to standard procedures.[15] Prior to use, the solvents were stored over 4-Å molecular sieves. The adduct THF·BH$_3$, L-(−)-proline, (*S*)-(+)-mandelic acid, CF$_3$CO$_2$H, tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III) [Eu(hfc)$_3$], and tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III) [Eu(fod)$_3$] (Aldrich) were used as supplied, and HOC$_6$H$_4$-*p*-Cl and HO(CH$_2$)$_3$OH (Aldrich) were vacuum distilled prior to use. Tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III) [Eu(tfc)$_3$] was used as supplied (Willow Brook Laboratories). ^{31}P NMR spectra were obtained on a Bruker HX-90 spectrometer at 30 °C. Phosphoric acid (85%) was used as the external standard in a 1-mm capillary tube held coaxially in the sample tube by a Teflon vortex plug. Low-resolution mass spectra were obtained on a Finnigan 4000 mass spectrometer interfaced with a gas chromatograph.

P(OPh)(OC$_6$H$_4$-*p*-Cl)(OC$_6$H$_4$-*p*-Me) ((±)-1). A solution of 3.30 g (25.7 mmol) of HOC$_6$H$_4$-*p*-Cl, 2.77 g (25.7 mmol) of HOC$_6$H$_4$-*p*-Me, and 5.19 g (51.3 mmol) of Et$_3$N in 200 mL of dry Et$_2$O was added dropwise over a period of 2 h to a solution of 5.00 g (25.7 mmol) of PhOPCl$_2$[17] in 500 mL of Et$_2$O at 0 °C under N$_2$. After the addition was complete, the reaction was allowed to stir for 1 h at 0 °C followed by filtration of the precipitated amine hydrochloride, which, after being washed with 50 mL of cold Et$_2$O and drying, was recovered in 99% yield. The ether was evaporated, giving a colorless oil (^{31}P NMR (acetone-d_6) δ 127.8 (51%, P(OPh)(OC$_6$H$_4$-*p*-Cl)$_2$, 128.4 (28%, P(OPh)(OC$_6$H$_4$-*p*-Me)$_2$), 127.3 (21%)). Chromatography of the mixture on silica gel (4:1 *n*-C$_6$H$_{14}$/CHCl$_3$) gave pure (±)-**1** in the middle fraction (^{1}H NMR (CDCl$_3$) δ 2.28 (s, CH$_3$), 6.61–7.42 (m, 2 C$_6$H$_4$, 1 C$_6$H$_5$); Ms *m/e* 358 (calcd 358)). Rapid flame distillation of the mixture (150 °C, 0.5 torr) increased the concentration of (±)-**1** to about 50%. Very similar results were obtained by starting with Cl$_2$POC$_6$H$_4$-*p*-Me or Cl$_2$POC$_6$H$_4$-*p*-Cl (made analogously to PhOPCl$_2$[17]) and simultaneously adding a solution of the other two phenols.

The phosphate derivatives of (±)-**1** were made as follows. Under N$_2$, 1.00 g (26.7 mmol) of (±)-**1** was dissolved in 50 mL of CH$_2$Cl$_2$ and the solution cooled to −30 °C. Gaseous N$_2$O$_4$ was bubbled through the solution until it became greenish. The reaction mixture was allowed to stir for 0.5 h at −30 °C and was then warmed slowly to room temperature. After the mixture was washed with 75 mL of 5% aqueous sodium bicarbonate followed by 150 mL of distilled water, the organic layer was separated and dried over sodium sulfate. The solvent was then evaporated to obtain a slightly yellowish oil in 88% yield (^{31}P NMR (CDCl$_3$) δ −17.20).

***cis*-Cl$_2$Pt[(±)-1]$_2$.** In method A, a solution of 0.5437 g (15.17 mmol) of (±)-**1** in 25 mL of CH$_2$Cl$_2$ was added dropwise to a solution of 0.7160 g (15.17 mmol) of *cis*-Cl$_2$Pt(NCPh)$_2$[18] in 50 mL of CH$_2$Cl$_2$ at 0 °C under N$_2$. The colorless reaction mixture was allowed to warm slowly to room temperature and stir overnight. To this solution was added 25 mL of EtOH, and the methylene chloride was evaporated until the colorless complex began to crystallize. After the mixture was allowed to stand at 0 °C for 24 h, the crystals were filtered, washed with cold Et$_2$O, and dried under vacuum (Yield 59%; mp 135–136 °C; ^{31}P NMR (CDCl$_3$) δ 60.39 ($^{1}J_{PtP}$ = 5784 Hz)).

In method B, a solution of 0.826 g (4.24 mmol) of PhOPCl$_2$[17] in 10 mL of CHCl$_3$ was added to a solution of 1.00 g (2.12 mmol) of *cis*-Cl$_2$Pt(NCPh)$_2$ in 25 mL of CHCl$_3$. The reaction mixture was refluxed for 1.5 h under N$_2$. The mixture was then cooled to 0 °C, and a solution of 0.458 g (4.24 mmol) of HOC$_6$H$_4$-*p*-Cl and 0.429 g (4.24 mmol) of Et$_3$N in 50 mL of CHCl$_3$ was added dropwise. After the addition was complete, the reaction was allowed to stir for 0.5 h while the temperature was maintained at 0 °C. To this mixture was added dropwise a solution of 0.545 g (4.24 mmol) of HOC$_6$H$_4$-*p*-Cl and 0.429 g (4.24 mmol) of Et$_3$N in 50 mL of CHCl$_3$. The solution was allowed to warm to room temperature with stirring continued for 1 h. CHCl$_3$ was evaporated, and to the residue was added 75 mL of Me$_2$CO. The Et$_3$NHCl was then filtered off, washed twice with 25 mL of EtOH, and dried to give a 91%

(11) It was hoped that the stronger interaction of chiral shift reagents with phosphoryl oxygens would facilitate checking the optical purity. Hence **1** was oxidized by N$_2$O$_4$, which is well-known to oxidize P(III) compounds stereoretentively (see Experimental Section).

(12) Wroblewski, A. E.; Socol, S. M.; Okruszek, A.; Verkade, J. G. *Inorg. Chem.* **1980**, *19*, 3713.

(13) Successful separation of the diastereomers of **5** would have allowed stereoretentive displacement of the amino function by CF$_3$O$_2$C$_6$H$_4$-*p*-Me (for such reactions with similar compounds, see: Horner, L.; Jordan, M. *Phosphorus Sulfur* **1980**, *8*, 235) to give the enantiomers of **1**. Attempts to separate the diastereomers of **5** were made by using HPLC on Porasil, analytical and preparative chiral stationary phase HPLC using CSP IV and CSP XIII (Snyder, L. R.; Kirkland, J. J. "Introduction to Modern Liquid Chromatography"; Wiley: New York, 1974), TLC on neutral alumina, silica gel, and cellulose (all with a variety of solvent systems), and spinning-band vacuum distillation. The only success attained was partial separation with TLC on silica gel using 4:1 PhH/CHCl$_3$. A large silica gel-to-compound ratio (>200:1) and very slow solvent flow rates resulted only in simultaneous elution of the diastereomers of **5**, however. Similar results were obtained with preparative TLC.

(14) Attempts to separate the diastereomers **6** (a more polar derivative of **5**) by column chromatographic techniques revealed merely more broadening of the adduct band than for **5**.

(15) Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972; p 445.

(16) Shibaski, M.; Tereshimai, S.; Yamadai, S. *Chem. Pharm. Bull.* **1975**, *23*, 279.

(17) Schwartz, R.; Gewlen, H. *Chem. Ber.* **1957**, *90*, 954.

(18) Church, M. H.; Mays, M. *J. Inorg. Nucl. Chem.* **1971**, *33*, 253.

yield. Me_2CO was evaporated and the residue recrystallized from CH_2Cl_2/EtOH to give the crude product in 30% yield. The yield of crude product was raised to 51% by running the above reactions at −25 °C. Chromatography (silica gel, $CHCl_3$) gave the pure product as the third fraction (R_f 0.34) following the corresponding $(PhOP(OC_6H_4\text{-}p\text{-}Me)_2)_2$ (R_f 0.82; ^{31}P NMR ($CDCl_3$) δ 59.7 ($^1J_{PtP}$ = 5797 Hz)) and $(PhOP(OC_6H_4\text{-}p\text{-}Cl)_2)_2$ (R_f 0.65; ^{31}P NMR ($CDCl_3$) δ 61.0 ($^1J_{PtP}$ = 5761 Hz)) complexes, which were identified by comparison of their R_f and ^{31}P NMR data with those of authentic samples prepared analogously.

Resolution of (±)-1. Halide exchange of *cis*-$Cl_2Pt[(\pm)\text{-}1]_2$ to the corresponding diiodide was carried out by following a previously reported method.[19] Chromatography (silica gel, CH_2Cl_2) of the crude material gave the desired product in 88% yield (mp 130 °C; ^{31}P NMR (acetone-d_6) δ 59.6 ($^1J_{PtP}$ = 5496 Hz)). In 150 mL of dry C_6H_6 were dissolved 0.2000 g (0.2021 mmol) of *cis*-$I_2Pt[(+)\text{-}3]_2$ (see Scheme I), 0.2357 g (0.2021 mmol) of *cis*-$I_2Pt[(\pm)\text{-}1]_2$, and 0.002 g of (+)-**3**. The reaction mixture was refluxed for 10 h under N_2. The solution was then filtered and the solvent evaporated to yield a yellow powder, which was dissolved in a minimum of CH_2Cl_2 and chromatographed (70 g of silica gel, CH_2Cl_2) at a flow rate of 1.0 mL/min. Five-milliliter fractions were collected and monitored by TLC. Four different fractions were collected and identified by ^{31}P NMR spectroscopy (band 1 R_f 0.72, *cis*-$I_2Pt[(\pm)\text{-}1]_2$, band 2 R_f 0.41, diastereomer **4a** (see Scheme I); ^{31}P NMR ($CDCl_3$) δ 64.8 ($^1J_{PtP}$ = 5869 Hz), 63.6 ($^1J_{PtP}$ = 5481 Hz); band 3 R_f 0.31, diastereomer **4b** (see Scheme I); ^{31}P NMR ($CDCl_3$) δ 66.6 ($^1J_{PtP}$ = 5852 Hz), 64.5 ($^1J_{PtP}$ = 5487 Hz); band 4 R_f 0.14, *cis*-$I_2Pt[(-)\text{-}3]_2$). To a solution of 0.1020 g (0.08718 mmol) of one of the resolved diastereomeric complexes **4a** or **4b** dissolved in 75 mL of CH_2Cl_2 was added 0.0340 g (0.8728 mmol) of dry NaCN. The solution turned colorless immediately and was allowed to stir at room temperature overnight under N_2. The colorless precipitate was filtered and the solvent evaporated to yield a colorless oil, which was dissolved in a minimum of C_6H_6 and chromatographed (silica gel, C_6H_6), giving (+)-**1** or (−)-**1** in the first fraction (R_f 0.76; yield 40%; $[\alpha]^{25}_{589}$ +21.4 ($CHCl_3$), −18.6 ($CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 127.8) with (+)-**3** (F_f 0.09[12]) arriving in the second fraction.

PhOP(OEt)[N(CH$_2$)$_3$CHCO$_2$Et] (5). To 3.979 g (20.41 mmol) of $PhOPCl_2$ in 1.0 L of Et_2O at 0°C were added dropwise over a period of 2 h a solution of 2.923 g (20.41 mmol) of ethyl L-prolinate and 2.067 g (20.41 mmol) of Et_3N in 75 mL of Et_2O and a solution of 0.9390 g (20.41 mmol) of EtOH and 2.067 g (20.41 mmol) of Et_3N in 100 mL of Et_2O. The amine hydrochloride, after filtration, washing, and drying, gave 97% of the expected amount. The solvent was evaporated to an oil, which was purified by chromatography (silica gel, 8:1 $C_6H_6/CHCl_3$) to give both diastereomers in a single fraction (^{31}P NMR ($CDCl_3$) δ 141.2, 139.9; MS *m/e* 311 (P^+) (calcd 311)). Efforts[13] to separate the diastereomers failed.

PhOP(OEt)[N(CH$_2$)$_3$CHCO$_2$Et]·BH$_3$ (6). Under dry N_2, 1.774 g (5.705 mmol) of **5a,b** was dissolved in 175 mL of Et_2O. After this solution was cooled to 0 °C, a 1.0 M solution containing 6.848 mmol (20% stoichiometric excess) of THF·BH_3 was added dropwise over a period of 10 min. The reaction was allowed to warm slowly to room temperature followed by evaporation of the solvent. The crude product was obtained as a viscous oil, which was purified by chromatography (silica gel, 9:1 $C_6H_6/CHCl_3$). Upon evaporation of the eluant, the diastereomeric product was obtained as a colorless oil (^{31}P NMR ($CHCl_3$) δ 73.3, 70.2) that resisted separation efforts.[14]

Acknowledgment. J.G.V. thanks the National Science Foundation for a grant in support of this research.

Registry No. (±)-**1**, 96455-46-8; (+)-**1**, 96455-47-9; (−)-**1**, 96455-48-0; (+)-**3**, 75045-93-1; **4** (isomer 1), 96455-53-7; **4** (isomer 2), 96553-61-6; **5a**, 96455-49-1; **5b**, 96481-06-0; **6a**, 96455-54-8; (±)-**1**, phosphate derivative, 96455-52-6; **6b**, 96553-62-7; *cis*-$Cl_2Pt[(\pm)\text{-}1]_2$, 96455-55-9; *cis*-$I_2Pt[(\pm)\text{-}1]_2$, 96455-56-0; *cis*-$Cl_2Pt(NCPh)_2$, 15617-19-3; *cis*-$I_2Pt[(+)\text{-}3]_2$, 72316-69-9; $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)_2$, 96455-50-4; $P(OPh)(OC_6H_4\text{-}p\text{-}Me)_2$, 96455-51-5; $PhOPCl_2$, 3426-89-9; $HOC_6H_4\text{-}p\text{-}Cl$, 106-48-9; $HOC_6H_4\text{-}p\text{-}Me$, 106-44-5; ethyl L-prolinate, 5817-26-5.

(19) Jenkins, J. M.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 2250.

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Technetium Electrochemistry. 3.[1] Spectroelectrochemical Studies on the Mixed-Ligand Technetium(III) Complexes *trans*-$[Tc(PR_2R')_2L]^+$ Where L Is a Tetradentate Schiff Base Ligand and PR_2R' Is a Monodentate Tertiary Phosphine Ligand

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The redox chemistry of a series of eight well-characterized, robust, cationic technetium(III) complexes of the general formula *trans*-$[Tc(PR_2R')_2L]^+$, where PR_2R' represents a monodentate tertiary phosphine with R and R' being ethyl and/or phenyl and L represents a tetradentate Schiff base ligand, has been investigated in propylene carbonate by using spectroelectrochemistry with a gold minigrid optically transparent thin-layer electrode. The *trans*-$[Tc(PR_2R')_2L]^+$ complexes undergo a reversible 1-equiv reduction of Tc(III) to Tc(II) and a reversible 1-equiv oxidation of Tc(III) to Tc(IV). $E^{\circ\prime}$ values for the Tc(III)/Tc(II) couple range from −1.11 to −0.69 V (vs. Ag/AgCl/NaCl (3 M)) while $E^{\circ\prime}$ values for the Tc(IV)/Tc(III) couple range from +0.62 to +0.79 V (vs. the same reference). The difference between $E^{\circ\prime}_{IV/III}$ and $E^{\circ\prime}_{III/II}$ ranges from 1.5 to 1.75 V, reflecting the large range of stability of the Tc(III) state. The formal potentials of both redox processes depend on the nature of the phosphine and Schiff base ligands. These dependencies are readily explained in terms of π back-bonding from low-valent technetium to both the phosphine and Schiff base ligands. All the technetium complexes, including the electrogenerated Tc(II) and Tc(IV) species, exhibit characteristic metal-to-ligand charge-transfer (MTLCT) bands in the visible region of the spectrum. The energies of these MTLCT transitions are a function of the oxidation state of the technetium, the nature of the phosphine ligands, and the nature of the Schiff base ligand. The energy of the Tc(III) MTLCT band is linearly related to the redox potential of the Tc(IV)/Tc(III) couple.

Introduction

We have been investigating the electrochemistry of technetium complexes[1,3-5] both in order to characterize the chemistry of this relatively unstudied element and also in order to understand the biological behavior of technetium-99m complexes developed for use in diagnostic nuclear medicine.[6-8] Of particular concern to

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