Synthesis, Resolution, and Chemistry of Chiral Octahedral Complexes of the Type *fac*-[RuX(CO)L(triphos)]X' (L = Tertiary Phosphine, Isocyanide; X = Halide, Alkyl; X' = Halide, PF6-; triphos = 1,1,1-Tris((diphenylphosphino)methyl)ethane)

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Treatment of complexes of the type [RuR(CO)$_2$(triphos)]$^+$ (R = alkyl) with several isocyanides and tertiary phosphines in the presence of trimethylamine oxide leads to the formation of complexes of the type *fac*-[RuR(CO)L(triphos)]$^+$, the ease of CO substitution being limited by the steric requirements (cone angles) in the cases of the phosphines. The new complexes are chiral, and resolution has been achieved in the case of [RuMe(CO)(t-BuNC)(triphos)]$^+$, which has been isolated enantiomerically pure as the hexa-fluorophosphate and (R,R)-hydrogendibenzoyltartrate (HBDT) salts. The crystal structure of [RuMe-(CO)(t-BuNC)(triphos)][HDBT] (monoclinic space group $P2_1$; a = 19.356 (5) Å, b = 10.841 (3) Å, c = 15.262 (3) Å, β = 108.33 (2)°, Z = 2; structure refined to R = 0.032, R_w = 0.049) shows that the absolute configuration of the complex cation can be designated by the Sloan modification of the Cahn–Ingold–Prelog procedures as OC-6-43-A. Electrophilic cleavage reactions of the resolved methyl complex with HCl, Cl$_2$, I$_2$, and HgBr$_2$ proceed cleanly and quantitatively to yield the corresponding haloruthenium complexes and CH$_4$, MeCl, MeI, or MeHgCl, respectively. All reactions appear to be stereoselective, at least, but the halo products are configurationally labile and neither the extent of the stereoselectivity nor the absolute configurations can be determined. Attempts to determine the stereoselectivity by NMR spectroscopy utilizing chiral shift reagents were inconclusive. The second-order ^{13}C{^{1}H} NMR spectra of a series of chiral complexes [RuX(CO)(^{13}CO)(triphos)]$^+$ (X = alkyl, halide) in the carbonyl region are analyzed in detail, and reasonable suggestions concerning the absolute signs of ^2J(P–C) (cis and trans) are made.

We have recently reported the synthesis of a series of new ruthenium(II) hydrido and alkyl complexes, prepared via oxidative addition reactions of the ruthenium(0) complex Ru(CO)$_2$(triphos) (triphos = MeC(CH$_2$PPh$_2$)$_3$) with protonic acids HX and alkyl halides RX (R = Me, Et, PhCH$_2$, allyl).[1] The alkyl complexes [RuR(CO)$_2$(triphos)]$^+$ were generally found to be thermally quite robust, while the hydride product [RuH(CO)$_2$(triphos)]$^+$ was, to our surprise, found to be a Brønsted acid of medium strength. Furthermore, the products of oxidative addition of acetyl chloride were found to be ketene and the above-mentioned hydride, apparently formed via an unprecedented elimination from the initially formed acetyl complex [Ru(COMe)(CO)$_2$(triphos)]$^+$.

The series of triphos–ruthenium(II) complexes is also of potential interest because substitution of a carbonyl group by another ligand L would result in the formation of the series of octahedral organometallic complex cations [RuR(CO)L(triphos)]$^+$. As the triphos is constrained in such complexes to coordinate only to a triangular face of an octahedron, the so-formed facial complexes would be chiral at the metal and should in principle be resolvable. Studies of the stereochemistry of their reactions should thus throw light on organometallic reaction mechanisms, in a manner complementary to the by now large body of information available for the series of compounds of the type CpML'L''L'''.[2] Relatively few octahedral organometallic compounds chiral at the metal have been reported, and those which have, *fac*-M(CO)$_3$(L–L')(L'') (M = Mn, Cr, Mo, W; L–L' = unsymmetrical, bidentate ligand; L'' = Br, CO, PPh$_3$)[3] and (polypyrazolylborate)M(CO)(NO)L

(M = Mo, W; L = neutral ligand)[4] have not yet been exploited for mechanistic purposes.

We now describe in detail the synthesis, characterization, resolution, and aspects of the chemistry of compounds of the general formula [RuR(CO)L(triphos)]$^+$ (R = Me, CH$_2$Ph; L = isocyanides, tertiary phosphines). We also discuss analyses of the second-order carbonyl resonances in the ^{13}C{^{1}H} NMR spectra of the chiral complexes [RuX(CO)(^{13}CO)(triphos)]$^+$ and [RuR(CO)(^{13}CO)(triphos)]$^+$. Aspects of this work have been communicated previously.[5]

Experimental Section

All reactions were carried out under purified nitrogen; solvents were dried by using standard procedures. Infrared (IR) spectra were run on Beckman 4240 and Bruker IFS 85 FTIR spectrometers, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra on a Bruker AM 400 NMR spectrometer; chemical shifts are relative to internal Me$_4$Si (^{1}H, ^{13}C) or external concentrated phosphoric acid (^{31}P), with downfield chemical shifts being positive. NMR data are listed in Tables I–III and VIII. NMR spectral simulations were carried out iteratively utilizing the Bruker Panic program and the Aspect 2000 computer of the IFS 85. ORD spectra were measured at 589, 578, 546, 436, and 365 nm using Perkin-Elmer 141 and 241 polarimeters (data in Table IV), while CD spectra were run on a Jasco J-500 CD spectrometer (spectra, in Figure 1). Elemental analyses were carried out by Canadian Microanalytical Services, Vancouver.

Salts of the ruthenium complexes [RuMe(CO)$_2$(triphos)]$^+$, [Ru(CH$_2$Ph)(CO)$_2$(triphos)]$^+$, and [RuX(CO)$_2$(triphos)]$^+$ (X = Cl, I) were prepared as previously described.[1] The compounds (S)-(–)-PPh$_2$NHCHMePh,[6] *sec*-BuNC,[7] PhMeCHNC,[8] silver

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Table I. ^{1}H NMR Data (δ, Internal Me$_4$Si)^a

compd	triphos			other
	Me	CH$_2$	Ph	
I^b	1.69 (m)	2.2–2.4 (2 H, m), 2.5–2.9 (4 H, m)	6.6–7.6 (m)	–0.41 (qd, J(H–P) = 6.5 (cis), 3 (trans) Hz, Ru–Me); 1.36 (dd, J(H–P) = 8, 1 Hz, P–Me); 1.52 (dd, J(H–P) = 8, 1 Hz, P–Me)
II^c	1.47 (m)	2.2–2.6 (m)	6.7–7.9 (m)	0.61 (dt, J(H–P) = 6.5 (cis), 3.5 (trans) Hz, Ru–Me)
III^c	1.70 (m)	2.35–2.5 (3 H, m), 2.55–2.85 (3 H, m)	6.9–7.6 (m)	–0.15 (m, Ru–Me); 3.57 (d, J(H–P) = 10 Hz, PO–Me)
IV^c	1.48 (m)	2.2–2.7 (m)	6.7–8.0 (m)	0.49 (dt, J = 6.5 (trans), 3.5 (cis) Hz, Ru–Me)
V^c	1.55 (m)	2.1–2.6 (m)	6.6–8.1 (m)	0.44 (m, Ru–Me)
VII^c	1.64 (m)	2.2–2.7 (m)	6.9–7.6 (m)	0.11 (td, J(H–P) = 6 (cis), 3 (trans) Hz, Ru–Me); 1.45 (s, *t*-Bu)
VIII^b	1.69 (m)	2.3–2.8 (m)	7.0–7.8 (m)	1.43 (s, *t*-Bu)
IX^c	1.74 (m)	2.4–2.8 (m)	6.9–7.7 (m)	1.39 (s, *t*-Bu)
X^b	1.61 (m)	2.2–2.7 (m)	6.8–7.8 (m)	0.18 (m, Ru–Me); 1.05/1.06^d (t, J(H–H) = 6 Hz, C–Me); 1.26/1.28^d (d, J(H–H) = 6 Hz, C–Me); 1.65 (m, CH$_2$); 3.77/3.84^d (m, CH)
XI^b	1.70 (m)	2.3–2.8 (m)	6.9–7.7 (m)	1.06 (t, J(H–H) = 7 Hz, C–Me); 1.18/1.21^d (d, J(H–H) = 6.5 Hz, C–Me); 1.63 (m, CH$_2$); 3.8 (m, CH)
XII^b	1.64 (m)	2.2–2.8 (m)	6.9–7.5 (m)	1.25 (s, *t*-Bu); Ru–CH$_2$ obscured ~2.2–2.8; ~7 (benzylic Ph)
XIII^b	1.64 (m)	2.3–2.8 (m)	6.9–7.6 (m)	0.78 (t, J(H–H) = 7 Hz, C–Me); 1.05/1.11^d (d, J(H–H) = 7 Hz, C–Me); 1.4 (m, CH$_2$); 3.48/3.52^d (m, CH); 2.92 (m, 1 benzylic H); other obscured ~2.3–2.8

^{a}Abbreviations: m = multiplet; d = doublet; s = singlet; qd = quartet of doublets; dt = double triplet; td = triplet of doublets. ^{b}CD$_2$Cl$_2$. ^{c}CDCl$_3$. ^{d}Resonances of different diastereomers.

Table II. ^{13}C{^{1}H} NMR Data (δ, Internal Me$_4$Si, CD$_2$Cl$_2$)^{a,b}

compd	triphos	CO	other
I	34.2, 35.1, 38.1 (all m, CH$_2$); 36.7 (q, J = 4 Hz, tert C); 38.4 (q, J = 9 Hz, Me); 128–140 (m, Ph)	206.1 (m)	–3.8 (dq, J = 38 (trans), 8 (cis) Hz, Ru–Me); 16.2 (br d, J = 27 Hz, P–Me); 17.4 (br d, J = 33 Hz, P–Me)
III	32.6, 33.3, 36.3 (all m, CH$_2$); 36.7 (br s, tert C), 38.3 (q, J = 9 Hz, Me); 127–139 (m, Ph)	204 (m)	–10.9 (br d, J = 35 Hz, Ru–Me); 54.6 (d, J = 11 Hz, PO–Me)
VII	31.4, 33.2, 34.3 (all m, CH$_2$); 37.6 (q, J = 4 Hz, tert C); 38.5 (q, J = 10 Hz, Me); 128–138 (m, Ph)	202.1 (ddd, J = 84, 10, 6 Hz)	–11.2 (br d, J = 38 Hz, Ru–Me); 146.5 (br d, J = 90 Hz, CN); 59.0 (s, *C*Me$_3$); 30.4 (s, C-*Me*)
VIII	31.4, 32.6, 33.1 (all m, CH$_2$); 37.9 (br s, tert C); 38.2 (q, J = 10 Hz, Me); 128–136 (m, Ph)	194.9 (dt, J = 90, 9 Hz)	59.8 (s, *C*Me$_3$); 29.9 (s, C-*Me*); CN not observed
IX	30.7, 31.6, 34.0 (all m, CH$_2$); 37.7 (m, Me + tert C); 128–136 (m, Ph)	194.5 (dt, J = 93, 9 Hz)	139.3 (br d, J = 95 Hz, CN); 59.7 (s, *C*Me$_3$); 29.8 (s, C-*Me*)
X	31.4, 33.3, 34.4 (all m, CH$_2$); 37.6 (q, J = 4 Hz, tert C); 38.6 (q, J = 10 Hz, Me); 128–138 (m, Ph)	202.2 (m)	–11.5/–11.6^c (br d, J = 37 Hz, Ru–Me); 149 (m, CN); 56.0 (CH); 30.1/30.2,^{c} 20.8/20.9,^{c} 10.5 (all s, Me + Et)
XI	30.8, 31.8, 34.4 (all m, CH$_2$); 38.0 (m, Me + tert C); 128–136 (m, Ph)	194.7 (br d, J = 93 Hz)	141 (m, CN); 56.5 (br s, CH); 29.9, 20.3, 10.3 (all s, Me + Et)
XII	32.7, 34.0, (all m, CH$_2$); 37.4 (q, J = 4 Hz, tert C); 38.6 (q, J = 10 Hz, Me); 128–138 (m, Ph)	201.7 (ddd, J = 84, 11, 7 Hz)	14.6 (dt, J = 36 (trans), 5 (cis) Hz, Ru–CH$_2$); 153.8 (br s, ipso C); 145.2 (m, CN); 59.9 (s, *C*Me$_3$); 30.1 (C-*Me*)
XIII	31.7, 34.3, 34.6 (all m, CH$_2$); 37.3 (br s, tert C); 38.6 (q, J = 10 Hz, Me); 123–137 (m, Ph)	not observed	14.3 (br d, J = 35 Hz, Ru–CH$_2$); 153.4/153.5^c (s, ipso C); 56.0/56.2^c (s, CH); 10.1/10.5^c (Me), 19.8/20.4,^{c} 29.2/29.7^c (s, Me, CH$_2$)

^{a}All spin–spin couplings are to phosphorus. ^{b}Abbreviations: m = multiplet; s = singlet; d = doublet; q = quartet; dt = doublet of triplets; dq = doublet of quartets; ddd = double double doublet. ^{c}Resonances of different diastereomers.

(*R,R*)-hydrogendibenzoyltartrate,^{9} and silver (+)-camphor-10-sulfonate^{10} were prepared as in the literature, triphos and *t*-BuNC were purchased from Strem Chemicals, and the chiral shift reagents [3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]$_3$M (M(hpc)$_3$) (M = Eu, Yb) and [3-(trifluoromethyl)-hydroxymethylene)-*d*-camphorato]$_3$M (M(tfc)$_3$) (M = Pr, Yb) were

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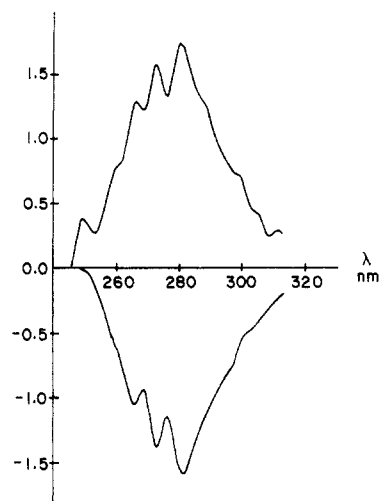(10) Maryanoff, C. A.; Hayes, K. S.; Mislow, K. *J. Am. Chem. Soc.* **1977**, *99*, 4412.

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[RuMe(CO)(PMe$_2$Ph)(triphos)]PF$_6$ (I). To a solution of 3.3 g (3.3 mmol) of [RuMe(CO)$_2$(triphos)]I in 120 mL of acetonitrile was added an acetonitrile solution of 0.55 g (3.2 mmol) of silver nitrate. After a few minutes, the precipitated silver iodide was removed by filtration, the solvent was removed under reduced pressure, and the residue was dissolved in 40 mL of methylene chloride. The solution was filtered once more, was treated with 1.5 mL (10.5 mmol) of PMe$_2$Ph and 0.3 g (4.0 mmol) of trimethylamine *N*-oxide, and was stirred for 10 min. About 20 mL of ethanol was added, the volume was reduced by half under reduced pressure, and a further 20 mL of ethanol was added to form a white precipitate. The mixture was cooled (0 °C), and the precipitate was collected by filtration, washed with ether, and

Figure 1. CD spectra of (+)- and (−)-[RuMe(CO)(CNBu-t)-(triphos)]PF$_6$ in methylene chloride.

Table III. ^{31}P{^{1}H} NMR Data (δ, External H$_3$PO$_4$)^a

compd	chemical shifts (J, Hz)
I^b	−5.7 (ddd, J = 219, 35, 20); 1.2 (ddd, J = 31, 25, 20); 11.3 (ddd, J = 40, 35, 31); 18.8 (ddd, J = 219, 40, 25)
II^c	−5.4 (dd, J = 20, 32); −3.7 (dd, J = 32, 38); 44.2 (dd, J = 20, 38)
III^b	2.7 (m); 8–15 (m, 2 P); 127.2 (ddd, J = 352, 36, 25)
IV^b	−4.5 (dd, J = 33, 19); −0.9 (dd, J = 39, 33); 47.0 (dd, J = 39, 19)
V^b	0.0–0.5 (m, 2 P); 48.0 (m)
VII^b	6.1 (dd, J = 31, 28); 12.4 (dd, J = 43, 31); 15.4 (dd, J = 43, 28)
VIII^b	−3.7 (dd, J = 43, 34); 0.7 (dd, J = 43, 31); 26.5 (dd, J = 34, 31)
IX^b	−0.9 (dd, J = 44, 34); 2.7 (dd, J = 44, 31); 31.8 (dd, J = 34, 31)
X^b	5.4/5.6^d (dd, J = 30, 27); 12.3/12.4^d (dd, J = 43, 30); 16.0^d/16.4 (dd, J = 42, 27)
XI^c	−1.3/−1.4^d (dd, J = 45, 34); 2.5/2.8^d (dd, J = 45, 32); 31.6/31.8^d (dd, J = 34, 32)
XII^c	4.4 (dd, J = 31, 26); 6.7 (dd, J = 42, 31); 14.4 (dd, J = 42, 26)
XIII^c	4.3/4.5^d (dd, J = 32, 28); 9.0 (dd, J = 41, 32); 12.2/12.4^d (dd, J = 41, 28)

^{a} All spin–spin couplings are to phosphorus. ^{b} CDCl$_3$. ^{c} CD$_2$Cl$_2$. ^{d} Resonances of different diastereomers.

dried in vacuo; yield 2.15 g (66%) of white, slightly air-sensitive material. Treatment of a solution of I in ethanol with a solution of sodium hexafluorophosphate in ethanol yielded the analytically pure hexafluorophosphate salt (ν(CO) = 1967 cm^{-1}). Anal. Calcd for C$_{51}$H$_{53}$F$_6$OP$_5$Ru: C, 58.23; H, 5.08. Found: C, 57.36; H, 5.01.

Although I is reasonable stable, the dimethylphenylphosphine ligand can be substituted by other ligands. Thus heating a solid sample of the iodide salt of I at 100 °C for 4 h resulted in partial conversion to a yellow material which was not obtained pure but which appeared on the basis of its IR (ν(CO) = 1973 cm^{-1}) and NMR spectra (Tables I and III) to be RuMe(CO)I(triphos) (II). Compound II was also obtained more slowly on treatment of a solution of I in CDCl$_3$ with excess tetrabutylammonium iodide at room temperature, while treatment of an acetonitrile solution of I with carbon monoxide (380 psi) for 2 days resulted in conversion to [RuMe(CO)$_2$(triphos)]PF$_6$.[2] In NMR experiments, it was found that treatment of I in CDCl$_3$ with P(OMe)$_3$ or t-BuNC resulted in the slow formation of the P(OMe)$_3$ or t-BuNC analogues III or VII, respectively.

[RuMe(CO){P(OMe)$_3$}(triphos)]PF$_6$ (III). The synthesis of this complex was as for I except that 1 h was allowed for the CO substitution reaction, and the nitrate salt was precipitated with ethyl ether rather than with ethanol; yield of nitrate salt (prior to conversion to hexafluorophosphate salt) 2.9 g (77%) (ν(CO) = 1985 cm^{-1}). Anal. Calcd for C$_{46}$H$_{51}$F$_6$O$_4$P$_5$Ru: C, 53.24; H, 4.95. Found: C, 52.50; H, 4.87.

In contrast to I, a solution of III in acetonitrile did not react with CO (380 psi) over 3 days. Attempts to prepare substituted complexes with P(OPh)$_3$, PEt$_3$, PPh$_3$ and PPh$_2$NHCH(Ph)Me[4] by routes similar to those described above generally resulted in formation of monocarbonyl species (IR) which did not contain the phosphorus donor. Although the new species were not characterized by elemental analyses, their spectroscopic properties (Tables I and III) were consistent with substitution of CO by counterion and formation of complexes of the type RuMeX-(CO)(triphos) (X = Cl (IV, ν(CO) = 1978 cm^{-1}), I (II), NO$_3$ (V, ν(CO) = 1990 cm^{-1})). The only exception was the mixture of products obtained from the reaction of PEt$_3$; on the basis of a new complex ruthenium–methyl multiplet in the ^{1}H NMR spectrum, this appeared to contain some [RuMe(CO)(PEt$_3$)-(triphos)]$^+$ (VI).

[RuMe(CO)(CNBu-t)(triphos)]PF$_6$ (VII). To a solution of 2.7 g (2.9 mmol) of [RuMe(CO)$_2$(triphos)]I, and 1.0 mL (12 mmol) of t-BuNC in 20 mL of methylene chloride was added 0.3 g (4 mmol) of Me$_3$NO. The mixture was stirred at room temperature for 40 min, after which time crude iodide salt was precipitated by adding ethyl ether. The solvent was removed by syringe, and the residue was dissolved in 80 mL of ethanol. Addition of an ethanol solution of NaPF$_6$ gave white, crystalline VII, which was collected by filtration, washed with ethyl ether, and dried in vacuo; yield 2.48 g (86%) (ν(CO) = 2000, ν(CN) = 2167 cm^{-1}). Anal. Calcd for C$_{48}$H$_{51}$F$_6$NOP$_4$Ru: C, 57.83; H, 5.16. Found: C, 57.54; H, 5.12.

In an NMR experiment involving 0.02 g of VII with 2 equiv of P(OMe)$_3$ in 0.5 mL of CD$_2$Cl$_2$, there had been no reaction after 22 h at room temperature. Similarly there was no reaction after treatment of a methylene chloride solution of VII with >100 psi of CO for 16 h.

[RuI(CO)(CNBu-t)(triphos)]PF$_6$ (VIII). To a solution of 1.1 g (1.1 mmol) of the iodide salt of VII, prepared as described above, in 10 mL of methylene chloride was added a solution of 0.27 g (1.1 mmol) of iodine in 20 mL of methylene chloride. On the addition of 20 mL of heptane and concentration at reduced pressure, an oil formed; this crystallized on addition of a little methylene chloride and was collected by filtration; yield 1.1 g (90%). The material was converted to the pale yellow hexafluorophosphate salt as above (ν(CO) = 2033, ν(CN) = 2186 cm^{-1}). Anal. Calcd for C$_{47}$H$_{48}$F$_6$INOP$_4$Ru: C, 50.91; H, 4.36. Found: C, 50.68; H, 4.32.

[RuCl(CO)(CNBu-t)(triphos)]PF$_6$ (IX). This complex was prepared essentially as was VIII, but using chlorine gas (ν(CO) = 2043, ν(CN) = 2193 cm^{-1}). Anal. Calcd for C$_{47}$H$_{48}$ClF$_6$NOP$_4$Ru: C, 55.49; H, 4.76; N, 1.38. Found: C, 55.50; H, 4.93, N, 1.36.

[RuMe(CO)(CNBu-sec)(triphos)]PF$_6$ (X). To 0.82 g (0.9 mmol) of [RuMe(CO)$_2$(triphos)]I and 0.2 mL (2 mmol) of sec-BuNC dissolved in 10 mL of methylene chloride was added 0.08 g (1.1 mmol) of Me$_3$NO. After a few minutes, addition of 10 mL of heptane yielded an oil, which was in turn dissolved in ethanol. The ethanol solution was filtered, 0.045 g (0.27 mmol, 0.3 equiv) of NaPF$_6$ in 5 mL of ethanol was added, and the mixture was cooled to −78 °C for several hours. A small amount of product precipitated which was collected by filtration, washed with ethanol, and dried. To the remaining solution was added 0.126 g (0.76 mmol, 0.85 equiv) of NaPF$_6$, giving a crystalline precipitate which was collected as above. The two batches of material were found to be identical (IR, NMR); combined yield of 0.42 g (47%) (ν(CO) = 1998, ν(CN) = 2173 cm^{-1}). Anal. Calcd for C$_{48}$H$_{51}$F$_6$NOP$_4$Ru: C, 57.83, H, 5.16. Found: C, 57.73; H, 5.18.

Table IV. Specific Rotations [α]^{25} of (+)- and (−)-VII in Methylene Chloride (c 3 × 10^{-3} M)

			λ, nm		
	589	578	546	436	365
(+)-VII	26.9°	27.7°	32.3°	60.8°	116.5°
(−)-VII	−27.9°	−28.7°	−33.5°	−63.0°	−118.3°

A similar attempt to prepare the analogous complex of 1-phenylethyl isocyanide did not yield a characterizable compound.

[RuCl(CO)(CNBu-*sec*)(triphos)]PF$_6$ (XI). To a solution of 0.42 g (0.42 mmol) of X in 20 mL of methylene chloride was added 0.15 g (0.55 mmol) of HgCl$_2$. After 7 min, 20 mL of ethanol was added, and concentration under reduced pressure gave a white precipitate of product, which was collected, washed with ethanol and pentane, and dried; yield 0.3 g (70%) (ν(CO) = 2042, ν(CN) = 2197 cm^{-1}). Anal. Calcd for C$_{47}$H$_{48}$ClF$_6$NOP$_4$Ru: C, 55.49; H, 4.76; N, 1.38. Found: C, 55.42; H, 4.85; N, 1.37.

[Ru(CH$_2$Ph)(CO)(CNBu-*t*)(triphos)]PF$_6$ (XII). To 0.37 g (0.36 mmol) of [Ru(CH$_2$Ph)(CO)$_2$(triphos)]PF$_6$ and 0.2 mL (2.3 mmol) of *t*-BuNC dissolved in 20 mL of methylene chloride was added 0.04 g (0.5 mmol) of Me$_3$NO. The solution was stirred at room temperature for 30 min, 20 mL of heptane was added, and concentration at reduced pressure gave an oil. The oil was dissolved in 30 mL of ethanol containing about 0.2 g of NaPF$_6$, the solution was taken to dryness, the residue was dissolved in 5 mL of methylene chloride, and sufficient ethyl ether was added to induce crystallization of product. After the mixture was cooled, the product was collected by filtration, recrystallized from acetone/ethanol, washed with ether, and dried; yield 0.15 g (39%) (ν(CO) = 2001, ν(CN) = 2165 cm^{-1}). Anal. Calcd for C$_{54}$H$_{55}$F$_6$NOP$_4$Ru: C, 60.45; H, 5.17; N, 1.31. Found: C, 60.00; H, 5.25; N, 1.36.

[Ru(CH$_2$Ph)(CO)(CNBu-*sec*)(triphos)]PF$_6$ (XIII). To a solution of 0.35 g (0.34 mmol) of [Ru(CH$_2$Ph)(CO)$_2$(triphos)]PF$_6$ and 0.20 mL (2.3 mmol) of *sec*-BuNC in 20 mL of methylene chloride was added 0.05 g (0.7 mmol) of Me$_3$NO. The solution was stirred for 25 min at room temperature, 15 mL of ethanol was added, the solution was concentrated to 5 mL under reduced pressure, and 20 mL of ethyl ether was added to give a crystalline precipitate of product which was collected, washed with ether, and dried; yield 0.27 g (73%) (ν(CO) = 2000, ν(CN) = 2176 cm^{-1}). Anal. Calcd for C$_{54}$H$_{55}$F$_6$NOP$_4$Ru: C, 60.45; H, 5.17; N, 1.31. Found: C, 60.37; H, 5.34; N, 1.35.

Resolution of [RuMe(CO)(CNBu-*t*)(triphos)]PF$_6$. A mixture of 2.22 g (2.27 mmol) of the iodide salt of VII and 1.10 g (2.36 mmol) of silver (*R,R*)-hydrogendibenzoyltartrate (AgHDBT) in 70 mL of ethanol was stirred for 30 min. at 40 °C. The mixture was cooled and centrifuged, and the supernatant was collected, concentrated and cooled to yield a white precipitate of [RuMe(CO)(CNBu-*t*)(triphos)][HDBT]. Five recrystallization from methylene chloride/ethyl ether yielded the HDBT salt of the pure (constant rotation) (+)-isomer of the cationic ruthenium complex, which was dissolved in a mixture of ethanol and methylene chloride and treated with a solution of NaPF$_6$ in ethanol. A white crystalline precipitate of pure (+)-VII formed which was collected, recrystallized from methylene chloride/ethanol, washed with ethanol, and dried in vacuo.

The combined mother liquors from the recrystallizations were concentrated to dryness, and the residue was worked up as above to give pure (−)-VII.

X-ray Structure Determination of (+)-VII. A colorless crystal of the HDBT salt of (+)-VII, 0.20 × 0.20 × 0.18 mm, was chosen for the collection of intensity data on an Enraf-Nonius CAD 4 diffractometer. The unit cell parameters were obtained by a least-squares analysis of 25 centered reflections in the range 18.6 ≤ 2θ ≤ 59°. The data were collected by the θ–2θ scan technique with variable scanning rate, using monochromated Cu radiation. A total of 4771 unique reflections were measured in the range 1 ≤ 2θ ≤ 120°, of which 4650 were considered observed, i.e., $I > 3\sigma(I)$. Three standard reflections were measured every 7200 s of radiation time and showed no significant variation during the course of data collection. The intensities were corrected for Lorentz and polarization effects. A numerical absorption correction was applied to the data; the transmission factors varied between 0.50 and 0.63.

The ruthenium and phosphorus atoms were found by the Patterson technique. Difference Fourier map calculations revealed the rest of the structure, including the positions of 50 of the 64 hydrogen atoms in the asymmetric unit. The positions of the remaining hydrogens were calculated. Hydrogen atoms were assigned temperature factors equal in magnitude to the equivalent isotropic values of their parent atoms and were included in the calculations but not refined. Full-matrix least-squares refinement

Table V. Summary of Crystallographic Data

Crystal Parameters	
crystal system: monoclinic	space group: $P2_1$
a = 19.356 (5) Å	Z = 2
b = 10.841 (3) Å	d_{calcd} = 1.321 g cm^{-3}
c = 15.262 (3) Å	T = 20 °C
β = 108.33 (2) Å	μ(Cu Kα) = 33.34 cm^{-1}
V = 3040.0 Å^3	

| Measurements of Intensity Data	
diffractometer	Enraf-Nonius CAD-4
radiation	Cu Kα (λ = 1.5418 Å)
monochromator	graphite crystal
scan type	θ–2θ
scan speed	variable, from 0.7 to 4°/minute
scan range	1° ≤ 2θ ≤ 120°
reflcts measd	+h,+k,±l
reflcts collected	4771 unique reflcts, 4650 with $I \geq 3\sigma$ (I)
check reflcts	3 measured every 7200 s
R	0.032
R_w	0.049
largest shift, final cycle (Δ/σ)	0.09
final diff map ($\Delta\rho$) max, min peak, e Å^{-3}	0.548, −0.686
stand dev obsvn of unit weight (σ)	1.572
isotropic secondary extinction correction, g	1.81 × 10^{-6}
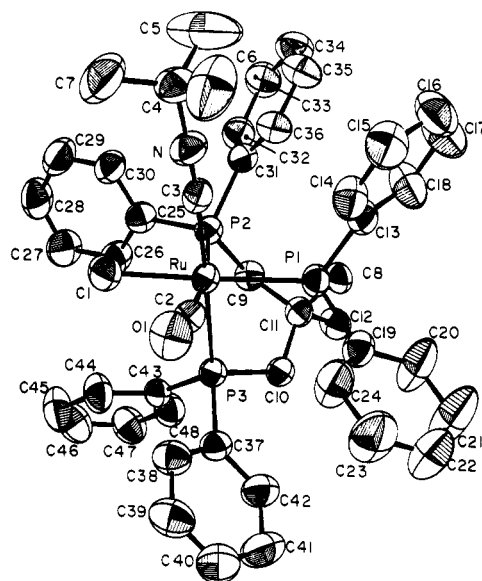
Figure 2. Ortep drawing of (+)-[RuMe(CO)(CNBu-*t*)(triphos)]$^+$ with atomic labeling scheme.

minimizing the function $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/(\sigma^2(F^2) + (0.06F^2)^2)$, with anisotropic temperature factors for the non-hydrogen atoms, resulted in R = 0.032 and R_w = 0.049. The esd of an observation of unit weight was 1.572, the maximum shift to error ratio was 0.09, and the final difference Fourier synthesis was essentially featureless except for several peaks [−0.686 to +0.548 e/Å^3] in the vicinity of the ruthenium atom. A correction for isotropic secondary extinction effect was included in the refinement: g = 1.81 × 10^{-6}. The scattering factors used were those of Cromer and Waber.[11] The anomalous dispersion coefficients were taken from Cromer.[12]

All calculations were performed on a PDP 11/23 computer using the structure determination package of Enraf-Nonius, SDP.[13] The program Ortep[14] was used for the preparation of the illus-

(11) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.
(12) Cromer, D. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.
(13) Enraf-Nonius SDP, Structure Determination Package, revised by B. A. Frenz; Enraf-Nonius: Delft, 1979.

Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-H Atoms with Esd's in Parentheses
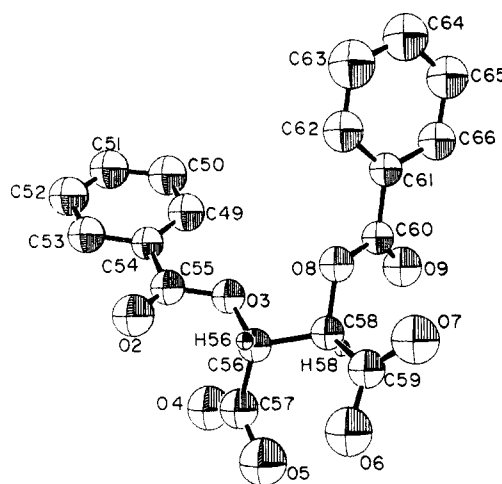
	x	y	z	B, Å²		x	y	z	B, Å²
Ru	0.19829 (1)	0.000	0.02166 (2)	3.251 (5)	C35	0.6263 (3)	0.3872 (7)	0.1685 (4)	5.8 (1)
P1	0.31664 (6)	0.0911 (1)	0.08231 (7)	3.59 (2)	C36	0.6713 (3)	0.3985 (6)	0.1127 (3)	4.7 (1)
P2	0.74449 (5)	0.3087 (1)	-0.00776 (7)	3.44 (2)	C37	0.8169 (2)	0.5554 (5)	0.7526 (3)	4.00 (9)
P3	0.21404 (5)	-0.0576 (1)	0.17895 (7)	3.37 (2)	C38	0.8856 (3)	0.6047 (6)	0.7891 (3)	4.9 (1)
O1	0.9027 (2)	0.7172 (4)	0.9907 (3)	6.1 (1)	C39	0.9115 (3)	0.6932 (7)	0.7403 (4)	6.3 (1)
N	0.8310 (2)	0.5755 (5)	0.1844 (3)	4.69 (9)	C40	0.8677 (3)	0.7314 (7)	0.6559 (5)	6.9 (2)
C1	0.9095 (3)	0.4129 (6)	0.0383 (3)	5.0 (1)	C41	0.7994 (4)	0.6856 (8)	0.6184 (4)	7.3 (2)
C2	0.8610 (3)	0.6393 (5)	0.9790 (3)	4.2 (1)	C42	0.7729 (3)	0.5634 (7)	0.6655 (4)	5.6 (1)
C3	0.8160 (2)	0.5436 (5)	0.1083 (3)	3.93 (9)	C43	0.8288 (2)	0.3041 (5)	0.7919 (3)	3.60 (9)
C4	0.8512 (3)	0.6145 (7)	0.2811 (3)	5.8 (1)	C44	0.0955 (3)	0.7858 (6)	0.1644 (4)	5.3 (1)
C5	0.7974 (5)	0.558 (2)	0.3206 (5)	13.6 (4)	C45	0.0600 (3)	0.6862 (7)	0.1857 (5)	6.5 (1)
C6	0.8442 (5)	0.7527 (9)	0.2818 (6)	9.7 (2)	C46	0.0977 (3)	0.5999 (6)	0.2489 (4)	6.1 (1)
C7	0.9277 (5)	0.576 (1)	0.3281 (5)	9.3 (2)	C47	0.1700 (3)	0.6168 (6)	0.2947 (4)	5.7 (1)
C8	0.6151 (2)	0.4724 (5)	0.8659 (3)	3.8 (1)	C48	0.2060 (3)	0.7175 (6)	0.2729 (4)	4.8 (1)
C9	0.3208 (2)	0.7623 (5)	0.1212 (3)	0.84 (9)	O2	0.1527 (2)	0.6280 (5)	0.6492 (3)	6.3 (1)
C10	0.6879 (2)	0.4201 (5)	0.7586 (3)	3.71 (9)	O3	0.2162 (2)	0.6592 (4)	0.5523 (2)	4.39 (7)
C11	0.6414 (2)	0.3668 (5)	0.8150 (3)	3.62 (9)	O4	0.1740 (2)	0.4315 (5)	0.5119 (3)	7.6 (1)
C12	0.5726 (2)	0.3098 (5)	0.7462 (3)	4.4 (1)	O5	0.2737 (2)	0.3468 (4)	0.5988 (4)	7.9 (1)
C13	0.6442 (3)	0.6742 (5)	-0.0042 (3)	4.4 (1)	O6	0.3953 (2)	0.4235 (5)	0.6775 (3)	7.0 (1)
C14	0.3134 (3)	0.2609 (6)	0.9456 (4)	5.3 (1)	O7	0.4615 (2)	0.5855 (5)	0.6694 (4)	7.2 (1)
C15	0.3394 (4)	0.3288 (6)	0.8850 (4)	6.5 (2)	O8	0.6508 (2)	0.2200 (3)	0.4198 (2)	4.36 (7)
C16	0.4110 (3)	0.3064 (8)	0.8849 (4)	7.2 (2)	O9	0.6206 (2)	0.2121 (4)	0.5493 (2)	6.13 (9)
C17	0.4510 (3)	0.2220 (9)	0.9392 (5)	7.8 (2)	C49	0.8804 (3)	0.3314 (7)	0.5486 (4)	6.1 (1)
C18	0.5753 (3)	0.6550 (7)	-0.0012 (4)	6.5 (1)	C50	0.9275 (4)	0.4164 (8)	0.5975 (5)	7.2 (2)
C19	0.3311 (3)	0.2120 (5)	0.1698 (3)	4.3 (1)	C51	-0.0053 (4)	0.4316 (7)	0.5794 (5)	6.9 (2)
C20	0.3989 (4)	0.2387 (7)	0.2294 (6)	8.1 (2)	C52	0.0099 (3)	0.3692 (7)	0.5129 (5)	6.5 (2)
C21	0.4087 (5)	0.3381 (9)	0.2899 (6)	10.0 (2)	C53	0.0415 (3)	0.7848 (6)	0.5410 (4)	5.3 (1)
C22	0.3515 (4)	0.4119 (8)	0.2921 (5)	7.8 (2)	C54	0.8946 (2)	0.2664 (5)	0.4780 (3)	4.3 (1)
C23	0.2870 (4)	0.3891 (8)	0.2325 (6)	8.7 (2)	C55	0.1588 (3)	0.6784 (6)	0.5818 (3)	4.5 (1)
C24	0.2741 (3)	0.2864 (7)	0.1710 (5)	6.7 (2)	C56	0.2654 (2)	0.5671 (5)	0.5987 (3)	4.0 (1)
C25	0.1954 (3)	0.6774 (5)	0.9680 (3)	4.1 (1)	C57	0.2333 (3)	0.4404 (6)	0.5657 (4)	5.6 (1)
C26	0.1730 (3)	0.6012 (5)	0.0275 (4)	5.1 (1)	C58	0.3377 (2)	0.5892 (5)	0.5785 (3)	4.02 (9)
C27	0.1220 (3)	0.5087 (6)	-0.0062 (4)	6.2 (1)	C59	0.4038 (2)	0.5303 (5)	0.6465 (3)	4.6 (1)
C28	0.0943 (3)	0.4896 (7)	0.9010 (4)	6.4 (1)	C60	0.6272 (2)	0.2697 (5)	0.4852 (3)	4.0 (1)
C29	0.1155 (4)	0.5638 (7)	0.8409 (4)	6.2 (1)	C61	0.6118 (2)	0.4017 (5)	0.4697 (3)	4.2 (1)
C30	0.1632 (3)	0.6580 (6)	0.8745 (3)	5.1 (1)	C62	0.6386 (3)	0.4714 (6)	0.4121 (4)	6.0 (1)
C31	0.6885 (2)	0.2982 (5)	0.0694 (3)	3.98 (9)	C63	0.6241 (4)	0.5946 (8)	0.3998 (5)	7.9 (2)
C32	0.3395 (3)	0.6813 (6)	0.9180 (3)	4.8 (1)	C64	0.5799 (4)	0.6504 (7)	0.4444 (5)	7.5 (2)
C33	0.3827 (3)	0.6695 (6)	0.8606 (4)	5.7 (1)	C65	0.5517 (3)	0.5830 (7)	0.5021 (4)	6.5 (1)
C34	0.6000 (3)	0.2721 (7)	0.1826 (4)	5.9 (1)	C66	0.5683 (3)	0.4601 (6)	0.5145 (4)	5.4 (1)

tration. Crystal data appear in Table V, final non-hydrogen positional parameters and selected interatomic distances for the cation in Tables VI and VII, respectively. Figure 2 shows the geometry of the (+)-cation along with the atom labelling scheme, Figure 3 the geometry of the HDBT anion.

Electrophilic Cleavage Reactions of VII. A series of experiments was carried out in which about 0.1 g of VII dissolved in 1 mL of CDCl₃ was treated with an excess of anhydrous hydrogen chloride, chlorine, mercuric chloride, or iodine. The reactions were monitored by ¹H NMR spectroscopy and in all cases were found to proceed quickly and quantitatively to the corresponding haloruthenium complexes [RuX(CO)(CNBu-t)(triphos)]PF₆ (X = Cl, I). Other products detected were MeCl from Cl₂, MeHgCl from HgCl₂ (quantitative yield), and MeI from I₂ (quantative yield).

Treatment of 0.05 g of (–)-VII in 10 mL or methylene chloride with excess HCl, followed by rapid concentration at reduced pressure (to remove the HCl) and dilution to 10 mL, resulted in a solution of the chloro complex which exhibited a negative optical rotation which was 14% of the original rotation. The rotation decreased to 5% after 13 h and 2% after 1.5 days. Very similar results were obtained with chlorine and mercuric chloride. Cleavage with iodine presented problems of absorption if an excess of iodine was used, and therefore an experiment with a slight deficiency of iodine was carried out. In a reaction with (+)-VII, the rotation of the solution remained positive but fell quickly to about 20% of the original value. The rotation slowly decreased to about 11% of the original value over 2 days.

Attempts To Resolve [RuI(CO)(CNBr-t)(triphos)]⁺. To 1.0 g (0.8 mmol) of [RuMe(CO)(CNBu-t)(triphos)][HDBT] in 10

(14) Johnson, C. K. Ortep, Report ORNL-3974; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Figure 3. Ortep drawing of the (R,R)-HDBT anion with the atomic labeling scheme.

mL of methylene chloride was added 0.2 g (0.8 mmol) of iodine. The solution was stirred for 15 min, after which time all the methyl complex had been converted to the iodo complex (IR). All attempts to attain diastereomeric separation via crystallization from methylene chloride/heptane, methylene chloride/ethyl ether, acetonitrile/ether, and acetone/ether failed to give crystalline material.

Alternatively, 1.44 g (1.47 mmol) of [RuMe(CO)(CNBu-t)-(triphos)]I in 40 mL of ethanol was combined with 0.5 g (1.47 mmol) of silver d-camphor-10-sulfonate. The mixture was stirred 30 min, filtered to remove silver iodide, and taken to dryness under

Table VII. Selected Bond Lengths (Å) and Angles (deg) in the Cation

Bond Lengths			
Ru-P1	2.397 (1)	Ru-C1	2.209 (5)
Ru-P2	2.392 (1)	Ru-C2	1.895 (5)
Ru-P3	2.405 (1)	Ru-C3	1.972 (4)
P1-C8	1.835 (4)	P2-C9	1.863 (4)
P1-C13	1.837 (4)	P2-C25	1.818 (4)
P1-C19	1.829 (5)	P2-C31	1.839 (4)
P3-C10	1.852 (4)	C8-C11	1.556 (6)
P3-C37	1.829 (4)	C9-C11	1.522 (6)
P3-C43	1.834 (4)	C10-C11	1.540 (6)
N-C4	1.465 (6)	C11-C12	1.542 (5)
N-C3	1.158 (6)	C4-C5	1.489 (10)
O1-C2	1.143 (6)	C4-C6	1.505 (11)
C4-C7	1.488 (9)		

Bond Angles			
P1-Ru-P2	88.76 (4)	P1-Ru-P3	85.17 (3)
P1-Ru-C1	177.9 (1)	P1-Ru-C2	100.2 (1)
P1-Ru-C3	96.0 (1)	P2-Ru-P3	86.93 (3)
P2-Ru-C1	89.8 (2)	P2-Ru-C2	170.8 (1)
P2-Ru-C3	92.3 (1)	P3-Ru-C1	96.3 (1)
P3-Ru-C2	95.7 (1)	P3-Ru-C3	178.6 (1)
C1-Ru-C2	81.2 (2)	C8-C11-C9	113.2 (3)
C1-Ru-C3	82.5 (2)	C8-C11-C10	110.1 (3)
C2-Ru-C3	84.9 (2)	C8-C11-C12	106.6 (3)
Ru-P1-C8	110.4 (1)	C9-C11-C10	112.9 (3)
C9-C11-C12	106.0 (4)	C10-C11-C12	107.5 (3)
Ru-P2-C9	110.5 (1)	Ru-P3-C10	109.6 (1)
Ru-C2-O1	170.6 (4)	Ru-C3-N	172.7 (4)
C3-N-C4	179.0 (5)	C5-C4-C6	109.4 (9)
C5-C4-C7	114.0 (8)	C6-C4-C7	110.6 (7)
N-C4-C5	106.9 (5)	N-C4-C6	107.4 (6)
N-C4-C7	108.3 (5)	P1-C8-C11	115.3 (2)
P2-C9-C11	116.3 (3)	P3-C10-C11	116.5 (3)

reduced pressure. The residue was dissolved in 40 mL of methylene chloride and filtered, and the solvent was removed again to yield 1.5 g (90% yield) of the *d*-camphor-10-sulfonate salt of the methyl complex as an oil. This was dissolved in 30 mL of methylene chloride and treated with a solution of 0.34 g (1.34 mmol, 1 equiv) of iodine in 20 mL of methylene chloride. An IR spectrum showed that the iodo salt had been formed cleanly, but again all attempts to effect diastereomeric separation via fractional crystallization failed.

In a different approach, 0.71 g (0.91 mmol) of Ru(CO)₂(triphos) in 10 mL of methylene chloride was converted to [RuI(CO)₂(triphos)]I via treatment with 0.22 g (0.86 mmol) of iodine in 16 mL of methylene chloride. To the resulting soluton was added 0.08 mL (0.9 mmol) of *t*-BuNC and a solution of 0.07 g (0.93 mmol) of Me₃NO in 3 mL of methylene chloride. The solution was stirred for 2 h and concentrated to 5 mL, and sufficient ether was added to induce crystallization of the [RuI(CO)(CNBu-*t*)(triphos)]I. Yield after recrystallization from methylene chloride/ether was 0.74 g (74%, 0.67 mmol). The iodide salt was then stirred with 0.3 g (0.64 mmol) of AgHBDT in 25 mL of ethanol, yielding [RuI(CO)(CNBu-*t*)(triphos)][HDBT] after removal of the precipitated silver iodide. All attempts to effect diastereomeric separation via fractional crystallization failed.

Experiments with Chiral Shift Reagents. In a typical experiment, about 10 mg of [RuI(CO)(CNBu-*t*)(triphos)][HDBT] was dissolved in 0.5 mL of CD₂Cl₂. A ¹H NMR spectrum was run, and then 50–60 mg of a shift reagent (Pr(tfc)₃, Yb(tfc)₃, Eu(hpt)₃, or Yb(hpt)₃) was added. In most cases there was very little change in the spectra, and certainly no distinction between diastereomers. The largest relative shift of any resonance was 1.7 ppm for the triphos methyl resonance, effected by using Yb(tfc)₃. Addition of 4 equiv of Eu(tfc)₃ to a solution of [RuMe(CO)(CNBu-*t*)(triphos)]PF₆ in methylene chloride had essentially no effect, although addition of 2 equiv of the same shift reagent to the HDBT salt caused a 0.4 ppm shift of the triphos methyl resonance.

Results and Discussion

The original aim of this research was to synthesize a series of stable, chiral complexes of the type [RuR(CO)-

(L)(triphos)]⁺ and to investigate their chemistry, in particular that involving "insertion" and cleavage reactions of the alkyl groups R. Representative alkyl complexes would then be resolved, as would be any interesting products of reactions involving the alkyl groups. The absolute configurations would be determined crystallographically in all cases, and thus information concerning the stereochemistry of the reactions would be obtained. Eventually, it was anticipated that sufficient ORD/CD spectra would become available that correlations of these types of spectroscopic data with absolute configurations would be possible.

While the complex [RuMe(CO)₂(triphos)]⁺ is generally inert to substitution reactions under mild conditions, it reacts readily with a variety of ligands in the presence of trimethylamine *N*-oxide,[15] substituting one carbonyl group. In all cases, the pair of ν(CO) at frequencies >2000 cm⁻¹ is replaced by a single band at a lower frequency. The chiral derivative containing PMe₂Ph (I) was readily formed in this way, and, as anticipated, the magnetic nonequivalence of the two ligand methyl resonances was reflected in both the ¹H and the ¹³C NMR spectra. Similarly there were four phosphorus resonances in the ³¹P NMR spectrum, with cis *J*(P-P) = 20–40 Hz and trans *J*(P-P) = 219 Hz. The methyl group attached to the metal exhibits spin-spin coupling to all four phosphorus atoms in both the ¹H and the ¹³C NMR spectra. As with [RuMe(CO)₂(triphos)]PF₆,[1] coupling of the ruthenium–methyl protons to the trans phosphorus atom is less than is coupling to the coupling to the cis phosphorus atoms.

These spectroscopic data were the first indications which we had that the anticipated new series of chiral compounds would at the very least not racemize rapidly on the NMR time scale via some fluxional process but would in principle be resolvable. The phosphine ligand of I is somewhat labile, however, and is slowly replaced by CO, by P(OMe)₃, by *t*-BuNC, and even by iodide ion. The product of the last reaction RuMeI(CO)(triphos) (II) was not obtained analytically pure but was characterized spectroscopically. Thus II exhibits a single ν(CO) at 1973 cm⁻¹ and three resonances in its ³¹P NMR spectrum, while the ruthenium–methyl resonance in the ¹H NMR spectrum exhibits coupling to three phosphorus atoms. In view of the lability of I, no attempts were made at its resolution.

The synthesis and spectroscopic properties of the P-(OMe)₃ complex III were very similar to those of I. Interestingly, although the phosphite is a weaker donor than is the phosphine, as is shown by the higher ν(CO) of III (1985 vs. 1967 cm⁻¹), III is considerably more stable with respect to ligand substitution. As mentioned above, I can be converted to III although the reverse does not appear to be true. Similarly, although I reacts with CO to give the dicarbonyl species, III is inert to CO under the same conditions.

As mentioned in the Experimental Section, attempts to form similar complexes with P(OPh)₃, PPh₃ and (*S*)-PPh₂NHCHMePh yielded only compounds in which a CO had been substituted by iodide (II), chloride (IV), or nitrate (V). As none of these compounds was obtained pure, all were characterized spectroscopically as described above for II. Only in the case of PEt₃ was a phosphine complex (VI) possibly formed in small amounts. On the basis of the information available, the ease of formation of complexes containing phosphorus donors decreases in the order P(OMe)₃ > PMe₂Ph > PEt₃ > PPh₃. The relative sta-

(15) (a) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53. (b) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255.
(16) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

bilities thus correlate well with the relative ligand steric requirements, as indicated by their cone angles which increase in the order $P(OMe)_3$ (107°) < PMe_2Ph (112°) < PEt_3 (132°) < PPh_3 (145°).[16] Space-filling molecular models of the Ru(triphos) moiety and the crystal structure of (+)-VII suggest that the triangular face opposite the triphos is very crowded, with the six phenyl groups forming an "umbrella" over the other three coordination positions. Thus steric control of much of the coordination chemistry of the compounds described here seems quite reasonable.

The methyl and benzyl complexes containing *t*-BuNC, VII and XII, respectively, were readily synthesized and purified, and all spectroscopic data are consistent with their formulation. The isocyanide ligand was found not to undergo substitution on treatment with CO or $P(OMe)_3$, and the methyl compound VII was chosen for attempts at resolution (see below).

The methyl complex containing *sec*-BuNC (X) was synthesized because the isocyanide ligand is chiral, and thus X should be formed as mixture of diastereomers, with different spectroscopic properties. The diastereomers do in fact exhibit different ^1H, ^{13}C, and ^{31}P NMR spectra, but all attempts to effect their separation failed and attempts to utilize X for stereochemical studies were abandoned. The complexes of the chiral ligands $PPh_2NHCHMePh$ and PhMeCHNC were sought for the same reason, and indeed complexes of the chiral phosphine have been utilized successfully for separation of diastereomers of organometallic compounds.[6] However, as mentioned above, the phosphine appears to be too bulky to coordinate and the desired complex would not be obtained. In contrast, the complex of the chiral isocyanide was readily formed (ν(CO) = 1998 cm^{-1} (br), ν(CN) = 2164 cm^{-1} (br)) but exhibited very complicated NMR spectra which were uninterpretable. In view of the relatively large steric requirements of this particular isocyanide and its undoubtedly sterically congested environment, we suspect that the complications in the spectra are a result of the presence of rotational isomers of the two diastereomers. The complex was not investigated in further detail.
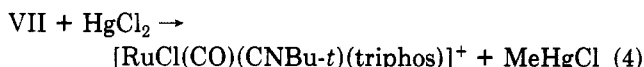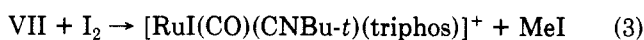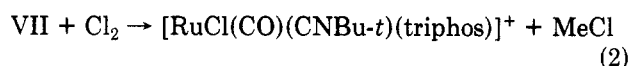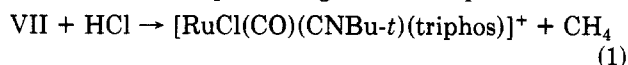
Resolution of VII. Complex VII was chosen for our initial attempts at resolving a triphos complex because of its relatively high stability, which presumably arises in part because of the linear array of the CNC moiety and the resulting relatively low steric requirements of the ligand. Although several approaches to separation of the enantiomers via the formation of diastereomeric salts using chiral anions were attempted, resolution was best effected with the conjugate base of (*R,R*)-dibenzoyltartaric acid (H$_2$DBT), available from the benzoylation of (*R,R*)-tartaric acid with benzoyl chloride.[17] As outlined in the Experimental Section, treatment of racemic [RuMe(CO)-(CNBu-*t*)(triphos)]I with AgHDBT yielded, after removal of precipitated AgI, a solution containing the diastereomers of [RuMe(CO)(CNBu-*t*)(triphos)][HDBT]. Fractional crystallization followed by metathesis with NaPF$_6$ yielded both enantiomers of VII, apparently in high optical purity. ORD data are listed in Table IV, while the CD spectra are shown in Figure 1. The CD spectra were difficult to obtain because relatively intense phenyl absorptions in the region of interest in the UV–vis spectrum necessitated the use of relatively dilute solutions.

The structure of the (+)-enantiomer of VII was determined by carrying out an X-ray crystal structure determination of its HDBT precursor, the absolute configuration being readily ascertained on the basis of the known

absolute configuration of (*R,R*)-tartaric acid.[18] Ortep drawings of the cation and anion are shown in Figures 2 and 3, respectively; selected bond lengths and angles of the cation are listed in Table VII. The complex cation is, as expected, essentially octahedral. The three Ru–P bond distances are marginally different and suggest that the trans influences of the three carbon donor ligands are similar but decrease in the order *t*-BuNC > Me > CO; all three Ru–P distances appear to be relatively long.[19] The ruthenium–carbon distances decrease in the order Ru–Me > Ru–CNBu-*t* > Ru–CO, consistent with changes in both carbon hybridization and degrees of back-donation. Comparisons with similar data in the literature would be rather meaningless.

In order to denote the absolute configuration of the cationic complex, one may employ modifications of the Cahn–Ingold–Prelog (CIP) procedures, as advocated for octahedral complexes by Sloan.[20] On this basis, the configuration of the cation is to be denoted OC-6-43-A.[20]

Electrophilic Cleavage Reactions. NMR experiments showed that the methyl group of VII is cleaved cleanly by a number of electrophilic reagents as in eq 1–4. In view

$$VII + HCl \rightarrow [RuCl(CO)(CNBu-t)(triphos)]^+ + CH_4 \quad (1)$$

$$VII + Cl_2 \rightarrow [RuCl(CO)(CNBu-t)(triphos)]^+ + MeCl \quad (2)$$

$$VII + I_2 \rightarrow [RuI(CO)(CNBu-t)(triphos)]^+ + MeI \quad (3)$$

$$VII + HgCl_2 \rightarrow$$
$$[RuCl(CO)(CNBu-t)(triphos)]^+ + MeHgCl \quad (4)$$

of the general importance of the stereochemistry of such reactions as an aid in deducing their mechanisms,[21] we have carried out all four reactions with resolved VII. In all cases, ORD studies suggested that the reactions proceed with at least partial stereoselectivity but that the halo products racemize over a few hours; in addition, all attempts at resolving the halo products failed.[22] CD spectra could not be obtained for the products, in part because of the weakness of the optical rotations and in part because intense electronic absorptions over the frequency range of interest necessitated the use of very dilute solutions. Although we cannot therefore deduce the stereochemical implications (whether retention or inversion) of reaction 1–4, we have found that cleavage reactions with deficiencies of iodine and mercuric chloride did not induce significant racemization of unreacted VII. As partial racemization of resolved compounds of the type CpFe(CO)(PPh$_3$)R in such

(17) Butler, C. L.; Cretcher, L. H. *J. Am. Chem. Soc.* **1933**, *55*, 2605.

(18) For a survey of relevant publications, see: Buding, H.; Deppisch, B.; Musso, H.; Snatzke, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 513.

(19) For a summary of relevant data, see: Wilkes, L. M.; Nelson, J. H.; Mitchener, J. P.; Babich, M. W.; Riley, W. C.; Helland, B. J.; Jacobson, R. A.; Cheng, M. Y.; Seff, K.; McCusker, L. B. *Inorg. Chem.* **1982**, *21*, 1376.

(20) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1. Normal CIP priorities are assigned for all ligands, i.e., P (priority no. 1) > CO > BuNC > Me (priority no. 4). Within the set of equivalent P atoms, preference (highest seniority) is assigned to that which is trans to the donor of lowest priority ("trans maximum difference rule"), i.e., P1 (trans to Me) > P3 (trans to BuNC) > P2 (trans to CO). The principal axis is defined by P1 and Me (C1). OC-6 refers to the fact that the complex is octahedral, 6-coordinated, 4 is the priority number of the ligating atom trans to the most preferred atom of priority 1 (P1), 3 is the priority number of the atom trans to the most preferred ligating atom in the plane perpendicular to the principal axis, and A signifies anticlockwise ordering of CIP priority numbers of the ligating atoms in the plane perpendicular to the principal axis when viewed from the atom of lowest priority number.

(21) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.

(22) While we do not know the mechanism of the racemization process, it seems possible that the halo ligands are labilized with respect to dissociation because of the large trans influence of the triphos donor atoms. See ref 1 for other possible manifestations of the trans influence of the triphos in these types of complexes.

Table VIII. ^{13}C NMR Data for the Complexes [RuX(CO)(^{13}CO)(triphos)]$^+$ and [Ru(CO)$_2$(^{13}CO)(triphos)]$^{2+}$

X	J(C-P')^a	J(C-P'')^a	J(C-P''')^a	J(P'-P'')^a	J(P'-P''')^a	J(P''-P''')^a	$\lvert\delta_{P'}-\delta_P\rvert^b$
Cl	89	7	12	44	32	32	0.02
Br	87	8	10	44	31	31	0.02
I	85	7	11	45	31	31	0.02
H	69	7	12	45	29	29	0.01
Me	78	6	13	45	30	30	0.02
PhCH$_2$	77	7	13	45	30	30	0.03
C$_3$H$_5$	78	6	12	44	30	30	0.01
CHO	64	8	8	44	30	30	0.015
CO	70	10	10	33	33	33	0.03

^{a} Hz. ^{b} ppm.

experiments has been taken as evidence of oxidative mechanisms[23] and 17-electron, fluxional intermediates, it may be that the reactions studied here involve classical S_E2 processes.[2,21] The similarities in behavior of the four systems certainly suggest a common reaction path.

In an unsuccessful effort to obtain a quantitative measure of the degree of racemization accompanying the cleavage reactions, attempts were initiated to prepare diastereomeric complexes of the chiral ligands sec-BuNC and PhMeCHNC; a similar approach has been taken elsewhere.[4b,24] We also assessed the utility of the chiral shift reagents M(hpc)$_3$ (M = Eu, Yb) and M(tfc)$_3$ (M = Pr, Yb). While VII contains no donor atoms with which to coordinate, we anticipated that the PF$_6^-$ would bind to the lanthanide complexes and that the so-formed chiral anions would form ion pairs with the chiral cation, thus hopefully leading to diastereomeric discrimination. The europium compound Eu(tfc)$_3$ has recently been used in this way to distinguish between the enantiomers of [Ru(o-phenanthroline)$_3$]Cl$_2$.[25] While the ^{1}NMR spectrum of VII changed very little on the addition of the chiral shift reagents to its solutions, suggesting little interaction, the corresponding HDBT salt did exhibit changes in its ^{1}H NMR spectrum, albeit primarily with the triphos methyl resonance. Similar observations were made with the PF$_6$ and HDBT salts of the iodo analogue.[26] However, as the desired diastereomeric discrimination was not achieved in either case, the approach was abandoned.

^{13}C NMR Spectra of the Complexes [RuX(CO)(^{13}CO)(triphos)]$^+$ (X = Cl, Br, I, H, Me, PhCH$_2$, η^2-Allyl, CHO) in the Carbonyl Region.

Dicarbonyl complexes containing ^{13}C at natural abundance are chiral and the two phosphorus atoms, P' and P'', trans to the carbonyl groups are non-equivalent, as in A. The ^{13}C

A
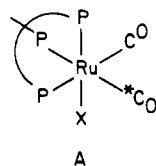
NMR spectra in the carbonyl region thus exhibit the X parts of ABKX spin systems (A, B, K = ^{31}P), and the observed second-order patterns of the carbonyl resonances (example in Figure 4) depend on the phosphorus chemical shifts and both the magnitudes and the relative signs of ^2J(P-P) and ^2J(C-P).

In contrast to the situation with ^{31}P NMR spectroscopy of complexes of tertiary phosphines, where the signs of many spin–spin coupling constants between ^{31}P and magnetic nuclei of other donor atoms are known,[27] there are available relatively few data pertaining to the signs of coupling constants of the ^{13}C of a coordinated CO with, for instance, the ^{31}P of a coordinated phosphine. The only data available appeared in 1981[28] and dealt with carbonyl phosphine complexes of chromium, molybdenum, and tungsten. It was found that cis ^2J(C-P) is negative for compounds of all three metals but that the corresponding two bond trans couplings are positive for molybdenum and tungsten but negative for chromium. The pattern of signs is thus identical to that found for ^2J(P-P) for similar compounds.[27,32]

To our knowledge, no data concerning the signs of ^2J(C-P) for carbonyl complexes of the platinum metals have been reported, although molecular orbital studies suggest that such data can throw much light on the nature of the bonding in such complexes.[29] By making reasonable assumptions concerning certain of the NMR parameters, however, it has been possible to simulate the spectra of the dicarbonyl complexes listed above and reported previously,[1] thereby obtaining the first information available concerning the relative signs of ^2J(C-P). While the results to be presented below retain an element of ambiguity, their confirmation must await spin tickling studies on ^{13}C-enriched materials.

As a representative example, the carbonyl resonance of the bromo complex at 100.6 MHz is illustrated in Figure 4a. Simulation of the spectrum required input concerning the three ^{31}P chemical shifts and the three ^2J(P-P), and it was assumed (a) that the chemical shift of P''' is identical with that in the ^{31}P{^{1}H} NMR spectrum of the ^{13}C-free material[30] and (b) that J(P'''-P') and J(P'''-P'') are equal to the value of J(P-P) obtained on inspection of the spectrum of the ^{13}C-free material.[1] It was also assumed that all values of ^2J(P-P) have the same sign, presumably negative.[27] A wide variety of P' and P'' chemical shift and ^2J(C-P) data were then assessed, and the best fits were found utilizing the data of Table VIII; the simulation is illustrated in Figure 4b.

To successfully simulate the spectra, it was found necessary that the chemical shifts of P' and P'' differ by about 0.2 ppm (too small to be resolved in the ^{31}P spectra; sign of the isotope shift unknown) and that the large ^2J(C-P) and the larger of the two small ^2J(C-P) be of opposite sign.

(23) (a) Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33. (b) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619.

(24) Johnson, B. V.; Sturtzel, D. P.; Shade, J. E. *Inorg. Chim. Acta* **1979**, *32*, 243.

(25) Barton, J. K.; Norwick, J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1650.

(26) These observations suggest that ion pairing occurs primarily at the "backside" of the triphos ligand. In agreement with this conclusion, the triphos methyl chemical shifts of several of the cationic complexes reported here are relatively sensitive to the nature of the counterion.

(27) (a) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}NMR of Transition Metal Complexes*; Springer-Verlag: Berlin, 1979. (b) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.

(28) (28) Colquoun, I. J.; Grim, S. O.; McFarlane, W.; Mitchell, J. D.; Smith, P. H. *Inorg. Chem.* **1981**, *20*, 2516.

(29) See, for instance: Koie, Y.; Shinoda, S.; Saito, Y. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 147.

(30) Trans influences on ^{31}P chemical shifts are normally much greater than cis influences,[27] and thus the chemical shift of P''' should be relatively unaffected by substitution of ^{12}CO by ^{13}CO.
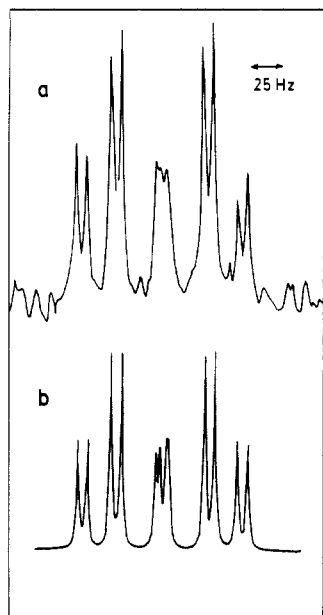
Figure 4. (a) Carbonyl resonance of [RuBr(CO)(^{13}CO)(triphos)]$^+$ at 100.6 MHz. (b) Simulated spectrum.

Since (a) there are two small and one large J(C–P) and (b) trans ^2J(P–P) of platinum metal compounds are generally $\gg$cis ^2J(P–P),[27] we assign the large carbon–phosphorus coupling to J(C–P′). The absolute values of each of the two small J(C–P) vary little and are $\gg$0, and thus each is probably of constant sign. Although they need not be of the same sign, as mentioned above cis ^2J(P–P) of such complexes are negative and we suggest that the same is true of cis ^2J(C–P). We tentatively assign the smaller, less variable of the two to J(C–P″), as greater variation is to

be anticipated for P‴, which is trans to X, than for P″, which is trans to CO.

We have also simulated the carbonyl spectrum of the related achiral complex [Ru(CO)$_2$(^{13}CO)(triphos)]$^{2+}$.[31] Assuming that trans ^2J(C–P) is large and $\gg$0 and cis ^2J-(C–P) is small and <0, it was possible to show that P (trans to ^{13}CO) lies about 0.03 ppm upfield relative to P (trans to ^{12}CO). This appears to be the first determination of a carbon isotope shift on a trans phosphorus atom.

(31) Hommeltoft, S. I. Ph.D. Thesis, Queen's University, 1985.
(32) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 2694.