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Preliminary communication

SYNTHESIS AND RESOLUTION OF A NOVEL SERIES OF OCTAHEDRAL ORGANOMETALLIC COMPLEXES CHIRAL AT THE METAL ATOM

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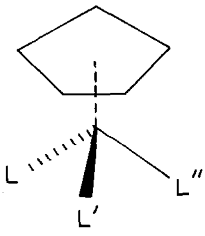
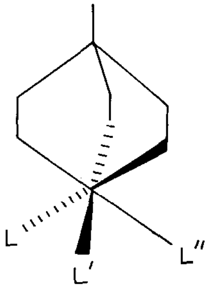
Summary

A series of chiral complexes of the type [RuX(CO)L(triphos)]X′ (X,X′ = anions, L = neutral ligands, triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane) has been synthesized, and the chemistry studied. The compound [RuMe(CO)(CNBu^t)(triphos)] PF$_6$ has been resolved, and the absolute configurations of the (+)-enantiomer have been determined.

Optically active organotransition metal complexes containing chiral metal atoms have found widespread applications in stereochemical studies in recent years [1]. Many investigations have utilized four coordinate, pseudo-tetrahedral complexes of type A, and reactions studied mechanistically include insertion, alkyl cleavage, ligand exchange and racemization processes [1]. In spite of the progress made, however, it is not at all clear to what extent the results of in-



(A)



(B)

vestigations involving compounds of type A can be generalized, especially to six coordinate, octahedral systems. Relatively few octahedral organometallic compounds chiral at the metal have been reported, and examples that have, i.e. *fac*-$Mn(CO)_3(L—L')Br$ (L—L' = bidentate ligand containing different donor atoms) [2] and $Bpz_4M(CO)(NO)L$ (Bpz_4 = polypyrazolyl borate, L = neutral ligand, M = Mo, W) [3,4] have not been exploited for various reasons.

We wish now to report the synthesis and resolution of a new type of organometallic, octahedral complex chiral at the metal. Chirality is achieved by coordination of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to an octahedral system as in B. The ligand triphos was chosen because of its great proclivity to coordinate comfortably to a triangular face of an octahedron; all complexes in which this ligand behaves as a tridentate chelate exhibit PMP bond angles of about 90° regardless of the nature and number of the other ligands [5]. Thus complexes of the type triphosMLL'L" can be expected to be stable with respect to dissociation of a coordinated phosphorus atom or isomerization of the facial MP_3 moiety [6].

Our initial studies have involved ruthenium. Oxidative addition reactions of halogens [7], methyl iodide, and hydrogen chloride with $Ru(CO)_2$(triphos) [7] proceed smoothly to give the complexes $[RuX(CO)_2$triphos$]X'$ (X = Br, I, Me, H; X' = halide). Subsequent treatment of these complexes with a variety of neutral ligands L (L = t-BuNC, s-BuNC, $P(OMe)_3$, PMe_2Ph, but not PEt_3 or PPh_3, which have larger cone angles) in the presence of trimethylamine-*N*-oxide yields chiral complexes of the types [RuX(CO)L(triphos)]X'. While an extensive series of such chiral complexes has been prepared, of particular interest at this stage is $[RuMe(CO)(CNBu^t)$triphos$]PF_6$ (I), which has been characterized by elemental analyses and IR, ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy*.

Compound I has been successfully resolved by treatment of $[RuMe(CO)(CNBu^t)$triphos$]I$ in refluxing ethanol with the silver salt of (+)-dibenzoyl hydrogentartrate [8]. After removal of silver iodide and concentration of the solution, white crystals of $(+)\text{-}[RuMe(CO)(CNBu^t)$triphos$][(PhCO_2CHCO_2)_2H]$ (II) were obtained. This compound was recrystallized (CH_2Cl_2/Et_2O) to constant rotation at 589 nm, and then the resolved cation was obtained as the PF_6^- salt by adding $NaPF_6$ to an ethanolic solution of the dibenzoyl hydrogentartrate salt. The PF_6^- salt of the other enantiomer was obtained in much the same way from the mother liquor resulting from the silver iodide precipitation. Specific rotations of the two enantiomeric materials are listed in Table 1.

TABLE 1

SPECIFIC ROTATIONS $[\alpha]_\lambda^{25}$ OF (+)- AND (−)-I IN $CHCl_3$ (*c* 3 × 10^{-3} *M*)

λ (nm)	589	578	546	438	365
(+)-I	+25.4	+26.7	+31.0	+59.5	+112.9
(−)-I	−27.7	−28.1	−31.8	−59.6	−110.9

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*^1H NMR ($CDCl_3$) δ (ppm for TMS): 0.11 (Me—Ru, doublet of triplets, $J(PH)_{cis}$ 5.7 Hz, $J(PH)_{trans}$ 3.2 Hz), 1.45 (Me_3CNC, s), 1.60 (MeC, q, $J(PH)$ ~1 Hz), 2.0—2.9 (CH_2, m), 6.7—7.8 (Ph, m). $^{31}P\text{-}\{^1H\}$ NMR $CDCl_3$ δ (ppm from ext H_3PO_4): 6.1 (1P, t, $J(PP)$ ~30 Hz), 12.4 (1P, dd, $J(PP)$ 31, 43 Hz), 15.4 (1P, dd, $J(PP)$ 28, 43 Hz); IR (CH_2Cl_2): 2005 cm^{-1} ($\nu(CO)$), 2175 cm^{-1} ($\nu(CN)$).

In order to determine the absolute configuration of the resolved, chiral cation, we have carried out a single crystal X-ray diffraction study of (+)-II, the precursor of (+)-I, with the optically active anion.

Crystal data: II crystallized in space group $P2_1$, with a 19.356(5), b 10.841(3), c 15.262(3) Å, β 108.33(2)°, V 3040.0 Å^3, $Z = 2$, D_{calc} 1.321 Mg m^{-3}, μ 33.338 cm^{-1}. Data were collected on an Enraf—Nonius CAD-4 diffractometer using a crystal measuring 0.20 × 0.20 × 0.18 mm. Of the 4771 unique reflections measured, 4650 were considered observed, i.e. $I \geqslant 3\sigma(I)$. 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 intensity statistics indicated the space group to be noncentrosymmetric, confirming the choice of space group $P2_1$ over $P2_1/m$. The ruthenium and phosphorus atoms were found by the Patterson technique [9]. Difference Fourier map calculations revealed the rest of the structure, including the positions of fifty of the sixty-four hydrogen atoms in the asymmetric unit. Full matrix least-squares refinement minimizing $\Sigma w||F_o| - |F_c||^2$, 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 absolute configuration of the crystal structure was determined from the known absolute configuration of the anion. The crystallographic calculations were performed using the structure determination package of Enraf—Nonius SDP (1979) [10].

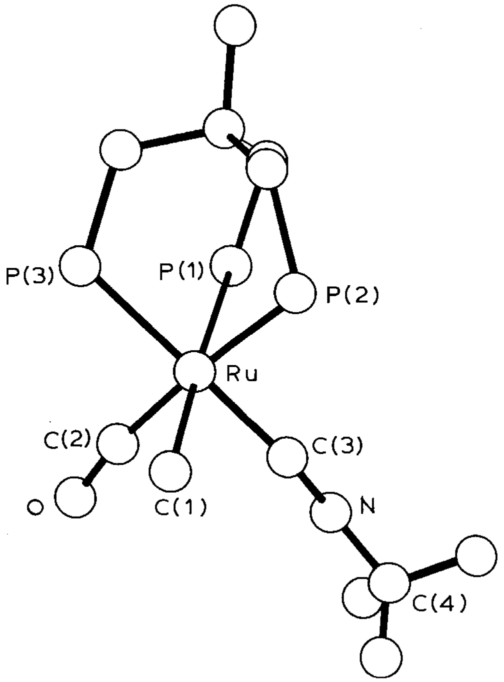

Fig. 1. The molecular structure of (+)-[RuMe(CO)(CNBu^t)triphos]$^+$. The phenyl groups and hydrogen atoms are omitted for clarity.

The structure of the complex cation is depicted in Fig. 1, while important bond lengths and angles are listed in Table 2. As can be seen, the appropriate CIP stereochemical descriptor of (+)-I is OC-6-43-A [11].

TABLE 2

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)[a]

Bond lengths		Bond angles	
Ru—P(1)	2.397(1)	P(1)—Ru—P(2)	88.76(4)
Ru—P(2)	2.392(1)	P(1)—Ru—P(3)	85.17(3)
Ru—P(3)	2.405(1)	P(2)—Ru—P(3)	86.93(3)
Ru—C(1)	2.209(5)	C(1)—Ru—C(2)	81.2(2)
Ru—C(2)	1.895(5)	C(1)—Ru—C(3)	82.5(2)
Ru—C(3)	1.972(4)	C(2)—Ru—C(3)	84.9(2)
N—C(3)	1.158(6)	Av. C—Ru—P	95.1±5.3
O—C(2)	1.143(6)		178.1±0.5

[a] Fractional atomic coordinates, anisotropic thermal parameters and lists of structure factors can be obtained from the authors.

Preliminary experiments indicate that (+)-I and (−)-I are stable with respect to racemization in methylene chloride solution at room temperature for at least 24 h, and that the methyl group is cleaved smoothly with a number of electrophilic reagents, is

$$\mathrm{I + HCl \rightarrow [RuCl(CO)(CNBu^t)triphos]PF_6 + CH_4} \tag{1}$$

$$\mathrm{I + I_2 \rightarrow [RuI(CO)(CNBu^t)triphos]PF_6 + MeI} \tag{2}$$

$$\mathrm{I + HgCl_2 \rightarrow [RuCl(CO)(CNBu^t)triphos]PF_6 + MeHgCl} \tag{3}$$

Corresponding reactions of (+)- and (−)-I in all cases proceeded to give solutions exhibiting optical rotations of the same signs as the reactants, but with only about 15% of the initial values. On standing, even these rotations decreased to zero, and thus it seems that all reactions were stereoselective, but that the halide products are unstable with respect to racemization. We have been unable to resolve any of the halo complexes, and thus the mechanistic implications of the results of the cleavage reactions are not yet clear. However, chiral octahedral triphos complexes undoubtedly hold great promise of providing mechanistic information for reactions of organometallic complexes, and further studies are in progress.

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9 The origin of the unit cell was selected by assigning a value of 0 to the y fractional coordinate of the ruthenium atom. Because of the space group symmetry, the Patterson synthesis does not yield a unique set of coordinates for the phosphorus atoms. Sign ambiguity remains in their y coordinates resulting in four non-equivalent enantiomorphic pairs of fractional coordinates. The initial choice of coordinates was based on geometrical considerations.
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