The broad *o*-H signal expected near −4.9 ppm[23] is obscured by the free thiol signal. From the relative intensities of *m*-H signals the ratio t^{2-}:d^{2-} is ~1.8:1. This value requires a net decrease in Fe atom mean oxidation state upon product formation, accounting for the appearance of disulfide in the spectrum. Formation of $[Fe_2S_2(SPh)_4]^{2-}$ could not be directly detected in spectrophotometric experiments because its visible spectrum (λ_{max} (ϵ_M) 493 (11 600) nm in Me_2SO[6]) is obscured by the more intense 458-nm absorption.

In contrast to the results with benzenethiol, treatment of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ with ≥30 equiv of 1,1-dimethylethanethiol gave no reaction and with 40 equiv of ethanethiol afforded a product with a broad, isotropically shifted resonance at −15.8 ppm. This signal does not correspond to that of $[Fe_4S_4(SEt)_4]^{2-}$ (−12.5 ppm in Me_2SO[42]) and is assigned to the methylene protons of $[Fe_6S_9(SEt)_2]^{4-}$. These observations suggest that core disruption may require protonation of core sulfur atoms, a process facilitated by the more acidic nature of aryl vs. alkyl thiols.

Summary. The species $[Fe_6S_9(SR)_2]^{4-}$ represents a fourth characterized structural type of Fe/S/SR clusters. With inclusion of $[Fe_6S_8(PEt_3)_6]^{2+}$ these Fe–S core units having the indicated (idealized) symmetries have now been established: $[Fe_2S_2]^{2+}$ (D_{2h}[6-8]), $[Fe_4S_4]^{2+}$ (D_{2d}[9,10]), $[Fe_4S_4]^{+}$ (D_{2d},[11a] C_{2v}[11b]), $[Fe_6S_8]^{2+}$ (O_h[15]), $[Fe_3S]^{4+}$ (C_{3v}[35]), $[Fe_6S_9]^{2-}$ (C_{2v}). All but $[Fe_3S]^{4+}$ may be regarded as constructed of planar or nonplanar Fe_2S_2 units **6**. The clusters $[Fe_6S_9(SR)_2]^{4-}$ exhibit certain properties in common with **1–3**: (i) visible RS → core charge-transfer spectra, which shift to lower energies when R = aryl vs. alkyl; (ii) antiferromagnetically coupled Fe sites; (iii) contact-shifted ^1H NMR spectra; (iv) electron-transfer series whose members are interrelated by chemically reversible one-electron reactions with potentials less negative for R = aryl vs. alkyl; (v) electronically delocalized structures in mixed-valence clusters as revealed by Mössbauer spectroscopy and the absence of structurally distinct Fe(II,III) sites from X-ray diffraction results; (vi) facile thiolate substitution reactions with retention of core structure. That disruption of the $[Fe_6S_9]^{2-}$ core with large excesses of benzenethiol produces $[Fe_2S_2(SPh)_4]^{2-}$ and $[Fe_4S_4(SPh)_4]^{2-}$ is not surprising in view of the stability of their core structures containing the unit **6**. Lastly, as observed in our initial report[17] of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{2-}$, the Fe_6S_9 core may be considered a candidate for structurally uncharacterized redox sites in Fe–S proteins. As with clusters containing Fe_2S_2 and Fe_4S_4 (but not as yet Fe_3S_3) cores, it can be readily assembled from simple reactants in a manner similar to the reconstitution of protein 2-Fe and 4-Fe sites with Fe(II,III) and sulfide reagents. However, as yet no analytically well-characterized proteins with the ratio S^{2-}:Fe > 1 are known, and we are not aware of any protein with an absorption spectrum closely similar to that of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ (Figure 5). The synthesis and properties of a fifth structural type of Fe/S/SR clusters, $[Fe_3S_4(SR)_4]^{3-}$ containing the core unit **9**, will be described elsewhere.[16]

Acknowledgment. This research was supported by NIH Grants GM-28856 (Harvard University) and HL-13157 (Northwestern University). We thank K. S. Hagen for experimental assistance.

Registry No. $(Me_3NCH_2Ph)_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$, 80976-82-5; benzenethiol, 108-98-5.

Supplementary Material Available: Positional and thermal parameters of all non-hydrogen atoms, bond distances and angles for cations and methanol solvate molecules, and calculated and observed structure amplitudes (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

Metal Complexes Containing Diastereoisomers and Enantiomers of *o*-Phenylenebis(methylphenylarsine) and Its Phosphorus Analogue. 3. Preparation and Stereochemistry of Octahedral Bis(bidentate)dichlororuthenium(II) Complexes

STEPHEN C. GROCOTT and STANLEY BRUCE WILD*[1]

Received December 15, 1981

A detailed investigation of the stereochemistry of *cis*- and *trans*-$[RuCl_2(bidentate)_2]$ containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue has been undertaken. The trans complexes were prepared in high yield from the ligands and a prereduced form of commercial ruthenium(III) chloride in the presence of aqueous formaldehyde. The optically active, racemic, meso, syn, and anti forms of the *trans*-dichloro complexes were isolated for both ligands, and each of these was subsequently isomerized to the corresponding cis compound by reaction with triethylaluminum. The various diastereoisomeric *cis*-dichloro compounds were also separated and characterized. Whereas the *trans*-dichloro isomers were relatively inert, the cis complexes readily underwent stereospecific halogen substitution by iodide ions and carbon monoxide.

Introduction

Bivalent ruthenium forms stable octahedral complexes containing chelating di(tertiary arsines) and phosphines of the type *cis*- and *trans*-$[RuX_2(bidentate)_2]$. In general, symmetrical bidentates have been employed as ligands,[2,3] although an investigation of the stereochemistry of trans complexes derived from 1,2-bis(methylphenylphosphino)ethane has been carried out by Horner and co-workers.[4] We have emphasized elsewhere[5,6] the value of using dissymmetric bidentates in their different stereoisomeric forms as probes for investigating the

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0020-1669/82/1321-3526$01.25/0

Table I. Some Physical Properties of the Complexes *trans*-[$RuCl_2$(bidentate)$_2$]

compd	mp, °C	δ(EMe)[a] Me···Me	δ(EMe)[a] Me···Ph
$(+)_{589}$-*trans*-[$RuCl_2$((*SS*)-diars)$_2$]	>315		1.55 s
meso-trans-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)]	>315	1.90 s[b]	
rac-trans-[$RuCl_2$((*RR,SS*)-diars)$_2$]	166–168		1.55 s
anti-trans-[$RuCl_2$((*RS*)-diars)$_2$]	>315		1.33
syn-trans-[$RuCl_2$((*RS*)-diars)$_2$]	295–296	1.90 s	
$(+)_{589}$-*trans*-[$RuCl_2$((*SS*)-diphos)$_2$]	>315		1.57 br s
meso-trans-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)]	>315	2.03 br s[b]	
rac-trans-[$RuCl_2$((*RR,SS*)-diphos)$_2$]	309–310		1.57 br s
anti-trans-[$RuCl_2$((*RS*)-diphos)$_2$]	>315		1.33 br s[b]
syn-trans-[$RuCl_2$((*RS*)-diphos)$_2$]	310	2.08 br s	
rac-trans-[$RuCl_2$((*RR,SS*)-diphos)((*RS*)-diphos)][c]	292–293	2.23 br d, 1.96 br d	1.39 br d, 1.28 br d

[a] Chemical shift values quoted relative to Me_4Si for $CDCl_3$ solutions of the complexes unless otherwise noted. [b] CH_2Cl_2 solution. [c] The ^1H NMR spectrum of this compound in the PMe region is available as supplementary material (Figure 9).

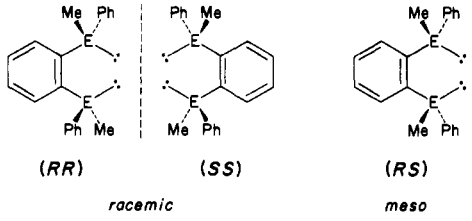

Figure 1. Stereoisomers of *o*-phenylenebis(methylphenylarsine) (E = As) and its phosphorus analogue (E = P).

dynamic behavior and reaction mechanisms of metal complexes in solution and also as a means of unambiguously assigning stereochemistries with NMR spectroscopy.

In this paper we describe in detail the preparation and properties of the complexes *cis*- and *trans*-[RuX_2(bidentate)$_2$] containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine)[7] and the corresponding di(tertiary phosphine).[8]

Results and Discussion

Stereochemistry. The stereoisomers of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue are depicted in Figure 1. The different forms of both ligands are air-stable crystalline solids.[7,8] Moreover, the asymmetric donor atoms in the free ligands are pyramidally stable under the conditions used to prepare the complexes described here.

In Figure 2 the stereochemistries of the complexes *trans*-[RuX_2(bidentate)$_2$] are summarized. For clarity, the relative arrangement of the methyl groups only is shown in each structure. The enantiomers of either ligand react to give optically active trans products of D_2 symmetry. The racemic forms of the ligands, however, yield pairs of internal diastereoisomers. The meso and racemic complexes cannot be interconverted by internal rotation. It is noteworthy that a racemic complex can always be identified in solution by comparing its NMR spectrum with that of the corresponding optically active material. The internally compensated meso forms of the ligands react to give achiral syn- and anti-trans isomers (syn and anti refer to the disposition of methyl groups in both cis and trans complexes).

In Figure 3 the products of the isomerization of the optically active complexes *trans*-[RuX_2((*SS*)-bidentate)$_2$] to corresponding cis compounds are shown. A pair of epimers is produced, differing in chirality only at the metal center. The symmetry of each is C_2, and consequently a pair of methyl resonances would be expected in the ^1H NMR spectrum of either compound. Isomerization of the corresponding racemic complexes, *rac-trans*-[RuX_2((*RR,SS*)-bidentate)$_2$], obviously produces the corresponding pair of racemic cis epimers. A racemic cis product of C_1 symmetry is obtained upon internal isomerization of the meso-trans complex, however (Figure 4). All four methyl groups in this isomer are magnetically nonequivalent. The isomerization of *syn*- or *anti-trans*-[RuX_2((*RS*)-bidentate)$_2$] leads to a potentially more complicated situation.[11] The products that may be obtained are depicted in Figure 5.

Preparation of Trans Complexes. A convenient method of preparing the compounds *trans*-[$RuCl_2$(bidentate)$_2$] was found. The procedure avoided the usual use of excess tertiary arsine or phosphine ligand as reductant. Commercial ruthenium trichloride[12] was dissolved in methanol and a stream of hydrogen passed through the solution at its boiling point for ca. 100 min. The reaction mixture at this stage was red-brown: further reduction led to the formation of Ru(II) species, as indicated by a green tinge in the solution.[14] The addition of this ruthenium(III) chloride solution to a mixture of 2 equiv of the appropriate ligand and excess aqueous formaldehyde in boiling methanol gave the complexes [$RuCl_2$(bidentate)$_2$] in 81–95% yield. The products were free from contamination by ruthenium metal and other byproducts often found when alternative methods of preparation are used.[4] Interestingly, neither the di(tertiary arsine) nor the phosphine appeared to react with a solution of ruthenium(II) chloride[15] in the absence of oxygen. However, if the reaction mixture was exposed to the atmosphere, after heating, the complexes [$RuCl_2$(bidentate)$_2$] precipitated in moderate yields.

1. Optically Active Trans Complexes. The reaction of 2 equiv of (*RR*)-diphos with prereduced commercial ruthenium(III) chloride, as described above, afforded optically active *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] in 81% yield (Table I). (In this paper diphos is defined as *o*-phenylenebis(methylphenylphosphine) and diars as *o*-phenylenebis(methylphenylarsine). Small quantities of the corresponding Λ-anti-cis material (5%) (see Figure 3) and *trans*-[$RuCl_2$((*SS*)-diphos)((*SS*)-*o*-C_6H_4(PMePh)(POMePh))] (7%) were also isolated from the reaction mixture. Fractional crystallization and column chromatography were used to separate the mixture. The ^1H NMR spectrum of *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] contained a

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Table II. Some Physical Properties of the Complexes *cis*-[$RuCl_2$(bidentate)$_2$]

compd	mp, °C	δ(EMe)[a]
(+)$_{589}$-Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diars)$_2$]	>320	1.44 s, 2.20 s
rac-anti-cis-C_2-[$RuCl_2$((*RR,SS*)-diars)$_2$]	207–209	1.44 s, 2.20 s
rac-cis-C_1-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)]	220–230	0.51 s, 1.22 s, 1.46 s, 2.35 s
rac-syn-cis-C_2-[$RuCl_2$((*RS*)-diars)$_2$]	>300	1.19 s, 2.34 s
rac-cis-C_1-[$RuCl_2$((*RS*)-diars)$_2$]	186–188	0.19 s, 2.00 s, 2.19 s, 2.36 s
(+)$_{589}$-Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diphos)$_2$]	305	1.65 br d, 2.33 br t
rac-anti-cis-C_2-[$RuCl_2$((*RR,SS*)-diphos)$_2$]	283–285	1.65 br d, 2.33 br t
rac-cis-C_1-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)][b]	232–233	0.65 br d, 1.14 br s, 1.64 d, 2.51 t
rac-syn-cis-C_2-[$RuCl_2$((*RS*)-diphos)$_2$]	>320	1.30 br d, 2.54 t

[a] Chemical shift values quoted relative to Me_4Si for 0.05 M solutions in $CDCl_3$. [b] The ^1H NMR spectrum of this compound (and the diiodo analogue) in the PMe region is available as supplementary material (Figure 10).

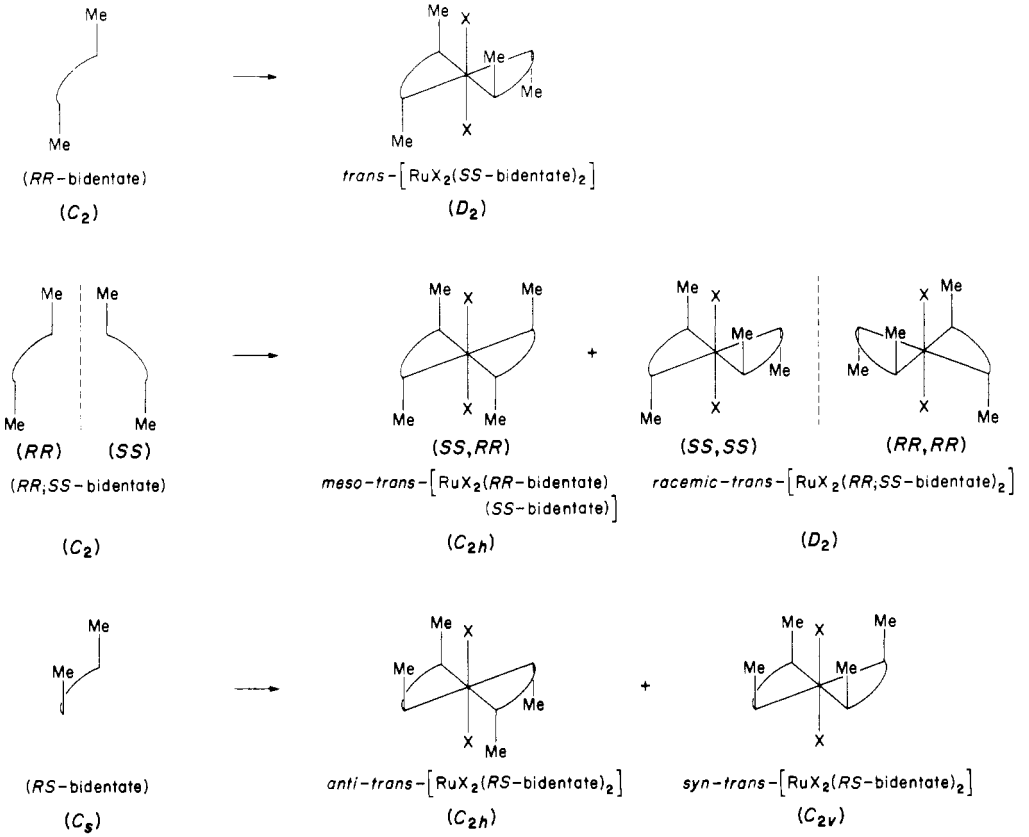

Figure 2. Representation of the stereochemistry of the complexes *trans*-[RuX_2(bidentate)$_2$]. Note: the donor atoms are asymmetric.[9]

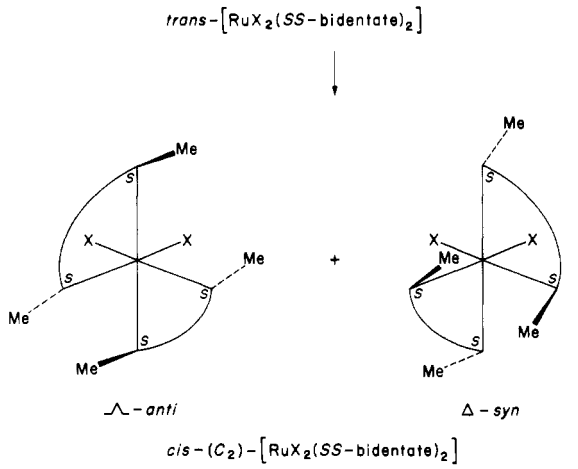

Figure 3. Epimers arising from the isomerization of the optically active trans complexes.

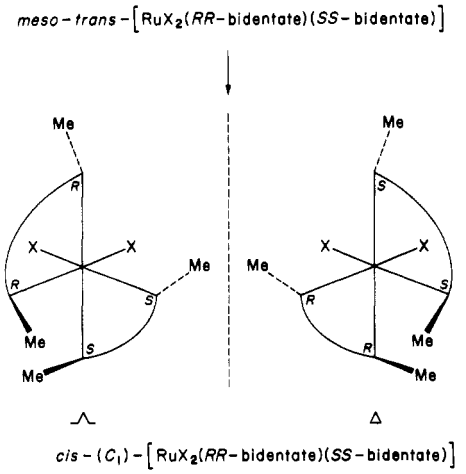

Figure 4. Isomerization of the meso-trans complexes.

broad singlet at δ 1.57 for the equivalent methyl groups. The Λ-anti-cis isomer exhibited the expected pair of resonances due to the nonequivalent pairs of methyl groups in the C_2 structure (Table II). The latter was also prepared directly from the optically active trans material (vide infra). The structure of the phosphine oxide complex was confirmed by

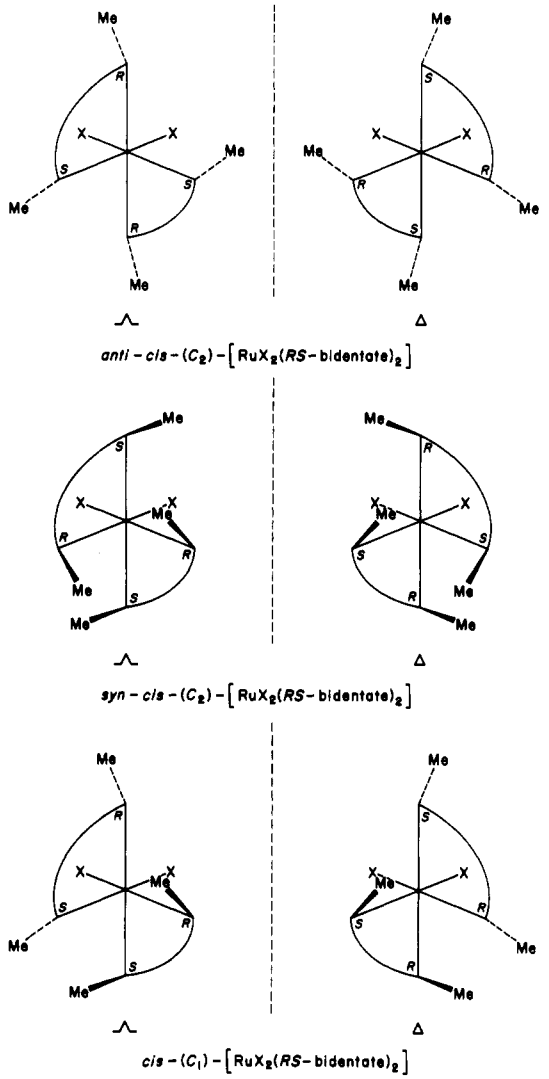

Figure 5. Products of the isomerization of *syn-trans-* and *anti-trans*-[RuX_2((*RS*)-bidentate)$_2$].

an X-ray crystal structure analysis.[16] It crystallized as deep red plates from a dichloromethane/hexane mixture. Four PMe resonances were found in the ^{1}H NMR spectrum of the complex, and a strong ν(PO) absorption at 1155 cm^{-1} was observed in the infrared spectrum in dichloromethane. Free (*RS*)-*o*-C_6H_4(PMePH)(POMePh) exhibited a strong band at 1183 cm^{-1} in the same solvent. The shift of the ν(PO) absorption to lower frequencies upon coordination is typical.[17]

The optically active di(tertiary arsine) (*RR*)-diars reacted with ruthenium(III) chloride under similar conditions to give a mixture of products consisting of deep red cubes of *trans*-[$RuCl_2$((*SS*)-diars)$_2$] (60%) and orange yellow rosettes of Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diars)$_2$] (33%). The ^{1}H NMR spectrum of the trans complex contained a sharp AsMe resonance at δ 1.55 in $CDCl_3$ and the cis material sharp singlets at δ 2.20 and 1.44 (Table II).

2. Racemic- and Meso-Trans Complexes. A mixture of the diastereoisomeric *rac-trans* and *meso-trans*-dichlororuthenium(II) complexes (Figure 2) arose from the interaction of the racemic di(tertiary phosphine) with ruthenium(III) chloride under the usual reducing conditions. Moreover, the extent of phenyl–phenyl group interference appeared to play an important part in determining the proportions of diastereoisomers formed (racemic:meso = 49:36). The preponderance of racemic product is compatible with the weaker steric interactions present in this structure. The racemic- and meso-trans complexes were identified by ^{1}H NMR spectroscopy. For example, the chemical shift of the PMe groups in *rac-trans*-[$RuCl_2$((*RR*,*SS*)-diphos)$_2$] occurred at δ 1.57 in $CDCl_3$, identical with the value found for *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] in the same solvent. The corresponding resonance in the meso complex occurred at δ 2.03. The relative upfield shift observed for the methyl protons in racemic complexes (compared to that in meso complexes) is due to diamagnetic shielding of the methyl protons by phenyl groups in the racemic structure.[5] This may be appreciated by inspection of the two structures shown in Figure 2. Interconversion between the diastereoisomers was not observed over a wide range of conditions, even in the presence of added bidentate ligand or chloride ions. The individual diastereoisomeric complexes were therefore kinetically inert to bidentate ligand redistribution under these circumstances. Small amounts of *rac-anti-cis*-C_2-[$RuCl_2$((*RR*,*SS*)-diphos)$_2$] and *rac-cis*-C_1-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)] were also isolated from the reaction mixture. The deliberate preparation of these cis complexes will be discussed subsequently. Two other byproducts were also isolated. One was identified as *rac-trans*-[$RuCl_2$((*RR*,*SS*)-diphos)((*RR*,*SS*)-*o*-C_6H_4(PMePh)(POMePh))] by comparison of its spectroscopic properties with those of the corresponding optically active material of known structure. The other was apparently an isomer of this complex.

The corresponding reaction with (*RR*,*SS*)-diars also proceeded in high yield (94%). However, the proportion of cis products was much greater in this case. The mixture of products was readily separated into its crystalline components by fractional crystallization and column chromatography. The distribution of products was the following: *rac-trans*-[$RuCl_2$(*RR*,*SS*-diars)$_2$], 38%; *meso-trans*-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)], 16%; *rac-anti-cis*-C_2-[$RuCl_2$((*RR*,*SS*)-diars)$_2$], 13%; *rac-cis*-C_1-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)], 27%. The increased proportion of cis products in the mixture may have arisen as a consequence of the relatively longer Ru–As and As–C bonds. The racemic-cis and -trans products were identified by comparison of their ^{1}H NMR spectra with those of the corresponding optically active compounds. Again, redistribution of the bidentate ligands could not be induced. The effect of solvent polarity upon the proportions of cis and trans products was also briefly investigated. When the reaction was performed in methanol/water (9:1) there was a marginal increase in the proportion of cis products formed, but the overall yield was reduced by 13%. In ethanol, the proportion of cis products was also larger, but the overall yield was even less (66%).

3. Syn- and Anti-Trans Complexes. High yields of *syn-trans-* and *anti-trans*-$RuCl_2$(bidentate)$_2$] were obtained from the reaction of the meso bidentates with ruthenium(III) chloride in the usual way. The pure anti-trans di(tertiary phosphine) complex crystallized from the reaction mixture upon cooling (46% yield), but the more soluble syn-trans isomer (36%) was best purified by column chromatography. Again, steric factors presumably accounted for the higher proportion of anti product formed. (In five-coordinate nickel(II) complexes of this type, the anti isomer was produced exclusively.[5]) Under similar conditions, however, the meso di(tertiary arsine) yielded a mixture of cis and trans products. The syn- and anti-trans geometric isomers were formed in equal amounts and accounted for 52% of the product. The remainder consisted of *rac-syn-cis*-C_2-[$RuCl_2$((*RS*)-diars)$_2$] and *rac-cis*-C_1-[$RuCl_2$((*RS*)-diars)$_2$] (see Figure 5), which were formed to the extent of 19 and 17%, respectively. The various products were readily identified by NMR spectroscopy.

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Because of pronounced shielding by the phenyl groups, the resonances due to the equivalent AsMe and PMe groups in the anti-trans complexes occurred well upfield of the corresponding signals in the syn-trans isomers (Table I). The cis-C_2 and cis-C_1 isomers exhibited the expected two and four AsMe resonances, respectively (vide infra). It was not found possible to thermally interconvert the internally related syn- and anti-trans isomers. The pure complex *syn-trans*-[$RuCl_2$((*RS*)-diphos)$_2$] was heated in dimethyl-d_6 sulfoxide to 420 K without evidence of the formation of the anti-trans isomer.

4. *rac-trans*-[$RuCl_2$((*RR,SS*)-diphos)((*RS*)-diphos)]. A molecule of this stereochemistry was required in order to unambiguously determine the stability of the complexes *trans*-[$RuCl_2$(diphos)$_2$] toward internal rearrangement in solution. The four methyl groups in this molecule are magnetically nonequivalent in the static structure. However, since the methyl groups of the racemic ligand are related by a C_2 axis bisecting the metal chelate ring, rapid internal rotation about this axis would lead to an internal exchange process identifiable by variable-temperature NMR spectroscopy.[5]

The mixed-bidentate-ligand complex could not be prepared by the stepwise reaction of the two ligands (*RR,SS*)-diphos and (*RS*)-diphos with ruthenium(III) chloride under the usual conditions or with a number of ruthenium(II) precursors. The addition of the first equivalent of di(tertiary phosphine) invariably led to the corresponding bis(bidentate) derivative. However, when an equimolar mixture of the two ligands was reacted with prereduced ruthenium(III) chloride in the presence of formaldehyde, a 33% yield of the desired product was isolated from the resulting mixture of products by careful column chromatography and fractional crystallization. The PMe resonances of the complex appeared as broadened doublets and were assigned (Table I) on the basis of relative shielding effects due to proximal phenyl groups, as well as by comparison with the spectra of related platinum complexes.[6] The ^{1}H NMR spectrum of the complex in dimethyl-d_6 sulfoxide did not alter when the solution was heated to 420 K.

Preparation of Cis Complexes. In general, these were prepared by dissolving the trans complex in triethylaluminum, allowing the reaction to proceed for ca. 2 h, and then decomposing the triethylaluminum with absolute ethanol. An intermediate compound precipitated at this juncture, which was dissolved in dichloromethane and the solution treated with concentrated hydrochloric acid. The cis product was then isolated from the organic layer. Chemical yields averaged 90%.

Isomerization of the Optically Active *trans*-Dichloro Complexes. A suspension of *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] in triethylaluminum was stirred for 2 h at 75 °C, after which time the colorless upper layer (excess triethylaluminum) was removed by washing with petroleum ether. The extremely air-sensitive residue was then cooled to −10 °C and carefully treated with ethanol. The resulting yellow solution was immediately evaporated to dryness. The remaining solid contained aluminum triethoxide, which was removed by the addition of hydrochloric acid at −78 °C. The product was extracted into dichloromethane and isolated by the usual method. The infrared spectrum of the compound contained a peak at 1976 cm^{-1}, which was attributed to a ν(RuH) absorption.[18] The ^{1}H NMR spectrum in $CDCl_3$ exhibited a pair of triplets due to PMe groups and a 1:4:6:4:1 quintet centered at δ −19.57 (Figure 7).[19] The quintet (J_{PH} = 21.5 Hz) is consistent[18] with a structure involving a hydridic proton coupled to four cis ^{31}P nuclei (two almost equivalent pairs in this case), viz., *trans*-[RuHCl((*SS*)-diphos)$_2$]. Upon recrystallization from benzene it was isolated as a benzene disolvate. The same compound was obtained by $LiAlH_4$ reduction of Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diphos)$_2$] (vide infra) and treatment of [$RuHCl(PPh_3)_3$] with (*RR*)-diphos. However, if the air-sensitive solid from the triethylaluminum reaction, perhaps [RuH((*SS*)-diphos)$_2$][$AlCl_2Et_2$], was stirred in ethanol for 3.5 h at room temperature (rather than for a brief time at −78 °C) the hydride was not observed. Instead, a 93% yield of a single dichloro species was obtained. Two PMe resonances were observed in the ^{1}H NMR spectrum of the complex (Table II), which was an indication of C_2 symmetry within the molecule. The downfield triplet was assigned to the methyl groups associated with the strongly coupled trans phosphorus nuclei[20] and the "filled-in" doublet to those bound to the pair of weakly coupled cis phosphorus nuclei.[21] Although an unambiguous assignment of the structure of this compound cannot be made on the basis of available physical data, molecular models indicate that the Λ-anti-cis-C_2 stereochemistry (Figure 3) is less hindered.

The complex *trans*-[RuHCl((*SS*)-diphos)$_2$] is remarkably stable to acid. In $CDCl_3$ solution in the presence of 10 M HCl, 35% of the hydride was still present after a 2-week period, the remainder having been converted into Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diphos)$_2$]. The reaction was faster in ethanol, 1–2 h at room temperature or several minutes at its boiling point being required for the conversion. Evidently, the isomerization of *trans*-dichloro complexes of this type in triethylaluminum proceeds via hydrido intermediates. The elimination of ethylene from a σ-ethyl intermediate would provide a mechanism for their formation. Indeed, we have shown, by use of MeOH-d_4 to hydrolyze the intermediate, that the hydridic proton does not arise from the alcohol.

Despite its stability, the Λ-anti epimer underwent slow isomerization, accompanied by epimerization of the coordinated tertiary phosphine centers, upon standing in solution for several weeks. Small quantities of all possible trans complexes were identified by thin-layer chromatography of a dichloromethane solution of the complex after this period, along with unchanged cis material. The complexes containing (*RS*)-diphos must have arisen through epimerization of coordinated tertiary phosphine groups. The epimerization of coordinated tertiary arsines within chelate rings has been previously observed in complex chlorides.[22] However, we were unable to catalyze epimerization of the tertiary phosphine or arsine centers under similar conditions[22] in the case of the ruthenium complexes.

The more stable epimer only was isolated from the isomerization of *trans*-[$RuCl_2$((*SS*)-diars)$_2$] with triethylaluminum. It may be recalled that this particular cis complex was also obtained in 33% yield from the reaction of (*SS*)-diars with prereduced ruthenium(III) chloride in the presence of formaldehyde.

The isomerization of the racemic-trans complexes was also investigated. As expected, both the chlorohydrido and the anti-cis-C_2 complexes could be isolated from the isomerization of *rac-trans*-[$RuCl_2$((*RR,SS*)-diphos)$_2$] but only the racemic-anti-cis epimer from the corresponding di(tertiary arsine) complex (Table II).

The internally compensated complexes *meso-trans*-[$RuCl_2$((*RR*)-bidentate)((*SS*-bidentate)] isomerized to the expected racemic cis product, viz., *rac-cis*-C_1-[$RuCl_2$((*RR*)-bidentate)((*SS*)-bidentate)] (Figure 4). This was found to be the case for both ligands. The C_1 symmetry of the products was verified by NMR spectroscopy: four PMe or

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(19) The ^{1}H NMR spectrum of this compound in the hydride region is available as supplementary material.
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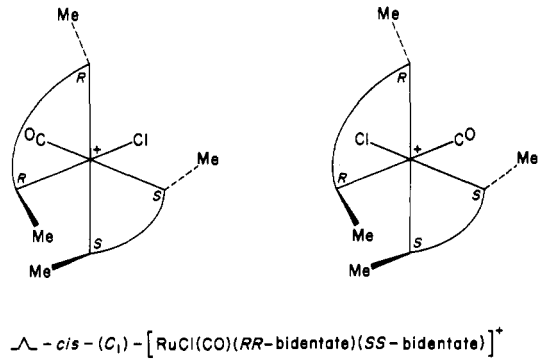
AsMe resonances were clearly evident in the spectra of the respective complexes (Table II). The doublets in the spectrum of the phosphine complex were assigned to the methyl groups located on the cis phosphorus nuclei (weak ^{31}P–^{31}P coupling) and the broad singlet and triplet resonances to those associated with the strongly coupled trans phosphorus nuclei.

The isomerization of *syn-trans* or *anti-trans*-[$RuCl_2$((*RS*)-bidentate)$_2$] was expected to lead to a mixture of products (Figure 5). However, a single cis complex was formed in each case, regardless of the starting material. The symmetry of the product was C_2 since a pair of AsMe or PMe resonances was observed in the NMR spectrum of each product (Table II). Inspection of molecular models of the two possible cis-C_2 products indicated considerably less steric congestion in the syn-cis structure. The ordering of stabilities of the alternative structures appeared to be syn-cis-C_2 > cis-C_1 >> anti-cis-C_2 on steric grounds. Although it is tempting to rationalize the formation of the cis isomers on the basis of intramolecular edge displacement of donor atoms in the parent trans complexes,[11] an intermediate five-coordinate cation of the type [RuCl(bidentate)$_2$]$^+$ (arising from the decomposition of an intermediate hydrido compound) is more likely. Indeed, [$RuCl(Ph_2P(CH_2)_3PPh_2)_2$]$PF_6$ has been isolated.[23] Consistent with this notion, anhydrous aluminum chloride isomerized the trans complexes to cis species to the extent of ca. 50% in dichloromethane. Interestingly, both the syn-cis-C_2 and the cis-C_1 diastereoisomers were formed in the reaction between ruthenium(III) chloride and (*RS*)-diars under reducing conditions (19% and 17% yields, respectively), as well as the expected syn-trans and anti-trans products (vide infra).

Whereas the *trans*-dichloro compounds required forcing conditions, the cis complexes readily underwent substitution with iodide ions. The displacement was completely stereospecific. The di(tertiary phosphine) complexes reacted much faster than the corresponding arsine compounds, in agreement with the increased trans labilizing effect of tertiary phosphine donors. A striking feature of the ^1H NMR spectra of the *cis*-diiodo complexes was the large downfield shift of the methyl resonances relative to those in the parent dichloro compounds (Table II). We have attributed this to deshielding by the adjacent iodine atoms. The relative ease of substitution of cis compared to trans complexes was also reflected by their conductivities in solution. Both sets of complexes behaved as nonelectrolytes in dichloromethane. However, in dimethyl sulfoxide the complexes Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-bidentate)$_2$] conducted as uni-univalent electrolytes after equilibrium had been reached (ca. 1 h at 25 °C for the di(tertiary phosphine) and 1 h at 90 °C for the arsine complex). On the other hand, prolonged heating of the trans complexes containing either ligand in dimethyl sulfoxide did not lead to conducting solutions. Furthermore, silver chloride precipitated immediately upon the addition of aqueous silver nitrate to solutions of the cis complexes in tetrahydrofuran, but the corresponding trans derivatives showed no evidence of this, even upon heating the solution.

Carbonyl Derivatives. The compound *trans*-[$RuCl_2$($Ph_2PCH_2PPh_2$)$_2$] reacts with carbon monoxide to give the salt *trans*-[RuCl(CO)($Ph_2PCH_2PPh_2$)$_2$]Cl.[24] The coordinatively unsaturated salts [$RuX(Ph_2P(CH_2)_3PPh_2)_2$]$PF_6$ (where X = Cl and Br) have also been isolated and subsequently converted to similar octahedral carbonyls.[23] We were unable to isolate the cation [RuCl((*SS*)-diphos)$_2$]$^+$ from *trans*-[$RuCl_2$((*SS*)-diphos)$_2$], or from the more reactive Λ-anti-cis isomer, by use of the conditions described by Bressan and Rigo.[23] However, when carbon monoxide was passed into a suspension of Λ-*anti-cis*-C_2-[$RuCl_2$((*SS*)-diphos)$_2$] in boiling ethanol, the yellow starting material rapidly dissolved to produce a colorless solution. The addition of NH_4PF_6 to this precipitated Λ-*anti-cis*-C_1-[RuCl(CO)((*SS*)-diphos)$_2$]PF_6 in almost quantitative yield. The carbonyl crystallized from a acetone/diethyl ether mixture as colorless plates. The ^{31}P-decoupled ^1H NMR spectrum of the salt contained four sharp PMe resonances as expected for C_1 symmetry. The average positions of the cis and trans PMe resonances in the salt (1.76 and 2.30 ppm, respectively) were similar to those found in the starting material (1.65 and 2.33 ppm), implying that the overall Λ-anti-cis geometry of the bidentate ligands had been retained. The ν(CO) adsorption in the salt was situated at 2026 cm^{-1} in dichloromethane solution. The reaction between *trans*-[$RuCl_2(CO)_2$((*SS*)-diphos)][25] and (*RR*)-diphos also led to the more stable epimeric cation Λ-*anti-cis*-C_1-[RuCl(CO)((*SS*)-diphos)$_2$]$^+$, which was isolated in 86% yield as its hexafluorophosphate, further emphasizing the stability of the Λ geometry.



Λ-*cis*-(C_1)-[RuCl(CO)(*RR*-bidentate)(*SS*-bidentate)]$^+$

Figure 6. Diastereoisomeric carbonyl derivatives of Λ-*cis*-C_2-[$RuCl_2$((*RR*)-bidentate)((*SS*)-bidentate)].

The large trans effect of the hydrido ligand in *trans*-[RuHCl((*SS*)-diphos)$_2$] was reflected in its reaction with carbon monoxide. The chloro ligand was readily and stereospecifically substituted to give the species *trans*-[RuH(CO)((*SS*)-diphos)$_2$]$^+$, which was precipitated as its hexafluorophosphate. The ν(RuH) absorption in the infrared was apparently obscured by the ν(CO) band at 1999 cm^{-1}, although the proton was observed in the ^1H NMR spectrum of the compound as an almost symmetrical 1:4:6:4:1 quintet centered at δ −8.45 (Figure 8).[19] The complex crystallizes from acetone as an acetone disolvate. The structure of the latter has been confirmed by an X-ray crystal structure analysis.[16] The hydride is remarkably stable to acid. An ethanol solution of the complex 3 M in hydrochloric acid was boiled for ca. 1 h without decomposition.

The compounds *rac-anti-cis*-C_2-[$RuCl_2$((*RR*,*SS*)-diphos)$_2$] and *rac-trans*-[RuHCl((*RR*,*SS*)-diphos)$_2$] were also reacted with carbon monoxide. As expected, substitution was again completely stereospecific. The racemic hexafluorophosphate salts were isolated in the usual way. Similarly, *rac-anti-cis*-C_1-[RuCl(CO)((*RR*,*SS*)-diars)$_2$]PF_6 was prepared in 88% yield from *rac-anti-cis*-C_2-[$RuCl_2$((*RR*,*SS*)-diars)$_2$].

The chlorine atoms in the enantiomers of *cis*-C_1-[$RuCl_2$((*RR*)-bidentate)((*SS*)-bidentate)] are diastereotopic (Figure 4). Consequently, reaction of the racemic complex with carbon monoxide led to a pair of internally diastereoisomeric products (Figure 6), which were isolated as a mixture of hexafluorophosphate salts.

It is noteworthy that substitution in all of the complexes was stereospecific, retention of the overall cis or trans arrangement of the bidentate ligands being retained. This implies that the stereochemistry of the intermediate species [RuX(bidentate)$_2$]$^+$

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(where X = Cl and H) is rigid or that their lifetime is very short.

Experimental Section

Reactions involving air-sensitive materials were performed in a nitrogen atmosphere with use of the Schlenk technique. Solvents were purified and degassed by distillation through a stream of pure nitrogen. The petroleum ether used had the bp 60–80 °C. Ruthenium trichloride was purchased from Johnson Matthey Chemicals Ltd. and triethylaluminum from Alfa Inorganics Inc. The neutral alumina used for column chromatography was Unilab Activity I and the silica for thin-layer chromatography Merck GF 254 (Type 60). All new compounds gave satisfactory elemental analyses. The ^{1}H NMR spectra were recorded at 35 °C with a Bruker HX-90 spectrometer and ^{31}P-decoupled ^{1}H NMR spectra with a Varian HA 100 spectrometer. The infrared spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer. Optical rotations were measured at 21 °C with a Perkin-Elmer Model 241 polarimeter.

Improved methods of synthesis of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue are reported although the seperation of diastereoisomers and resolutions were carried out as previously described.[7,8]

Methylphenylarsine. A mixture of dimethylphenylarsine (793.4 g) and sodium wire (205.3 g) in liquid ammonia (3.6 L) was stirred for 3.5 h. Water (1.2 L) was then cautiously added and the ammonia allowed to evaporate off overnight. The resulting two layers were separated, and the aqueous component was extracted with diethyl ether (200 mL). The organic fractions were combined, dried ($MgSO_4$), and distilled to afford methylphenylarsine as a colorless mobile liquid: bp 56–58 °C (2 mmHg); 637.5 g (87%); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3, J = 6.5 Hz, AsMe), 3.11 (q, 1, J = 6.5 Hz, AsH), 7.0–7.45 (m, 5, aromatics).

(*RR*,*SS*)- and (*RS*)-*o*-Phenylenebis(methylphenylarsine). The mixture of diastereoisomers was prepared as described in ref 7 except that Na[AsMePh] was generated from methylphenylarsine and sodium foil. The yield was 89%.

(*RR*,*SS*)- and (*RS*)-*o*-Phenylenebis(methylphenylphosphine). Sodium foil (44.7 g) was added to a solution of methylphenylphosphine) (241.5 g)[8] in tetrahydrofuran and the mixture heated under reflux for 30 min. The reaction mixture was then cooled to room temperature and filtered. The filtrate was cooled to −78 °C and *o*-dichlorobenzene (109.4 mL) added over a 5-h period. The temperature was maintained at −78 °C and stirring continued for 12 h. At this stage the reaction mixture was warmed to room temperature and then heated under reflux for 30 min. Water (250 mL) was slowly added and the bulk of the tetrahydrofuran removed by distillation. The two layers that resulted were separated and the aqueous component extracted once with diethyl ether (150 mL). The organic fractions were combined, dried ($MgSO_4$), and distilled to afford an equimolar mixture of the desired diastereoisomers (271.9 g, 87%).[8]

(*RS*)-Methyl[2-(methylphenylphosphino)phenyl]phenylphosphine Oxide. A solution of [*o*-C_6H_4(PMePh)(PBzMePh)]Br[8] (0.42 g) in methanol (15 mL) was heated under reflux with aqueous NaOH solution (5 mL, 10 M) for 15 h. The methanol was removed by distillation and the residue extracted with dichloromethane (2 × 15 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated to leave a pale brown oil, which was dissolved in ethyl acetate and crystallized by adding petroleum ether. The product formed white balls: mp 131–133 °C (yield 0.20 g, 69%); ^{1}H NMR ($CDCl_3$) δ 1.30 (d of d, 3, J_{PH} = 30 Hz, $J_{P(O)H}$ = 4 Hz, PMe), 2.33 (d, 3, $J_{P(O)H}$ = 44 Hz, P(O)Me), 6.9–7.8 (m, 14, aromatics); IR (CH_2Cl_2) 1183 cm^{-1} (ν_{PO}).

(+)$_{589}$-*trans*-Dichlorobis((*SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II) and (+)$_{589}$-Λ-*anti*-*cis*-C_2-Dichlorobis((*SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II). Commercial hydrated ruthenium(III) chloride (0.42 g) was reduced by bubbling hydrogen through a solution of it in methanol (45 mL) at its boiling point for 100 min. The color of the solution changed from blackish red to a clear reddish brown during this period. The solution of prereduced ruthenium(III) chloride was then added to a solution of (*RR*)-diars (1.35 g) and aqueous formaldehyde (2 mL, 40% w/v) in methanol at its boiling point. The trans complex precipitated immediately and was crystallized from dichloromethane (15 mL) by the addition of petroleum ether (20 mL). More of the product was obtained from the filtrate by evaporating it to dryness and chromatographing the residue on alumina with dichloromethane/hexane (60:40) as eluent. The pure trans complex formed deep orange-red prisms: mp >315 °C (yield 0.96 g, 60%); $[\alpha]_D$ + 371° (*c* 0.631, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 12, AsMe), 7.3–7.6 (m, 28, aromatics). Further elution of the column with a more polar solvent mixture (dichloromethane/tetrahydrofuran (90:10)) yielded Λ-*anti*-*cis*-C_2-[$RuCl_2$((*SS*)-diars)$_2$] as canary yellow needles after recrystallization from dichloromethane/ethanol mixture: mp >320 °C (yield 0.53 g, 33%); $[\alpha]_D$ + 141° (*c* 0.136, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 6, cis-AsMe), 2.20 (s, 6, trans-AsMe), 6.85–7.7 (m, 28, aromatics). This compound was also prepared in 75% yield by isomerization of *trans*-[$RuCl_2$((*SS*)-diars)$_2$] with triethylaluminum.

***meso*-*trans*- and *rac*-*cis*-C_1-Dichloro((*RR*)-*o*-phenylenebis(methylphenylarsine))((*SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II) and *rac*-*trans*- and *rac*-*anti*-*cis*-C_2-Dichlorobis((*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II).** The reaction of a solution of prereduced ruthenium(III) chloride (2.98 g) in methanol (200 mL) with a boiling solution of (*RR*,*SS*)-diars (9.76 g) and aqueous formaldehyde (5 mL, 40% w/v) in methanol resulted in the precipitation of a yellow powder. This was collected and recrystallized from dichloromethane (200 mL) by slowly evaporating the solution over a 2-day period and then adding petroleum ether (50 mL). The pure meso-trans complex formed yellow microcrystals: mp >315 °C (yield 1.37 g, 12.1%); ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 12, AsMe), 7.1–7.65 (m, 28, aromatics). The combined filtrates were evaporated to dryness, and the residue was chromatographed on alumina. Elution of the column with dichloromethane/petroleum ether (60:40) afforded the racemic-trans complex as orange blocks after recrystallization from the same solvent mixture; mp 166–168 °C (yield 4.30 g, 38%). The ^{1}H NMR ($CDCl_3$) was identical with that of the optically active material. Continued elution of the column with the same mixture of solvents produced additional meso-trans complex (0.23 g, 2%). Subsequent elution of the column with dichloromethane/tetrahydrofuran mixture (99:1) gave *rac*-*cis*-C_1-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)] as bright yellow needles after recrystallization from dichloromethane/ethanol: mp 220–230 °C (yield 3.10 g, 27%); ^{1}H NMR ($CDCl_3$) δ 0.51 (s, 3, AsMe), 1.22 (s, 3, AsMe), 1.46 (s, 3, AsMe), 2.35 (s, 3, AsMe), 6.9–7.9 (m, 28, aromatics). This compound was also obtained in 67% yield by isomerization of *meso*-*trans*-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)] with triethylaluminum. Use of dichloromethane/tetrahydrofuran (90:10) as eluent yielded *rac*-*anti*-C_2-[$RuCl_2$((*RR*,*SS*)-diars)$_2$] as yellow needles after recrystallization from dichloromethane/ethanol: mp 207–209 °C (yield 1.51 g, 13%); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 6, cis-AsMe), 2.20 (s, 6, trans-AsMe), 6.85–7.7 (m, 28, aromatics). The optically active compound Λ-*anti*-*cis*-C_2-[$RuCl_2$((*SS*)-diars)$_2$] had an identical NMR spectrum. The overall yield of cis and trans complexes was 92%. The racemic-anti-cis-C_2 compound was also prepared by reaction of *rac*-*trans*-[$RuCl_2$((*RR*,*SS*)-diars)$_2$] with triethylaluminum (vide infra).

***anti*-*trans*-, *syn*-*trans*-, *rac*-*syn*-*cis*-C_2-, and *rac*-*cis*-C_1-Dichlorobis((*RS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II).** The addition of a solution of prereduced ruthenium(III) chloride (1.11 g) in methanol (65 mL) to a boiling solution of (*RS*)-diars and aqueous formaldehyde (2.3 mL, 40% w/v) in methanol led to the formation of an orange-yellow precipitate. This was dissolved in dichloromethane (400 mL) and filtered, and the volume was reduced to 50 mL. The gradual addition of petroleum ether (15 mL) to the concentrated solution afforded the anti-trans complex as orange microcrystals, mp >315 °C. The combined filtrates were then evaporated, and the residue was chromatographed on alumina. Elution of the column with dichloromethane/petroleum ether (40:60) yielded additional anti-trans complex: net yield 1.13 g (26%); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.33 (s, 12, AsMe), 7.1–7.8 (m, 28, aromatics). Elution of the column with dichloromethane/petroleum ether (45:55) gave the corresponding syn-trans complex as orange blocks, mp 295–296 °C, after recrystallization from dichloromethane/ethanol (1.14 g, 26%): ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 12, AsMe), 6.7–7.5 (m, 28 aromatics). Further elution with a more polar solvent mixture afforded the two cis complexes. Dichloromethane/tetrahydrofuran (99:1) eluted the racemic-syn-cis-C_2 species, which was obtained as orange needles, mp >300 °C, after recrystallization from dichloromethane/ethanol (0.81 g, 19%): ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 6, cis-AsMe), 2.34 (s, 6, trans-AsMe), 6.45–7.85 (m, 28, aromatics). Subsequent elution of the column with dichloromethane/tetrahydrofuran (97:3) yielded the remaining racemic-cis-C_1 isomer as bright yellow blocks after recrystallization from dichloromethane/ethanol: mp 186–188 °C (yield 0.73 g, 17%); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3, AsMe), 2.00 (s, 3,

AsMe), 2.19 (s, 3, AsMe), 2.36 (s, 3, AsMe), 6.05–8.05 (m, 28, aromatics).

Interestingly, only *rac-syn-cis-C*$_2$-[$RuCl_2$((*RS*)-diars)$_2$] was isolated (51% yield) from the isomerization of *syn-trans-* or *anti-trans*-[$RuCl_2$((*RS*)-diars)$_2$] in triethylaluminum.

(+)$_{589}$-*trans*-Dichlorobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II). A solution of commercial hydrated ruthenium(III) chloride (2.99 g) was reduced in the usual way and added to a boiling solution of (*RR*)-diphos (7.7 g) and aqueous formaldehyde (5 mL, 40% w/v) in methanol (500 mL). The product separated as a golden yellow precipitate, which was filtered off and recrystallized from dichloromethane (18 mL) by the addition of petroleum ether (60 mL). More of the product was obtained from the filtrate by evaporating it to dryness and chromatographing the residue on alumina with dichloromethane/hexane (70:30) as eluent. The pure product formed orange prisms: mp >320 °C (yield 7.52 g, 81%); $[\alpha]_D$ +411° (*c* 9.22, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.57 (br s, 12, PMe), 7.38 (br s, 28, aromatics). Small quantities of two other products of the reaction were also eluted from the column by using a more polar solvent mixture (dichloromethane/tetrahydrofuran (90:10)). The first was shown to be *trans*-[$RuCl_2$((*SS*)-diphos)((*RS*)-*o*-C_6H_4(PMePh)[P(O)MePh])]. It formed deep red plates from dichloromethane/petroleum ether: mp 301–302 °C (yield 0.71 g, 7%); $[\alpha]_D$ + 350° (*c* 1.01, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.22 (d, 3, *J* = 10.5 Hz, PMe), 1.73 (d of d, 3, *J* = 1.9, 7.9 Hz, PMe), 2.23 (d, 3, *J* = 13.9 Hz, PMe), 2.31 (d of d, 3, *J* = 2.1, 9.0 Hz, P(O)Me), 6.9–7.9 (m, 28, aromatics); IR (CH_2Cl_2) 1155 cm^{-1} (ν_{PO}). The second band contained Λ-*anti-cis-C*$_2$-[$RuCl_2$((*SS*)-diphos)$_2$] (0.47 g, 5%), which is described in detail subsequently.

***meso-trans*-Dichloro((*RR*)-*o*-phenylenebis(methylphenylphosphine))((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II) and *rac-trans*-Dichlorobis((*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II).** Reaction of a solution of prereduced ruthenium(III) chloride (3.78 g) in methanol (190 mL) with a boiling solution of (*RR*,*SS*)-diphos (9.6 g) and aqueous formaldehyde (6 mL, 40% w/v) in methanol (630 mL) led to the precipitation of a yellow solid. This was filtered off and dissolved in boiling dichloromethane (2 L), and the solution was filtered and reduced to ca. 350 mL. Upon standing this precipitated orange crystals of the pure meso-trans complex: mp >315 °C; ^{1}H NMR (CH_2Cl_2) δ 2.03 (br s, 12, PMe), 6.8–7.5 (m, 28, aromatics). The filtrate was concentrated to ca. 80 mL, whereupon orange blocks of the racemic-trans complex deposited: mp 309–310 °C; ^{1}H NMR ($CDCl_3$) δ 1.57 (br s, 12, PMe), 7.39 (br s, 28, aromatics). Additional small quantities of both trans isomers were obtained from the combined filtrates by column chromatography on alumina. A dichloromethane/petroleum ether mixture (40:60) eluted first the racemic-trans complex and then the remainder of the meso-trans compound. Net yields: meso-trans, 4.24 g, 36%; racemic-trans, 5.77 g, 49%. Subsequent elution of the column with dichloromethane/tetrahydrofuran (90:10) gave small amounts of two of the three possible corresponding cis complexes: *rac-cis-C*$_1$-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)] (0.47 g, 4%) and *rac-anti-cis-C*$_2$-[$RuCl_2$((*RR*,*SS*)-diphos)$_2$] (0.71 g, 6%). Both of these will be described in detail subsequently.

***anti-trans*- and *syn-trans*-Dichlorobis((*RS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II).** To a boiling solution of (*RS*)-diphos (4.21 g) in methanol (220 mL) containing aqueous formaldehyde (3 mL, 40% w/v) was added prereduced ruthenium(III) chloride (1.63 g) in methanol (100 mL). The reaction mixture was heated under reflux for 1 h and then cooled to 5 °C. A bright yellow precipitate formed, which was dissolved in hot dichloromethane (200 mL). The solution was filtered and concentrated to ca. 75 mL; orange blocks of the anti-trans complex crystallized: mp >315 °C; ^{1}H NMR (CH_2Cl_2) δ 1.33 (br s, 12, PMe), 7.2–7.6 (m, 28, aromatics). The solvent was evaporated from the filtrate and a little dichloromethane added to redissolve the residue, followed by ethanol. The syn-trans isomer crystallized from this mixture as yellow prisms: mp 310 °C; ^{1}H NMR ($CDCl_3$) δ 2.08 (br s, 12, PMe), 6.9–7.5 (m, 28, aromatics). The filtrates were combined and evaporated to dryness, and the residue was chromatographed on alumina to yield further small quantities of, first, the anti-trans complex, followed by the syn-trans complex. Yields: anti-trans, 2.33 g, 46%; syn-trans, 1.83 g, 36%.

***trans*-Dichloro((*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine))((*RS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II).** A solution of prereduced ruthenium(III) chloride (0.57 g) in methanol (50 mL) was added to a boiling solution of (*RR*,*SS*)-diphos (0.78 g) and (*RS*)-diphos (0.78 g) in methanol (100 mL) containing aqueous formaldehyde (1 mL, 40% w/v). The precipitate was discarded, the filtrate evaporated to dryness, and the residue chromatographed on alumina. Elution of the column with dichloromethane/hexane (40:60) followed by fractional crystallization afforded yellow needles of the almost pure product: mp 292–293 °C (yield 0.62 g, 33%); ^{1}H NMR ($CDCl_3$) δ 1.28 (br d, 3, *J* = 5.6 Hz, PMe), 1.39 (br d, 3, *J* = 6.8 Hz, PMe), 1.96 (br d, 3, *J* = 4.9 Hz, PMe), 2.33 (br d, 3, *J* = 7.0 Hz, PMe), 6.1–7.9 (m, 28, aromatics). The spectrum also contained resonances due to the complex *rac-trans*-[$RuCl_2$(*RR*,*SS*-diphos)$_2$] (<5%).

(+)$_{589}$-Λ-*anti-cis-C*$_2$-Dichlorobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II). Finely ground *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] (1.99 g) was suspended in triethylaluminum (5 mL) and the reaction mixture stirred at 75 °C for 2 h. Two clear layers separated during this period. The mixture was cooled to −10 °C and ethanol (20 mL) slowly added, giving a pale yellow solution. This was stirred at room temperature for 3.5 h; the color of the solution deepended and a greenish yellow compound precipitated. The solvent was removed (20 mmHg, 50 °C) and the residue dissolved in dichloromethane (50 mL). Concentrated hydrochloric acid (20 mL, 10 M) was then cautiously added and the organic layer separated and dried (Na_2CO_3). The pure product was obtained as lemon yellow flakes, mp 305 °C, from dichloromethane by the addition of ethanol. A further small quantity of the product was obtained from the filtrate by column chromatography: yield 1.84 g (93%); $[\alpha]_D$ +27° (*c* 0.24, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.65 (filled-in d, 6, *J* = 8.0 Hz, cis-PMe), 2.33 (t, 6, *J* = 3.6 Hz, trans-PMe), 6.5–7.7 (m, 28, aromatics).

(+)$_{589}$-*trans*-Chlorohydridobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II) Benzene Disolvate. The colorless mixture obtained from the reaction of *trans*-[$RuCl_2$((*SS*)-diphos)$_2$] (1.46 g) with triethylaluminum (4 mL) was diluted with dichloromethane (35 mL) and then cooled to −78 °C. Ethanol (25 mL) was slowly added, and the combined solvents were evaporated (20 mmHg, 50 °C). The solution became yellow as it warmed to room temperature. The residue was redissolved in dichloromethane and, once again, cooled to −78 °C and cautiously treated with hydrochloric acid (30 mL, 10 M). The organic layer was separated and dried (Na_2CO_3) while being maintained at −78 °C. Evaporation of the solvent left a yellow solid, which was recrystallized from benzene. The product was isolated as a pale yellow benzene disolvate: mp 160–162 °C (yield 0.93 g, 61%); $[\alpha]_D$ + 320° (*c* 4.92, CH_2Cl_2). Anal. Calcd for $C_{46}H_{47}ClP_4Ru$: C, 66.6; H, 5.7; Cl, 3.8. Found: C, 66.2; H, 5.8; Cl, 3.9. ^{1}H NMR ($CDCl_3$): δ −19.57 (q, 1, *J* = 21.5 Hz, RuH), 1.26 (br t, 6, cis-PMe), 1.63 (br d, 6, *J* = 3.1 Hz, trans-PMe), 7.1–7.6 (m, 35, aromatics (including C_6H_6)). This compound was also prepared as follows. A solution of *cis*-[$RuCl_2$((*SS*)-diphos)$_2$] (0.11 g) in tetrahydrofuran (15 mL) was stirred with excess lithium aluminum hydride for 20 min. The gray hydride was removed by filtration, leaving a pale yellow solution. This was evaporated to dryness and the residue dissolved in dichloromethane and treated with hydrochloric acid (5 mL, 2 M). Separation of the organic layer, followed by drying (Na_2CO_3), evaporation of the solvent, and recrystallization of the residue from benzene afforded the *trans*-chlorohydrido complex as the benzene disolvate in almost 95% yield. The same complex was obtained by reaction of [$RuHCl(PPh_3)_3$]·C_6H_6 with (*RR*)-diphos (41% yield).

***rac-anti-cis-C*$_2$-Dichlorobis((*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II)** was prepared from *trans*-[$RuCl_2$((*RR*,*SS*)-diphos)$_2$] by using the same method as that used for the optically active Λ-anti-cis-C_2 complex: lemon yellow rods; mp 283–285 °C (89% yield). The ^{1}H NMR ($CDCl_3$) was identical with that of the optically active material.

***rac-trans*-Chlorohydridobis((*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II) Benzene Disolvate.** The synthesis was the same as that for the optically active complex, but racemic starting material was used. The ^{1}H NMR ($CDCl_3$) was identical with that of the pure enantiomer.

***rac-cis-C*$_1$-Dichloro((*RR*)-*o*-phenylenebis(methylphenylphosphine))((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II)** was prepared from *meso-trans*-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)] (2.08 g) and $AlEt_3$ (3 mL) by the usual method. The pure product crystallized from dichloromethane/ethanol as beautiful lemon yellow needles: mp 232–233 °C (yield 1.80 g, 86%); ^{1}H NMR ($CDCl_3$) δ 0.65 (br d, 3, *J* = 8.2 Hz, cis-PMe), 1.14 (br s, 3,

trans-PMe), 1.64 (d, 3, J = 9.8 Hz, cis-PMe), 2.51 (t, 3, J = 4.1 Hz, trans-PMe), 6.3–8.05 (m, 28, aromatics).

***rac-syn-cis-*C_2-Dichlorobis((*RS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II).** Interaction of either *anti-trans-* or *syn-trans-* [$RuCl_2$((*RS*)-diphos)$_2$] with triethylaluminum following the usual procedure gave the pure racemic-syn-cis-C_2 product: mp >320 °C (69% yield); ^{1}H NMR ($CDCl_3$) δ 1.30 (filled-in d, 6, J = 9.4 Hz, cis-PMe), 2.54 (t, 6, J = 4.1 Hz, trans-PMe), 5.8–7.8 (m, 28, aromatics).

$(+)_{589}$-Λ-*anti-cis-*C_2-Diiodobis((*SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II). A solution of Λ-*anti-cis-*C_2-[$RuCl_2$((*SS*)-diars)$_2$] in tetrahydrofuran containing a 10–30 × excess of lithium iodide was heated at reflux temperature for ca. 30 min. The solvent was then removed, and the product was extracted into dichloromethane and crystallized by the addition of ethanol. The product formed orange needles: mp 309 °C (84% yield); $[\alpha]_D$ +122° (c 1.02, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6, cis-AsMe), 2.58 (s, 6, trans-AsMe), 6.2–7.8 (m, 28, aromatics).

The following compounds were prepared similarly. *rac-anti-cis-*C_2-[RuI_2((*RR,SS*)-diars)$_2$]: orange needles; mp 264–266 °C (96%); ^{1}H NMR ($CDCl_3$) identical with that of the corresponding enantiomer; *rac-cis-*C_1-[RuI_2((*RR*)-diars)((*SS*)-diars)]: deep red plates; mp 203–205 °C (yield 89%); ^{1}H NMR (CH_2Cl_2) δ 0.47 (s, 3, AsMe), 1.43 (s, 3, AsMe), 1.57 (s, 38 AsMe), 2.70 (s, 3, AsMe), 6.5–7.9 (m, 28, aromatics).

$(+)_{589}$-Λ-*anti-cis-*C_2-Diiodobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II). This complex was prepared in the same way as the corresponding di(tertiary arsine) compounds, although the rate of substitution was faster (reaction time required: 1–3 min). The pure enantomer crystallized as orange needles: mp 309–310 °C (86% yield); $[\alpha]_D$ +68.7° (c 0.150, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.77 (filled-in d, 6, J = 6.3 Hz, cis-PMe), 2.79 (t, 6, J = 3.5 Hz, trans-PMe), 5.75–7.9 (m, 28, aromatics).

Prepared similarly were the following. *rac-anti-cis-*C_2-[RuI_2((*RR,SS*)-diphos)$_2$]: yellow orange needles; mp 294–295 °C (yield 83%); ^{1}H NMR ($CDCl_3$) identical with that of the corresponding enantiomer. *rac-cis-*C_1-[RuI_2((*RR*)-diphos)((*SS*)-diphos)]: red blocks; mp 201–203 °C (89%); ^{1}H NMR (CH_2Cl_2) δ 0.56 (d, 3, J = 8.2 Hz, PMe), 1.35 (br d, 3, J = 4.5 Hz, PMe), 1.82 (d, 3, J = 7.3 Hz, PMe), 3.00 (d of d, J = 3.9, 7.6 Hz, PMe), 6.4–8.0 (m, 28, aromatics).

$(+)_{589}$-Λ-*anti-cis-*C_1-Carbonylchlorobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II) Hexafluorophosphate. Carbon monoxide was passed into a boiling suspension of Λ-*anti-cis-*C_2-[$RuCl_2$((*SS*)-diphos)$_2$] (0.21 g) in ethanol for 15 min. The neutral starting material dissolved to give a colorless solution of the desired cation. An excess of aqueous ammonium hexafluorophosphate solution was then slowly added to the clear reaction mixture. The product separated as a flocculent precipitate, which was filtered off, washed with water, and dried. Recrystallization of the crude material from acetone by the addition of diethyl ether gave the pure product as colorless prisms: mp >300 °C (yield 0.23 g, 93%); $[\alpha]_D$ +41.4° (c 0.826, CH_2Cl_2); ^{1}H NMR (100 MHz, ^{31}P decoupled, CD_2Cl_2) δ 1.77 (s, 3, PMe), 1.80 (s, 3, PMe), 2.23 (s, 3, PMe), 2.37 (s, 3, PMe), 6.75–8.0 (m, 28, aromatics); IR (CH_2Cl_2) 2026 cm^{-1} (ν_{CO}); Λ_M (CH_2Cl_2) 48.8 cm^2 Ω^{-1} mol^{-1} (0.873 × 10^{-3} M) (1:1). An alternative method of preparation of this salt was the following. A suspension of *trans*-[$RuCl_2(CO)_2$((*SS*)-diphos)$_2$][24] (0.10 g) and (*RR*)-diphos (0.06 g) in ethanol (3 mL) was heated under refluxing conditions for 40 min. During this time the solids dissolved and the yellow color of the solution faded. Aqueous NH_4PF_6 was then added and the precipitate filtered off and recrystallized as above. This method gave an 86% yield of the pure Λ-anti-cis-C_1 isomer.

$(+)_{589}$-*trans*-Carbonylhydridobis((*SS*)-*o*-phenylenebis(methylphenylphosphine))ruthenium(II) Hexafluorophosphate. Carbon monoxide was passed into a boiling solution of the corresponding *chlorohydride* in ethanol (10 mL) for 10 min, causing the deep yellow color to fade. An excess of aqueous NH_4PF_6 was added to the reaction mixture while the CO stream was maintained. The reaction mixture was cooled to −10 °C, and the white solid was isolated, washed with water, and dried. Recrystallization of the product from acetone (10 mL) by the addition of diethyl ether (50 mL) yielded white flakes of the pure product, which, after drying at 100 °C (0.1 mmHg), had mp 194–195 °C (yield 1.11 g, 80%) and $[\alpha]_D$ +333° (c 1.06, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.33 (br s, 6, PMe), 1.68 (br s, 6, PMe), 7.0–8.0 (m, 28, aromatics). IR (CH_2Cl_2): 1999 cm^{-1} (ν_{CO}). Λ_M (CH_2Cl_2): 55.4 cm^2 Ω^{-1} mol^{-1} (1.99 × 10^{-3} M) (1:1). The sample for X-ray crystal structure analysis was air-dried and analyzed as the acetone disolvate.

The corresponding racemic compounds were prepared similarly: *rac-anti-cis-*[RuCl(CO)((*RR,SS*)-*o*-C_6H_4($PMePh_2$)$_2$)$_2$]PF_6, mp 200–201 °C (yield 93%); *rac-trans-*[RuH(CO)((*RR,SS*)-*o*-C_6H_4-($PMePh_2$)$_2$)]PF_6, mp 184–185 °C (yield 86%).

***rac-anti-cis-*C_1-Carbonylchlorobis((*RR,SS*)-*o*-phenylenebis(methylphenylarsine))ruthenium(II) Hexafluorophosphate.** Carbon monoxide was bubbled into a boiling suspension of *rac-anti-cis-*C_2-[$RuCl_2$((*RR,SS*)diars)$_2$] (0.2 g) and NH_4PF_6 (0.06 g) in ethanol (10 mL) for 20 min. The resulting solution was cooled to room temperature and then treated with water (25 mL). The CO stream was stopped and the pale yellow powder filtered off, washed with water, and dried. The pure product was obtained as pale yellow rods from acetone/diethyl ether: mp 187–189 °C (yield 0.20 g, 88%); ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3, AsMe), 1.73 (s, 3, AsMe), 2.19 (s, 3, AsMe), 2.25 (s, 3, AsMe), 6.0–7.9 (m, 28, aromatics); IR (CH_2Cl_2) 2010 cm^{-1} (ν_{CO}); Λ_M (CH_2Cl_2): 47.4 cm^2 Ω^{-1} mol^{-1} (1.01 × 10^{-3} M) (1:1).

Acknowledgment. This work was supported by the Australian Research Grants Committee.

Registry No. $(+)_{589}$-*trans*-[$RuCl_2$((*SS*)-diars)$_2$], 82338-47-4; *meso-trans*-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)], 82442-82-8; *rac-trans*-[$RuCl_2$((*RR,SS*)-diars)$_2$], 82373-44-2; *anti-trans*-[$RuCl_2$-((*RS*)-diars)$_2$], 82443-56-9; *syn-trans*-[$RuCl_2$((*RS*)-diars)$_2$], 82443-55-8; $(+)_{589}$-*trans*-[$RuCl_2$((*SS*)-diphos)$_2$], 82338-48-5; *meso-trans*-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)], 82442-81-7; *rac-trans*-[$RuCl_2$((*RR,SS*)-diphos)$_2$], 82373-45-3; *anti-trans*-[$RuCl_2$-((*RS*)-diphos)$_2$], 82443-57-0; *syn-trans*-[$RuCl_2$((*RS*)-diphos)$_2$], 82467-17-2; *rac-trans*-[$RuCl_2$((*RR,SS*)-diphos)((*RS*)-diphos)], 82373-46-4; $(+)_{589}$-Λ-*anti-cis-*C_2-[$RuCl_2$((*SS*)-diars)$_2$], 82442-80-6; *rac-anti-cis-*C_2-[$RuCl_2$((*RR,SS*)-diars)$_2$], 82442-76-0; *rac-cis-*C_1-[$RuCl_2$((*RR*)-diars)((*SS*)-diars)], 82442-79-3; *rac-syn-cis-*C_2-[$RuCl_2$((*RS*)-diars)$_2$], 82338-49-6; *rac-cis-*C_1-[$RuCl_2$((*RS*)-diars)$_2$], 82373-47-5; $(+)_{589}$-Λ-*anti-cis-*C_2-[$RuCl_2$((*SS*)-diphos)$_2$], 82373-48-6; *rac-anti-cis-*C_2-[$RuCl_2$((*RR,SS*)-diphos)$_2$], 82442-77-1; *rac-cis-*C_1-[$RuCl_2$((*RR*)-diphos)((*SS*)-diphos)], 82442-78-2; *rac-syn-cis-*C_2-[$RuCl_2$((*RS*)-diphos)$_2$], 82373-49-7; *trans*-[$RuCl_2$((*SS*)-diphos)-((*RS*)-*o*-C_6H_4(PMePh)[P(O)MePh])], 82338-50-9; $(+)_{589}$-*trans*-[RuHCl((*SS*)-diphos)$_2$], 82338-51-0; *rac-trans*-[RuHCl((*RR,SS*)-diphos)$_2$], 82373-50-0; $(+)_{589}$-Λ-*anti-cis-*C_2-[RuI_2((*SS*)-diars)$_2$], 82338-52-1; *rac-anti-cis-*C_2-[RuI_2((*RR,SS*)-diars)$_2$], 82373-51-1; *rac-cis-*C_1-[RuI_2((*RR*)-diars)((*SS*)-diars)], 82442-75-9; $(+)_{589}$-Λ-*anti-cis-*C_2-[RuI_2((*SS*)-diphos)$_2$], 82338-53-2; *rac-anti-cis-*C_2-[RuI_2((*RR,SS*)-diphos)$_2$], 82442-73-7; *rac-cis-*C_1-[RuI_2(*RR*)-diphos)((*SS*)-diphos)], 82442-74-8; $(+)_{589}$-Λ-*anti-cis-*C_1-[Ru(CO)-Cl((*SS*)-diphos)$_2$]PF_6, 82338-55-4; $(+)_{589}$-*trans*-[Ru(CO)H((*SS*)-diphos)$_2$]PF_6, 82338-57-6; *rac-anti-cis*-[RuCl(CO)((*RR,SS*)-diphos)$_2$]PF_6, 82373-53-3; *rac-trans*-[RuH(CO)((*RR,SS*)-diphos)$_2$]PF_6, 82373-55-5; *rac-anti-cis-*C_1-[RuCl(CO)((*RR,SS*)-diars)$_2$]PF_6, 82338-59-8; (*RS*)-methyl[2-(methylphenylphosphino)phenyl]-phenylphosphine oxide, 82323-92-0; [*o*-C_6H_4(PMePh)(PBzMePh)]Br, 82312-36-5; $RuHCl(PPh_3)_3$, 55102-19-7.

Supplementary Material Available: ^{1}H NMR spectra (Figures 7–10) (4 pages). Ordering information is given on any current masthead page.