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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. 4. Preparation and Properties of Carbonyl Halide Derivatives of Ruthenium(II)

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

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Octahedral complexes of the type [RuCl$_2$(CO)$_2$(bidentate)] have been prepared from the meso, racemic, and optically active forms of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue. Methods are described for the production of either the *cis*- or *trans*-dichloro isomers. The salts [RuCl(CO)$_3$(bidentate)]Cl were also isolated in the case of the di(tertiary phosphines) and shown to contain a meridional arrangement of carbonyl ligands. The neutral dicarbonyls underwent reversible decarbonylation to form the chloro-bridged dimers [RuCl$_2$(CO)(bidentate)]$_2$. Reaction of the dimers or neutral dicarbonyls with dimethyl sulfoxide gave exclusively the *cis*-dichloro complexes [RuCl$_2$(CO)(bidentate)(Me$_2$SO-*S*)]. The latter were shown to undergo a slow epimerization at the metal center which was facilitated by heating, according to variable-temperature ^{1}H NMR studies. The structures of the various stereoisomeric complexes were assigned on the basis of spectroscopic data and, in two instances, X-ray crystallography.

Introduction

Whereas numerous carbonyl halides of bivalent ruthenium containing unidentate tertiary arsines and phosphines are known, few derivatives of the corresponding chelating di(tertiary) species have been reported.[2] The latter of necessity give rise to the relatively uncommon cis arrangement of group 5B donor atoms in the [RuX$_2$(CO)$_2$L$_2$] system.[3] By utilization of the various stereoisomers of *o*-phenylenebis(methylphenylarsine)[4] and its phosphorus analogue[5] we have been able to investigate in detail the substitution patterns of the common carbonyl chlorides of ruthenium(II), as well as some of the resulting derivatives. In the previous article[6] methods of preparation and the stereochemistry of the complexes *cis*- and *trans*-[RuCl$_2$(bidentate)$_2$] containing the same sets of ligands were reported.

Results and Discussion

1. *trans*-Dichloro Complexes. The reaction of [RuCl$_2$(CO)$_2$]$_n$ with 1 equiv of the appropriate stereoisomer of either ligand in boiling ethanol or 2-methoxyethanol gave the *trans*-dichloro complexes, *trans*-[RuCl$_2$(CO)$_2$(bidentate)], in ca. 80% yield. Excessive reaction time led to the formation of insoluble dimers by the loss of carbon monoxide (see Figure 5). The monomeric derivatives were obtained as yellow (di(tertiary arsine)) or orange (di(tertiary phosphine)) crystalline solids, the spectroscopic properties of which are summarized in Table I. The spectroscopic data in support of the various structural assignments are unequivocal. The observation of singlet ^{1}H and ^{13}C resonances for the AsCH$_3$ and a singlet ^{13}C resonance for the Ru–CO groups in the NMR spectra of the complex containing (*RS*)-diars was sufficient evidence to assign to it structure **1b** (Figure 1). (In this paper diars is defined as *o*-phenylenebis(methylphenylarsine) and diphos as *o*-phenylenebis(methylphenylphosphine).) The corresponding compound containing (*RR,SS*)-diars, or its enantiomers, had the same *trans*-dichloro structure according to spectroscopic studies (Table I). However, in this case IR spectroscopy was required in order to distinguish between **1a** and the alternative C_2 structure containing *cis*-dichloro ligands trans to the bidentate donor atoms. Long-range ^{31}P coupling to the methyl protons complicated the NMR spectra of the di(tertiary phosphine) complexes: the PMe resonances in both cases appeared as "filled-in" doublets in the ^{1}H NMR spectra.[7] A five-line pattern of resonances was observed for these groups in the ^{13}C NMR spectra of the complexes, however, where they are part of an AA′XX′ spin system.[8]

2. *cis*-Dichloro Complexes. The *cis*-dichloro complexes were less stable than the corresponding trans isomers. They were prepared from [RuCl$_2$(CO)$_3$]$_2$ and the appropriate ligand in ethanol at room temperature. When the reagents were mixed, carbon monoxide was evolved and the colorless products precipitated. The reaction of (*RS*)-diars was stereoselective, the racemate corresponding to **2c** being the only compound isolated (89% yield; see Figure 2). The AsMe resonances in this complex were situated ca. 0.3 ppm downfield of the resonance found for the corresponding trans complex (**1b**), which indicated that the axial carbonyl ligand was adjacent to and deshielded the methyl groups. A small amount of the stereoisomer **2d** and its enantiomer may have remained in the filtrate after removal of the main product, however. The residue from the filtrate exhibited a broad ^{1}H NMR signal centered at δ 2.00, although a crystalline material could not be isolated. The stereoselectivity of the reaction is noteworthy.

The axial coordination sites cis to the chelated dissymmetric forms of the bidentate ligands are diastereotopic. Thus there are two epimeric *cis*-dichloro complexes, [RuCl$_2$(CO)$_2$((*RR,SS*)-bidentate)]. These are illustrated in Figure 2 for the products derived from the *RR* form of the bidentates. The reaction between [RuCl$_2$(CO)$_3$]$_2$ and (*RR*)-diars yielded **2a** in 49% yield. The corresponding racemic complex was prepared similarly and its structure determined by X-ray crystallography.[9] Although **2b** could not be isolated, there was NMR evidence indicating that it was present to the extent of ca. 25%.

The solid-state coordination geometry of the *cis*-dichloro complexes was retained in solution. A pair of ν(CO) absorptions was observed in the infrared spectra of both the optically active and the racemic complexes, as well as a pair of AsMe singlets in the ^{1}H NMR spectra (Table I). Furthermore, the ^{13}C NMR spectra of both complexes contained two singlets corresponding to the carbon nuclei of the carbonyl ligands.

A suggested pathway for the formation of the epimers is shown in Figure 3. The starting material contains a facial

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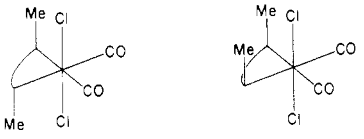
Table I. Spectroscopic Data and Structural Assignment of the Complexes *cis-* and *trans-*[$RuCl_2(CO)_2$(bidentate)]

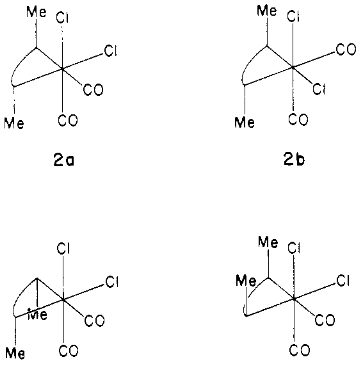
			^{1}H NMR[b]		^{13}C NMR[c]			
bidentate	structure	IR[a] ν(CO)	δ(EMe)	*J*(PH)	δ(EMe)	*J*(PC)	δ(CO)	*J*(PC)
(*SS*)-diars	**1a**	2065, 2012	2.05 s		9.39 s		193.66 s	
(*RR,SS*)-diars	**1a**	2065, 2012	2.05 s		9.39 s		193.66 s	
(*SS*)-diphos	**1a**	2070, 2021	2.17 fd	9.9	12.97 q	16.0[d]	193.10 q (AB)	109.9 (trans) 18.3 (cis)
(*RR,SS*)-diphos	**1a**	2070, 2021	2.17 fd	9.9	12.97 q	16.0[d]	193.10 q (AB)	109.9 (trans) 18.3 (cis)
(*RS*)-diars	**1b**	2065, 2013	2.02 s		9.56 s		193.55 s	
(*RS*)-diphos	**1b**	2066, 2021	2.16 fd	10.6	14.28 q	16.0[d]	192.95 q (AB)	109.8 (trans) 19.5 (cis)
(*SS*)-diars	**2a**	2072, 2000	1.88 s 2.29 s		7.51 s 16.50 s		189.62 s 192.30 s	
(*RR,SS*)-diars	**2a**	2072, 2000	1.88 s 2.29 s		7.51 s 16.50 s		189.62 s 192.30 s	
(*RR,SS*)-diphos	**2a**	2079, 2005	2.00 d 2.45 d	9.7 12.0	9.42 d 21.35 d	35.5 36.6	192.6 m	
(*RS*)-diars	**2c**	2069, 2004	2.28 s 2.30 s		7.65 s 11.29 s		190.14 s 191.56 s	

[a] Recorded in CH_2Cl_2. [b] Chemical shifts (*J* in Hz) relative to Me_4Si in $CDCl_3$ (*J* in Hz; fd = filled-in doublet). Aromatic protons appeared as unresolved multiplets at δ 7–8 ppm for all complexes. [c] Spectra recorded in $CDCl_3$. Chemical shifts are quoted relative to Me_4Si (*J* in Hz). Aromatic nuclei gave unresolved multiplets at δ 125–145. [d] Apparent coupling constant.



Ia Ib

Figure 1. Stereoisomers of the *trans*-dichloro complexes *trans*-[$RuCl_2(CO)_2$(bidentate)].



2c 2d

Figure 2. Stereoisomers of the complexes *cis*-[$RuCl_2(CO)_2$(bidentate)].

arrangement of carbonyl ligands in the solid state.[10] In polar solvents, e.g., alcohols, the dimers disproportionate into species of the type [$RuCl_2(CO)_3(ROH)$]. The reaction of the solvated monomer with the bidentates appears to proceed stereospecifically to produce substituted cations in which the three carbonyl ligands are meridionally disposed to one another. Tricarbonyl cations of this stereochemistry were isolated for both (*RR,SS*)-diphos and (*RS*)-diphos (vide infra). However, di(tertiary arsine) derivatives of this type could not be isolated in a state of purity due to their ready loss of carbon monoxide. Substitution of one or the other of the diastereotopic axial carbonyl ligands by chloride produces the respective neutral dicarbonyls **2a** and **2b**.

The yields of the *cis*-dichloro di(tertiary phosphine) complexes were lower than those of the corresponding arsenic compounds. In the former case the rates of formation and decomposition (to dimers) of the neutral dicarbonyls appeared to be similar. However, the latter decarbonylation was inhibited by excess carbon monoxide. Thus, a 55% yield of **2a** and its enantiomer was obtained from the reaction of [$RuCl_2(CO)_3]_2$ and (*RR,SS*)-diphos in ethanol under 600 psi of carbon monoxide. As for the di(tertiary arsine) system, it was not found possible to isolate compounds of the type **2b**.

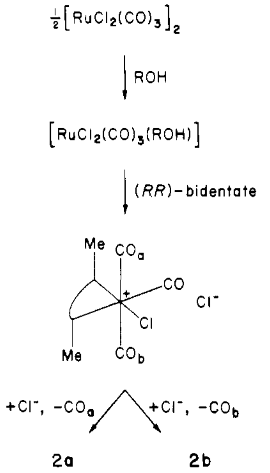


Figure 3. Suggested mechanism of formation of the epimeric complexes *cis*-[$RuCl_2(CO)_2$((*SS*)-bidentate)].

Spectroscopic details for the various stereoisomeric *cis*- and *trans*-dichloro complexes are summarized in Table I.

3. Tricarbonyl Complexes. In the presence of carbon monoxide the di(tertiary phosphines) reacted with [$RuCl_2(CO)_3]_2$ to give high yields of the salts [$RuCl(CO)_3$(diphos)]Cl. In boiling propan-2-ol the yields were ca. 90%. However, the products were invariably contaminated with small quantities of neutral dicarbonyls; the latter were not readily removed due to further decarbonylation of the tricarbonyls to more of the neutral dicarbonyls. The corresponding di(tertiary arsine) tricarbonyls were even more sensitive to decarbonylation and could not be isolated in a state of purity.

The infrared spectra of the pure tricarbonyl cations containing either (*RR,SS*)-diphos or (*RS*)-diphos were almost superimposable in the ν(CO) region. Three strong carbonyl stretches were observed for each complex, suggesting the presence of a single complex cation in each case. For the tricarbonyl cation containing (*RS*)-diphos there is a chiral stereoisomer containing a meridional arrangement of carbonyl

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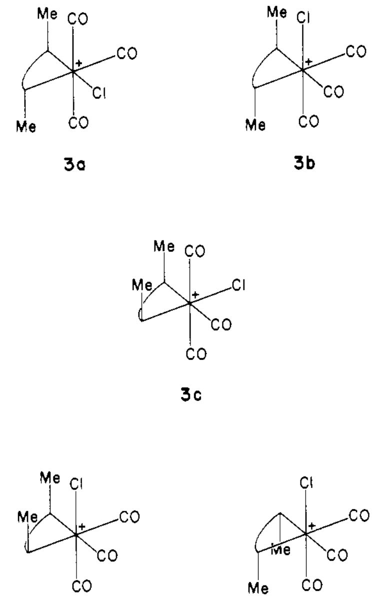
(10) Benedetti, E.; Braca, G.; Sbrana, G.; Salvetti, F.; Grassi, B. *J. Organomet. Chem.* **1972**, *37*, 361.



3a **3b** **3c** **3d** **3e**

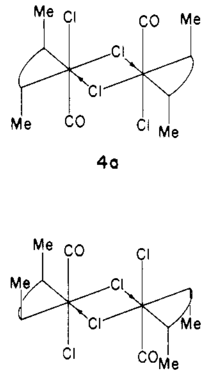
Figure 4. Stereoisomers of the *fac*- and *mer*-tricarbonyl cations [RuCl(CO)$_3$(bidentate)]$^+$.

ligands (**3c**), as well as two achiral facial isomers (**3d** and **3e**) (Figure 4). The cations *fac*-[RuCl(CO)$_3$((*RS*)-diphos)]$^+$ contain equivalent PMe groups. In the meridional structure the PMe groups are nonequivalent. Since a pair of PMe doublets was observed in the ^{1}H NMR spectrum of [RuCl(CO)$_3$((*RS*)-diphos)]Cl and its physical properties and IR spectrum are consonant with the presence of a single cation only, we have assigned to it the chiral structure **3c**. The complex derived from (*RR*,*SS*)-diphos is considered to be composed of **3a** and its enantiomorph.

The tricarbonyl salts conducted as uni-univalent electrolytes in dichloromethane. In ethanol solution they decomposed with the evolution of carbon monoxide upon exposure to sunlight.

4. Dimeric Complexes. The neutral *cis*- and *trans*-dichloro complexes [RuCl$_2$(CO)$_2$(bidentate)] dimerized through loss of carbon monoxide upon prolonged heating in ethanol or, better, 2-methoxyethanol. The extent of the reaction was conveniently monitored by IR spectroscopy. For example, the ν(CO) bands at 2065 and 2012 cm^{-1} in the spectrum of *trans*-[RuCl$_2$(CO)$_2$((*RR*,*SS*)-diars)] decreased in intensity as decarbonylation proceeded and a new band at 1997 cm^{-1} appeared. The latter continued to grow until another new band at 1975 cm^{-1} became evident, whereupon a yellow solid began to precipitate. The product was sparingly soluble in common solvents and was analyzed as [RuCl$_2$(CO)(diars)]. However, the decarbonylation of the corresponding optically active complex **1a** was not accompanied by precipitation. Although the new band at 1997 cm^{-1} appeared, the lower energy absorption did not. We therefore propose that the yellow solid contains an enantiomeric pair of di(tertiary arsine) ligands; that is, it has the internally compensated meso structure **4a** (Figure 5). The band at 1997 cm^{-1}, which was observed during both the optically active and the racemic decarbonylations, may be attributed to the solvated intermediate [RuCl$_2$(CO)((*RR*,*SS*)-diars)(ROH)] (or the pure enantiomer in the case of the optically active system). We were unable to isolate an optically active dimer under any of the conditions tried. It is perhaps noteworthy that similar relative solubilities exist between the complexes *trans*-[RuCl$_2$((*SS*)-diars)$_2$] and *meso-trans*-[RuCl$_2$((*RR*)-diars)((*SS*)-diars)].[6]

Decarbonylation of either *cis*- or *trans*-[RuCl$_2$(CO)$_2$((*RS*)-diars)] also produced an insoluble dimer. The low solubility of the dimer was reminiscent of the properties of the complex *anti-trans*-[RuCl$_2$((*RS*)-diars)$_2$], which contains an anti arrangement of the methyl and phenyl groups.[6] This observation, combined with the presence of a single ν(CO) absorption at 1974 cm^{-1} in the IR (Nujol spectrum) has led us to assign to it the anti structure **4b**.



4a **4b**

Figure 5. Proposed structures of the complexes *meso*-[Ru$_2$Cl$_4$(CO)$_2$((*RR*)-bidentate)((*SS*)-bidentate)] (**4a**) and *anti*-[Ru$_2$Cl$_4$(CO)$_2$((*RS*)-bidentate)$_2$] (**4b**).

The corresponding dimeric complexes containing the di(tertiary phosphine) were also readily prepared. Again, a peak of higher energy (1999 cm^{-1}) first appeared, which was followed by one at 1974 cm^{-1} at the same time as the yellow product was precipitated. Both analogues of type **4a** and **4b** were insufficiently soluble for the ^{1}H NMR spectra to be recorded. Again, the optically active dimer could not be isolated.

Both sets of dimers were obtained in equal yield from either the *cis*- or the *trans*-dichloro monomeric precursors.

5. Dimethyl Sulfoxide Complexes. The μ-chloro bridges in the dimers were readily cleaved by dimethyl sulfoxide. For example, the di(tertiary arsine) derivative of type **4b** dissolved in warm dimethyl sulfoxide to give a pale yellow solution from which a colorless compound that was analyzed as [RuCl$_2$(CO)(Me$_2$SO)(diars)] could be isolated. Its infrared spectrum in dichloromethane contained a sharp ν(CO) absorption at 1983 cm^{-1} and a ν(SO) band at 1103 cm^{-1}. The latter was attributed to the S–O stretch of an S-bonded Me$_2$SO ligand. In the same solvent, free Me$_2$SO absorbs at 1055 cm^{-1}. The shift of the band to higher energy upon coordination is typical of this mode of coordination.[11]

The ^{1}H NMR spectrum of [RuCl$_2$(CO)((*RS*)-diars)(Me$_2$SO)] in CDCl$_3$ exhibited singlets at δ 2.29 and 2.26 for the AsMe groups. These values may be compared to those of δ 2.30 and 2.28 for the related di(tertiary arsine) complex of structure **2c**. Clearly, the carbonyl ligand occupies an axial site adjacent to the AsMe in the bridge-split complex. In the compound of type **1b**, the AsMe resonance occurs at δ 2.02. The SMe resonances occur at δ 3.41 and 3.31. In the same solvent, free Me$_2$SO has a resonance at δ 2.61. The pronounced downfield shift of the SMe resonance upon coordination adds further support to assignment of an S-bonded Me$_2$SO ligand. In cases of O bonding the position of the SMe resonance is very little different from that of the free ligand.[11] Furthermore, a *cis*-dichloro formulation is implied by the color of the substance: *trans*-dichloro *cis*-dicarbonyls of Ru(II) are usually yellow, and *cis*-dichloro *cis*-dicarbonyls, white. It therefore appears that the Me$_2$SO splits the μ-chloro bridge with retention of the relative stereochemistry of CO and the (*RS*)-diars ligand. The same compound was also obtained by heating either of the *trans*- or *cis*-dichloro monomers, **1b** or

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[11] Kitching, W.; Moore, C. J.; Doddrell, D. *Inorg. Chem.* **1970**, *9*, 541 and references therein.

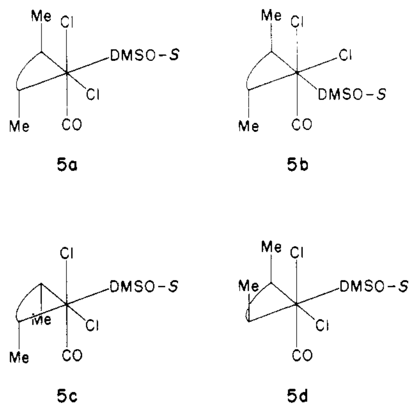

Figure 6. Stereoisomers of the *cis*-dichloro complexes [$RuCl_2(CO)$(bidentate)(Me_2SO-*S*)].

2c, in Me_2SO until CO evolution ceased (ca. 3 h).

On the basis of spectroscopic evidence and knowledge of the crystal structure of [$RuCl_2(CO)$((*RR,SS*)-diphos)(Me_2SO)] (vide infra), the compound [$RuCl_2(CO)$((*RS*)-diphos)(Me_2SO)] and its arsenic analogue have been assigned structure **5c** rather than **5d** (Figure 6). The ^{13}C NMR spectrum of the di(tertiary phosphine) compound contains an approximate triplet for the ^{13}CO resonance due to weak, almost equal, coupling of the ^{13}C nucleus with the nonequivalent cis ^{31}P nuclei, which is typically of the order 15–25 Hz. On the other hand, if the carbonyl ligand had been in the plane of the chelate ring, a strong coupling of the carbonyl ^{13}C to a trans ^{31}P (ca. 110 Hz) would have been evident, in addition to a weaker cis ^{13}C–^{31}P interaction. The deshielded position of the PMe resonances also points to structure **5c**. Since the coordination sites trans to the bidentate donors are enantiotopic, the product isolated from the reaction mixture was racemic. However, the same sites in complexes containing the dissymmetric forms of the bidentates are diastereotopic. Thus, the epimeric structures **5a** and **5b** are possible for the Me_2SO adducts. Both species have been observed. In the solid state, a crystal of [$RuCl_2(CO)$((*RR,SS*)-diphos)(Me_2SO)] was shown by X-ray crystallography to be a racemic compound of **5b** and its enantiomorphs.[9] However, dissolution of this complex, or any of its analogues, in $CDCl_3$ resulted in epimerization of the metal center and observation of NMR signals due to both **5a** and **5b**. Furthermore, mutarotation of the optically active complexes was found. An equilibrium rotation of the complexes was reached only after solutions of the optically active complexes had stood for 48 h. The addition of excess Me_2SO-d_6 to solutions of any of the complexes resulted in a slow exchange of the coordinated Me_2SO, which was readily monitored by ^1H NMR spectroscopy. Thus the complexes [$RuCl_2(CO)$(bidentate)(Me_2SO-d_6)] could be prepared by warming [$RuCl_2(CO)$(bidentate)(Me_2SO)] in Me_2SO-d_6 or directly by mixing either *cis*- or *trans*-[$RuCl_2(CO)_2$(bidentate)] and Me_2SO-d_6 in boiling 2-methoxyethanol.

The rate of intermolecular exchange of the coordinated Me_2SO in these complexes was slow (relative to the NMR time scale) at 30 °C. For the complexes [$RuCl_2(CO)$((*RS*)-bidentate)(Me_2SO-*S*)] the diastereotopicity of the SMe resonances and the nonequivalence of the PMe or AsMe resonances were clearly evident at this temperature. However, as the temperature of a solution of [$RuCl_2(CO)$((*RS*)-diphos)(Me_2SO-*S*)] in *o*-$C_6H_4Cl_2$ was raised (Figure 7), the resonances due to the PMe groups broadened, coalesced (T_c = 376 K), and reemerged as a doublet, which corresponds to an approximate $\Delta G^{\ddagger}$ of 19.7 K cal mol^{-1}. The SMe resonances behaved similarly. Upon heating the doublet of resonances observed at 303 K broadened, coalesced (T_c = 386 K), and reemerged as a singlet ($\Delta G^{\ddagger}$ = 19.9 K cal mol^{-1}). Above 120 °C this complex, and its analogues, lost Me_2SO and the hitherto described dimeric complexes were precipitated. The complexes were sufficiently stable to be repeatedly crystallized from a dichloromethane/methanol mixture without decomposition, however. On the other hand, [$RuCl_2(CO)(Me_2SO$-$O)(PPh_3)_2$] is reported to eliminate Me_2SO under these conditions.[12]

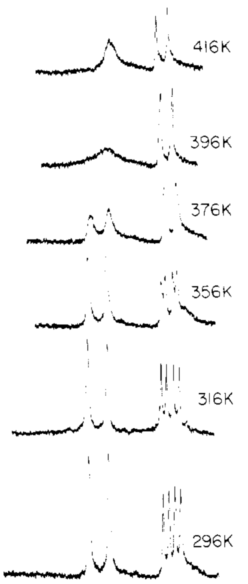

Figure 7. Variable-temperature ^1H NMR spectra of *syn-cis*-[$RuCl_2(CO)(Me_2SO$-*S*)((*RS*)-diphos)] in *o*-$C_6H_4Cl_2$ in the methyl region.

6. Isomerization of Dicarbonyl Complexes. The decarbonylation of the monomeric dicarbonyls to dimers is reversible. Thus, the reaction of the dimeric di(tertiary arsine) complex of the type **4b** with carbon monoxide in ethanol at its boiling point produced in high yield a 95:5 mixture of *cis*-dichloro monomers **2d** and **2c**, respectively. The dimer **4a**, under the same conditions, produced a 70:30 mixture of the di(tertiary arsine) compounds **2a** and **2b**, respectively. The exclusive formation of products in which the chlorine atoms are cis to one another presumably reflects the participation of a five-coordinate intermediate with a common arrangement of donor atoms, which is carbonylated stereospecifically. The same ratios of stereoisomeric *cis*-dichloro products were obtained when carbon monoxide was passed into a boiling solution of **1a** or **1b** in ethanol.

The monomeric *cis*- and *trans*-dichloro complexes of both sets of ligands isomerize upon heating in solution or exposure to sunlight. The colorless cis complexes are converted to the more stable yellow- to orange-colored trans species in boiling ethanol. Prolonged heating resulted in decarbonylation and dimer formation, however.

The mechanism of the thermal and photochemical rearrangement of complexes of the type *cis*- or *trans*-[$RuX_2(CO)_2L_2$] (where X = Cl, Br, and I and L = PR_3) has been discussed elsewhere.[3] Our findings are consistent with these observations. In the present system, the di(tertiary phosphine) derivatives were less amenable to isolation and characterization than the corresponding di(tertiary arsine) compounds. For example, the rates of decarbonylation of the various compounds [$RuCl_2(CO)_2$(diphos)] (to the respective dimers) were comparable to the rates of decarbonylation of [$RuCl(CO)_3$(diphos)]Cl. Isomerization of the complexes *trans*-[$RuCl_2(CO)_2$(diphos)] to the corresponding *cis*-dichloro isomers using CO in boiling ethanol was also only partially effected. How-

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(12) James, B. R.; Markham, L. D.; Hui, B. C.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2247.

ever, the corresponding di(tertiary arsine) derivatives clearly underwent the appropriate transformations in very high yield.

Experimental Section

Reactions were performed with reagents and conditions described in part 3.[6] All new compounds gave satisfactory C and H analyses.

Dicarbonyldichlororuthenium(II). Commercial hydrated ruthenium trichloride (1 g) was dissolved in 2-methoxyethanol (50 mL) and the solution heated under reflux as a stream of carbon monoxide was passed into it. The initial deep red-brown solution suddenly turned a clear yellow after 170–210 min, whereupon the solvent was removed (100 °C, 20 mmHg) and the yellow powder isolated (0.87 g, 100%). Prolonged treatment with carbon monoxide under these conditions led to $[RuCl_2(CO)_3]_2$.

Hexacarbonyldichlorobis(μ-chloro)diruthenium(II). This compound was prepared by the method of Colton and Farthing.[13]

***rac-trans*-Dicarbonyldichloro[(*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-33-(*RR*,*SS*)]**[14] **(Structure 1a and Its Enantiomorph).** A mixture of $[RuCl_2(CO)_2]_n$ (from 0.503 g of commercial "$RuCl_3 \cdot 3H_2O$") and (*RR*,*SS*)-diars (0.788 g) in ethanol (25 mL) was heated under reflux for 2 min. When the mixture cooled, the solution deposited the racemic trans complex as orange prisms, mp 190–191 °C (yield 0.81 g). Chromatography of the filtrate produced further complex, net yield 1.04 g (85%).

$(-)_{589}$-*trans*-Dicarbonyldichloro[(*SS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-33-(*SS*)] (structure 1a) was prepared in the same way but with (*RR*)-diars: orange needles from dichloromethane/ethanol; mp 195–196 °C (yield 61%); $[\alpha]_D - 12°$ (c 0.560, CH_2Cl_2).

***trans*-Dicarbonyldichloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-44-(*RS*)] (structure 1b)** was prepared from (*RS*)-diars under the same conditions. The pure complex crystallized as orange-yellow needles from dichloromethane/petroleum ether; mp 169–170 °C (yield 72%).

***rac-trans*-Dicarbonyldichloro[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]ruthenium(II) [*OC*-6-13-(*RR*,*SS*)] (structure 1a and Its Enantiomorph).** A mixture of $[RuCl_2(CO)_2]_n$ (from 0.508 g of "$RuCl_3 \cdot 3H_2O$") and (*RR*,*SS*)-diphos (0.626 g) in ethanol (40 mL) was heated under reflux for 2 min, in the presence of a stream of carbon monoxide. The reaction mixture was filtered while hot and the filtrate evaporated to dryness. The residue was then dissolved in dichloromethane and the pure racemic complex precipitated by the addition of ethanol. It crystallized as yellow flakes, mp 194–195 °C (yield 0.675 g). Additional material was obtained from the mother liquor by use of column chromatography (net yield 0.96 g, 90%).

Prepared in the same way were the following: **$(-)_{598}$-*trans*-dicarbonyldichloro[(*SS*)-*o*-phenylenebis(methylphenylphosophine)]ruthenium(II) [*OC*-6-13-(*SS*)] (structure 1a)**, lemon yellow needles from dichloromethane/methanol, mp 230–231 °C dec (yield 72%), $[\alpha]_D$ −80.5° (c 0.757, CH_2Cl_2); ***trans*-dicarbonyldichloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]ruthenium(II) [*OC*-6-14-(*RS*)] (structure 1b)**, lemon yellow prisms from dichloromethane/methanol, mp 190–191 °C dec (yield 78%).

$(-)_{589}$-*cis*-Dicarbonyldichloro[(*SS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-32-*A*-(*SS*)] (Structure 2a). A mixture of $[RuCl_2(CO)_3]_2$ (from 0.498 g of "$RuCl_3 \cdot 3H_2O$") and (*RR*)-diars (0.782 g) in ethanol (20 mL) was heated under reflux for 3.5 h in the presence of a stream of carbon monoxide. The reaction mixture was then cooled to −10 °C for 1 h, whereupon colorless crystals of the product precipitated: mp 209–211 °C (yield 0.598 g, 49%); $[\alpha]_D$ −31.2° (c 0.112, CH_2Cl_2).

The corresponding derivatives of the racemic and meso ditertiary arsines were prepared similarly: ***rac-cis*-dicarbonyldichloro[(*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)] (structure 2a and its enantiomorph)**, white prisms, mp 222–223 °C (yield 64%); ***rac-cis*-dicarbonyldichloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)]ruthenium(II) [*OC*-6-(43,34)-*A*-(*RS*)] (structure 2c and its enantiomorph)**, white needles, dec pt 170–180 °C, mp 275–280 °C (yield 89%).

***rac-cis*-Dicarbonyldichloro[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]ruthenium(II) [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)] (Structure 2a and Its Enantiomorph).** A solution of $[RuCl_2(CO)_3]_2$ (from 0.520 g "$RuCl_3 \cdot 3H_2O$") and (*RR*,*SS*)-diphos (0.642 g) in ethanol (50 mL) was pressurized to 600 psi with carbon monoxide for 3 h. After this period the autoclave was depressurized and the crystalline product isolated by filtration. Additional product was obtained from the filtrate by concentration. The pure racemic complex formed colorless prisms, mp 225 °C (net yield 0.603 g, 55%).

***rac-mer*-Tricarbonylchloro[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]ruthenium(II) Chloride [*OC*-6-23-(*RR*,*SS*)] (Structure 3b and Its Enantiomorph).** The dimer $[RuCl_2(CO)_3]_2$ (from 0.376 g of "$RuCl_3 \cdot 3H_2O$") and (*RR*,*SS*)-diphos (0.463 g) were reacted together in boiling propan-2-ol (5 mL) for 10 min, in the presence of a rapid stream of carbon monoxide. The colorless product crystallized from the reaction mixture when it was cooled to room temperature (0.765 g, 92%). Recrystallization of this material from dichloromethane/diethyl ether gave the pure salt as white needles: mp >220 °C dec (yield 0.350 g, 42%); ^1H NMR (CH_2Cl_2) δ 2.20 (d, 3, J_{PH} = 6.1 Hz, PMe), 2.27 (d, 3, J = 7.4 Hz, PMe), 6.85–7.6 (m, 14, aromatics); IR (CH_2Cl_2) 2124 s, 2046 s, 1984 s cm^{-1} (ν_{CO}); Λ_M (CH_2Cl_2) 25.0 $cm^2\ \Omega^{-1}\ mol^{-1}$ (1.03×10^{-3} M) (1:1). The hexafluorophosphate salt was not precipitated upon addition of NH_4PF_6.

***rac-mer*-Tricarbonylchloro[(*RS*)-*o*-phenylenbis(methylphenylphosphine)]ruthenium(II) Chloride [*OC*-6-(24,34)-(*RS*)] (Structure 3e and Its Enantiomorph).** This compound was prepared with use of the method described for the derivative of (*RR*,*SS*)-diphos. The yield, after recrystallization, was 21% as white needles: mp >220 °C dec; ^1H NMR (CH_2Cl_2) δ 1.31 (d, 3, J_{PH} = 10.0 Hz, PMe), 1.57 (d, 3, J = 7.0 Hz, PMe), 7.25–7.75 (m, 14, aromatics); IR (CH_2Cl_2) 2125 s, 2045 s, 1980 s cm^{-1} (ν_{CO}); Λ_M (CH_2Cl_2) 26.9 $cm^2\ \Omega^{-1}\ mol^{-1}$ (1.02×10^{-3} M) (1:1). The hexafluorophosphate salt was not precipitated upon addition of NH_4PF_6.

***meso*-Dicarbonyldichlorobis(μ-chloro)[(*RR*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]diruthenium(II) and Its Phosphorus Analogue (Structure 4a).** A solution of the *trans*-dichloro complex [*OC*-6-13-(*RR*,*SS*)]-$[RuCl_2(CO)_2(diars)]$ (0.150 g) in 2-methoxyethanol (2 mL) was heated under reflux for 16 h. Carbon monoxide was evolved, and a yellow compound was precipitated. The reaction mixture was cooled and the solid filtered off, washed with ethanol and diethyl ether, and dried (0.136 g, 95%): mp >300 °C; IR (Nujol) 1961 cm^{-1} (ν_{CO}). The sparingly soluble product had the empirical formula $C_{21}H_{20}As_2Cl_2RuO$. The isosteric di(tertiary phosphine) compound was prepared under similar conditions from [*OC*-6-13-(*RR*,*SS*)]-$[RuCl_2(CO)_2(diphos)]$. It was isolated in 43% yield as a pale yellow powder: mp >310 °C; IR (Nujol) 1969 cm^{-1} (ν_{CO}).

***anti*-Dicarbonyldichlorobis(μ-chloro)bis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]diruthenium(II) and Its Phosphorus Analogue (Structure 4b).** These are prepared by decarbonylating [*OC*-6-44-(*RS*)]-$[RuCl_2(CO)_2(diars)]$ and [*OC*-6-14-(*RS*)]-$[RuCl_2(CO)_2(diphos)]$ as described above. The di(tertiary arsine) dimer was isolated as bright yellow needles: mp >300 °C (97% yield); IR (Nujol) 1974 cm^{-1} (ν_{CO}). The isosteric di(tertiary phosphine) compound was obtained in 94% yield: mp >320 °C; IR (Nujol) 1973 cm^{-1} (ν_{CO}).

Reaction of any of the dimers with carbon monoxide in ethanol at its boiling point led to the respective monomeric *cis*-dichloro compounds. The di(tertiary arsine) monomers were considerably easier to isolate, however. Although spectroscopic evidence suggested compounds of structure **2d** may have formed to the extend of ca. 30%, pure crystals could not be isolated for either ligand system.

[*OC*-6-32-*C*-(*SS*)]-Carbonyldichloro(dimethyl sulfoxide)[*o*-phenylenebis(methylphenylarsine)]ruthenium(II) (Structure 5b in the Solid State). A solution of the *trans*-dichloro complex [*OC*-6-33-(*SS*)]-$[RuCl_2(CO)_2(diars)]$ (0.543 g) in dimethyl sulfoxide (5 mL) was heated to 170 °C for 3 h. Carbon monoxide was evolved, and the solution, which was initially bright yellow, become paler. At this stage the excess Me_2SO was removed under reduced pressure (20 mmHg). The residual yellow oil was then heated in propan-2-ol for ca. 1 min, whereupon a mass of white crystals formed. The propan-2-ol solution was carefully diluted with diethyl ether (5 mL) and the product collected by filtration (0.492 g, 84%). The epimer had mp 234–236

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(14) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273. *Note*: The presence or nonpresence of the "chirality symbols" *A* or *C* in the stereochemical descriptors has no bearing on whether or not the molecule as a whole is chiral; for example, see compounds having structures **3a–e** (Figure 4). The order of priority of the ligands follows the Cahn–Ingold–Prelog standard sequence rule.[15] For the complexes described here the order of priority of the donor atoms is (*R*)-As, (*S*)-As, Cl, Me_2SO-*S*, (*R*)-P, (*S*)-P, CO.

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°C and $[\alpha]_D$ (equilibrium) −37.3° (*c* 1.07, CH_2Cl_2). ^1H NMR ($CDCl_3$; **5b**:**5a** ca. 1.83:1): δ 1.94 (s, 3.9, $AsMe_{5a}$), 2.00 (s, 2.1, $AsMe_{5b}$), 2.28 (br s, 6, $AsMe_{5a,b}$), 2.81 (s, 3.9, SMe_{5a}), 3.28 (s, 2.1, SMe_{5b}), 3.37 (br s, 6, $SMe_{5a,b}$), 7.3–7.7 (m, 14, aromatics). ^{13}C NMR ($CDCl_3$): δ 9.11 (s, $AsMe_{5a}$), 14.80 (s, $AsMe_{5a}$), 10.36 (s, $AsMe_{5b}$), 13.55 (s, $AsMe_{5b}$), 41.85 (s, SMe_{5a}), 45.38 (s, SMe_{5a}), 41.05 (s, SMe_{5b}), 46.57 (s, SMe_{5b}) 128–143 (m, aromatics), 194.76, 195.10 (s, $CO_{5a,5b}$). IR (CH_2Cl_2): 1978 (ν_{co}), 1103 cm^{-1} (ν_{SO}).

The following compounds were prepared similarly. **[*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-(RuCl$_2$(CO)(diars)(Me$_2$*S*O-*S*)] (structure 5a and its enantiomorph in the solid state)**: white needles; mp 284–285 °C dec (91% yield); ^1H NMR and IR spectra identical with those of the pure epimer. **[*OC*-6-(34,43)-*A*-(*RS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)] (structure 5c and its enantiomorph)**: white needles; mp 281–282 °C dec (yield 93%); ^1H NMR ($CDCl_3$) δ 2.26 (s, 3, AsMe), 2.29 (s, 3, AsMe), 3.31 (s, 3, SMe), 3.41 (s, 3, SMe), 7.3–7.8 (m, 14, aromatics); IR (CH_2Cl_2) 1983 (ν_{CO}), 1103 cm^{-1} (ν_{SO}). **[*OC*-6-43-*A*-(*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)]**: white needles; mp 238–242 °C (yield 92%); $[\alpha]_D$ (equilibrium) −58.9° (*c* 0.774, CH_2Cl_2); ^1H NMR (CH_2Cl_2; **5b**:**5a** ca. 1.2:1) δ 2.12 (d, J_{PH} = 9.7 Hz, PMe_{5b}), 2.19 (d, J_{PH} = 9.9 Hz, PMe_{5a}), 2.39 (d, J_{PH} = 11.7 Hz, PMe_{5b}), 2.51 (br s, SMe_{5a}), 3.10 (br s, SMe_{5b}), 3.22 (br s, $SMe_{5a,b}$), 7.3–7.8 (br m, aromatics); IR (CH_2Cl_2) 1983 (ν_{CO}), 1102 cm^{-1} (ν_{SO}). **[*OC*-6-43-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)]**: white prisms; mp >300 °C (yield 92%); ^1H NMR and IR spectra identical with those of the pure epimer. The sample for X-ray structural analysis was obtained by slow crystallization of this material from a $Me_2SO/MeOH/H_2O$ mixture. **[*OC*-6-(53-*A*-,54-*C*)-(*RS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-S)] (structure 5c and its enantiomorph)**: white needles; mp 250–255 °C (yield 93%); ^1H NMR (CH_2Cl_2) δ 2.36 (d, 3, J_{PH} = 12.0 Hz, PMe), 2.42 (d, 3, J = 11.9 Hz, PMe), 3.17 (s, 3, SMe), 3.30 (s, 3, SMe), 7.3–7.85 (m, 14, aromatic); ^{13}C NMR ($CDCl_3$) δ 12.50 (d, 1, J_{PC} = 40.05 Hz, PMe), 12.55 (d, 1, J_{PC} = 28.61 Hz, PMe), 40.65 (d, 1, J_{PC} = 2.79 Hz, S(O)Me), 45.66 (s, 1, S(O)Me), 128–146 (m, 14, aromatics), 194.63 (t, 1, J_{PC} = 13–16 Hz, CO); IR (CH_2Cl_2) 1991 (ν_{CO}), 1103 cm^{-1} (ν_{SO}).

The Me_2SO derivatives can also be prepared in high yield from the appropriate cis complexes. The Me_2SO-d_6 compounds were prepared from the appropriate dicarbonyl precursors by reacting them with a tenfold excess of Me_2SO-d_6 in boiling 2-methoxypropanol for 3 h. The products were isolated by evaporating the solvent and recrystallizing the residue as described for the non-deuterated compounds.

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Registry No. [*OC*-6-33-(*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82338-42-9; [*OC*-6-33-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-33-9; [*OC*-6-13-(*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82338-43-0; [*OC*-6-13-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-34-0; [*OC*-6-44-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-34-0; [*OC*-6-44-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-35-1; [*OC*-6-14-(*RS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-36-2; [*OC*-6-32-*A*-(*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-37-3; [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-38-4; [*OC*-6-32-(*A*,-*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-39-5; [*OC*-6-(43,34)-*A*-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-40-8; [*OC*-6-23-(*RS*-*SS*)]-[RuCl(CO)$_3$(diphos)]Cl, 82338-44-1; [*OC*-6-(24,34)-(*RS*)]-[RuCl(CO)$_3$(diphos)]Cl, 82373-41-9; *meso*-[((*RR*)-diars)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*SS*)-diars)], 82338-45-2; *meso*-[((*RR*)-diphos)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*SS*)-diphos)], 82338-46-3; *anti*-[((*RS*)-diars)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*RS*)-diars)], 82373-42-0; *anti*-[((*RS*)-diphos)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*RS*)-diphos)], 82373-43-1; [*OC*-6-32-*C*-(*CS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82373-32-8; [*OC*-6-32-*A*-(*SS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82373-31-7; [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82338-41-8; [*OC*-6-(34,43)-*A*-(*RS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82398-54-7; [*OC*-6-43-*A*-(*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82373-30-6; [*OC*-6-43-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82442-83-9; [*OC*-6-(53-*A*,54-*C*)-(*RS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82373-29-3; [RuCl$_2$(CO)$_2$]$_n$, 28986-72-3; [RuCl$_2$(CO)$_3$]$_2$, 22594-69-0; [*OC*-6-43-*C*-(SS)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82338-40-7.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Reactions of Alkyl Isocyanides with Polyhydride Complexes of Rhenium and with Binuclear Dirhenium Complexes Containing Quadruple or Triple Bonds: Nonreductive and Reductive Cleavage of Re-Re Multiple Bonds To Afford Mononuclear Isocyanide Complexes of Rhenium(I) and Rhenium(III)

JOE D. ALLISON, THOMAS E. WOOD, ROBERT E. WILD, and RICHARD A. WALTON*

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Treatment of the dinuclear quadruply bonded complexes $Re_2(O_2CR)_4Cl_2$ (R = CH_3 or C_6H_5) with alkyl isocyanides (RNC; R = CMe_3 or C_6H_{11}) affords solutions from which salts of the $[Re(CNR)_6]^+$ cations can be isolated in good yield. While $[Re(CNR)_6]^+$ is inert to substitution by monodentate tertiary phosphines, routes to species of the type $[Re(CNR)_4(PR_3)_2]^+$ are afforded by (a) the reductive cleavage of the triply bonded complexes $Re_2Cl_4(PR_3)_4$ by RNC ligands or (b) the reductive elimination of H_2 from the polyhydride complexes $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_2L$ in the presence of an excess of RNC. In contrast to the preceding reductive-cleavage reductions, the "halide-rich" salts $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) react with *tert*-butyl isocyanide to give mononuclear seven-coordinate rhenium(III) species $[Re(CNCMe_3)_5X_2]^+$, which have been isolated as their PF_6^- salts. The mixed isocyanide–halide–phosphine complexes of rhenium(III) $[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$ and $[Re(CNCMe_3)_3(dppe)Cl_2]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$) are likewise prepared by isocyanide cleavage of quadruply bonded $Re_2Cl_6(PEtPh_2)_2$ and dimeric $Re_2Cl_6(dppe)_2$ (the latter containing $Re(\mu\text{-}Cl)_2Re$ bridges but no Re–Re bond). The spectroscopic and electrochemical properties of these complexes are reported, and the significance of the cleavage reactions by π-acceptor ligands (such as RNC) is discussed in the context of their constituting an important synthetic route to mononuclear transition-metal complexes.

Introduction

While six-coordinate homoleptic rhenium(I) isocyanide species of the type $[Re(CNR)_6]^+$ have been known for many years,[1] little in the way of reaction chemistry or photochemistry of these systems has been developed, particularly when contrasted with the more thoroughly studied manganese systems.[1-3] The synthetic methods available for their preparation include the reactions of alkyl and aryl isocyanides with starting

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