pairing which would correlate with an excited state when the pressure is suddenly released. This mechanism of TL excitation by molecular distortion is attractive because the major effect of pressure on a crystal is the shortening of intermolecular distances rather than the bond distances.[22] Because the bending force constants are much lower than the stretching force constants, a geometry change is energetically more likely to occur as a result of the increased intermolecular repulsions.

The important role of the counterion dependence on the emission energy vs. pressure graphs is illustrated by $(MePh_3P)_2MnCl_4$ and $(pyH)_2MnCl_4$. The former complex contains the largest cation and shows a stronger coupling with pressure (slope -39 cm^{-1}/kbar) than the latter complex (slope -20 cm^{-1}/kbar). In addition, the latter complex displays a characteristic unique among those of all other Mn(II) complexes studied here. With increasing pressure, the luminescence spectrum develops a large band in the red region. The $^4T_1 \rightarrow {}^6A_1$ emission becomes a small shoulder on the much larger red band. The luminescence changes reversibly from green to red with pressure. Two possible origins of the red emission are (a) luminescence from a low-spin tetrahedral complex formed at high pressure and (b) luminescence from an octahedral complex formed under high pressure containing coordinated pyridine. This phenomenon is currently under further investigation.

No unambigous choice can be made between the various mechanisms on the basis of the spectral data. The observation of the high-energy emission from the absorbed molecular nitrogen strongly implicates an electrical mechanism. However, the intensity of the nitrogen emission is very weak compared to that observed in aniline hydrochloride[4] or sucrose.[5] Thus, electrification may be a minor component of the overall excitation process. Furthermore, frictional electrification does not appear to be important. Thermal population of the excited states under pressure is likely in the manganese system based on the high-pressure spectroscopic results. However, this mechanism may not be unique even in centrosymmetric cyrstals because crystal defects could provide a small number of sites where the centricity is destroyed and electrification could be important. Thus, several of the proposed mechanisms may be operating simultaneously.

Note Added in Proof. Recent x-ray structural determinations of the quinolinium and pyridinium salts of $MnCl_4^{2-}$ have found both crystals to have the centrosymmetric space group $P\bar{1}$.[24] Neither crystal is triboluminescent. To date, all of the manganese complexes with known space groups are centrosymmetric and are not triboluminescent. No generalizations can be made until the space groups of some triboluminescent crystals are known. We thank Professor R. Willett for communicating his results on the quinolinium salt to us prior to publication.

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Registry No. $Mn(Ph_3PO)_2Cl_2$, 14494-86-1; $Mn(Ph_3PO)_2Br_2$, 14552-77-3; $(MePh_3P)_2MnCl_4$, 60451-52-7; $(Et_4N)_2MnBr_4$, 2536-14-3; $(Bu_4N)_2MnI_4$, 21790-92-1; $(pyH)_2MnCl_4$, 18497-10-4.

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Complexes of Alkyl and Aryl Cyanides. 9.[1] Reactions of *cis*-$ReCl_4(CH_3CN)_2$ with Bidentate Phosphorus and Arsenic Donors: Cis–Trans Isomerization in Complexes of the Type $ReCl_4L_2$

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The reactions of *cis*-$ReCl_4(CH_3CN)_2$ with the ligands bis(diphenylphosphino)methane (dppm), bis(1,2-diphenylphosphino)ethane (dppe), and 1-diphenylphosphino-2-diphenylarsinoethane (arphos) lead to the formation of the six-coordinate complexes of the types *cis*-$ReCl_4$(LL), polymeric *trans*-$ReCl_4$(LL), or monomeric *trans*-$ReCl_4(LL)_2$, depending upon the choice of reaction conditions. The cis and trans isomers of $ReCl_4$(LL), where LL = dppe or arphos, are a novel series of complexes since these are the first geometric isomers to have been isolated in which bidentate tertiary phosphine or arsine ligands containing the ethane skeleton are either in the gauche (chelating) or trans (bridging) conformations. The factors which control the course of these reactions are discussed.

Introduction

The reduction of rhenium(V) chloride by acetonitrile to yield *cis*-tetrachlorobis(acetonitrile)rhenium(IV) was first reported in 1968.[2] It was found that this complex reacts with a variety of monodentate donors to yield substitution products of the type *trans*-$ReCl_4L_2$, where L = PPh_3, $AsPh_3$, etc.[2] The coordinated acetonitrile groups were also found[2] to undergo nucleophilic addition when reacted with primary aromatic amines, to yield N-substituted amidines, or with alcohols, to yield complexes of imidate esters.

More recently an improved synthesis of this complex has been developed[3] via the chlorine oxidation of $Re_2(CO)_{10}$ in acetonitrile. In addition, we have isolated[1] *trans*-$ReCl_4(CH_3CN)_2$ by a careful workup of the same $ReCl_5$–CH_3CN reaction mixtures which yield[2] the cis isomer as the major reaction product.

Although it might be anticipated that the reaction of *cis*-$ReCl_4(CH_3CN)_2$ with potentially chelating bidentate tertiary phosphines and arsines of the type $Ph_2XCH_2CH_2YPh_2$, where X and Y = P and/or As, would simply yield complexes of the type *cis*-$ReCl_4$(LL), we have found that these systems are unexpectedly complicated and afford both the cis and trans isomers of this stoichiometry. To our knowledge this behavior is novel for ligands of this type. Furthermore, these results are of additional interest in view of the relatively rare occurrence of both the cis and trans isomers of 1:2 adducts of metal tetrahalides with neutral donor molecules.[1] Our results are now reported in detail.

Experimental Section

Starting Materials. *cis*-Tetrachlorobis(acetonitrile)rhenium(IV) was prepared from $Re_2(CO)_{10}$ by the method of Edwards and Marshalsea.[3] The following commercially available ligands, which were recrystallized from acetonitrile prior to use, are listed together with their abbreviations: bis(1,2-diphenylphosphino)ethane, dppe; bis(diphenylphosphino)methane, dppm; 1-diphenylphosphino-2-diphenylarsinoethane, arphos; bis(1,2-diphenylarsino)ethane, dpae.

All solvents were dried by reflux and/or distillation from calcium hydride, phosphorus pentoxide, or anhydrous calcium sulfate and were deoxygenated prior to use. *All reactions were carried out in a nitrogen atmosphere.*

Reactions of *cis*-$ReCl_4(CH_3CN)_2$. A. Bis(diphenylphosphino)methane. (i) *cis*-$ReCl_4$(dppm). *cis*-$ReCl_4(CH_3CN)_2$ (0.2 g) was dissolved in 12 ml of acetonitrile and 0.19 g of dppm was added to the resulting apple green solution. An orange coloration appeared within seconds of mixing of reagents, and within 5 min of reflux, brilliant orange crystals had formed on the boiling stick. After 10 min of reflux, the solution was cooled and filtered. The orange crystals were washed with acetonitrile and diethyl ether and dried in vacuo. A further crop of crystals was obtained from the chilled filtrate. Anal. Calcd for $C_{25}H_{22}Cl_4P_2Re$: C, 42.13; H, 3.09. Found: C, 42.21; H, 3.02; yield 75%; mp 285 °C dec.

(ii) $ReCl_4(dppm)\cdot{}^1/_3CH_2Cl_2$ and $ReCl_4(dppm)\cdot(CH_3)_2CO$. These products formed as orange crystals upon reacting equimolar proportions of *cis*-$ReCl_4(CH_3CN)_2$ and dppm in refluxing dichloromethane and acetone, respectively. Anal. Calcd for $C_{25.3}H_{22.7}Cl_{4.7}P_2Re$: C, 41.08; H, 3.02; Cl, 22.35. Found: C, 40.43; H, 2.90; Cl, 22.31; yield 70%; mp 275 °C dec. Calcd for $C_{28}H_{28}Cl_4OP_2Re$: C, 43.60; H, 3.64; Cl, 18.44. Found: C, 43.41; H, 3.72; Cl, 18.20; yield 86%; mp 268 °C dec.

The infrared spectrum of the acetone solvate contains bands associated with the coordinated dppm ligand together with a sharp intense band at 1705 cm^{-1} assigned to ν(C=O) of lattice acetone. When a suspension of this complex is refluxed with carbon tetrachloride, the acetone of solvation is readily lost as indicated by the absence of the 1705-cm^{-1} band in the infrared spectrum of the recovered complex. A mass spectrum of this solvate contains a peak at m/e 58 due to acetone.

(iii) $ReOCl_3$(dppm). If the acetone reaction mixture described in section A(ii) is allowed to reflux for 48 h, the initial orange rhenium(IV) complex reacts further by oxygen abstraction from the solvent to afford a pale green insoluble powder. This was filtered off, washed with cold acetone and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{25}H_{22}Cl_3OP_2Re$: C, 43.35; H, 3,18; Cl, 15.32. Found: C, 43.39; H, 3.42; Cl, 15.71; yield 100%; mp 180–190 °C dec.

The infrared spectrum of this complex in the region 4000–200 cm^{-1} is similar to that of $ReOCl_3$(dppe) which was prepared[4] by aerial oxidation of a dichloromethane solution of $Re_2Cl_6(dppe)_2$. In particular, both the dppe and dppm complexes exhibit an absorption at ~990 cm^{-1} assigned to ν(Re=O).

(iv) *trans*-$ReCl_4(dppm)_2$. A quantity of dppm (0.6 g) was dissolved in 15 ml of acetone and this solution was added to 0.3 g of *cis*-$ReCl_4(CH_3CN)_2$ in an equal volume of acetone. The initial green solution rapidly changed to orange and after 30 min of reflux dark purple crystals of the complex had formed. The reaction was continued for 1 h (longer reflux times reduce the yield), and the product was filtered off, washed with acetone and diethyl ether, and dried, in vacuo. Anal. Calcd for $C_{50}H_{44}Cl_4P_4Re$: C, 54.74; H, 4.01; Cl, 12.96. Found: C, 54.15; H, 4.00; Cl, 12.34; yield 83%; mp 192 °C dec.

B. Bis(diphenylphosphino)ethane. (i) *cis*-$ReCl_4$(dppe). This complex was prepared in a manner similar to that described for *cis*-$ReCl_4$(dppm) in section A(i). The reflux time in acetonitrile was 30 min, and the resulting orange solution was reduced in volume until orange crystals separated. The product was filtered off, washed with cold CCl_4 and diethyl ether, and dried. Its infrared spectrum was identical with that of an authentic sample of this complex prepared by an alternative route involving the carbon tetrachloride oxidation of $Re_2Cl_6(dppe)_2$.[5] Anal. Calcd for $C_{26}H_{24}Cl_4P_2Re$: C, 42.98; H, 3.31; Cl, 19.56. Found: C, 42.65; H, 3.26; Cl, 19.60; yield 93%; mp 260 °C.

This complex could also be prepared using dichloromethane as the reaction solvent. The reaction mixture was maintained at 0 °C for 1 h and the solvent then removed under reduced pressure at 0 °C.

(ii) *trans*-$ReCl_4$(dppe). Dichloromethane (10 ml) was added to a mixture of *cis*-$ReCl_4(CH_3CN)_2$ and dppe (1:1 molar proportions) at 20 °C. After 30 min of reaction at room temperature a dark red solid precipitated. This red product was filtered off, washed with dichloromethane, acetone, acetonitrile, and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{26}H_{24}Cl_4P_2Re$: C, 42.98; H, 3.31; Cl, 19.56; P, 8.54. Found (for separate preparative samples): C, 41.17, 42.45; H, 3.40, 3.83; Cl, 19.65, ...; P, 9.06, ...; yield ~25–50%; mp 240 °C. This complex is insoluble in all common organic solvents.

Workup of the orange filtrate from this reaction afforded a quantity of *cis*-$ReCl_4$(dppe).

C. 1-Diphenylphosphino-2-diphenylarsinoethane. (i) *cis*-$ReCl_4$(arphos). This orange complex was prepared as described for the dppe analogue in section B(i), except that the reflux time in acetonitrile was 1 h. The complex was washed with carbon tetrachloride and diethyl ether and dried prior to analysis. Anal. Calcd for $C_{26}H_{24}AsCl_4PRe$: C, 40.52; H, 3.12; Cl, 18.44. Found: C, 40.51; H, 3.15; Cl, 18.75; yield 80%; mp 255 °C.

(ii) *trans*-$ReCl_4$(arphos). *cis*-$ReCl_4(CH_3CN)_2$ (0.1 g) was dissolved in 12 ml of acetone and 0.11 g of arphos was added. Within a few seconds at 20 °C, the solution had acquired a dark red-orange color and after 1–5 min a dark red precipitate formed. The reaction mixture was allowed to stand for 30 min under nitrogen and then filtered. The insoluble red product was washed with acetone, acetonitrile, and diethyl ether. Finally, the red complex was extracted with chloroform for 36 h and dried at 100 °C in vacuo for 8 h prior to analysis. Anal. Calcd for $C_{26}H_{24}AsCl_4PRe$: C, 40.52; H, 3.12; Cl, 18.44. Found: C, 41.73; H, 3.51; Cl, 17.81; yield 67%; mp 230 °C dec.

A small quantity of *cis*-$ReCl_4$(arphos) was isolated on workup of the orange filtrate; yield 20%.

(iii) *trans*-$ReCl_4(arphos)_2$. *cis*-$ReCl_4(CH_3CN)_2$ and arphos were reacted in 1:2 molar proportions in refluxing acetone. After 6 h the reaction mixture was cooled and filtered. The purple insoluble crystals were washed with acetone and diethyl ether. This product could be purified by dissolving it in chloroform (without heating), filtering, and quickly adding acetone to reprecipitate the purple complex. Anal. Calcd for $C_{52}H_{48}As_2Cl_4P_2Re$: C, 51.48; H, 3.97; Cl, 11.72; mol wt 1212. Found: C, 51.21; H, 4.01; Cl, 12.00; mol wt in $CHCl_3$ 1182; yield 41%. This complex is soluble in dimethylformamide, chloroform, and dichloromethane but these solutions decompose on standing.

D. Bis(1,2-diphenylarsino)ethane. The reaction of *cis*-$ReCl_4(CH_3CN)_2$ with dpae in dichloromethane or acetone or as a melt failed to produce the complex $ReCl_4$(dpae) under any of the reaction conditions we used.

E. Reactions of the Rhenium(IV) Complexes. (i) *cis*-$ReCl_4$(dppm). A quantity of this complex (0.1 g) was dissolved in 15 ml of acetone to which 0.1 g of dppm had been added. The resulting yellow solution was refluxed. Within about 5 min a purple precipitate began to form, and as the reaction proceeded, dark purple crystals commenced to grow on the boiling stick. After 40 min, the reaction mixture was cooled to room temperature and the purple insoluble product *trans*-$ReCl_4(dppm)_2$ (0.12 g) filtered off and washed with acetone and diethyl ether. Anal. Calcd for $C_{50}H_{44}Cl_4P_4Re$: C, 54.74; H, 4.01. Found: C, 54.65; H, 4.04; yield 77%.

(ii) *trans*-$\mathbf{ReCl_4(dppm)_2}$. A purple solution of *trans*-$ReCl_4(dppm)_2$ (0.1 g) in dichloromethane (35 ml) turned yellow-orange after heating for 5 min. This solution was cooled and poured into 80 ml of cold *n*-hexane. The resulting yellow powder (0.034 g) was centrifuged off and washed with diethyl ether and dried; yield 52%. The identity of this complex was confirmed by a comparison of its melting point and infrared spectrum with those of an authentic sample of *cis*-$ReCl_4(dppm)$.

(iii) *cis*-$\mathbf{ReCl_4}$(arphos). By use of a procedure similar to that described in section E(i), but with a reflux time of 3.5 h, *cis*-$ReCl_4$(arphos) was converted to *trans*-$ReCl_4(arphos)_2$. Anal. Calcd for $C_{52}H_{48}As_2Cl_4P_2Re$: C, 51.48; H, 3.97. Found: C, 51.64; H, 3.87; yield 47%.

(iv) *trans*-$\mathbf{ReCl_4(arphos)_2}$. (a) This complex (0.1 g) was dissolved in 30 ml of chloroform to afford a purple solution. This solution turned bright yellow after it had been refluxed for 3.5 h. It was cooled and then evaporated to dryness using a rotary evaporator. The orange residue was treated with diethyl ether and the mixture filtered. The resulting insoluble product was carefully washed with a small quantity of *cold* acetone (the product is soluble in acetone) and then with diethyl ether and finally was dried in vacuo to afford the pure orange-yellow complex *cis*-$ReCl_4$(arphos) (0.04 g). Anal. Calcd for $C_{26}H_{24}AsCl_4PRe$: C, 40.52; H, 3.12. Found: C, 40.44; H, 3.27; yield ~62%. *trans*-$ReCl_4(arphos)_2$ was similarly converted to *cis*-$ReCl_4$(arphos) in dimethylformamide.

(b) *cis*-$ReCl_4(CH_3CN)_2$ (0.1 g) was dissolved in 10 ml of acetone and 0.15 g of *trans*-$ReCl_4(arphos)_2$ was added to this solution. The reaction mixture was refluxed for 1 h and then filtered while still warm. The resulting red insoluble residue of *trans*-$ReCl_4$(arphos) (0.03 g) was washed with acetone, acetonitrile, dichloromethane, and diethyl ether until the washings were colorless. Its identity was confirmed by its melting point and infrared spectral properties.

F. Synthesis of $\mathbf{ReCl_4(CH_3CN)(PPh_3)}$. A mixture of *cis*-$ReCl_4(CH_3CN)_2$ (0.2 g) and triphenylphosphine (0.128 g) was added to 10 ml of dry, deoxygenated acetonitrile. The resulting solution was heated *gently* until the color had changed from the initial green to dark orange, a procedure which generally requires 1 min or less to occur. The solution was then poured quickly into a cold hexane–diethyl ether solvent mixture. A dark orange precipitate formed and was filtered off after it had been allowed to stand at ~0 °C for 30 min. This product (0.13 g) was washed with hexane and diethyl ether and then dried in vacuo. It was finally recrystallized from acetonitrile in which the major contaminant *trans*-$ReCl_4(PPh_3)_2$ is insoluble. Anal. Calcd for $C_{20}H_{18}Cl_4NPRe$: C, 38.02; H, 2.85; Cl, 22.46; N, 2.22. Found: C, 37.92; H, 2.74; Cl, 21.75; N, 2.30; yield 45%; mp ~168–172 °C dec.

The molar conductivity (Λ_m) of a solution of $ReCl_4(CH_3CN)(PPh_3)$ in acetonitrile (1.58×10^{-3} M) was 4.0 Ω^{-1} cm^2 mol^{-1}, consistent with this complex having a nonionic structure.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Electronic spectra were recorded on Cary 14 and Beckman DU-2 spectrophotometers. X-ray photoelectron spectra were measured on a Hewlett-Packard 5950A ESCA spectrophotometer using Al Kα (1486.6 eV) radiation. Magnetic moments were obtained using a Gouy balance system with $Hg[Co(SCN)_4]$ as the calibrant. Corrections for the ligand diamagnetism were estimated from Pascal's constants.

Analytical Procedures. Elemental microanalyses and molecular weight measurements were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

In our studies dealing with the reactivity of $ReCl_4(CH_3CN)_2$, we have restricted our attention to the cis isomer. While the trans isomer has been prepared,[1] it can only be isolated in low yield and does not appear to be very soluble in suitable reaction solvents.[1]

Synthesis and Preliminary Characterization. The expected products from the reactions between *cis*-$ReCl_4(CH_3CN)_2$ and the bidentate donors dppm, dppe, arphos, and dpae are substitution products of the type *cis*-$ReCl_4$(LL), where LL represents a bidentate chelating ligand molecule. With the exception of dpae, these complexes are readily synthesized in excellent yields when acetonitrile is used as the reaction solvent. The ligand dpae did not yield a pure product when reacted under either reflux or melt reaction conditions. It also failed to yield the cis complex when reacted under reduced pressure in cyclohexanone, although transient orange solutions were noted. These conditions are similar to those employed by Rouschias and Wilkinson[2] in the successful reaction of *cis*-$ReCl_4(MeCN)_2$ with triphenylarsine to yield *trans*-$ReCl_4(AsPh_3)_2$.

The unreactive dpae ligand is contrasted with very reactive dppe which forms the cis complex in 60% yield even at 0 °C. Despite the formation of a four-membered ring, dppm yields the cis complex within minutes of reflux in acetonitrile but fails to react at 0 °C. With the latter ligand, use of acetone or dichloromethane as the reaction solvent also afforded *cis*-$ReCl_4$(dppm) but in these instances it crystallized as a solvate. $ReCl_4(dppm)\cdot(CH_3)_2CO$ is qualitatively converted to green $ReOCl_3$(dppm) on prolonged reflux in deoxygenated acetone, presumably via oxygen abstraction from the solvent.

The low-frequency infrared spectra of the three cis complexes were very similar (Table I), displaying ν(Re–Cl) patterns which were characteristic of MCl_4L_2 chromophores of C_{2v} symmetry.[6] In addition, their electronic absorption spectra were typical of octahedral rhenium(IV) species (Table I). In the case of *cis*-$ReCl_4$(dppe), its spectral properties were essentially identical with those of a sample of this complex prepared[5] by the carbon tetrachloride oxidation of the chlorine-bridged dimer $Re_2Cl_6(dppe)_2$. Since the carbon tetrachloride solvate $ReCl_4(dppe)\cdot{}^3/_4CCl_4$ has been fully characterized structurally,[7] there is no doubt that our stereochemical assignments are correct.

During the reaction of 1:1 molar proportions of *cis*-$ReCl_4(CH_3CN)_2$ and dppe in dichloromethane at 22 °C, two products each analyzing as $ReCl_4$(dppe) were formed. The soluble orange chelate was produced initially, followed by precipitation of a dark red material. Under similar reaction conditions but by using acetone as solvent, the arphos ligand yielded analogous products. This behavior was not observed upon reacting *cis*-$ReCl_4(CH_3CN)_2$ with dppm. Available evidence supports these red complexes being formulated as polymeric *trans*-$ReCl_4$(LL), in which the dppe and arphos ligands are in a trans, bridging conformation.[8]

Their low-frequency infrared spectra (Table I) each contain a single intense ν(Re–Cl) band at 331 cm^{-1}, very close in frequency to the related mode in the spectra of other complexes of the type *trans*-$ReCl_4L_2$, such as *trans*-$ReCl_4(PEt_3)_2$[9] and *trans*-$ReCl_4(CH_3CN)_2$.[1] Such species of idealized D_{4h} symmetry are expected to exhibit a single infrared-active ν(Re–Cl) mode, of E_u symmetry.[6] In addition, between 2000 and 400 cm^{-1} the spectra are less complex for *trans*-$ReCl_4$(LL) than they are for the related cis isomers, consistent with a difference in ligand conformation. The electronic absorption spectra (Table I) and magnetic properties ($\mu_{eff} = 3.84\ \mu_B$ for *trans*-$ReCl_4$(dppe) and 3.38 μ_B for *trans*-$ReCl_4$(arphos) at 22 °C) are indicative of rhenium(IV) in an octahedral environment. The dark red colors of these complexes are also in accord with their proposed structure, resembling closely the colors of the related triphenylphosphine and triphenylarsine derivatives *trans*-$ReCl_4L_2$.

Both complexes are involatile, very resistant to chemical degradation (heating in a H_2O_2/NaOH solution results in decomposition only after 1 h), and amorphous to x rays.

When either arphos or dppm is reacted with *cis*-$ReCl_4(CH_3CN)_2$ using 2:1 molar proportions of reagents, complexes of the type $ReCl_4(LL)_2$ are produced. $ReCl_4(dppm)_2$ and $ReCl_4(arphos)_2$ are strikingly similar with respect to their physical and chemical properties. Both complexes are clearly rhenium(IV) derivatives as evidenced by their electronic

Table I. Spectral Properties of Rhenium(IV) Complexes Prepared from *cis*-$ReCl_4(CH_3CN)_2$

		Electronic absorption maxima × 10^{-3}, cm^{-1}					Infrared spectra,[b] cm^{-1}	
Complex	Medium[a] for electronic spectra	$^4A_{1g} \rightarrow$ $^2T_{1g}(\Gamma_8)$, $^2E_g(\Gamma_8)$	$^2T_{1g}(\Gamma_6)$	$^2T_{2g}(\Gamma_7)$	$^2T_{2g}(\Gamma_8)$	CT[c]	ν(Re–Cl)	Other bands
cis-$ReCl_4$(dppe)	NM	7.8 w	8.2 w	12.7 w, br	15.4 m	21.4 s	346 m, 331 s, ~305 s	381 w, 262 w
	CH_2Cl_2	7.85 w	8.15 w	12.7 w, br		21.5 s		
cis-$ReCl_4$(arphos)	NM	7.0 vw, br	8.3 vw, br	12.5–13.3 w	15.4 w	20.8 s	344 m, 331 s, 312 s	271 w
	DR			12.9 w, br	15.1 w, br	21.05 s		
cis-$ReCl_4$(dppm)	NM	6.7 vw, br	8.2 w, br	12.0 w, 13.1 w	14.3 w		341 m, 331 s, 306 s	378 w, 365 w, 264 w
cis-$ReCl_4$(dppm)·$(CH_3)_2CO$	NM		8.1 w, br	12.1 w, 13.1 w	14.3 w	>25.0		
trans-$ReCl_4$(dppe)	NM	6.65 w	8.0 w, 8.9 w	12.95 w	17.4 sh	20.4 s	348 sh, 331 s	
	DR			13.0 w	17.4 sh	20.4 s		
trans-$ReCl_4$(arphos)	NM	7.2 w	7.9 w	13.1 m	17.8 sh	20.2 s	331 s	362 sh, 277 w
	DR			12.9 w	17.3 sh	20.0 s		
trans-$ReCl_4(dppm)_2$	NM	7.2 w	7.8 w	13.1 w	~16.0 sh	18.9 s	330–320 s[d]	371 w
	DR			13.1 w	~16.0 sh	18.8 s		
trans-$ReCl_4(arphos)_2$	NM	7.2 w	7.8 w	13.1 w, br	17.1 sh	20.0 s	331–320 s[d]	372 w, 306 sh, 281 w
	DR			13.1 w	17.0 sh	19.6 s		
cis-$ReCl_4(CH_3CN)(PPh_3)$	NM	7.1 vw	8.0 w, 8.5 w	12.7 sh, 13.1 m			357 m, 326 s, 309 m–s, 303 sh?	
	DR			13.1 m		20.4 s		

[a] Abbreviations: NM, Nujol mull; DR, diffuse reflectance. [b] 400–200 cm^{-1} only. [c] CT = charge-transfer band. [d] Doublet.

absorption spectra (Table I) and magnetic properties (μ_{eff} = 3.64 μ_B for $ReCl_4(arphos)_2$ and 3.65 μ_B for the dppm analogue). The molar conductivity of a dimethylformamide solution of $ReCl_4(arphos)_2$ was 8.0 Ω^{-1} cm^2 mol^{-1} at 24 °C thus precluding an ionic formulation for this complex, and a molecular weight determination in chloroform confirmed its monomeric formulation. $ReCl_4(dppm)_2$ dissolves in dichloromethane and chloroform but these solutions decompose over extended periods of time. Both complexes exhibit similar x-ray powder patterns.

The low-frequency infrared spectra of the $ReCl_4(LL)_2$ complexes are virtually identical (Table I). The ν(Re–Cl) modes are observed as a closely spaced doublet between 330 and 320 cm^{-1}, similar in frequency to ν(Re–Cl) of trans-$ReCl_4$(LL), where LL = dppe or arphos (Table I). The splitting of this band suggests a slight lowering in symmetry from idealized D_{4h}, but nonetheless these spectral properties and the color of the complexes leave little doubt that they have a trans-octahedral structure.[10]

X-Ray Photoelectron Spectra. The rhenium 4f and chlorine 2p binding energies of several of these complexes were recorded and these data are presented in Table II. These energies are similar to those previously reported[5,11] for *trans*-$ReCl_4(PPh_3)_2$ and *cis*-$ReCl_4$(dppe). In all cases, the chlorine 2p spectra reveal a well-resolved $2p_{1/2,3/2}$ spin–orbit doublet characteristic of a single type of chlorine environment.[12] A comparison of the phosphorus 2p spectra of *cis*-$ReCl_4$(dppm) and *trans*-$ReCl_4(dppm)_2$ is consistent with the monodentate nature of dppm in the latter complex. While the fwhm values of the rhenium 4f and chlorine 2p peaks are very similar for these two complexes, the phosphorus 2p peak of *trans*-$ReCl_4(dppm)_2$ is significantly broader than that of *cis*-$ReCl_4$(dppm) (see Table II), consistent with the presence of both bound and unbound phosphorus atoms.

Reactivity of the Complexes. The extreme insolubility of the complexes *trans*-$ReCl_4$(LL), where LL = dppe or arphos, precluded a study of their solution chemistry; consequently our investigations into the reactivities of these complexes were restricted to the monomeric complexes of the types *cis*-$ReCl_4$(LL) and *trans*-$ReCl_4(LL)_2$, where LL = dppm or arphos. When acetone solutions of *cis*-$ReCl_4$(dppm) and dichloromethane solutions of *cis*-$ReCl_4$(arphos) were treated with an *excess* of the appropriate ligand, they turned red-purple and afforded the crystalline 1:2 adducts *trans*-$ReCl_4(LL)_2$. In contrast, solutions of *cis*-$ReCl_4$(dppe) were completely stable in the presence of excess dppe under reflux conditions. These differences in behavior are readily rationalized in terms of *trans*-$ReCl_4(LL)_2$ being the thermodynamically favored product for the dppm and arphos systems but not for dppe. With *cis*-$ReCl_4$(dppm), the strained four-membered chelate ring is unstable in the presence of excess dppm. Although a more stable five-membered ring is present in *cis*-$ReCl_4$(arphos), the formation of a second Re–P bond provides the driving force for its conversion to *trans*-$ReCl_4(arphos)_2$. On the other hand, when dichloromethane, chloroform, or dimethylformamide solutions of *trans*-$ReCl_4(LL)_2$ were maintained at room temperature for many hours or heated for short periods, the orange complexes *cis*-$ReCl_4$(LL) were regenerated, provided that excess ligand was not present. The course of these reactions is clearly favored by an increase in entropy upon loss of one of the bidentate ligands.

It would seem logical that the reaction of *cis*-$ReCl_4(CH_3CN)_2$ with *trans*-$ReCl_4(arphos)_2$ should afford polymeric *trans*-$ReCl_4$(arphos). This in fact occurs when acetone is used as the reaction solvent.[13] While $ReCl_4(dppm)_2$ failed to react under similar conditions, it must also be emphasized that *trans*-$ReCl_4$(dppm) has not been isolated by any other route.

Table II. X-Ray Photoelectron Spectra[a]

Complex	Re		Cl		P 2p
	$4f_{5/2}$	$4f_{7/2}$	$2p_{1/2}$	$2p_{3/2}$	
cis-$ReCl_4$(dppm)	45.2 (1.1)	42.7 (1.2)	199.7 (1.2)	198.2 (1.1)	131.2 (1.4)
trans-$ReCl_4(dppm)_2$	45.5 (1.2)	43.0 (1.2)	200.0 (1.2)	198.4 (1.1)	130.9 (2.0)
cis-$ReCl_4$(dppe)[b]	45.4 (1.5)	43.1 (1.4)	199.8 (1.6)	198.3 (1.4)	
trans-$ReCl_4$(arphos)	45.7 (1.5)	43.3 (1.7)	199.9 (1.5)	198.6 (1.4)	131.5[c]
trans-$ReCl_4(arphos)_2$	45.2 (1.2)	42.7 (1.4)	199.7 (1.4)	198.2 (1.2)	131.0 (1.5)
trans-$ReCl_4(PPh_3)_2$[d]	45.5	43.0	199.8	198.3	

[a] Binding energies are quoted relative to a value of 284.0 eV for the carbon 1s binding energy of graphite; fwhm values are given in parentheses. [b] Data taken from ref 5. [c] Peak too weak for reliable fwhm value to be quoted. [d] Data taken from ref 11.

The fact that dppm does not form bridged complexes of this type may be due to unfavorable steric effects caused by a shorter P–P distance in dppm as compared to that in dppe.

Few studies have been carried out on substitution reactions of rhenium(IV) and no information is yet available on their mechanism. Since our work has led to the isolation of the cis and trans isomers of a complex of the type MX_4L_2, it is perhaps pertinent if we briefly discuss some mechanistic implications of our results. While we have no information on whether the reactions between *cis*-$ReCl_4(CH_3CN)_2$ and dppe or arphos occur by dissociative or associative pathways, the factor which probably determines whether *cis*- or *trans*-$ReCl_4$(LL) is isolated is the rate of cis → trans isomerization of the reaction intermediate, *cis*-$ReCl_4(CH_3CN)$(LL), in which LL is bound in a *monodentate* fashion. We have not been able to isolate this intermediate in any of these reactions, but its isomerization is preferred over the alternative one of *cis*-$ReCl_4(CH_3CN)_2$ → *trans*-$ReCl_4(CH_3CN)_2$, since we have been unable to effect this latter transformation when the cis isomer is dissolved in various solvents. It can be argued that the rate of cis → trans isomerization of $ReCl_4(CH_3CN)$(LL) is dramatically reduced in acetonitrile at all temperatures and in solvents such as dichloromethane at 0 °C. This is illustrated by the reaction of *cis*-$ReCl_4(CH_3CN)_2$ with dppe in dichloromethane. At room temperature, a mixture of *trans*- and *cis*-$ReCl_4$(dppe) is isolated but at 0 °C only the cis isomer is formed.

The factor which most likely prevented our isolation of $ReCl_4(CH_3CN)$(LL), where LL = dppe or arphos, is that this intermediate is itself a donor molecule, containing as it does an unbound tertiary phosphine or arsine group. Consequently, either rapid intermolecular nucleophilic attack upon another rhenium(IV) species or intramolecular displacement of acetonitrile and ring closing can be expected to occur. Consistent with these possibilities we observe that dilution of the *cis*-$ReCl_4(CH_3CN)_2$/LL reaction mixture lowers the yield of polymeric *trans*-$ReCl_4$(LL) relative to the monomeric cis isomer. As an alternative approach to obtaining information on the stability and structure of a mixed-ligand complex of the type $ReCl_4(CH_3CN)(PR_3)$, we attempted to isolate $ReCl_4(CH_3CN)(PPh_3)$ from the reaction between *cis*-$ReCl_4(CH_3CN)_2$ and triphenylphosphine. Rouschias and Wilkinson[2] have shown previously that this reaction affords *trans*-$ReCl_4(PPh_3)_2$ but they did not report any attempts to isolate a reaction intermediate. We have prepared this dark orange complex from the reaction between *cis*-$ReCl_4(CH_3CN)_2$ and triphenylphosphine in acetonitrile using a very short reaction time (see Experimental Section). Its infrared spectrum showed characteristic CH_3CN absorptions[14] at 2322 and 2295 cm^{-1}, in addition to the usual bands due to coordinated triphenylphosphine. The complexity of its low-frequency infrared spectrum in the ν(Re–Cl) region (Table I) is clearly consistent[6] with a cis-octahedral stereochemistry. Recrystallization of this complex from acetonitrile or refluxing a solution of it in dichloromethane did not convert it to the trans isomer. However, reaction with an equimolar quantity of triphenylphosphine in dichloromethane led to the rapid formation of *trans*-$ReCl_4(PPh_3)_2$, showing that cis → trans isomerization occurs only in the presence of a source of "free" tertiary phosphine (or arsine). This result is pertinent to the reactions of *cis*-$ReCl_4(CH_3CN)_2$ with dppe or arphos, since it suggests that the reaction intermediate $ReCl_4(CH_3CN)$(LL) has a cis stereochemistry. It is only upon substitution of the remaining acetonitrile ligand that isomerization occurs.

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Registry No. *cis*-$ReCl_4$(dppm), 60260-06-2; $ReOCl_3$(dppm), 60260-17-5; *trans*-$ReCl_4(dppm)_2$, 60260-07-3; *cis*-$ReCl_4$(dppe), 16920-07-6; *trans*-$ReCl_4$(dppe), 60260-45-9; *cis*-$ReCl_4$(arphos), 60260-08-4; *trans*-$ReCl_4$(arphos), 60319-14-4; *trans*-$ReCl_4(arphos)_2$, 60260-09-5; $ReCl_4(CH_3CN)(PPh_3)$, 60260-10-8; *cis*-$ReCl_4(CH_3CN)_2$, 16853-53-5.

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