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Unusual Reactivity Associated with the Triply Bonded Re_2^{4+} Core: Facile Reaction of $Re_2Cl_4(Ph_2PCH_2PPh_2)_2$ with Nitriles To Afford the Cations $[Re_2Cl_3(Ph_2PCH_2PPh_2)_2(NCR)_2]^+$

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The triply bonded complex $Re_2Cl_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) reacts with nitriles (RCN) to form complexes of stoichiometry $[Re_2Cl_3(dppm)_2(NCR)_2]X$ (X = Cl^-, PF_6^-; R = CH_3, C_2H_5, C_6H_5, 4-PhC_6H_4). The use of $^{31}P\{^1H\}$ NMR spectroscopy to monitor the formation of $[Re_2Cl_3(dppm)_2(NCC_2H_5)_2]Cl$ in the reaction between $Re_2Cl_4(dppm)_2$ and propionitrile indicates that these reactions occur by a two-step process in which a nitrile first coordinates to one of the rhenium atoms of $Re_2Cl_4(dppm)_2$ to generate a 1:1 adduct, possibly possessing the chlorine-bridged structure $(C_2H_5CN)ClRe(\mu\text{-}Cl)(\mu\text{-}dppm)_2ReCl_2$, followed by the addition of a second nitrile ligand to the same rhenium atom with concomitant loss of chloride ion to generate the ionic bis(nitrile) complex. The complex $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$ has been structurally characterized by X-ray crystallography. The red crystals were orthorhombic, space group *Cmcm*, with *a* = 15.606 (2) Å, *b* = 24.604 (4) Å, *c* = 18.326 (3) Å, *V* = 7037 (3) Å^3, and *Z* = 4. The Re–Re bond distance is 2.270 (1) Å. The complex cation is twisted about the Re–Re bond, with a torsion angle P–Re–Re–P of 22.2°, and the twisted molecules are packed in a systematically disordered manner.

Introduction

The bidentate tertiary phosphine ligand bis(diphenylphosphino)methane (dppm) forms complexes with transition metals in which this ligand can be encountered in a monodentate or in a bidentate chelating or bridging mode.[2,3] In complexes that contain two metal centers, dppm often preferentially bridges the two metal atoms, thereby affording a quite stable five-membered ring.[2-4] This strong tendency to bridge dimetal units thus makes dppm particularly suitable for stabilizing multiply bonded pairs of metal atoms.[3,5,6]

In our continuing efforts to explore both the reaction chemistry and electrochemical properties of multiply bonded dirhenium complexes containing dppm[5-8] we have discovered that the triply bonded complex $Re_2Cl_4(dppm)_2$ reacts smoothly with nitriles (RCN) to generate, in high yield, complexes of stoichiometry $[Re_2Cl_3(dppm)_2(NCR)_2]X$ (X = Cl^-, PF_6^-). This reaction is rather surprising since other dirhenium complexes that contain the electron-rich Re_2^{4+} core, e.g. $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane),[5,9] show no great tendency to react with nitriles under comparable conditions.

Herein, we report the details of these reactions, in which we have employed the nitriles CH_3CN, C_2H_5CN, C_6H_5CN, and 4-PhC_6H_4CN, along with the spectroscopic and electrochemical properties of the resultant complexes. A crystallographic study on $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$ confirmed the nature of these complexes, showing that both nitrile ligands are bound to the same rhenium atom.

Experimental Section

Starting Materials. The complex $Re_2Cl_4(dppm)_2$ was prepared according to the known literature procedure.[6] The various nitriles, along with solvents used in the preparation of the complexes, were of commercial grade and were thoroughly deoxygenated prior to use. Dichloromethane used in the electrochemical experiments was of the highest purity commercially available and was used without further purification.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere by using standard vacuum line techniques. However, we subsequently found that these reactions proceed in a similar fashion without recourse to the rigorous exclusion of air with little apparent sacrifice in product yield.

Preparation of the Complexes $[Re_2Cl_3(dppm)_2(NCR)_2]X$ (X = Cl^-, PF_6^-). The following procedure is a general one for the preparation of all the nitrile complexes: To a solution of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) and KPF_6 (0.20 g, 1.1 mmol) in acetone (10 mL) was added 0.5 g of the appropriate nitrile (RCN) and the mixture stirred for 15 min. The resulting solution was then added dropwise into diethyl ether and the mixture stirred for 15 min. The resulting solid was filtered off, washed with diethyl ether, and then extracted into dichloromethane (20 mL). The complex can be precipitated from dichloromethane by the addition of an excess of diethyl ether and then recrystallized from acetone/diethyl ether. In the case of the acetonitrile reaction, the product was found to be sparingly soluble in common solvents and, unlike the other derivatives, precipitates from the reaction solution without the addition of diethyl ether. Yield: R = CH_3, 0.11 g (96%); R = C_2H_5, 0.10 g (94%); R = C_6H_5, 0.11 g (90%); R = 4-PhC_6H_4, 0.11 g (81%). Microanalytical data were obtained in the case of the propionitrile complex $[Re_2Cl_3(dppm)_2(NCC_2H_5)_2]PF_6\cdot(CH_3)_2CO$. Anal. Calcd for $C_{59}H_{60}Cl_3F_6N_2OP_5Re_2$: C, 45.40; H, 3.87; N, 1.79; Cl, 6.81. Found: C, 46.03; H, 3.98; N, 1.63; Cl, 7.09. The presence of a molecule of acetone of solvation was confirmed by ^1H NMR spectroscopy.

The benzonitrile complex $[Re_2Cl_3(dppm)_2(NCPh)_2]PF_6$, whose structure was determined by X-ray crystallography, was also subjected to an elemental microanalysis. Anal. Calcd for $C_{64}H_{54}Cl_3F_6N_2P_5Re_2$: C, 48.08; H, 3.40. Found: C, 48.63; H, 3.85.

All the complexes exhibited essentially identical electrochemical properties and electronic absorption spectra, thereby confirming the similarity between them.

If the preceding reactions are carried out in the absence of KPF_6, the analogous chloride salts can be isolated. However, the reaction times required for complete reaction are now much longer (ca. 8 h). Alternatively, the chloride salts can be prepared by dissolving the complexes as their PF_6^- salts in acetone and adding an excess of $[(C_6H_5CH_2)(C_2H_5)_3N]Cl$. Precipitation with an excess of diethyl ether, followed by the extraction of the resulting solid with water and recrystallization from acetone/diethyl ether mixtures, yields the pure chloride salts in close to quantitative yield. The cyclic voltammograms of the chloride complexes were identical with those of their hexafluorophosphate analogues (Table III), except for the presence of an irreversible wave at ca. +1.1 V (vs. SCE), which signals the presence of the Cl^- ion.

Preparation of the 1:1 Adduct $Re_2Cl_4(dppm)_2(NCC_2H_5)$. A solution of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) and C_2H_5CN (0.75 mL) in dichloromethane (5 mL) was stirred for 2 min. The solution was then immediately added dropwise to a large volume of diethyl ether. This yielded a green solution to which was added an excess of petroleum ether (50 mL). The gray-green solid was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.10 g (96%). Anal. Calcd for $C_{53}H_{49}Cl_4NP_4Re_2$: C, 47.57; H, 3.69. Found: C, 46.57; H, 3.78.

Preparation of Single Crystals of the Benzonitrile Complex for Structure Determination. Crystals of $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$ were grown by layering a dichloromethane solution of the complex under diethyl ether and allowing the two layers to diffuse slowly together.

X-ray Crystallography. Crystal data, which are summarized in Table I, were taken from a red, prismatic crystal (dimensions 0.31 × 0.21 × 0.18 mm), mounted at the end of a glass fiber. Geometric and intensity data were taken by a CAD-4F diffractometer equipped with graphite-

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Table I. Summary of Crystallographic Data for $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$

formula	$Re_2Cl_3P_5F_6N_2C_{64}H_{54}$
fw	1598.8
space gp	*Cmcm*
syst abs	$(hkl)\ h + k = 2n + 1$; $(h0l)\ l(h) = 2n + 1$
a, Å	15.606 (2)
b, Å	24.604 (4)
c, Å	18.326 (3)
V, Å^3	7037 (3)
Z	4
d_{calcd}, g/cm^3	1.509
cryst size, mm	0.31 × 0.21 × 0.18
μ(Mo Kα), cm^{-1}	39.2
data collcn instrum	Enraf-Nonius CAD-4F
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
orientation reflcns: no.; range (2θ)	25; $19 < 2\theta < 27°$
temp, °C	25 ± 2
scan method	ω–2θ
data colcn range (2θ), deg	4–46
no. of unique data	
total	2062
no. with $F_o^2 > 3\sigma(F_o^2)$	1691
no. of parameters refined	173
transmissn factors; max, min	calcd 0.49, 0.20; obsd 1.00, 0.76.
R^a	0.0486
$R_w{}^b$	0.0507
quality-of-fit indicator^c	1.31
largest shift/esd, final cycle	0.12
largest peak, e/Å^3	1.17

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w^{1/2}(|F_o| - |F_c|)/\Sigma w^{1/2}|F_o|$; $w = 0.44/[\sigma^2(F_o) + 0.001|F_o|^2]$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

monochromated Mo Kα radiation, using previously described procedures.[10a] The unit-cell dimensions and orientation were identified automatically and were refined by a least-squares fit to 25 well-centered reflections in the range $19 < 2\theta < 27°$. The Laue class (*mmm*) was established through axial photography. Intensity data were gathered by the ω–2θ technique. Three check reflections measured after every hour of accumulated X-ray exposure did not change noticeably in intensity during the 51 h of beam time. Azimuthal scans of nine reflections were used as the basis of an empirical absorption correction.[10b,c]

Systematic absences were found to be consistent with the centric space group, *Cmcm*, and with the acentric groups, *C2cm* and *Cmc*2$_1$.

The positions of the two unique Re atoms were derived from a Patterson map, and successive iterations of least-squares refinement and difference Fourier maps led to the identification of all atomic positions.

Solution of the structure in all three possible space groups gave the same, well-defined pattern of disorder in the atomic positions. The pattern of occupied crystallographic sites fits all three space groups, and so the refinement was completed in the centric group, *Cmcm*, the highest symmetry representation of the motif at hand.

In order to explain as clearly as possible the nature of the disorder and the strategy used in the refinement, we shall now give a brief description of the structure as it is described in space group *Cmcm*. The space group has a mirror plane at $x = 0$ and another at $z = {}^1/_4$. The two crystallographically independent Re atoms (Re(1) and (Re(2)) lie on the twofold axis, $(0, y, {}^1/_4)$, which is the intersection of the two mirror planes. A pair of enantiomeric, dinuclear complex cations occupies this crystallographic site. Both cations occupy the same set of two unique rhenium positions (see Figure 2a for the structure of one isomer), as well as the same sites for the atoms bound to Re(1) (i.e., Cl(1), P(1), and N(1)) and for the bridging carbon atom (C(1)) of the dppm ligand. Atom Cl(1) is on the same twofold axis as are Re(1) and Re(2); atoms P(1) and C(1) of dppm are on the crystallographic mirror plane at $z = {}^1/_4$ (as are Re(1) and Re(2)); and atom N(1) of the benzonitrile ligand is on the crystallographic mirror plane at $x = 0$ (as, again, are Re(1) and Re(2)). Thus, each of the atoms bonded to Re(1) fully occupies a single, unique site.

The atoms bound to Re(2) are disordered about the two crystallographic mirror planes. The chemical coordination to Re(2) comprises two phosphorus atoms (from dppm) and two chlorine atoms, in a trans arrangement. The disorder can be conceptualized as the result of a twist of this end of the molecule, relative to the other end, about the Re–Re bond. Figure 2a shows the Δ conformer of the complex cation, which has a torsion angle of ca. 22°. The Λ conformer, which occupies the same crystallographic site, has a torsion angle of ca. −22° about the Re–Re bond. Figure 2b shows the overlay of the two conformers on the crystallographic site.

In order to establish that the observed disorder was not an artifact of our imposition of symmetry on the system, we developed the structure independently in the two acentric subgroups of *Cmcm*. Removing the mirror plane at $x = 0$ gives space group *C2cm*. Development of the structure in this group led to the same pattern of atomic positions, disordered across the *yz* plane. This validates the description of the structure in a space group with a mirror symmetry element at $x = 0$. In a similar fashion, we used space group *Cmc*2$_1$ to establish the disorder about the plane at $z = {}^1/_4$. Group *Cmc*2$_1$ has mirror symmetry at $x = 0$ but none at $z = {}^1/_4$. Development of the structure in *Cmc*2$_1$ led to the same pattern of atomic positions that we had observed in *Cmcm* and *C2cm*. The pattern of disordered atomic sites in the coordination shell of Re(2) had mirror symmetry about the plane $z = {}^1/_4$.

The development of the structure in space group *Cmc*2$_1$ also described a disorder of the phenyl groups attached to atom P(1). This part of the crystal structure comprises four half-occupied sites for phenyl groups—two pairs related approximately by reflection in the plane $z = {}^1/_4$. We expected this disorder, because the presence of the two conformers of the complex cation at the same crystallographic site gives a crystallographic disorder of the torsion angle about the P(1)–C(1) bond. We describe the disorder fully in the discussion.

We want to emphasize here that, after the derivation of the positions of the rhenium atoms, all other atoms were located in difference Fourier maps—that is, no a priori modeling of the chemical system was done.

In undertaking the refinement of a chemical structure with a complex, but well-defined, disorder, we relied upon modern methods that employ partial reparameterization via the inclusion of rigid groups and that also allow weighted distance restraints in the form of observational equations in the least-squares refinement.[10d] These methods are fully within the convolution approximation of X-ray diffraction, and they render feasible such complex refinements as the present one.

The model used for the final refinement incorporated the constraints and restraints needed for a stable refinement. All phenyl groups were treated as rigid bodies. For each phenyl ring of which disordered congeners were in close proximity (C(3)–C(8), C(9)–C(14), C(9A)–C(14A); see Figure 2 and the discussion section), a single set of anisotropic thermal parameters was used for all six atoms in the ring. For each phenyl ring lying near, and disordered across, a crystallographic mirror plane (C(3)–C(8), C(15)–C(20), the anisotropic thermal parameters were averaged across the appropriate symmetry element. In addition, three bond distances (P(1)–C(9), P(1)–C(9A), P(2)–C(1)) were restrained, via observational equations, to be 1.81 Å. In all, 173 variables were fitted to 1694 observations; the number of observations includes the three distance restraints. The final least-squares cycle did not shift any parameter by more than 0.12 times its estimated standard deviation. The final residuals (defined in Table I) are $R = 0.0486$ and $R_w = 0.0507$. No noteworthy correlation was observed, other than that which is expected, i.e., among the rotational and translational parameters of the rigid groups.

Table II contains the atomic coordinates and isotropic thermal parameters from the crystallographic analysis. Full tables of thermal parameters and structure factors are available as supplementary material.

Physical Measurements. Infrared spectra were recorded as Nujol mulls on IBM Instruments IR/32 Fourier transform (4000–400 cm^{-1}) and Digilab FTS-1MX 20 spectrometers (500–50 cm^{-1}). Electronic absorption spectra were recorded on an IBM Instruments 9420 UV-visible spectrophotometer. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values $[(E_{p,a} + E_{p,c})/2]$ were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H NMR spectra were also recorded on a Varian XL-200 spectrometer. Conductivities were measured on an Industrial Instruments Inc. Model RC 16B2 conductivity bridge. Microanalyses were performed by Dr. C.

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Table II. Positional Parameters and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$

atom	x	y	z	B,[a] Å^2
Re(1)	0.0000	0.34740 (4)	0.2500	3.57 (3)
Re(2)	0.0000	0.25515 (4)	0.2500	3.25 (3)
Cl(1)	0.0000	0.4521 (3)	0.2500	6.4 (2)
Cl(2)	−0.0633 (4)	0.2228 (3)	0.3585 (4)	4.9 (2)
P(1)	0.1576 (4)	0.3544 (2)	0.2500	7.3 (2)
P(2)	0.1434 (5)	0.2453 (2)	0.2998 (3)	3.7 (2)
P(3)	0.0000	0.2247 (6)	0.7500	10.7 (5)
F(1)	0.0000	0.161 (2)	0.7500	19 (1)*
F(2)	0.070 (1)	0.2224 (8)	0.693 (1)	19.0 (6)*
F(3)	0.0000	0.285 (2)	0.7500	21 (1)*
N(1)	0.0000	0.3550 (5)	0.3623 (8)	4.1 (4)
C(1)	0.2134 (9)	0.2906 (5)	0.2500	4.7 (5)
C(2)	0.0000	0.3648 (8)	0.422 (1)	4.5 (5)
C(3)	−0.002 (2)	0.3780 (9)	0.4974 (8)	8.2 (4)
C(4)	0.024 (2)	0.4296 (9)	0.5202 (8)	8.2 (4)
C(5)	0.012 (2)	0.4455 (9)	0.5925 (8)	8.2 (4)
C(6)	−0.026 (2)	0.4098 (9)	0.6421 (8)	8.2 (4)
C(7)	−0.052 (2)	0.3583 (9)	0.6194 (8)	8.2 (4)
C(8)	−0.040 (2)	0.3424 (9)	0.5470 (8)	8.2 (4)
C(9)	0.185 (2)	0.380 (1)	0.1605 (8)	11.6 (7)
C(10)	0.180 (2)	0.437 (1)	0.1511 (8)	11.6 (7)
C(11)	0.205 (2)	0.460 (1)	0.0850 (8)	11.6 (7)
C(12)	0.235 (2)	0.427 (1)	0.0283 (8)	11.6 (7)
C(13)	0.239 (2)	0.371 (1)	0.0377 (8)	11.6 (7)
C(14)	0.214 (2)	0.347 (1)	0.1038 (8)	11.6 (7)
C(9A)	0.224 (1)	0.4009 (7)	0.198 (1)	7.9 (4)
C(10A)	0.191 (1)	0.4283 (7)	0.138 (1)	7.9 (4)
C(11A)	0.246 (1)	0.4538 (7)	0.089 (1)	7.9 (4)
C(12A)	0.335 (1)	0.4520 (7)	0.100 (1)	7.9 (4)
C(13A)	0.367 (1)	0.4246 (7)	0.161 (1)	7.9 (4)
C(14A)	0.312 (1)	0.3991 (7)	0.210 (1)	7.9 (4)
C(15)	0.184 (1)	0.1763 (6)	0.289 (1)	5.5 (7)
C(16)	0.262 (1)	0.1655 (6)	0.254 (1)	6.4 (7)
C(17)	0.288 (1)	0.1119 (6)	0.243 (1)	10 (1)
C(18)	0.237 (1)	0.0691 (6)	0.267 (1)	7 (1)
C(19)	0.159 (1)	0.0799 (6)	0.301 (1)	9 (1)
C(20)	0.133 (1)	0.1334 (6)	0.312 (1)	10 (1)
C(21)	0.174 (1)	0.2632 (7)	0.3940 (9)	5.0 (7)
C(22)	0.257 (1)	0.2827 (7)	0.4081 (9)	7 (1)
C(23)	0.281 (1)	0.2953 (7)	0.4793 (9)	11 (1)
C(24)	0.223 (1)	0.2885 (7)	0.5365 (9)	10 (2)
C(25)	0.141 (1)	0.2690 (7)	0.5225 (9)	11 (2)
C(26)	0.116 (1)	0.2564 (7)	0.4512 (9)	7 (1)

[a] Starred values indicate atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

S. Yeh and Dr. H. D. Lee of the Purdue University microanalytical laboratory and by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

(a) Synthesis and Preliminary Characterization of $[Re_2Cl_3(dppm)_2(NCR)_2]X$ ($X = Cl^-$, PF_6^-; $R = CH_3$, C_2H_5, C_6H_5, 4-PhC_6H_4). Solutions of the complex $Re_2Cl_4(dppm)_2$ in 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)/dichloromethane exhibit well-defined electrochemical behavior, with reversible one-electron oxidations being observed at +0.27 and +0.80 V vs. Ag/AgCl as measured by the cyclic voltammetric technique.[6] Upon carrying out these measurements in 0.1 M TBAH/CH_3CN, we have observed quite different electrochemical behavior (Figure 1), the solutions now being characterized by a one-electron oxidation at $E_{1/2} \simeq +0.6$ V and a reduction close to −1.4 V. Since the clear implication is that acetonitrile reacts rapidly and essentially quantitatively with $Re_2Cl_4(dppm)_2$, we sought to identify the nature of this product. In the course of doing this, we have found that $Re_2Cl_4(dppm)_2$ undergoes a quite general reaction with nitriles to produce complexes of stoichiometry $[Re_2Cl_3(dppm)_2(NCR)_2]X$ ($X = Cl^-$, PF_6^-; $R = CH_3$, C_2H_5, C_6H_5, 4-PhC_6H_4).

In all instances these complexes exhibit essentially identical electrochemical properties (Table III), each showing a one-electron oxidation (by coulometry) at ca. +0.60 V (vs. Ag/AgCl) and a reduction at ca. −1.40 V. The oxidations are characterized by $i_{p,c}/i_{p,a}$ ratios approximately equal to unity, and constant $i_p/v^{1/2}$ ratios for sweep rates between 50 and 400 mV/s. The potential separation between the anodic and cathodic peaks, ΔE_p, was close to 75 mV for a sweep rate of 200 mV/s and increased slightly with increasing sweep rate. These observations are in accord with these oxidations being quasi-reversible electron-transfer processes. In addition to their similar electrochemical properties, these complexes exhibit very similar electronic absorption spectra and, as PF_6^- salts, they behave as 1:1 electrolytes in acetone (Table IV). Their IR spectra reveal a weak but observable $\nu_{C\equiv N}$ stretch at ca. 2250 cm^{-1} (Table IV) for all but the propionitrile derivative.

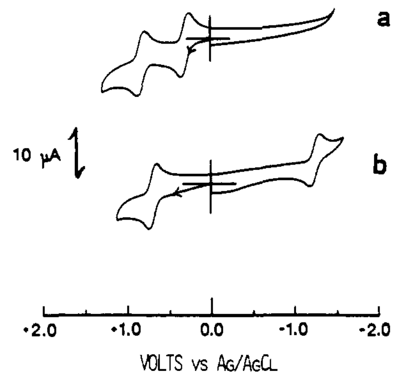

Figure 1. Cyclic voltammograms (measured at 200 mV/s at a Pt-bead electrode) of $Re_2Cl_4(dppm)_2$: (a) in 0.2 M TBAH/CH_2Cl_2; (b) in 0.1 M TBAH/CH_3CN. If the switching potential is increased to +1.5 V in (b), an irreversible oxidation is seen at $E_{p,c}$ = +1.2 V vs. Ag/AgCl; this is due to the Cl^- ion as is present in $[Re_2Cl_3(dppm)_2(NCCH_3)_2]Cl$.

Table III. $^{31}P\{^1H\}$ NMR Spectra and Electrochemical Data for Nitrile Complexes of Dirhenium(II)

	^{31}P δ[a]	$E_{1/2}$(ox)[b]	$E_{1/2}$(red)[b]
$[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$			
$R = CH_3$		+0.59 (85)	−1.39 (90)
$R = C_2H_5$	−7.0[c]	+0.59 (85)	−1.42 (100)
$R = C_6H_5$	−6.3[c]	+0.61 (90)	−1.34 (100)
$R = 4\text{-}PhC_6H_4$	−6.2[c]	+0.61 (85)	−1.33 (100)
$Re_2Cl_4(dppm)_2$	−3.3[d]		

[a] Positive chemical shifts measured downfield from 85% H_3PO_4. [b] $E_{1/2}$ values in volts vs. SCE using a Pt-bead electrode in dichloromethane with 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Values of $E_{p,a} - E_{p,c}$ (in millivolts) at sweep rates of 200 mV/s are given in parentheses. [c] AA'BB' multiplets: PF_6^- Resonance for complexes located at ca. δ −144 (hept, J_{P-F} = 712 Hz). [d] Singlet.

(b) Crystal Structure of $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$. Figure 2 shows the cation $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]^+$; Table V gives the more important bond distances and angles. The Re–Re triple-bond distance, 2.270 (1) Å, is greater than the distances observed in neutral, triply bonded dirhenium compounds that have relatively undistorted coordination shells about each Re atom.[5,11] The major causes of this effect are most likely a contraction of the Re–Re σ- and π-bonding orbitals, brought on by the charge of the present complex,[11a] and the presence of a single axially coordinated Cl atom. Mixing of nitrile π orbitals with Re–Re π^* levels could also contribute to this effect. The Re–Re distance is identical with that observed in $Re_2Cl_4(Ph_2Ppy)_2(PEt_3)$ (Ph_2Ppy ≡ 2-(diphenylphosphino)pyridine),[12] a neutral complex with a

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Table IV. Electronic Absorption and Infrared Spectra and Conductivity Data for Nitrile Complexes of Dirhenium(II)

	elec abs spec,[a,b] nm	Λ_m,[a] Ω^{-1} cm^2 mol^{-1}	IR abs ν(C≡N),[c] cm^{-1}
$[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$			
R = CH_3	*d*	*d*	2280 w
R = C_2H_5	645 (~100), 500 (~200)	117	NO[e]
R = C_6H_5	660 (~100), 510 (~200)	108	2250 w
R = 4-PhC_6H_4	660 (~100), 500 sh	104	2245 w

[a] Acetone solutions ((9.1–9.4) × 10^{-4} M). [b] Molar extinction coefficients given in parentheses. [c] Nujol mulls. [d] Too insoluble for solution measurements. [e] Not observed.

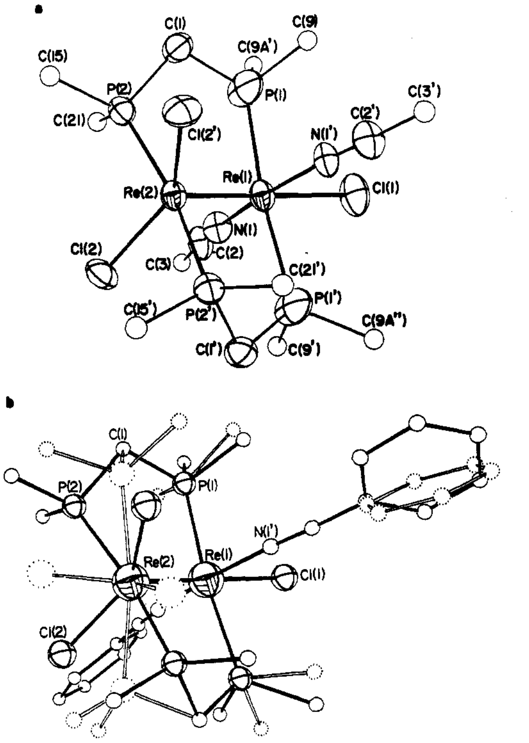

Figure 2. (a) ORTEP drawing of the structure of the Δ isomer of the $[Re_2Cl_3(dppm)_2(C_6H_5CN)_2]^+$ ion. For clarity, the secondary carbon atoms of each phenyl group have been omitted. The phenyl carbon atoms shown are represented by circles of arbitrary radius, while all other atoms are given as their 40% probability ellipsoids. (b) ORTEP drawing showing both enantiomers of $[Re_2Cl_3(dppm)_2(C_6H_5CN)_2]^+$ at the same crystallographic site. The Δ isomer is shown with solid bonds and with full circles representing the atoms. Crystallographically distinct features of the Λ isomer have hollow bonds and dotted circles for the atoms. Atoms Re(2), Re(1), and P(1) are at $Z = {}^1/_4$; and Re(2), Re(1), and N(1') define the plane $X = 0$.

single axial Cl ligand and somewhat more distortion about each Re atom than we observe in the present case.

The following detailed description of the crystallographic disorder is given with reference to Figure 2a,b. Figure 2a shows a single chemical unit, and Figure 2b shows this same unit and its enantiomer, which occupies the same crystallographic site.

The Δ conformer of the complex cation is the one shown in Figure 2a. The torsion angle P(1)–Re(1)–Re(2)–P(2) is 22.2°, and N(1)–Re(1)–Re(2)–Cl(2) is 26.4°. Both the Δ and the Λ conformations are present at the same crystallographic site. Atoms Re(1), Re(2), P(1), and C(1) all lie on a crystallographic mirror plane ($Z = 0.25$), and in the disordered congeners, atom P(2) lies 0.91 (1) Å above (in the Δ conformer) or below (Λ conformer) the plane.

The site symmetry for the complex cation is *mm*. The atoms coordinated to Re(1), two phosphorus atoms and two nitrogens in a trans arrangement, lie on mirror planes. The phosphorus and chlorine atoms coordinated to Re(2), lying off the mirror planes, are thus disordered about them. The two phenyl groups bound to P(2) (attached through atoms C(15) and C(21); see Figure 2) are, therefore, also disordered. In consequence of the disorder of the torsion angle Re(1)–P(1)–C(1)–P(2) (ca. ±31°), the phenyl groups on P(1) (attached through C(9) and C(9A)) are also disordered. In addtion, an unfavorable steric interaction between phenyl rings C(21)–C(26) (attached to atom P(2) of dppm) and C(3)–C(8) (of benzonitrile) is avoided via a tilting (with concomitant disorder) of the latter. That the 10 phenyl groups of the Δ conformer are crystallographically distinct from those of the Λ conformer is not surprising in this case of two enantiomers of C_2 symmetry residing on a crystallographic site of symmetry D_{2h}.

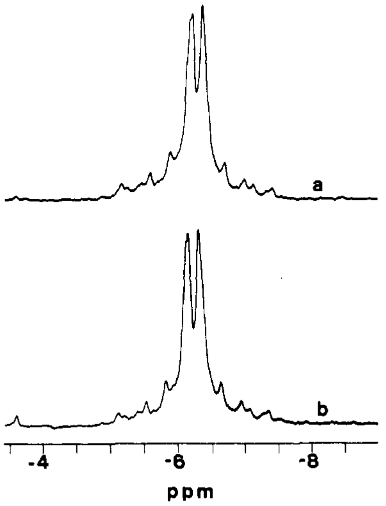

Figure 3. $^{31}P\{^1H\}$ NMR spectra: (a) $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$; (b) $[Re_2Cl_3(dppm)_2(NCC_6H_4\text{-}4\text{-}Ph)_2]PF_6$. The spectra were recorded on 1:1 CH_2Cl_2/acetone-d_6 solutions referenced against 85% aqueous H_3PO_4.

Potential steric interactions also impose an order among one set of neighboring molecules. For example, each Δ isomer at site $(0, y, {}^1/_4)$ must be accompanied by a Δ isomer at $({}^1/_2, {}^1/_2 - y, {}^3/_4)$; otherwise, there would be contacts as short as 2 Å between phenyl carbon atoms of adjacent molecules. Relief of steric crowding may also explain why each phosphorus atom subtends one Re–P–C angle greater than 120°.

The remaining major structural features of the cation $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]^+$—in particular, the bonds and angles about the Re atoms—present no surprises (Table V).

Since the disorder in the crystal structure comprises partial occupancy of a single site by two well-defined chemical moieties, no drastic drop in intensity of X-ray diffraction as a function of $(\sin\theta)/\lambda$ would be expected nor was any observed. Such a drop would be expected of a crystal that, unlike the present one, contained a substantial amount of electron density disordered over a large number of poorly defined sites.

(c) NMR Spectroscopy and the Identification of a Reaction Intermediate. The ^1H NMR spectra of the complexes, while otherwise relatively uninformative, show a broad and unresolved multiplet at ca. δ +6.1 that is assigned to the methylene resonance of the dppm ligands. The coordinated propionitrile resonances of the 1:2 adduct with this nitrile are at δ +0.52 (CH_3, t) and

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Table V. Important Distances (Å) and Angles (deg) and Their Estimated Standard Deviations[a] for $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Re(1)	Re(2)	2.270 (1)	Re(2)	P(2)	2.430 (7)	P(2)	C(15)	1.83 (2)
Re(1)	Cl(1)	2.575 (7)	P(1)	C(1)	1.796 (14)	P(2)	C(21)	1.85 (2)
Re(1)	P(1)	2.465 (6)	P(1)	C(9)	1.81 (2)	N(1)	C(2)	1.13 (2)
Re(1)	N(1)	2.066 (15)	P(1)	C(9A′)	1.81 (2)	C(2)	C(3)	1.41 (2)
Re(2)	Cl(2)	2.359 (7)	P(2)	C(1)	1.807 (13)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re(2)	Re(1)	Cl(1)	180	Cl(2)	Re(2)	Cl(2′)	140.5 (3)	Re(2)	P(2)	C(1)	107.7 (5)
Re(2)	Re(1)	P(1)	94.0 (1)	Cl(2)	Re(2)	P(2)	92.0 (2)	Re(2)	P(2)	C(15)	112.0 (7)
Re(2)	Re(1)	N(1)	95.2 (4)	Cl(2)	Re(2)	P(2′)	84.1 (2)	Re(2)	P(2)	C(21)	124.7 (7)
Cl(1)	Re(1)	P(1)	86.0 (1)	P(2)	Re(2)	P(2′)	168.6 (2)	C(1)	P(2)	C(15)	107.9 (9)
Cl(1)	Re(1)	N(1)	84.8 (4)	Re(1)	P(1)	C(1)	115.0 (5)	C(1)	P(2)	C(21)	99.6 (7)
P(1)	Re(1)	P(1′)	171.9 (2)	Re(1)	P(1)	C(9)	105 (1)	C(15)	P(2)	C(21)	103 (1)
P(1)	Re(1)	N(1)	89.64 (3)	Re(1)	P(1)	C(9A′)	127.8 (7)	Re(1)	N(1)	C(2)	173 (1)
N(1)	Re(1)	N(1′)	169.6 (5)	C(1)	P(1)	C(9)	101 (1)	P(1)	C(1)	P(2)	104.3 (7)
Re(1)	Re(2)	Cl(2)	109.7 (2)	C(1)	P(1)	C(9A′)	106.0 (8)	N(1)	C(2)	C(3)	178 (1)
Re(1)	Re(2)	P(2)	95.7 (1)	C(9)	P(1)	C(9A′)	97 (1)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

+1.86 (CH_2, quart). The $^{31}P\{^1H\}$ NMR spectra (Table III) show an expected AA′BB′ pattern for the dppm ligands, consistent with the structure of $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$. Surprisingly, the chemical shift difference between the two sets of inequivalent phosphorus atoms is apparently very small, and only in the case where phenyl groups are present on the ntirile ligands (i.e., C_6H_5CN and $4\text{-}PhC_6H_4CN$) are the two signals for this pattern resolvable (Figure 3). For the alkyl nitrile derivatives, an apparent singlet is observed but closer inspection shows clearly the presence of much weaker outer lines of the AA′BB′ pattern. As is typical in such cases where the chemical shift difference between the two sets of nuclei is very small, the inner lines emerge and grow in intensity at the expense of the outer lines, which eventually become too weak to be observed and the pattern collapses to a deceptively simple first-order singlet.[13-15] No attempt was made to analyze these spectra further.

The fact that the reaction of $Re_2Cl_4(dppm)_2$ with nitriles in the absence of KPF_6 is rather slow (see Experimental Section) afforded us the opportunity to follow the course of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy. Figure 4 shows the results of this study, which indicates that an intermediate is formed that subsequently reacts further to generate the bis(nitrile) product with concomitant loss of Cl^-. As far as the $^{31}P\{^1H\}$ spectral results are concerned, there is evidence for only one intermediate in the reaction of $Re_2Cl_4(dppm)_2$ with an *excess* of propionitrile (carried out in CH_2Cl_2/acetone-d_6 solutions) and this is characterized by an AA′BB′ pattern centered close to −8 ppm. The logical conclusion that this must be the 1:1 adduct $Re_2Cl_4(dppm)_2(NCC_2H_5)$ has been confirmed by the following experiments. The reaction of $Re_2Cl_4(dppm)_2$ with C_2H_5CN was carried out in CH_2Cl_2 for ca. 2 min and the reaction stopped at this stage by adding a large excess of diethyl ether. This gave a gray-green powder that analyzed closely for the 1:1 adduct (see Experimental Section). The ^1H NMR spectrum of $Re_2Cl_4(dppm)_2(NCC_2H_5)$ shows clearly that in CD_2Cl_2 this complex partially dissociates into $Re_2Cl_4(dppm)_2$ and C_2H_5CN, with the equilibrium constant (eq 1) being $\sim 4 \times 10^{-3}$ M at 293 K.[16] After due allowance has been

$$Re_2Cl_4(dppm)_2(NCC_2H_5) \rightleftharpoons Re_2Cl_4(dppm)_2 + C_2H_5CN \quad (1)$$

made for the resonances of $Re_2Cl_4(dppm)_2$ (this complex shows a characteristic methylene pentet at δ +5.21)[6] and free propionitrile [(δ +1.27 (CH_3, t), +2.35 (CH_2, quart)], the complex $Re_2Cl_4(dppm)_2(NCC_2H_5)$ can be seen to possess C_2H_5CN resonances at δ +0.51 and +1.94 and a complex AB multiplet centered at δ +5.68 that is due to the methylene bridge of the dppm ligands (δ_A = 5.76, δ_B = 5.60; J_{AB} = 14.0Hz, $J_{P\text{-}H}$ = 4.7 and 4.9 Hz). From these results we can conclude that the first step in the reaction of $Re_2Cl_4(dppm)_2$ with RCN is the formation of a relatively weak 1:1 adduct,[17] which in the presence of an *excess* of RCN adds a second nitrile ligand with concomitant dissociation of a chloride ligand, there being no spectroscopic evidence for a

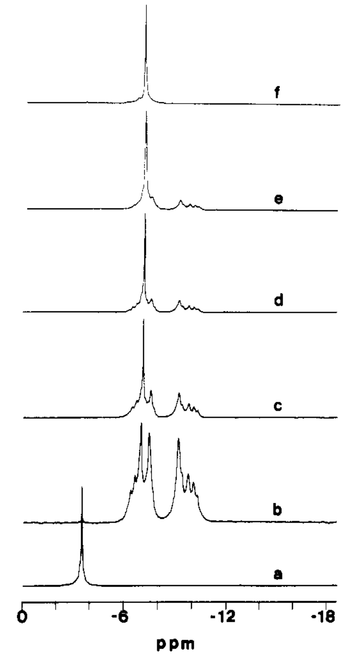

Figure 4. $^{31}P\{^1H\}$ NMR spectra of the timed reaction between $Re_2Cl_4(dppm)_2$ and excess C_2H_5CN: (a) $Re_2Cl_4(dppm)_2$; (b) t = 10 min; (c) t = 35 min; (d) t = 1.5 h; (e) t = 2.5 h; (f) pure $[Re_2Cl_3(dppm)_2(NCC_2H_5)_2]Cl$. The reaction solution consisted of 0.15 g of $Re_2Cl_4(dppm)_2$ in 2 mL of CH_2Cl_2/acetone-d_6 (1:1 v/v) to which was added 0.5 mL of C_2H_5CN.

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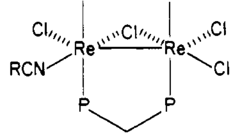
(16) This value was determined by comparing the intensities of the resonances associated with free nitrile and coordinated nitrile along with those due to the methylene protons of $Re_2Cl_4(dppm)_2$ in the ^1H NMR spectrum. This yielded a coordinated nitrile to free nitrile ratio of approximately 1.4/1 for a CD_2Cl_2 solution that was initially 1.4×10^{-2} M in $Re_2Cl_4(dppm)_2(NCC_2H_5)$.

(17) Other nitrogen σ-donor ligands can also form 1:1 adducts with $Re_2Cl_4(dppm)_2$. Thus, the addition of 4-methylpyridine (0.40 mL) to a solution of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) in acetone (5 mL) gave an insoluble green solid when the reaction mixture is stirred for 10 min. Anal. Calcd for $C_{56}H_{51}Cl_4NP_4Re_2$: C, 48.88; H, 3.74. Found: C, 48.89; H, 4.27. If this complex is dissolved in CD_2Cl_2, a purple solution results that shows in the ^1H NMR a pentet at δ +5.20 (4 H) and a singlet at δ +2.36 (3 H) and in the $^{31}P\{^1H\}$ NMR a singlet at δ −3.3 (vs. H_3PO_4). This indicates that this complex is only a weak adduct and completely dissociates in solution to generate $Re_2Cl_4(dppm)_2$ (purple solution) and free 4-methylpyridine. However, if excess 4-methypyridine is added to $Re_2Cl_4(dppm)_2$ a green solution results and the $^{31}P\{^1H\}$ NMR in CD_2Cl_2 exhibits an AA′XX′ pattern ($\nu_A - \nu_X$ = 830 Hz), indicating that like the nitrile derivatives the 1:1 adduct is stable in solution only if the ligand is present in excess.

second stable intermediate (see the $^{31}P\{^1H\}$ NMR spectral results in Figure 4).

At the present time we are uncertain as to the structure of $Re_2Cl_4(dppm)_2(NCC_2H_5)$ since attempts to grow crystals of it in the absence of excess nitrile have been thwarted by its ready dissociative decomposition. One intriguing possibility is that it possesses the A-frame structure **1**, which is analogous to that which



1

we have recently found is formed in the reaction of $Re_2Cl_4(dppm)_2$ with isocyanide ligands.[18] Indeed, certain dinuclear complexes that possess a trans dppm-bridged unit are known to undergo skeletal rearrangement via an A-frame type structure.[19] In support of structure **1**, we note that when an A-frame structure is present, the ^1H NMR spectrum of the methylene protons of the dppm ligands appears as a basic AB pattern with superimposed P–H coupling.[20–22] This is exactly what we observe in the spectrum of $Re_2Cl_4(dppm)_2(NCC_2H_5)$ (vide supra) and contrasts with the related NMR spectrum of $Re_2Cl_4(dppm)_2$ that shows[6] a pentet for the methylene resonance.

The formation of a bridged species such as **1** as a necessary prerequisite for these nitrile reactions to occur is also consistent with the fact that for $Re_2Cl_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) such a chlorine-bridged intermediate is unlikely to be accessible because of the bonding constraints imposed by the bridging dppe ligands.[23] In accord with this we find that $Re_2Cl_4(dppe)_2$ shows no tendency to react with nitriles under these same conditions.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE82-06117 to R.A.W. and Grant No. CHE82-11407 to F.A.C.) is gratefully acknowledged.

Supplementary Material Available: Full tables of anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors for the crystal structure of $[Re_2Cl_3(dppm)_2(NCC_6H_5)_2]PF_6$ (14 pages). Ordering information is given on any current masthead page.

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[18] The reaction of $Re_2Cl_4(dppm)_2$ with RNC gives the stable 1:1 adduct $Re_2Cl_4(dppm)_2(CNR)$. A single-crystal X-ray structure determination on the derivative where R = *t*-Bu has confirmed that this molecule has structure **1**, in which a multiply bonded dirhenium(II) unit is retained. A disorder problem is at present frustrating our attempts to refine the structure: Barder, T. J.; Powell, D.; Walton, R. A., unpublished results.

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New Isomeric Form of the "$M_2(OC_5H_3NCl)_4$" Core: A Polar Arrangement of the Four 6-Chloro-2-hydroxypyridinato (chp) Ligands in a Chlorodiruthenium(II,III) Complex, $Ru_2Cl(chp)_4$

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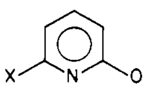
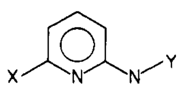
The compound $Ru_2Cl(chp)_4$ was prepared by reacting $Ru_2Cl(O_2CCH_3)_4$ with Hchp (6-chloro-2-hydroxypyridine) at 135 °C. Crystals of composition $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$ were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of $Ru_2Cl(chp)_4$. The crystalline compound was characterized analytically and spectroscopically. The structure has been determined by X-ray crystallography. The crystals are orthorhombic and belong to the space group *Pbcn* with a = 15.645 (4) Å, b = 11.861 (3) Å, c = 16.942 (4) Å, V = 3144 (2) Å^3, and Z = 4. The compound has four bridging chp ligands that are oriented in one direction to form a polar molecule. In $Ru_2Cl(chp)_4{\cdot}CH_2Cl_2$, the ruthenium having one axial chlorine atom is bonded to four oxygen atoms. The other ruthenium is bonded to four nitrogen atoms. The molecule is twisted away from an eclipsed conformation by approximately 19°. The CH_2Cl_2 molecule is present as a solvent of crystallization and does not interact with the complex molecule. The Ru–Ru bond length is 2.281 (1) Å, and the metal–metal bond order is 2.5. The Ru–Cl, average Ru–O, and average Ru–N bond lengths are 2.443 (2), 2.002 [5], and 2.085 [6] Å, respectively. The purple solution of the compound in CH_2Cl_2 exhibits a band at 536 nm (ϵ = 4740 M^{-1} cm^{-1}) in the electronic spectrum.

Introduction



1

hp: X=H
mhp: X=CH_3
chp: X=Cl
fhp: X=F



2

ap: X=Y=H
map: X=CH_3, Y=H
PhNpy: X=H, Y=C_6H_5

Bridging ligands of the types **1** and **2** are known[1] to be good stabilizers of dimetal units with short metal–metal bonds. It has been found that the steric and electronic nature of the substituents X and Y play a critical role in dictating the geometry and the metal–metal bond length of a complex molecule. In complexes of the types $M_2(mhp)_4$[2,3] and $M_2(chp)_4$[3,4] (M = Cr, Mo, W, Rh), the disposition of the four bridging ligands about the dimetal unit is generally such that each metal is coordinated to two O atoms and two N atoms, thus giving what we call the 2:2 arrangement. A similar arrangement has also been observed[5] in the $M_2(PhNpy)_4$ complexes of molybdenum and tungsten. In some dirhodium species a 3:1 arrangement of ligands has been observed.[3,6] In

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