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Reactions of the A-frame Complexes $[Rh_2(\mu\text{-}OH{\cdot}Cl)(CO)_2(\mu\text{-}dppm)_2]{\cdot}H_2O$ and $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (X = NCO, N_3, NCS, SCN) with CO and SO_2. Synthesis of a σ-π Bridging Cyanide Complex, $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$

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Reactions of the A-frame complexes $[Rh_2(\mu\text{-}OH{\cdot}Cl)(CO)_2(\mu\text{-}dppm)_2]{\cdot}H_2O$ and $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (X = OH, OMe, OEt, NCO, N_3, NCS and SCN) with CO and SO_2 are described and, where reactions occur, they are unusual in that the bridging ligand X is involved.

Thus, $[Rh_2(\mu\text{-}OH{\cdot}Cl)(CO)_2(\mu\text{-}dppm)_2]{\cdot}H_2O$ reacts with CO under pressure to yield trans-*$[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$. The pseudohalide A-frame complexes with X = N_3, NCS react with CO to give $[Rh_2(\mu\text{-}NCO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ and $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ respectively. The latter molecule is fluxional and possesses an unusual σ-π bridging cyanide ligand. With SO_2, $[Rh_2(\mu\text{-}OH{\cdot}Cl)(CO)_2(\mu\text{-}dppm)_2]$ affords $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2]HSO_4$ eventually, whereas all other complexes yield weak adducts involving an apparent Lewis acid-base interaction between SO_2 and the bridging ligand.*

Introduction

One reason for the continuing interest in the chemistry of binuclear complexes is the ability of certain members of the family to coordinate small molecules such as CO, SO_2, acetylene *etc.* in a bridging fashion, sometime reversibly. The largest number of examples of this behaviour is afforded by the metal–metal bonded dimers $[M_2L_2(\mu\text{-}dppm)_2]$ (dppm = bis(diphenylphosphino)methane; L = Cl, Br, I; M = Pd, Pt; L = CO, M = Rh) where both reversible and irreversible binding of a wide variety of molecules has been observed [1–4]. A large number of examples is also furnished by the so-called A-frame complexes of rhodium, $[Rh_2(\mu\text{-}X)L_2(\mu\text{-}dppm)_2]^{n+}$. Thus with L = CO, n = 1, coordination of CO is observed with X = Cl [5], Br, I (irreversibly) [6], H [3] and CH_3CO_2 at –70 °C) [7]. Reversible SO_2 addition to the complex with X = Cl also occurs [8]. Sulphur dioxide adducts with L = CO, X = Br and I have also been observed as products of the reaction of SO_2 with the A-frames having L = [Br, I], CO and X = CO [6a]. Interestingly, the complex $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$ forms an adduct with SO_2 but not with CO [9], unlike its iridium analogue [10].

A-frame complexes of the type having X = CO, SO_2 and L = Cl, Br also exhibit the ability to bind small molecules, often with ligand rearrangement. In particular, the complexes $[Rh_2X_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (X = Cl, Br, I) were found to react with activated acetylenes to yield the dimetallated olefin complexes, $[Rh_2X_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(\mu\text{-}dppm)_2]$ (R = CF_3, CO_2Me) [11]. A similar adduct has been observed between $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(\mu\text{-}dppm)_2]^+$ and dimethylacetylene dicarboxylate [7]. Although adducts of this type have not been observed with olefins, a correlation between the reversible formation of a CO adduct and catalytic hydrogenation activity has been observed for a variety of A-frames [12].

We have recently described the synthesis of a variety of A-frame complexes of the type $[Rh_2(CO)_2(\mu\text{-}X)(\mu\text{-}dppm)_2]^+$ with X = OR (R = H, Me, Et), OH·Cl, O_2CR (R = H, Me, CF_3, CH_2Cl, $CHCl_2$, CCl_3), NCO, NCS, SCN, and N_3 [13]. In this paper we describe the reactions of some of these with CO and SO_2 in which the principal reactions involve the bridging ligand, in contrast to the more usual situation in which bridging CO and SO_2 adducts prevail. In particular, we wish to report the unusual conversion of a bridging N-thiocyanate group into a bridging cyanide ligand by carbon monoxide.

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Experimental

Physical Measurements

Infrared spectra were recorded on Perkin Elmer 180 or 283B grating spectrophotometers either as Nujol mulls on KBr plates or CH_2Cl_2 solutions in NaCl cells. Calibration was achieved with either polystyrene or indene. ^1H and ^{13}C NMR spectra were recorded on a Varian Associates CFT 20 and the Nicolet 360 MHz spectrometer of the Atlantic Region Magnetic Resonance Centre. TMS (^1H) and CD_2Cl_2 (^{13}C) were used as internal calibrants. ^{31}P NMR spectra were obtained on a Varian Associates XL100 spectrometer of the National Research Council Atlantic Regional Laboratory, whose assistance is gratefully acknowledged. Samples were run either as CD_2Cl_2 solutions in 5 mm tubes or in CH_2Cl_2 in 12 mm concentric tubes with CD_2Cl_2 lock. In both cases, chemical shifts were determined relative to 85% phosphoric acid as an external standard. Conductivity measurements were determined by using an Industrial Instruments conductivity bridge with approximately 10^{-3} *M* solutions in dichloromethane or acetone at 25 °C. The cell constant was determined using 0.0100 *M* KCl solution. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical laboratories Ltd., Ontario and the Canadian Microanalytical Service Ltd., British Columbia.

Preparation of Complexes

All reagents were subject to vacuum drying prior to the recording of physical and analytical data, unless otherwise stated. Labelling of complexes with ^{13}CO was achieved by subjecting CH_2Cl_2 solutions of the compounds to ^{13}CO (Stohler isotopes, 90% C-13) at a partial pressure of *ca.* 250 mm Hg on a standard Toepler line. Under these conditions, exchange is essentially complete within 5 min for 30 mg samples.

Reactions with Carbon Monoxide

[Rh$_2$(μ-OH·Cl)(CO)$_2$(μ-dppm)$_2$]·H$_2$O. Preparation of trans-*[Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$]*

$[Rh_2(\mu\text{-}OH\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (0.10 g, 0.091 mmol) was dissolved in 10 ml of dichloromethane and subjected to CO under pressure (30 p.s.i.) at room temperature. After stirring for 2 h, the reaction vessel was vented and diethyl ether added to the red-brown solution. The orange precipitate was removed by filtration, washed with diethyl ether and dried *in vacuo* (0.033 g, 66% based on available chloride). Characterization was by comparison with that of an authentic sample [9].

[Rh$_2$(μ-N$_3$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. Preparation of [Rh$_2$(μ-NCO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$

A solution of $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.10 g, 0.085 mmol) in 10 ml of dichloromethane was subjected to CO pressure (40 psi, 25 °C) for 24 h. The addition of diethyl ether to the resultant yellow-orange solution precipitated bright yellow crystals of the product which were recrystallized from dichloromethane–diethyl ether (0.075 g, 75%). Characterization was by comparison with an authentic sample [13].

[Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. Preparation of [Rh$_2$(μ-CN)(μ-CO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$

$[Rh_2(\mu\text{-NCS})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.20 g, 0.17 mmol) was dissolved in 10 ml of dichloromethane and CO was bubbled slowly through the solution for a period of 10 min. The yellow-orange solution initially turned red-brown and gradually lightened to red-orange. The addition of diethyl ether resulted in the deposition of orange crystals of the complex. Recrystallization from dichloromethane–diethyl ether yielded the product as a dichloromethane solvate (0.16 g, 80%). M.Pt. 190–210 °C (dec). *Anal.* Found: C, 51.84; H, 3.81; N, 1.16; S, <0.2%. $C_{54}H_{46}NP_4Cl_3O_6Rh_2$ requires C, 52.05; H, 3.65; N, 1.11; S, 0.0%. Λ_M (acetone) = 133 cm^2 Ω^{-1} mol^{-1}. Evidence for the formation of the solvate comes from the ^1H NMR spectrum in d_6-acetone, 5.60 s, 2H.

Reactions with Sulphur Dioxide

[Rh$_2$(μ-OH·Cl)(CO)$_2$(μ-dppm)$_2$]·H$_2$O. Preparation of [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]HSO$_4$

Sulphur dioxide was passed slowly through a solution of $[Rh_2(\mu\text{-}OH\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (0.12 g, 0.11 mmol) in 10 ml of dichloromethane for 15 min. The slow addition of diethyl ether to the resultant magenta solution yielded a red-brown solid of crude $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)(CO)_2(\mu\text{-dppm})_2]HSO_4$. The crude material was redissolved in dichloromethane, purged with nitrogen for several minutes and the orange product precipitated by the addition of diethyl ether (0.07 g, 60%). M. Pt. 200–205 °C. *Anal.* Found: C, 54.06; H, 3.90; Cl, 4.72; S, 2.97%. $C_{52}H_{45}ClSP_4O_6Rh_2$ requires C, 53.70; H, 3.90; Cl, 3.05; S, 2.76%. Λ_M = 93 Ω^{-1} cm^2 mol^{-1}.

Reaction of [Rh$_2$(μ-OH·Cl)(CO)$_2$(μ-dppm)$_2$]·H$_2$O with H$_2$SO$_4$

To $[Rh_2(\mu\text{-}OH\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (0.15 g, 0.14 mmol) dissolved in 10 ml of dichloromethane was added conc. H_2SO_4 (0.03 ml) dissolved in 1 ml of ethanol. After stirring the mixture for 10 minutes, diethyl ether was added to precipitate the product as orange crystals which were recrystallized from dichloromethane-diethyl ether (0.15 g, 92%). Infrared spectroscopy established the product as being identical to that obtained in the preceding reaction.

$[Rh_2(\mu$-$OR)(CO)_2(\mu$-dppm$)_2]ClO_4$ (R = H, Me, Et)

Sulphur dioxide was bubbled through a solution of the appropriate complex (0.10 g, *ca.* 0.086 mmol) in 10 ml of dichloromethane for 10 min. The addition of SO_2 saturated diethyl ether to the resultant red solutions resulted in the precipitation of the orange products in *ca.* 85% yield. When ground or exposed to the atmosphere for 1 h, loss of SO_2 occurred resulting in regeneration of the yellow starting materials.

Reaction of $[Rh_2(\mu$-$OR)(CO)_2(\mu$-dppm$)_2]ClO_4$ with H_2SO_4

In a procedure analogous to that described for $[Rh_2(\mu$-OH$\cdot$Cl$)(CO)_2(\mu$-dppm$)_2]\cdot H_2O$ above, $[Rh_2(\mu$-OR$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (0.10 g, *ca.* 0.086 mmol) was reacted with conc. H_2SO_4 (0.03 ml) dissolved in 1 ml of ethanol. The red $[Rh_2(\mu$-$HSO_4)(CO)_2(\mu$-dppm$)_2]ClO_4$ was recrystallized from dichloromethane–diethyl ether (0.092 g, 91%). M. Pt. 185 °C (dec). Anal. Found: C, 51.14; H, 4.09; P, 10.13; S, 3.29%. $C_{52}H_{44}SP_4O_{10}ClRh_2$ requires C, 50.90; H, 3.70; P, 10.10; S, 2.61%. Λ_M = 118 Ω^{-1} cm^2 mol^{-1}.

$[Rh_2(\mu$-$X)(CO)_2(\mu$-dppm$)_2]ClO_4$ (X = N_3, NCO). Preparation of $[Rh_2(\mu$-$X{\cdot}SO_2)(CO)_2(\mu$-dppm$)_2]ClO_4$

A procedure analogous to that employed for the alkoxide complexes above yielded burgundy coloured solutions from which bright red crystalline complexes could be isolated in *ca.* 90% yield. The complexes were stable only in an atmosphere of SO_2 and lost SO_2 immediately on grinding or on standing 10–15 minutes in air.

$[Rh_2(\mu$-$NCS)(CO)_2(\mu$-dppm$)_2]ClO_4$

Bubbling SO_2 through a solution of $[Rh_2(\mu$-NCS$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (0.085 g) in 10 ml dichloromethane resulted in a colour change to a bright red-orange. The slow addition of diethyl ether to this solution, even while SO_2 was still being passed, resulted in a gradual lightening of colour and the deposition of yellow crystals of the starting material (0.07 g, 80%).

$[Rh_2(\mu$-$SCN)(CO)_2(\mu$-dppm$)_2]ClO_4$. Isomerization to $[Rh_2(\mu$-$NCS)(CO)_2(\mu$-dppm$)_2]ClO_4$

$[Rh_2(\mu$-SCN$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (0.11 g, 0.093 mmol) was dissolved in 10 ml of dichloromethane and SO_2 was bubbled through the solution for 15 min. The addition of SO_2 saturated diethyl ether to the wine red solution resulted in the deposition of a crude orange solid. Recrystallization of the crude material from dichloromethane–diethyl ether yielded yellow crystals of $[Rh_2(\mu$-NCS$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (0.08 g, 70%).

Results and Discussion

Reactions with Carbon Monoxide

Unlike their halide bridged analogues, the O-bridged A-frames $[Rh_2(\mu$-OH$\cdot$Cl$)(CO)_2(\mu$-dppm$)_2]\cdot H_2O$ and $[Rh_2(\mu$-OR$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (R = H, Me, Et) do not react with CO at room temperature and pressure. The situation is somewhat different, however, when these complexes are subjected to CO under pressure. Under 30 p.s.i. of CO, yellow $[Rh_2(\mu$-OH$\cdot$Cl$)(CO)_2(\mu$-dppm$)_2]\cdot H_2O$ reacts within 2 hours to give a red-brown solution which yields *trans*-$[Rh_2Cl_2(CO)_2(\mu$-dppm$)_2]$ upon the addition of diethyl ether. Characterization of the product was by comparison with an authentic sample; ν(CO) = 1974 vs, 1937 sh (Lit. 1976 vs, 1937 sh [14]). Based on the amount of chloride available, the yield of $[Rh_2Cl_2(CO)_2(\mu$-dppm$)_2]$ was 66%. There was, however, no attempt on our part to establish the stoichiometry of the reaction, nor were we successful in determining the fate of the remaining rhodium. The analogous iridium complex, $[Ir_2(\mu$-OH$\cdot$Cl$)(CO)_2(\mu$-dppm$)_2]$ [15] reacts with CO, under considerably more mild conditions, with oxidation of CO to CO_2. In view of the fact that $[Rh_2(\mu$-OH$\cdot$Cl$)(CO)_2(\mu$-dppm$)_2]\cdot H_2O$ is quite stable in the absence of CO, it would appear that a similar ligand reaction is taking place, possibly with the following stoichiometry;

$$2[Rh_2(\mu\text{-}OH{\cdot}Cl)(CO)_2(\mu\text{-dppm})_2] + 3CO \longrightarrow$$

$$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2 +$$

$$\{Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-dppm})_2\} + 2CO_2 + H_2$$

although it must be stressed that under the conditions employed, it proved impossible for us to detect gaseous by-products. Under CO pressure, the complexes $[Rh_2(\mu$-OR$)(CO)_2(\mu$-dppm$)_2]ClO_4$, R = H, Me, Et) also react slowly, although here the product resulting from the carbonylation of all three complexes is an unusual trimeric rhodium cluster, whose synthesis, structure and chemistry will be the subject of a forthcoming paper.

Of the pseudohalide bridged A-frame complexes $[Rh_2(\mu$-X$)(CO)_2(\mu$-dppm$)_2]ClO_4$ (X = NCO, N_3, NCS, SCN), none was observed to form a simple bridging CO adduct. All, however, with the exception of the cyanate, did react with CO. In a slow reaction, $[Rh_2(\mu$-$N_3)(CO)_2(\mu$-dppm$)_2]ClO_4$ reacts with CO (1 atom for 72 h or 40 p.s.i. for 24 h) to give $[Rh_2(\mu$-NCO$)(CO)_2(\mu$-dppm$)_2]ClO_4$ in good yield. Under 1 atm of CO the reaction was easily moni-

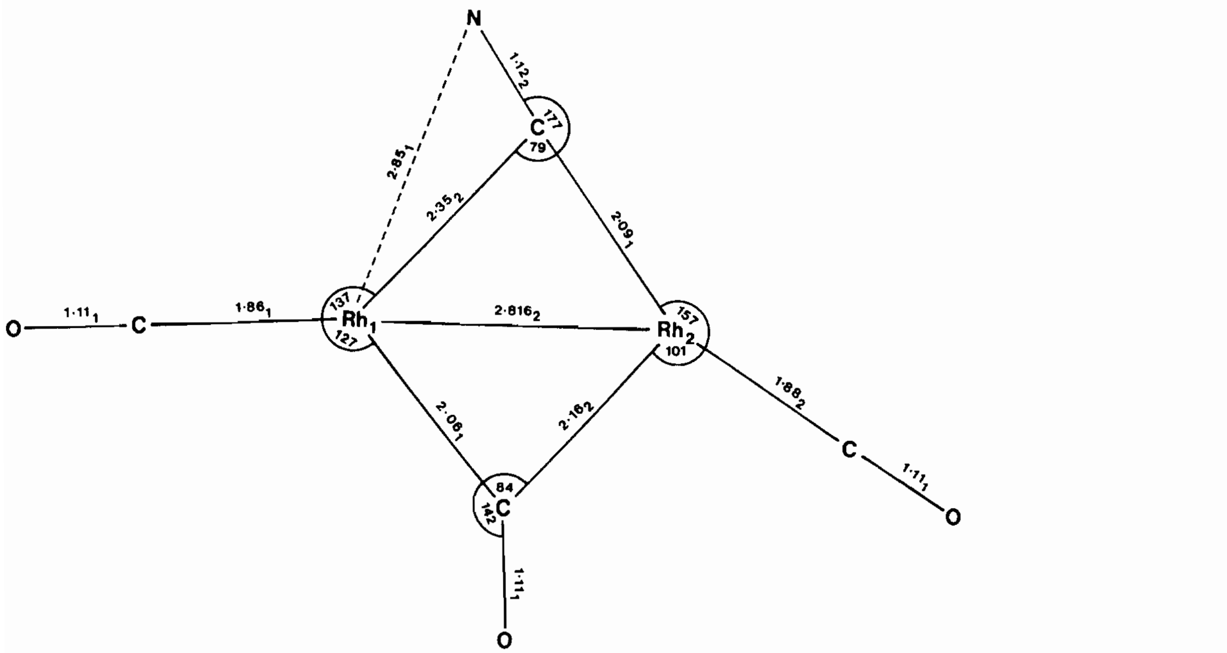


Fig. 1. Geometry of $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]^+$ in the rhodium–carbonyl plane (approximately to scale). Esd's on bond lengths are indicated by subscripts. All bond angles have been quoted to the nearest degree and have esd's < 1.

tored via the disappearance of νN_3 at 2077 and the concomitant growth of $\nu(NCO)$ at 2199 cm^{-1}. Conversion of terminal azide to cyanate groups on reaction with carbon monoxide is quite common but would appear to be less so when bridging azide ligands are involved [16]. It is worth noting at this point that the product tentatively identified by Sanger [6b] as $[Rh_2Cl(N_3)(CO)_2(dppm)_2]$ can probably best be regarded as a mixture of the A-frames $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-}dppm)_2]Cl$ and $[Rh_2(\mu\text{-}NCO)(CO)_2(\mu\text{-}dppm)_2]Cl$. The complex is prepared under an atmosphere of CO and the infrared bands reported at 2286 and 2080 cm^{-1} are probably better attributed to νNCO and νN_3 rather than νN_3 and νCO as proposed.

The reaction of $[Rh_2(\mu\text{-}SCN)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ with CO proved very complex and to date, at least, the products isolated have defied characterization. Bubbling CO through a solution of this complex results in a rapid colour change from orange to brown. The addition of diethyl ether to such solutions precipitates an amorphous green solid shown by elemental analysis to contain nitrogen and sulphur in an approximately 4:1 ratio. Infrared and ^{31}P NMR spectra of this material are uninformative so further characterization was not attempted. The reaction of the N–bound isomer $[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ with CO, however, proceeds smoothly to give a well defined product. Bubbling CO slowly through a dichloromethane solution of $[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ results in a progressive colour change from yellow to brown to orange over a period of several minutes. Addition of diethyl ether results in the deposition of orange crystals of the product whose structural formula has been established as $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot CH_2Cl_2$ through the use of infrared spectroscopy, ^1H, ^{13}C and ^{31}P NMR spectroscopy and X-ray crystallography [17].

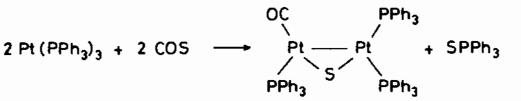
$[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ in dichloromethane solution exhibits $\nu(CO)$ bands at 2019 sh, 2000 vs and 1893 m which, on labelling with ^{13}CO, shift to 1978 sh, 1959 vs and 1851 m enabling $\nu(CN)$ to be identified at 2044 w. The value observed for $\nu(CN)$ is low by comparison with the range normally associated with bridging cyanide groups [18] and low also by comparison with terminal cyanide groups associated with other rhodium-dppm complexes [6b], presumably as a consequence of its unusual bridging mode (*vide infra*). At the present stage of refinement (R = 0.066 on 3440 independent reflections with $I > 3\sigma(I)$) the geometry of the cation in $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot CH_2Cl_2$ in the rhodium-carbonyl plane is as depicted in Fig. 1.

It should be noted here that the distinction made in the figure between the bridging cyano and carbonyl groups is as a result of consideration of the spectroscopic data given above and below, rather than on crystallographic grounds. The most striking feature of the structure is the unusual, distinctly asymmetric nature of the bridging cyano ligand. A similar example of an asymmetrically bridging CN group has been observed by Curtis *et al.* in $(NEt_4)[Cp_2Mo_2(\mu\text{-}CN)(CO)_3]$ [19]. The same authors have also discussed a criterion for distinguishing between 2-electron and incipient 4-electron (σ-π) donor behaviour of bridging CO and CN groups [20], in which the σ-π mode is characterized by essential invariance of the M–C–O or M–C–N bond angle with the asymmetry parameter, α (defined as $\alpha = (d_2\text{-}d_1)/d_1$ where d_1 and d_2 are the short and long M–C distances respectively). The Rh(2)–C–N bond angle of 177(1)° and low asymmetry parameter of $\alpha = 0.12$ clearly place the bridging cyanide group in this instance in the σ-π domain. This, of course, contrasts well with the value of 142(1)° and $\alpha = 0.05$ for the bridging CO, which places it on the published curve for simple 2-electron donor bridging ligands [20]. Counting the cyanide ligand as a 4-electron donor makes the dimer a 34 electron complex which formally should contain a Rh–Rh bond and, in fact, the Rh–Rh distance of 2.816(2) Å is within the range normally considered indicative of a metal–metal bond for this type of complex [21].

The unusual bridging mode of the cyanide ligand also results in some significant changes in the coordination geometries of the two metal atoms by comparison to more familiar A-frame carbon monoxide adducts such as $[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]\cdot BPh_4$, for example [22]. In the chloro bridged species, both metal centres are described as having severely distorted trigonal bipyramidal geometries with large C_t–Rh–Cl bond angles of *ca.* 140° and small C_b–Rh–Cl angles of *ca.* 103°. In the cyanide analogue, however, one centre only (Rh(1)) can best be described as being distorted trigonal bipyramidal, with an axial bond angle of 176.2(2)° and equatorial angles of 126.8(6)°, and (assuming a π-CN–Rh(1) interaction) *ca.* 125° and 108°. The second metal centre, on the other hand, is best described as a distorted square pyramid with *trans* basal angles of 157.2(6)° and 161.6(2)°, *cis* basal angles of 91.9(5)°, 86.1(4)°, 86.2(4)° and 88.8(3)°, and apical angles of 101.2(6)°, 101.5(5)°, 98.4(3)° and 99.5(3)°. Other bond angles and lengths in $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot CH_2Cl_2$ are in keeping with this type of complex and will be discussed in more detail with the full structural report.

NMR spectroscopy establishes $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ as a fluxional molecule with at least two different fluxional processes taking place. At 25 °C, the ^1H NMR shows only a broad, featureless, barely resolved doublet centred at 3.72 ppm for the dppm methylene protons. In the ^{13}C NMR spectrum of an enriched sample (40%) at the same temperature, only two broad, featureless resonances were seen at 203.4 ppm and 189.2 ppm in the approximate ratio of 1:2. On cooling to *ca.* –35 °C, both ^1H and ^{13}C spectra sharpened considerably. The dppm methylene protons at this temperature gave rise to two multiplets centred at 3.77 ppm and 3.56 ppm whereas in the ^{13}C NMR spectrum, the resonance attributed to the terminal carbonyls split into two multiplets (188.6 ppm, $^1J_{Rh-C_t} = 72.8$ Hz) and that attributed to the bridging carbonyl appeared as a triplet of quintets (203.4 ppm, $^1J_{Rh-C_b} = 36.2$ Hz, $^2J_{C_b-P} = 4.7$ Hz). As a result of the incomplete exchange of ^{13}CO and spectrometer resolution, we did not observe $^{13}C_t$–$^{13}C_b$ coupling, as seen for the chloro-bridged analogue, although all the other observations correspond closely [5]. We believe that both the ^1H and ^{13}C NMR spectra can be accounted for by invoking the same fluxional process. Both dppm methylene protons and terminal and bridging carbonyls can be rendered equivalent by 'walking' the CO and CN groups around the equatorial region of the complex *via* a series of terminal to bridging rearrangements, in much the same manner as observed for polynuclear carbonyls [23]. We have not, however, established the coalescence temperatures for the ^1H and ^{13}C NMR spectra (>25 °C), so the possibility still exists for the carbonyl scrambling to occur *via* an intermolecular process. At 25 °C, the $^{31}P\{^1H\}$ NMR spectrum consists of a broad, unresolved second order multiplet which, at –35 °C, sharpens to the characteristic A-frame AA′A″A‴XX′ pattern at 30.36 ppm with $|^1J_{RhP} + {}^xJ_{RhP}| = 97.1$ Hz. Since all four phosphorus atoms are equivalent, it is necessary to invoke either a symmetrically bridging cyanide group in solution or a fluxional process, akin to that seen in $(NEt_4)[Cp_2Mo_2(\mu\text{-}CN)(CO)_3]$, in which the cyanide flips from one metal to another in a 'windshield wiper' type motion. In view of the observed solid state structure, a fluxional process seems to be a more logical explanation for these observations. It did not prove possible to freeze this motion out, even at –80 °C. It is worth noting that a similar fluxional process, invoked to explain chemical equivalence of all phosphorus atoms in the σ-π acetylide complex $[Rh_2(\mu\text{-}C_2Bu^t)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ also remains fast at –80 °C [24].

Since there is no evidence for the deposition of elemental sulphur during the product of $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$, it is tempting to assume that the sulphur has been removed as COS. There are ample examples in the literature of COS breaking down in the presence of metal complexes to give products containing carbonyl and sulphide ligands; *e.g.*



[25]

Hence, it does not seem unreasonable to suspect that the reverse can take place. Running infrared spectra of the carbonylation reaction before it has gone to completion indicate the transitory existence of an intermediate (or intermediates) which exhibits bands at 2120 w, 2030 m and 1835 m cm^{-1}. Unfortunately, the existence of this species is so fleeting that little can be said other than it appears to have a bridging carbonyl and possibly a terminal NCS group. The possibility also exists that the 2120 band is due to free COS, detected before being purged by excess carbon monoxide.

Reactions with Sulphur Dioxide

Bubbling sulphur dioxide through a dichloromethane solution of $[Rh_2(\mu\text{-OH}\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ results in a dramatic colour change from yellow to magenta. The addition of diethyl ether to such solutions results in the deposition of a crude red-brown solid with solution infrared maxima at 2016 vs and 1991 s cm^{-1}. In the solid state spectrum, a number of S–O absorptions were seen in the 1300–800 cm^{-1} region at 1231 m, 1189 m, 1064 s and 855 m cm^{-1}. These data suggested that the crude material contains the cation $[Rh_2(\mu\text{-Cl})(\mu\text{-}SO_2)(CO)_2(\mu\text{-dppm})_2]^+$ (ν(CO) = 2015 s, 1985 s,sh (Nujol); νSO_2 = 1229 m, 1070 m [8]). The presence of a chloro bridged species was verified by recrystallizing the crude material after purging the solution with dinitrogen. The yellow-orange product exhibited an infrared spectrum identical to that of an authentic sample of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (ν(CO) = 1991 s, 1972 vs) with additional bands at 1231 m, 1063 m and 861 m cm^{-1}. Additional proof was afforded by recrystallizing the crude product in the presence of $NaClO_4$ which gave $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]ClO_4$ without the extra bands in the 1200–800 cm^{-1} region. The obvious candidates for the counterion in this reaction are HSO_3^- and HSO_4^-, with HSO_3^- being more readily explicable. Unfortunately, however, all evidence gathered to date supports formulation of the product as a bisulphate salt. For example, the free HSO_4^- ion normally exhibits infrared maxima between 1180–1160, 1080–1000 and 880–840 cm^{-1}, in keeping with the extra bands observed in spectra of the recrystallized product. Final verification of the identity of the anion was afforded by reacting $[Rh_2(\mu\text{-OH}\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ with H_2SO_4, which gave a product identical in every respect with that obtained from the SO_2 reaction. $[Rh_2(\mu\text{-OH}\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ has been observed on a number of occasions to react with non-coordinating acids HY affording $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]Y$ [26]. In order to verify that the HSO_4^- ion was not coordinated to the complex, a genuine sample of red $[Rh_2(\mu\text{-}HSO_4)(CO)_2(\mu\text{-dppm})_2]ClO_4$ was synthesized by adding H_2SO_4 to $[Rh_2(\mu\text{-OH})(CO)_2(\mu\text{-dppm})_2]ClO_4$ [13]. $[Rh_2(\mu\text{-}HSO_4)(CO)_2(\mu\text{-dppm})_2]ClO_4$ exhibits ν(CO) at 1996 s and 1966 s (2005 s, 1990 vs in CH_2Cl_2) with bands attributable to the HSO_4 group being observed at 1269 m and 935 w cm^{-1}. In addition to the spectroscopic differences, the physical and chemical properties of $[Rh_2(\mu\text{-}HSO_4)(CO)_2(\mu\text{-dppm})_2]ClO_4$ established it as being quite different from $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]HSO_4$.

The formation of the HSO_4^- ion under these circumstances is unusual but not entirely without precedence. A variety of d^8 osmium complexes react with sulphonyl chlorides, RSO_2Cl, to give salts containing the corresponding sulphonate anions [27]. *e.g.*:

$$Os(CO)_2(CNR)(PPh_3)_2 + CH_3SO_2Cl \longrightarrow$$

$$cis\text{-}[OsCl(CO)_2(CNR)(PPh_3)_2]CH_3SO_3$$

$$(R = \text{p-tolyl})$$

In this case, there was circumstantial evidence to suggest that the reaction was free radical in nature, with the sulphonate anion being produced *via* oxidation of the $RSO_2\cdot$ radical. A radical mechanism seems less likely in the case of $[Rh_2(\mu\text{-OH}\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$, however, since it is conceivable that the dimer itself might function as a catalyst for the oxidation of HSO_3^- to HSO_4^-. It is quite obvious that the chloride in $[Rh_2(\mu\text{-OH}\cdot Cl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ is essential to its reactivity with both CO and SO_2. By way of contrast, $[Rh_2(\mu\text{-OR})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = H, Me, Et) react with SO_2 with the formation of weak adducts only, the exact nature of which is as yet unknown. The orange complexes lose SO_2 in less than 1 hour on standing at room temperature and immediately on grinding. Hence we do not have any solid state infrared evidence regarding the nature of these adducts. In SO_2 saturated dichloromethane solution, a pronounced shift to higher wavenumbers was seen for the ν(CO) values; with R = Et, for example, the ν(CO) values changed from 1992 sh, 1981 vs to 2033 s, 1994 vs cm^{-1}. Such values are exactly as might be anticipated for complexes such as $[Rh_2(\mu\text{-OR})(\mu\text{-}SO_2)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Unfortunately, the changes in the infrared spectra are not reflected in the ^{31}P NMR spectra of these complexes. Thus, for example, the ethoxy species showed only slight changes when the ^{31}P NMR spectrum was run in SO_2 saturated CD_2Cl_2; 20.52 ppm, $|^1J_{RhP} + {}^xJ_{RhP}|$ = 126.0 Hz *versus* 20.67 ppm, $|^1J_{RhP} + {}^xJ_{RhP}|$ = 128.2 Hz for the parent complex. These data are more in keeping with the formation of a Lewis acid-base adduct between SO_2 and the bridging ligand (*vide infra*).

Bubbling SO_2 into yellow solutions of $[Rh_2(\mu\text{-X})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (X = N_3, NCO) results in a colour change to burgundy. From these solutions can be isolated unstable, bright red solids by the addition of SO_2 saturated diethylether. These solids are stable under 1 atmosphere of SO_2 or at −18 °C, but at room temperature in the absence of SO_2, they quickly lose SO_2 to regenerate the starting materials. As observed for the alkoxide complexes, SO_2 is lost immediately on grinding. Infrared spectra of the burgundy solutions show no change within experimental error, as do the ^{31}P NMR spectra. There is obviously an interaction of some description between these A-frame complexes and SO_2, either of the Lewis acid-base or charge transfer type, and we believe the site of this interaction is the free terminus of the bridging pseudohalide ligand. Similar SO_2 complexes of pseudohalide complexes such as $Pd(NCO)_2(PPh_3)_2$ and $IrX(CO)(PPh_3)_2$ (X = NCO, N_3)) have been described previously [28] and weak SO_2 adducts have been observed for the complexes $Os(X_2)(CO)_2(PPh_3)_2$ (X = S, Se) [29]. With the thiocyanate A-frame complexes, $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-}dppm)_2]ClO_4$, X = NCS, SCN, weak SO_2 adduct formation is seen only in the N–bound complex and even then, only in solution. Thus bubbling SO_2 through solutions of $[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ results in a colour change from yellow to red-orange, as observed for the axide and cyanate analogues. There appear to be no spectroscopic changes occurring along with the colour change. Adding SO_2 saturated diethyl ether to the orange solution causes a gradual lightening to pale orange and the deposition of the yellow starting material only. Adding SO_2 to orange solutions of $[Rh_2(\mu\text{-}SCN)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ results in a colour change to bright red. Infrared spectra of such solutions show only the presence of the N–bound isomer, however, indicating that isomerization has taken place. The manner in which SO_2 effects this isomerization is as yet unknown but presumably these results do indicate that, of the two different isomers, the N–bound form would appear to be the more stable.

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