isomer II and the shoulder arises from isomer I. The OMW_2 region contains two resonances. Since diastereomer I contains no OMW_2 oxygens and diastereomer II contains a single OMW_2 oxygen, O_B, diastereomer III must be present. The more intense OMW_2 resonance has about the same intensity as the two more intense OMNbW resonance and is therefore assigned to O_B in isomer II. The less intense resonance arises from diastereomer III.

Although the relative intensities of the resonance just discussed reflect the relative abundances of diastereomers I–III, the range of line widths present and overlapping nature of several resonances make a truly quantitative assessment of the isomer distribution impossible. A qualitative view is obtained easily, however. The ratio of the $OMNb_2$ resonance's intensity to the intensity of either of the more intense OMNbW resonances directly reflects the relative concentrations of diastereomers I and II, and II is clearly predominant. The ratio of the less intense OMW_2 resonance's intensity to the intensity of either of the more intense OMNbW resonances divided by 2 sets an upper limit on the ratio of isomer III concentration to isomer II concentration, and isomer II clearly predominates here also. The situation is complicated by the fact that the less intense OMW_2 resonance arises from the two O_B oxygens in isomer III and possibly the O_C oxygen in isomer III, depending upon the level of ^{17}O enrichment at this O_C site (see above). Since purely statistical factors favor the C_1 symmetry diastereomer II over the C_s diastereomers I and III by a factor of 2, the observed I:II:III isomer distribution approximates the 1:2:1 statistically random situation.

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Registry No. 1 (isomer I), 93530-16-6; 1 (isomer II), 93530-21-3; 1 (isomer III), 93564-54-6; 2 (isomer I), 93530-18-8; 2 (isomer II), 93530-23-5; 2 (isomer III), 93530-25-7; $[(OC)_3Mn(NCCH_3)_3]Br$, 93530-19-9; $(Nb_2W_4O_{19})[(n\text{-}C_4H_9)_4N]_4$, 60098-33-1; $[(OC)_3Re(NCCH_3)_3]PF_6$, 66610-18-2.

Supplementary Material Available: Crystal structure analysis report, Tables III (anisotropic thermal parameters for non-hydrogen atoms) and V (cation bond lengths and angles), Figure 3 (ORTEP drawing of the cation), and structure factor tables for the X-ray structural study of $[(OC)_3Mn(Nb_2W_4O_{19})][(n\text{-}C_4H_9)_4N]_3$ (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis of $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-}PPh_2CH_2PPh_2)_2]ClO_4$ (R = H, CH_3, C_2H_5) and Their Use as Synthetic Precursors to Other A-Frame Complexes

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General preparative methods for the synthesis of a variety of A-frame complexes, $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]^+$, are presented, including examples in which the bridgehead ligand X has an oxygen or nitrogen donor atom. The reaction of *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ with excess RO^- and $NaClO_4$ in the appropriate alcohol suspension yields $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = Me, Et). Recrystallizing the alkoxide complexes in the presence of excess $HClO_4$ gives $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$. A similar hydroxide complex $[Rh_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ results from the reaction of *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ with Na_2CO_3 in aqueous ethanol. The bridging ligands in $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = H, Me, Et) are acid labile, enabling a range of substitution reactions to be performed. Thus, complexes of the type $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with X = Cl, Br, I, O_2CH, O_2CCH_3, O_2CCF_3, NCO, and N_3 can be synthesized. The trifluoroacetate group in $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ is also labile, making this compound a useful synthon. With excess MX, complexes of the type $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ and $[RhX(CO)(dppm)]_2$ (X = NCO, NCS) can be isolated. With 1 equiv of NH_4NCS, $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ yields $[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-dppm})_2]ClO_4$. The N-bound isomer is also obtained when $[Rh_2(\mu\text{-}OEt)(CO)_2(\mu\text{-dppm})_2]ClO_4$ reacts with NH_4NCS in the presence of $HClO_4$, but when the acid is omitted, the S-bound isomer $[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$ results.

Introduction

Recently, the chemistry of the rhodium A-frame complexes, typified by $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-dppm})_2]^+$,[1] $Rh_2(\mu\text{-}CO)Cl_2(\mu\text{-dppm})_2$,[2] and $Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2$,[3] has attracted considerable attention, especially with respect to the ability of these compounds to coordinate small molecules such as carbon monoxide, sulfur dioxide, and acetylenes in a bridging fashion. This phenomenon has obvious relevance to catalytic processes occurring either on transition-metal clusters or on metal surfaces, and in fact, a number of A-frame complexes are capable of homogeneous hydrogenation,[1,4] hydroformylation, and catalysis of the water gas shift reaction.[4] Despite this, however, the relationship between catalytic activity and binding of the substrate in the bridging position has not been established.

In the chemistry of the rhodium A-frame complexes so far investigated, the principal function of the bridgehead ligand has been to link the two rhodium-containing square planes, thereby orienting the metal centers in the appropriate fashion. In addition, it is obvious that the bridging ligand has a profound effect upon the ability of the A-frame complex to coordinate small molecules in the endo pocket. Our work with A-frame complexes stems from a long-term interest in ligand reactivity. Since it seems natural to expect that certain bridging ligands should have an interesting

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[1] Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.

[2] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

[3] Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

[4] Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

chemistry in their own right, we have sought to develop synthetic routes to as wide a variety of A-frame complexes as possible and to examine their chemistry with respect to both their ability to bind small molecules and the chemistry of the bridging ligand. In this publication, we describe general methods for the synthesis of A-frame complexes $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]^+$ in which X is one of a wide variety of monoanionic ligands. Subsequent publications will deal with the effect that changing X has on the ability of these dimers to bind such molecules as CO, SO_2, and acetylene, etc., and on the chemistry of the bridging ligands themselves.

Experimental Section

Materials. Hydrated rhodium(III) chloride (Strem) and bis(diphenylphosphino)methane (dppm) (Strem) were used as received. All other reagents were of ACS quality or better and were also used without further purification. Hydrogen halide adducts of *N,N*-dimethylacetamide (DMA·HX) were prepared by bubbling the appropriate hydrogen halide into benzene solutions of DMA until precipitation was complete. The moisture- and air- (X = I) sensitive crystals were collected, washed with benzene, and stored appropriately after drying in vacuo. All solvents were appropriately dried and distilled before being stored over type 4A molecular sieves.

Physical Measurements. Infrared spectra were recorded on Perkin-Elmer 180 or 283B grating spectrophotometers as either Nujol mulls on KBr plates or CH_2Cl_2 solutions in NaCl cells. Calibration was achieved with either polystyrene or indene. ^1H NMR spectra were recorded either on Varian Associates CFT20 and FT80 spectrometers or on the Nicolet 360-MHz instrument of the Atlantic Regional Magnetic Resonance Centre using Me_4Si as internal calibrant. ^{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 a 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 .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 preparative procedures were routinely carried out under an atmosphere of prepurified nitrogen even though all complexes were found to be air stable, both in the solid state and in CH_2Cl_2 solution. Several complexes, however, proved subject to hydrolysis and alcoholysis and had to be handled accordingly. All complexes prepared were subject to vacuum drying prior to the recording of physical and analytical data, unless otherwise stated. *trans*-$[RhCl(CO)(dppm)]_2$ was prepared from a previously published procedure.[3] Labeling of complexes with ^{13}CO was achieved by subjecting CH_2Cl_2 solutions of the compounds to ^{13}CO (Stohler isotopes, 90% ^{13}C) at a partial pressure of ca. 250 mmHg on a standard Toepler line. Under these conditions, exchange is essentially complete within 5 min for 30-mg samples.

$[Rh_2(\mu\text{-}OCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (1). A suspension of *trans*-$[RhCl(CO)(dppm)]_2$ (0.25 g, 0.23 mmol) in absolute methanol was treated with freshly prepared sodium methoxide solution (0.070 g of sodium in 10 mL of methanol, 3.0 mmol). The turbid, yellow-orange solution that resulted after 15 min of stirring was filtered through Celite and excess sodium perchlorate monohydrate added (0.060 g, 0.43 mmol). The product separated on stirring and, when precipitation was judged complete, was removed by filtration, washed with methanol and hexane, and recrystallized from dichloromethane–methanol.

$[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (2). This complex was prepared by using the procedure described above for its methoxide analogue, with ethanol being used instead of methanol at all points. The complex was recrystallized from dichloromethane–ethanol as bright yellow crystals.

$[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (3). To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (2) (0.20 g, 0.17 mmol) in 5 mL of dichloromethane was added 2 mL of absolute ethanol containing perchloric acid (70%, 0.13 mL (8 drops)). The solution was allowed to stir for 5 min and the product made to crystallize by the addition of diethyl ether. Recrystallization from dichloromethane–diethyl ether in the presence of $HClO_4$ gave the complex in the form of yellow microcrystals.

$Rh_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-dppm})_2\cdot H_2O$ (4). A mixture of *trans*-$[RhCl(CO)(dppm)]_2$ (0.50 g, 0.45 mmol) and sodium carbonate decahydrate (0.50 g, 1.7 mmol) in 50 mL of 95% aqueous ethanol was stirred for 12 h. The yellow-orange suspension so formed was allowed to settle for 30 min and filtered through a pad of Celite, which was then washed with dichloromethane. The resultant filtrate was reduced to ca. 10 mL under reduced pressure and the product precipitated by the addition of excess diethyl ether. The precipitate was removed by filtration, washed with water and diethyl ether, and recrystallized from dichloromethane–diethyl ether to give the product as bright yellow crystals.

Reactions of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Although the procedures described here all use $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ as starting material, similar results were obtained with $[Rh_2(\mu\text{-}OCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ and $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ as precursors.

With Carboxylic Acids. Preparation of $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (5, R = H; 6, R = CH_3; 7, R = CF_3; 8, R = CH_2Cl; 9, R = $CHCl_2$; 10, R = CCl_3). A solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.25 g, 0.21 mmol) in 5 mL of dichloromethane was treated with 0.05 mL of the appropriate carboxylic acid, resulting in an immediate color change from yellow to deep red. Careful addition of diethyl ether resulted in the deposition of red crystals of the various products in excellent yields. Recrystallization of the complexes was from dichloromethane–diethyl ether.

For the preparation of the chloroacetates **8**–**10**, the above procedure was modified slightly with the addition of 3 equiv of acid for R = CH_2Cl and $CHCl_2$ and only 1 equiv in the case of R = CCl_3. The addition of excess Cl_3CCO_2H results in the formation of $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (60%).

With DMA·HX. Preparation of $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (X = Cl, Br; 11, X = I). To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.29 g, 0.17 mmol) in 10 mL of dichloromethane was added 1.0 equiv of solid DMA·HX. A red-orange solution (red for X = I) immediately resulted, the addition of diethyl ether to which resulted in the deposition of orange crystals. Recrystallization was from dichloromethane–diethyl ether. In the case X = Cl and Br, characterization was by comparison of the physical and chemical properties of the product with those of authentic samples.[1,5]

Substitution Reactions of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ and $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Synthesis of $[RhX(CO)(dppm)]_2$ (X = NCO; 12, X = NCS). To a solution of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.20 g, 0.16 mmol) in 10 mL of acetone was added 4.0 equiv of either KNCO or NH_4NCS dissolved in a minimum of water or acetone, respectively. The solution immediately turned red-orange and deposited the red-orange or golden-yellow product, which was removed by filtration and washed with water followed by ethanol. Recrystallization of small portions of the sparingly soluble products could be achieved from dichloromethane–diethyl ether. Characterization of $[Rh(NCO)(CO)(dppm)]_2$, formed in 70% yield, was by comparison with an authentic sample.[5]

Synthesis of $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (13, X = NCO; 14, X = NCS; 15, X = SCN). $[Rh_2(\mu\text{-}NCO)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Method A: To a solution of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.15 g, 0.12 mmol) in 5 mL of acetone was added KNCO (0.0098 g, 0.12 mmol) dissolved in a minimum of water. The addition of diethyl ether to the resultant yellow-orange solution precipitated the product, which was removed by filtration and washed with diethyl ether. Recrystallization from dichloromethane–diethyl ether gave bright yellow crystals of the complex.

Method B: To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.10 g, 0.085 mmol) dissolved in a dichloromethane–acetone mixture (5 mL; 1:4 v/v) was added 0.07 mL (4 drops) of 70% $HClO_4$ simultaneously with KNCO (0.0069 g, .085 mmol) dissolved in a minimum quantity of water. After the mixture was stirred for ca. 5 min, the product was crystallized by the addition of diethyl ether. Recrystallization of the product from dichloromethane–diethyl ether yielded bright yellow crystals.

$[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Method A: To a solution of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.25 g, 0.20 mmol) in 5 mL of dichloromethane was slowly added a solution of NH_4NCS (0.0153 g, 0.20 mmol) in 10 mL of acetone. After it was stirred for 25–30 min, the solution was filtered to remove $[Rh(NCS)(CO)(dppm)]_2$ and diethyl

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(5) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228.

ether added to the filtrate to precipitate the product, still contaminated with some of the neutral complex (0.16 g, ca. 67%). The yellow-orange crude material was purified by successive fractional dissolution–recrystallization cycles (dichloromethane–diethyl ether) until pure yellow in color, at which point the absence of a band at 2077 cm^{-1} in the infrared spectrum indicated that the product was free of $[Rh(NCS)(CO)(dppm)]_2$. Usually two to three cycles were necessary, resulting in overall yields of less than 55%, depending upon the scale used.

Method B: To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.10 g, 0.085 mmol) in 5 mL of dichloromethane–acetone (1:4 v/v) was added NH_4NCS (0.0065 g, 0.085 mmol) dissolved in 2 mL of acetone containing 0.07 mL of 70% $HClO_4$. The solution immediately turned orange, and on the addition of diethyl ether, a bright yellow crystalline material precipitated. The product was filtered and recrystallized from dichloromethane–diethyl ether as bright yellow crystals.

$[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$. To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.20 g, 0.17 mmol) in 5 mL of dichloromethane was added NH_4NCS (0.0129 g, 0.170 mmol) dissolved in 10 mL of acetone. The solution immediately turned dark red in color and on stirring deposited $[Rh(NCS)(CO)(dppm)]_2$ in 15–20% yield. After filtering, the filtrate was reduced in volume to ca. 7–8 mL, and upon addition of excess diethyl ether, an orange precipitate was obtained. Recrystallization from dichloromethane–diethyl ether yielded the product as an orange microcrystalline solid.

With Excess N_3^-. Preparation of $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (16). Method A: To a solution of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.15 g, 0.12 mmol) in 10 mL of acetone was added a solution of NaN_3 (0.032 g, 0.49 mmol) in a minimum of water. Addition of diethyl ether to the resultant yellow-orange solution yielded a crude yellow-orange product, which was removed by filtration and washed with water and diethyl ether. Recrystallization from dichloromethane–diethyl ether gave the product in the form of lustrous bright yellow plates.

Method B: To a solution of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.10 g, 0.085 mmol) dissolved in 5 mL of dichloromethane–acetone (1:4 v/v) was added NaN_3 (0.213 g, 0.328 mmol) dissolved in a minimum quantity of water to which was added 0.07 mL of 70% $HClO_4$. The solution was stirred for 5 min and the product isolated by the addition of diethyl ether. Recrystallization was as above.

Reactions. $[Rh_2(\mu\text{-NCS})(CO)_2(\mu\text{-dppm})_2]ClO_4$ with NH_4NCS. To a solution of $[Rh_2(\mu\text{-NCS})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.050 g, 0.042 mmol) in 5 mL of dichloromethane was added NH_4NCS (0.0032 g, 0.042 mmol) in 10 mL of acetone. The solution immediately turned red, and a golden yellow product deposited on stirring. The product, identified as $[Rh(NCS)(CO)(dppm)]_2$, was separated by filtration, washed with water and ethanol, and dried in vacuo; yield 0.0413 g (86%).

$[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with NH_4NCS. To a solution of $[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.100 g, 0.084 mmol) in 5 mL of dichloromethane was added NH_4NCS (0.0064 g, 0.084 mmol) in 10 mL of acetone. The solution immediately turned red and deposited a golden yellow precipitate of $[Rh(NCS)(CO)(dppm)]_2$, which was worked up in the above fashion; yield 0.080 g (83%).

Results and Discussion

Analytical, infrared, and NMR data for all new complexes are summarized in Tables I and II.

A-Frame Complexes with Bridging Oxygen Donor Ligands. *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$, in methanol suspension, reacts with freshly prepared sodium methoxide to yield a yellow solution that on addition of excess $NaClO_4$ deposits crystals of $[Rh_2(\mu\text{-OMe})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**1**). A similar procedure using ethanol yields the ethoxide analogue, $[Rh_2(\mu\text{-OEt})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**2**). Both **1** and **2** are readily characterized as typical A-frame complexes via infrared and NMR spectroscopy. Band envelopes in the $\nu(CO)$ region of the infrared spectra of **1** and **2** are virtually identical with that observed for the cation $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]^+$. In dichloromethane solution, the main peak at ca. 1982 cm^{-1} is accompanied by a higher frequency shoulder at ca. 1993 cm^{-1}. These values are somewhat lower than those observed for the halogen-bridged A-frame complexes, as is often found for alkoxide and hydroxide complexes. The only infrared evidence for coordinated alkoxide ligands occurs in the spectrum of **1**, where a weak band, assigned to the asymmetric CH stretching mode of the methoxide group, occurs at 2803 cm^{-1}. Such a band is frequently characteristic of methoxide complexes.[6]

Table I. Analytical and Physical Data for Complexes

complex	% found (% calcd) C	H	P	others	mp,[a] °C	% yield[b]	equiv conduct[c]
$[Rh_2(\mu\text{-}OCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$[e] (**1**)	53.40 (53.44)	3.98 (4.02)	10.75 (10.30)		190 dec	77, 79	43.0[d]
$[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**2**)	54.91 (55.19)	4.28 (4.20)	10.92 (10.54)		220 dec	85, 87	43.2[d]
$[Rh_2(\mu\text{-OH})(CO)_2(\mu\text{-dppm})_2)]ClO_4$ (**3**)	54.20 (54.45)	3.98 (3.96)	9.77 (10.80)	Cl, 3.18 (3.09)	215 dec	85	44.6[d]
$[Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (**4**)	55.88 (56.72)	4.22 (4.30)	11.41 (11.25)	Cl, 3.06 (3.22)	>176 dec	75–85	4.83[d]
$[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**5**)	54.42 (54.17)	3.60 (3.86)	10.68 (10.54)		195 dec	90	126
$[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**6**)	54.63 (54.55)	3.96 (3.98)	10.91 (10.42)		230 dec	95	121
$[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**7**)	52.11 (52.18)	3.49 (3.57)	10.24 (9.97)	F, 5.09 (4.58)	240 dec	95	115
$[Rh_2(\mu\text{-}O_2CCH_2Cl)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**8**)			...			89	123
$[Rh_2(\mu\text{-}O_2CHCl_2)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**9**)			...			79	126
$[Rh_2(\mu\text{-}O_2CCCl_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**10**)			...			71	117
$[Rh_2(\mu\text{-I})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**11**)	49.89 (49.68)	3.47 (3.53)	10.45 (9.86)		260 dec	90	115
$[Rh(NCS)(CO)(dppm)]_2$ (**12**)	56.48 (56.56)	3.71 (3.87)	...	N, 2.47 (2.44); S, 6.08 (5.59)	205 dec	96	
$[Rh_2(\mu\text{-NCO})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**13**)	54.31 (54.29)	3.78 (4.11)	...	N, 1.21 (1.19)	265 dec	70, 74	119
$[Rh_2(\mu\text{-NCS})(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**14**)	53.39 (53.57)	3.66 (3.73)		N, 1.21 (1.19); S, 2.56 (2.70)	205 dec	<55, 85	117
$[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**15**)	53.38 (53.57)	3.83 (3.73)	...	N, 1.52 (1.19); S, 2.90 (2.70)	185 dec	65–70	117
$[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**16**)	53.18 (53.29)	3.63 (3.78)	10.78 (10.57)	N, 3.50 (3.59)	204 dec	78, 92	117

[a] dec = melts with decomposition. [b] Where two yields are quoted, the values correspond to methods A and B, respectively. [c] In $cm^2\ \Omega^{-1}\ equiv^{-1}$ values obtained in acetone solution unless indicated otherwise. [d] CH_2Cl_2 solution. [e] Dichloromethane hemisolvate; $\delta(^1H\ (CH_2Cl_2)) = 5.32$ (s, 1 H).

Table II. Infrared and $^{31}P\{^1H\}$ and ^1H NMR Data

compd	$\nu(CO)$,[a] cm^{-1}	others,[b] cm^{-1}	$\delta(^{31}P)$[c]	$\delta(^1H)$ (assgnt)[d]
$[Rh_2(\mu\text{-}OCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (1)	1993 sh, 1982 vs	$\nu(CH)$ 2802 w	20.64 (128.1)	3.37 (s, OCH_3), 4.05, 3.22 m (CH_2)
$[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (2)	1992 sh, 1981 vs		20.67 (128.2)	0.62 (t, CH_3), 3.32 (q, OCH_2) 4.15, 3.34 (m, CH_2)
$[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (3)	1984 vs, 1978 sh	$\nu(OH)$ 3619 w	20.65 (128.1)	−0.13 (quintet, OH), 4.06, 3.24 (m, CH_2)
$[Rh_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (4)	1976 sh, 1966 vs	$\nu(OH)$ H_2O, 3670, 3400, 3200 w, br	20.79 (130.1)	3.75 (s, OH), 1.71 (s, H_2O), 5.29, 3.06 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (5)	2001 vs, 1991 s	$\nu(CO_2)$ 1568 s, $\nu(CH)$ 1352 m	23.83 (125.4)	4.05, 3.23 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (6)	2001 vs, 1985 s	$\nu(CO_2)$ 1545 m	23.00 (126.3)	0.73 (s, CH_3), 3.95, 3.43 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (7)	2009 vs, 1996 s	$\nu(CO_2)$ 1634 s	23.25 (122.4)	3.93, 3.13 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CCH_2Cl)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (8)	2002 vs, 1992 s	$\nu(CO_2)$ 1567 s, 1418 m	23.39 (125.1)	2.58 (s, CH_2Cl), 3.39, 3.80 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CCHCl_2)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (9)	2004 vs, 1993 sh	$\nu(CO_2)$ 1602 s, 1402 m	24.00 (124.0)	4.82 (s, $CHCl_2$), 3.15, 3.96 (m, CH_2)
$[Rh_2(\mu\text{-}O_2CCCl_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (10)	2005 vs, 1995 sh	$\nu(CO_2)$ 1625 s, 1376 s	24.77 (123.3)	2.97, 4.02 (m, CH_2)
$[Rh_2(\mu\text{-}I)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (11)	2003 s, 1991 vs		17.31 (108.6)	3.30, 4.60 (m, CH_2)
$[Rh(NCS)(CO)(dppm)]_2$ (12)	1994 vs[b]	$\nu(CN)$ 2077 s, $\nu(CS)$ 831 w		
$[Rh_2(\mu\text{-}NCO)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (13)	2003 sh, 1995 vs	$\nu(CO)$ 2196 vs	19.95 (117.0)	3.60, 3.88 (m, CH_2)[f]
$[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (14)	2005 sh, 1996 vs	$\nu(CN)$ 1952 s, $\nu(CS)$ 872, 842 w	21.18 (115.8)	3.51, 3.73 (m, CH_2)[f]
$[Rh_2(SCN)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (15)	1996 vs, 1952 w	$\nu(CN)$ 2073 m	23.0[e]	3.62, 3.89 (m, CH_2)[f]
$[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (16)	2002 sh, 1995 vs	$\nu(N_3)$ 2077 s	20.20 (119.7)	3.58, 3.81 (m, CH_2)[f]

[a] Recorded in CH_2Cl_2 solution unless noted otherwise. [b] Recorded as Nujol mulls. [c] ^{31}P chemical shifts relative to external 85% H_3PO_4, positive shifts downfield. $|^1J(RhP) + {}^xJ(RhP)|$ in parentheses. [d] ^1H chemical shifts relative to internal Me_4Si. Resonances due to phenyl protons (7.0–7.5 ppm) have not been included. [e] See text. [f] Obtained at 360 MHz.

Nevertheless, the presence of coordinated alkoxide groups is confirmed by the ^1H NMR spectra of **1** and **2**, which also established the sensitivity of these bridging groups toward hydrolysis. Thus, the ^1H NMR spectrum of **1** indicated the presence of both coordinated methoxide (3.37 ppm) and free methanol (3.44 ppm). A more clear demonstration of this lability was afforded by the ^1H NMR spectrum of **2**, which displayed triplets at 1.18 ppm (^2J = 7 Hz) and 0.65 ppm (^2J = 7 Hz) due to free and coordinated ethyl groups, respectively. The corresponding methylene quartets both overlapped the dppm methylene multiplets at ca. 3.5 ppm although it did prove possible to assign a value of 3.32 ppm for the shift of the methylene protons of the coordinated ethoxide. On addition of D_2O, hydrolysis of the alkoxide groups in **1** and **2** was immediate and signals due only to the free alcohol remained. The facile hydrolysis of **1** and **2** suggested that the complex $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**3**) was being formed. Accordingly, a sample of **2** was reacted with $HClO_4$ in dichloromethane–ethanol, and upon addition of diethyl ether, yellow crystals of **3** were obtained. A similar procedure employing $DClO_4$ in C_2H_5OD allows isolation of $[Rh_2(\mu\text{-}OD)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Direct spectroscopic evidence for the hydroxide group in **3** is seen in both the infrared spectrum (3619 w, $\nu(OH)$; 2672 w, $\nu(OD)$) and the ^1H NMR spectrum (−0.13 ppm (q, $^3J(H-P)$ = 3.1 Hz, 1 H)). There is no evidence for hydrogen–rhodium coupling in the ^1H NMR signal attributed to the μ-OH proton. The quintet shows a distinct 1.0:1.5:1.0 intensity ratio for the innermost lines, which is noticeably different from the 1.0:1.33:1.0 ratio to be expected if the quintet observed is merely the inner five lines of a septet resulting from having $^3J(H-P) \approx {}^2J(H-Rh)$. Similar behavior is exhibited by $[(C_5Me_5)_2Rh_2(\mu\text{-}OH)_3]BPh_4$, with the NMR signal of the hydroxyl protons remaining as a singlet down to −60 °C.[7] As expected, the addition of D_2O to solutions of **3** results in exchange of the OH proton, as evidenced by the disappearance of the multiplet at −0.13 ppm. As required by the assignment of A-frame type structures to complexes **1–3**, the $^{31}P\{^1H\}$ NMR spectra indicate a chemically equivalent environment for all four phosphorus atoms. The typical AA′A″A‴XX′ pattern exhibited by these complexes was also exhibited by all other complexes isolated in this study. No attempt has been made to simulate these spectra since confirmation of the structural assignments only was sought, for which only the chemical shift and the separation of the two major lines ($|^1J(Rh-P) + {}^xJ(Rh-P)|$) was deemed necessary. The $^{31}P\{^1H\}$ NMR spectra of compounds **1–3** are virtually superimposable in both pattern and position. The ^1H NMR spectra of the solutions of **1** and **2** used to obtain the ^{31}P spectra confirmed that some hydrolysis had taken place. This, coupled with the fact that no broadening was observed, must mean that the ^{31}P chemical shifts for **1** and **2** are essentially the same as that for **3**, regardless of the rate of OH/OR exchange.

If the procedure for the preparation of **1** and **2** is modified by using $Na_2CO_3\cdot 10H_2O$ as the base and eliminating the addition of $NaClO_4$, a yellow crystalline solid analyzing approximately as $[Rh_2(OH)Cl(CO)_2(dppm)_2]\cdot H_2O$ can be isolated. Both infrared and $^{31}P\{^1H\}$ NMR spectra favor the typical A-frame geometry for this complex. However, the compound is essentially nonconducting in dichloromethane (Λ_M = 4.9 Ω^{-1} cm^2 equiv^{-1}) by comparison to complexes **1–3**, which are 1:1 electrolytes (Λ_M = 43.0–44.6 Ω^{-1} cm^2 equiv^{-1} in CH_2Cl_2). On the basis of this and the evidence below, and by analogy with the recently structurally characterized iridium analogue,[8] this complex has been assigned the formula $[Rh_2(\mu\text{-}OHCl)(CO)_2(\mu\text{-dppm})_2]\cdot H_2O$ (**4**) in which the chloride ion is hydrogen bound to the bridging hydroxide ligand. Unlike the infrared spectra of **3**, spectra of **4** do not exhibit sharp maxima attributable to $\nu(OH)$. Instead, broad, medium

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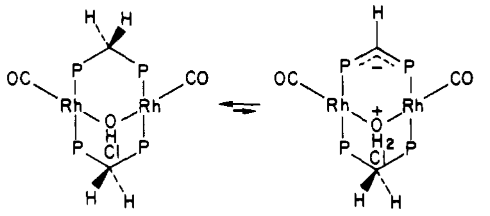
(6) Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149.
(7) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127.
(8) Cowie, M., personal communication.

to weak intensity bands at ca. 3670, 3400, and 3200 cm^{-1} (Nujol) are observed that undoubtedly originate from the hydrogen-bound OH and the clathrate water molecule, although no definite assignment has been attempted. In CD_2Cl_2 solution, the ^1H NMR spectrum of **4**, in addition to resonances due to phenyl (7.70 ppm (m, 45 H)) and methylene protons (5.29 ppm (m, 2.0 H), 3.06 ppm (m, 2.1 H)), exhibits resonances at 3.78 ppm (s, br, 1.1 H) and 1.71 ppm (s, br, 1.8 H) attributable to the OHCl and H_2O protons, respectively. This assignment is supported by the addition of D_2O since the resonance at 3.78 ppm vanishes and the resonance at 1.71 ppm changes in intensity and shifts approximately 0.08 ppm. Interestingly, prolonged exposure of the solutions of **4** to D_2O (typically ca. 1 h) results in exchange of the dppm methylene protons. Attempts to perform similar exchange reactions with other A-frame complexes such as $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]^+$ (X = OH, OR, Cl, etc.) met with failure, indicating that the bridging OHCl group is necessary. It seems probable that this exchange process occurs via tautomerism of the type depicted in eq 1, followed by deuterium exchange both at the bridging OHCl and at OH_2Cl groups and direct attack of D_2O on the bis(diphenylphosphino)methanide ligand in **4a**. The latter process has been observed directly in the reaction of $Pt(n\text{-}C_4H_9)(PEt_3)(PPh_2CHPPh_2)$ with water.[9] A similar deuterium-exchange reaction has also been observed with $[(C_5Me_5)_2Rh_2(\mu\text{-}OH)_3]^+$, providing further evidence of the extreme basicity of such bridging hydroxide groups.[7]



4 **4a** (1)

Reactions of $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = H, Me, Et) with Acids. All three oxygen-bridged A-frame complexes **1**–**3** react with coordinating acids with replacement of the bridging ligand. It did prove generally more convenient, however, to use the ethoxide **2** as the common precursor in these reactions.

Compound **2** reacts with excess carboxylic acids in dichloromethane solution to yield the red, bridging carboxylate complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**5**–**10**, R = H, CH_3, CF_3, CH_2Cl, $CHCl_2$, CCl_3). During the course of this investigation reports detailing independent syntheses of **5**[4] and **6**[10] (as PF_6^- and BF_4^- salts) have appeared. Neither infrared nor $^{31}P\{^1H\}$ NMR spectra can unambiguously distinguish between the monodentate and bidentate bridging modes for the carboxylate groups in these complexes. However, the existence of a proximity shifted charge-transfer band[11] at ca. 490 nm (CH_2Cl_2 solution) in all six compounds favors the bidentate mode. The shift to longer wavelengths for this band (cf. ca. 430 nm for **2**) implies a greater interaction of the metal d_{z^2} orbitals, which in turn can be explained by either a close approach of the metal centers and/or increased coplanarity of the metal coordination planes. Both of these effects are expected to be favored by having the carboxylate ligand bidentate bridging. A recently completed X-ray analysis of **7** confirms this mode of coordination for the trifluoroacetate group.[12] The physicochemical properties of **5** and **6** more or less coincide with those already published,[4,10] whereas **7** is characterized by an extreme lability not observed in its conjenors. For example, **7** readily undergoes hydrolysis or alcoholysis to yield compounds **1**–**3**, and the trifluoroacetate ion can be readily substituted with other anions (vide infra). Even dichloromethane solutions of **7** undergo exchange when in contact with sodium chloride cell windows to eventually yield $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-dppm})_2]ClO_4$, identified by the appearance of $\nu(CO)$ bands at 2005 (s) and 1989 (vs) cm^{-1}. The chemistry of compounds **8**–**10** has not been studied extensively, and their characterization has been by spectroscopic means only.

Compound **2** reacts with 1 equiv of the hydrogen halides, added in the form of their *N*,*N*-dimethylacetamide adducts, to yield the halogen-bridged A-frame complexes $[Rh_2(\mu\text{-}X)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (X = Cl, Br, I). Those with X = Cl[1] and Br[5] have been reported and characterized elsewhere, but the complex with X = I (**11**), although prepared by other groups working in this field, has not been reported.[9] As anticipated, complex **11** is spectroscopically similar to its chloro and bromo analogues. Cowie et al. have observed a cation isomeric with the cation in **11**, viz. $[Rh_2(\mu\text{-}CO)I(CO)(\mu\text{-dppm})_2]^+$, when in association with I^- as the counterion.[2] It was of interest, therefore, to see whether or not **11** would isomerize in solution. Accordingly a dichloromethane solution of **11** was sealed in an NMR tube and the $^{31}P\{^1H\}$ NMR spectrum obtained after 24 h. No evidence was seen for $[Rh_2(\mu\text{-}CO)I(CO)(\mu\text{-dppm})_2]ClO_4$. Instead, signals attributable to two new symmetric species appeared at the expense of the signal due to **11**. The lower field of the two new signals at 26.88 ppm, $|^1J(Rh\text{-}P) + {}^xJ(Rh\text{-}P)| = 93.6$ Hz, agrees favorably with that reported for $[Rh_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]I$ (26.6 ppm, $J = 92.7$ Hz),[2] whereas the new signal to higher field (19.3 ppm, $J = 114.0$ Hz) compares most favorably with that reported for the complex $[Rh_2I_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$.[13] The infrared spectrum of the solution reflected these changes with a new band appearing at 1870 cm^{-1} indicative of a bridging carbonyl. No $\nu(CO)$ band at lower frequency was observed, however, in keeping with the observation that $[Rh_2I_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$ appeared to be formed only in trace amounts (less than 10%).

Pseudohalide-Bridged A-Frame Complexes. It was initially anticipated that compounds **1**–**3** would react with pseudohalide salts under acidic conditions to yield pseudohalide-bridged A-frame complexes. This indeed proved to be the case, but for reasons of convenience, only **2** was used extensively for this purpose. Furthermore, it was found that the unusual lability of **7** also enabled a number of pseudohalide complexes to be synthesized via simple substitution reactions, sometimes in better yield. Thus, for example, reacting **7** with excess KOCN in aqueous acetone results in the immediate formation of $[Rh(NCO)(CO)(dppm)]_2$, which was characterized by a comparison of its physical properties with those of a genuine sample prepared by the reaction of $[RhCl(COD)]_2$ with KOCN, carbon monoxide, and dppm in methanol–acetone solution.[5] A similar reaction of **7** with excess NH_4NCS produces an insoluble, golden yellow material that we have formulated as $[Rh(NCS)(CO)(dppm)]_2$ (**12**), on the basis of elemental analysis and by analogy with the cyanate system. The infrared spectrum of **12** supports this formulation,[14] with bands attributable to $\nu(CN)$ and $\nu(CS)$ of the N-bound thiocyanate groups occurring at 2077 (s) and 831 (s) cm^{-1} (Nujol), respectively. Furthermore, the absorptions due to the perchlorate ion are no longer present. Unlike $[Rh(NCO)(CO)(dppm)]_2$, which has $\nu(CO)$ at 1969 (vs) cm^{-1}, **12** exhibits a single sharp $\nu(CO)$ absorption at 1994 (vs) cm^{-1}. Thus, **12** exhibits almost the same infrared spectrum as the compound previously reported as $[Rh(NCS)_2(CO)_4(dppm)_2]$[5] ($\nu(CN) = 2073$, $\nu(CS) = 830$, $\nu(CO) = 1992$ cm^{-1}), suggesting that the complexes may in fact be identical. Accordingly, a sample of $[Rh_2(NCS)_2(CO)_4(dppm)_2]$ was prepared according to the literature method (analogous to that for $[Rh(NCO)(CO)(dppm)]_2$), and on our instrumentation

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[9] Browning, J.; Bushnell, G. W.; Dixon, K. R. *J. Organomet. Chem.* **1980**, *198*, C11.

[10] Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.

[11] Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840.

[12] Cameron, T. S., personal communication.

[13] Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.

[14] Bailey, R. A.; Kozak, S. L.; Michelson, T. W.; Mills, W. N. *Coord. Chem. Rev.* **1971**, *6*, 407 and references therein.

proved to have exactly the same physical properties and ν(CN), ν(CS), and ν(CO) values as exhibited by **12**. Since compound **12** is prepared in 96% yield from a dicarbonyl precursor in the absence of carbon monoxide, it appears that $[Rh_2(NCS)_2(CO)_4(dppm)_2]$ should be reformulated.

The addition of 1 equiv of KOCN to either **7** or **2** (excess $HClO_4$ being added in the latter case) results in the formation of the A-frame complex, $[Rh_2(\mu\text{-}NCO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (**13**). The presence of the N-bound cyanate group is affirmed by the presence of an absorption band at 2196 (vs) cm^{-1} in the infrared spectrum attributable to ν_s(NCO), although the corresponding ν_{as}(NCO) band expected at around 1300–1350 cm^{-1} proved too weak to identify unambiguously. The ν(CO) band envelope in **13** is typical of that normally seen for A-frame complexes bridged by halide ions, for example, and the band positions of 2003 and 1995 cm^{-1} (CH_2Cl_2 solution) are also quite typical for this class of complex. The $^{31}P\{^1H\}$ NMR spectrum of **13** is also consistent with the A-frame structure proposed. The low-temperature $^{31}P\{^1H\}$ NMR spectra of **13** and its thiocyanate analogue (**14**, vide infra) were also run in an attempt to distinguish between formulations for these complexes containing either symmetrically bridging NCX ligands or fluxional, terminal NCX groups leading to equivalent phosphorus environments. No change was observed in the spectra of either complex at −70 °C. There is, however, ample precedent for symmetrically N-bridging cyanate ions, and the value for ν_s(NCO) of 2196 cm^{-1} obtained with **13**, is well within the range quoted for this vibration in such compounds.[14] The ^1H NMR spectrum of **13**, and indeed of all the heterocumulene-bridged complexes reported herein, is unusual in that the signals due to the nonequivalent methylene protons cannot be resolved at 80 MHz. At 360 MHz, however, the two characteristic complex multiplets can be identified around 3.6 and 3.8 ppm.

The addition of 1 equiv of NH_4NCS to **7** in dichloromethane–acetone solution results in a relatively slow reaction that sees the deposition of some $[Rh(NCS)(CO)(dppm)]_2$ from solution. After filtering, the addition of diethyl ether to the solution results in precipitation of a yellow-orange product. This material can be separated by repeated fractional dissolution into more **12** and yellow $[Rh_2(\mu\text{-}NCS)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (**14**). Unfortunately, the lengthy separation procedure required means that overall yields of **14** are low, usually 55%. The infrared spectrum of **14** in the solid state is unusual but in support of the bridging thiocyanate being N bound. In the carbonyl stretching region, three bands at 1997 (s), 1984 (vs), and 1957 (s) cm^{-1} are observed, although in dichloromethane solution the highest frequency band is less clearly defined and maxima at 2005 (sh, m), 1996 (vs), and 1952 (s) cm^{-1} can be identified. The band envelope of the 2005-, 1996-cm^{-1} pair is closely comparable to that of other A-frame complexes, implying that the band at 1952 cm^{-1} might be attributed to ν(CN), despite its rather low value. This assignment was confirmed by preparing $[Rh_2(\mu\text{-}NCS)(^{13}CO)_2(\mu\text{-}dppm)_2]ClO_4$ (**14a**) from labeled **2**. Solution infrared spectra of **14a** exhibit no bands other than $\nu(^{13}CO)$ at 1952 (vs) cm^{-1}, which overlaps the ν(CN) band at 1952 cm^{-1}. To the best of our knowledge, there is only one other example of a bridging N-bound thiocyanate.[15] In this complex, $(n\text{-}Bu_4N)_3[Re_2(NCS)_{10}]$,[15] two thiocyanate ligands bridge two rhenium atoms in a symmetric fashion. Both bridging ligands in this complex are linear, and despite the centrosymmetric structure of the anion, two strong absorptions at 1920 and 1885 cm^{-1} are attributed to these ligands. In light of this example, and the lower ν_s(NCO) range exhibited by N-bridging cyanate ligands,[14] the ν(CN) value of 1952 cm^{-1} in **14** seems perfectly reasonable. The existence of an N-bound thiocyanate ligand in **14** is also indicated by the appearance of two sharp but weak bands at 872 and 842 cm^{-1}, both of which lie in the region normally associated with ν(CS) of N-bound thiocyanate groups. Neither of these bands occurs in the other A-frame complexes examined in this study, suggesting that both can be assigned to ν(CS). Although splitting of ν(CS) in this fashion is not common, it has been observed occasionally.[14] Another interpretation of these two bands could have one assigned to ν(CS) and the other to the first overtone of δ(NCS), which in principle could also occur in this region. All attempts to assign a structure to **14** not involving a thiocyanate group have been rejected by noting that both qualitative and quantitative elemental analyses support the proposed formulation and that reacting **14** with exactly 1 equiv of NH_4NCS yields $[Rh(NCS)(CO)(dppm)]_2$ in 86% yield.

Reacting solutions of **2** with 1 equiv of NH_4NCS in the presence of excess $HClO_4$ also gives **14** in what appears to be the method of choice, since the workup is not complicated by the concomitant formation of **12**. However, reacting complex **2** with 1 equiv of NH_4NCS in dichloromethane–acetone solution in the absence of excess $HClO_4$ results in an immediate color change and the prompt deposition of **12** in ca. 14–20% yield. The addition of diethyl ether to the resultant solution yields an orange solid analyzing for $[Rh_2(SCN)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (**15**) in good yield. Both infrared and $^{31}P\{^1H\}$ NMR spectra establish that this complex differs from its isomer **14**. In the solid state, **15** exhibits bands at 2073 (m), 1987 (vs), and 1970 (sh) cm^{-1}. The band at 2073 cm^{-1} can be attributed to ν(CN) of the S-bound thiocyanate, and as often found for other thiocyanate complexes, it is at a higher frequency than the analogous band in **14**.[14] Also, no bands in the 800–900-cm^{-1} region attributable to ν(CS) are observed, in keeping with the S-bound formulation. The ν(CO) bands at 1987 and 1970 cm^{-1} are in the range normally associated with simple A-frame complexes such as **11**. Freshly made dichloromethane solutions of **15** exhibit infrared maxima at 2078 (m), 1996 (vs), and 1952 (w) cm^{-1}. The weak band at 1952 cm^{-1} we attribute to a small amount of the N-bound isomer **14**, although the possibility exists that it is an intrinsic feature of the spectrum of **15**. The maximum at 1996 cm^{-1} is asymmetric although it has no distinct shoulders present that can be assigned approximate values.

The infrared evidence is therefore not inconsistent with a simple A-frame formulation for **15**, in the solid state at least. The $^{31}P\{^1H\}$ NMR evidence, however, indicates that formulation of **15** as an A-frame complex is not appropriate. Spectra of freshly prepared solutions of **15** indicate the presence of two major and three minor components at −40 °C. One of the two major components is clearly the starting material **2**, present as a result of the formation of $[Rh_2(NCS)_2(CO)_2(dppm)_2]$ after the addition of 1 equiv of $(NH_4)NCS$. The other major component, easily the dominant product, gives rise at this temperature to a pattern, centered at ca. 23 ppm, attributed to an AA′BB′XY spin system by comparison with spectra derived from unsymmetrical species such as $[Rh_2Cl_2(CO)(SCNMe_2)(\mu\text{-}dppm)_2]BF_4$.[8] The minor products are present in considerably smaller quantities, and all appear to be symmetrical A-frame species. One of these ($\delta^{31}P$ = 20.8, $|^1J(Rh\text{–}P) + {}^xJ(Rh\text{–}P)|$ = 114.9 Hz) is probably the N-bound isomer **14**, and a second at ca. 16.8 ppm appears to be a byproduct, since its relative abundance varies considerably from one preparation to the next. The third minor component appears at $\delta(^{31}P)$ = 18.37, with $|^1J(Rh\text{–}P) + {}^xJ(Rh\text{–}P)|$ = 113.9 Hz. When the mixture is warmed to room temperature, changes occur in the spectrum consistent with some dynamic process taking place. The signals arising from the starting material **2** and the minor product at 16.8 ppm suffer no change except for a slight change in chemical shift. The multiplet at 23 ppm broadens extensively and loses all fine structure, and the multiplet at 18.37 does likewise. It was not possible to ascertain the fate of the signal at 20.8 ppm since it was buried by the broadened resonance at 23 ppm. Assuming that only two species are involved in the dynamic process taking place, these observations are not inconsistent with the following

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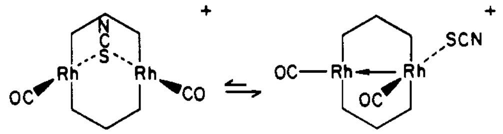
(15) Cotton, F. A.; Davison, A.; Ilsley, W. H.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 2719.

56 *Inorg. Chem.* **1985**, *24*, 56-61

equilibrium being responsible:



There is ample precedent for the nonbridged structure depicted above. For example, the $[Pt_2(CH_3)_3(\mu\text{-dppm})_2]^+$ cation[16] has been shown to possess a similar structure (albeit with a cis arrangement of phosphine ligands on one metal center), and a similar complex has been proposed as an intermediate in the A-frame inversion of $[Pd_2(CH_3)I(\mu\text{-I})(\mu\text{-dppm})_2]BF_4$.[17] The discomfort associated with identifying the expected S-bridged structure for **15** as the minor component of this equilibrium was somewhat alleviated for us by the observation that, to the best of our knowledge at least, no example of a stable, symmetrically S-bridged thiocyanate complex has been reported. It is also obvious, however, that the numerous different species identified in spectra of **15** and the observed tendency of this complex to decompose readily at room temperature admit interpretations other than that above. We have been attempting to grow single crystals of this complex for some time but without success. It appears that decomposition outpaces good crystal growth under all the conditions we have so far tried, and hence it may be some time before the true nature of **15** is verified.

Unlike the reactions with KOCN and NH_4NCS, the reaction of **7** or **2** with NaN_3 does not require the stoichiometry to be carefully controlled. Thus, solutions of **7** and acidified **2** react with excess NaN_3 to yield $[Rh_2(\mu\text{-}N_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**16**), in excellent yield. The infrared spectrum of **16** is closely comparable to those of the A-frame complexes described above with the exception of $\nu(N_3)$ at 2077 (s) cm^{-1}, and the $^{31}P\{^1H\}$ NMR spectrum is also consistent with the A-frame assignment. The absence of a neutral species in this reaction is somewhat surprising, but similar behavior has been observed in the reaction of $[RhCl(COD)]_2$ with NaN_3, dppm, and carbon monoxide.[5]

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Registry No. **1**, 91581-08-7; **2**, 91581-10-1; **3**, 91581-06-5; **4**, 91580-98-2; **5**, 93646-74-3; **6**, 93646-75-4; **7**, 93646-77-6; **8**, 93646-79-8; **9**, 93683-47-7; **10**, 93646-81-2; **11** (X = I), 93646-83-4; **11** (X = Cl), 93646-86-7; **11** (X = Br), 93646-87-8; **12** (X = NCO), 77010-18-5; **12** (X = NCS), 93646-88-9; **13**, 91581-01-0; **14**, 91581-03-2; **15** (isomer I), 91581-12-3; **15** (isomer II), 93646-85-6; **16**, 91581-00-9; *trans*-$[RhCl(CO)(dppm)]_2$, 22427-58-3.

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Modeling Macroscale Metal Vapor Reactions: Synthesis of Bis(η^6-naphthalene)titanium

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The interaction of metal vapors of Cr, V, and Ti with naphthalene, and selected naphthalene derivatives, has been studied by means of matrix-isolation UV-visible spectroscopy. The electronic spectra of the Cr and V products are analyzed in terms of their known bis(η^6-arene)metal conformations via a simple molecular orbital ordering scheme. On the basis of the data for Cr and V, the spectra of the Ti species appear to be best assigned to an analogous bis(η^6-naphthalene)titanium complex. Preliminary studies on the reactivity of this complex reveal that it is apparently thermally stable at 290 K under matrix conditions, although it exhibits high reactivity toward ether solvents even at 190 K.

Introduction

Metal vapor synthesis is now recognized as providing a valuable route to a wide range of organometallic complexes.[1] Indeed, a number of metal species have been generated from metal vapors for which no conventional synthesis exists. Molecules such as $(\eta^6\text{-}C_6H_{6-n}Me_n)_2M$ (M = Ti, Nb, Ta),[2,3] $(\eta^4\text{-}C_8H_{12})_2Fe$,[4] and $(\eta^6\text{-}C_6H_{6-n}Me_n)_2MPMe_3$ (M = Zr, Hf)[3,5] were unknown prior to their metal vapor preparations and still can be accessed only in this way.

Recently, it has been reported that naphthalene interacts with chromium, molybdenum, or vanadium vapors under macroscale synthetic conditions, by either cocondensation of reagents at 77 K or deposition of metals into solutions containing the aromatic molecule at 150 K, to give the corresponding bis(η^6-naphthalene)metal complexes.[6,7] This represents an important new area for study in metal vapor chemistry; no conventional route exists for the preparation of homoleptic (naphthalene)metal complexes (the well-known Fischer–Hafner synthetic scheme

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