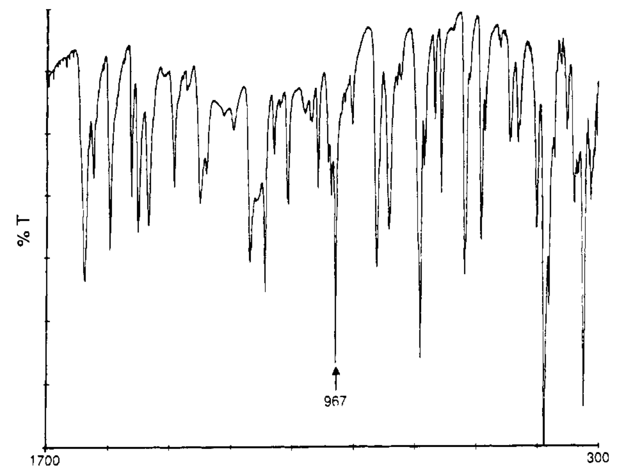

Figure 3. IR spectrum for the prism form of $V(O)L_2$.

Infrared spectra of both forms are presented, and show that the previous workers were in error in their assignment.

Experimental Section

Bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV) was prepared according to the procedure of Pasquali et al.[11] A yellow-brown solid was initially produced; upon recrystallization from carbon disulfide both yellow-brown prisms and needles were obtained, with the needle form predominating. Samples of the prism form and needle form were obtained by carefully separating individual crystals from the mixture and were sent for elemental analysis. Anal. Calcd for $VC_{26}H_{18}N_2O_3Cl_2$: C, 59.11; H, 3.43; N, 5.30; Cl, 13.42. Found (needle form): C, 57.91;[13] H, 3.41; N, 5.24; Cl, 13.41. Found (prism form): C, 59.13; H, 3.53; N, 5.25; Cl, 13.35.

Unit cell parameters of the prism form were obtained by mounting a suitable crystal on a Syntex P3 automated diffractometer. Least-squares refinement of the best angular positions for 10 independent reflections ($2\theta > 18°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å) yielded a monoclinic cell with $a = 10.973$ (6) Å, $b = 20.944$ (34) Å, $c = 9.931$ (9) Å, and $\beta = 99.50$ (6)°.

Infrared spectra of both the prism form and needle form in the solid state were recorded on a Nicolet 20 DXC Fourier-transform infrared spectrometer, using a Spectratech Model 300 continuously variable ATR attachment. Samples were finely ground and then mounted with double-sided tape. An angle of 60° was used to minimize interference by the tape. An IR spectrum was recorded for a carbon disulfide solution with the use of sodium chloride cells. Elemental analyses were performed by the Microanalysis Laboratory at the University of Massachusetts, Amherst, MA.

Results

Synthesis of bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV), subsequently referred to as $V(O)L_2$ (Figure 1), led to formation of both fine yellow-brown needles and brown prisms. The two forms were manually separated, and their IR spectra were recorded (Figures 2 and 3). The IR spectra of the two products are very similar between 1700 and 600 cm^{-1}, differing only in the position of the V–O stretch. For the needle form, a peak at 888 cm^{-1} can be assigned to this stretch. This agrees with the value of 885 cm^{-1} reported by Pasquali et al.[11] However, the IR spectrum of the prism form lacks this feature; instead, an intense peak at 967 cm^{-1} can be assigned to the V–O stretch. Minor differences in peak intensities are observed in the spectra below 650 cm^{-1}, where V–O and V–N stretches of the Schiff-base ligand occur.[4] Near 355 cm^{-1} there is a moderately strong peak present in the spectrum of the needle form, while the spectrum of the prism form shows two less intense peaks. The IR spectrum recorded for a carbon disulfide solution of the unseparated product mixture is also similar to the spectra recorded for the solid forms, except for peaks which may be assigned to the V–O stretch. In the solution spectrum there is no peak at either 967 or 888 cm^{-1}, but there is a peak at 988 cm^{-1} which is not present in the spectra recorded for the two solids.

Discussion

The unit cell parameters determined for the prism form isolated in this study ($a = 10.973$ (6) Å, $b = 20.944$ (34) Å, $c = 9.931$ (9) Å, and $\beta = 99.50$ (6)°) are in good agreement with values reported by Pasquali et al.[11] ($a = 11.08$ (2) Å, $b = 21.14$ (3) Å, $c = 10.06$ (2) Å, and $\beta = 99.0$ (2)°), indicating that the prism form of the product has the same structure as the form they reported. This form is monomeric and contains a vanadium which is five-coordinate.

The value for the V–O stretch of the prism form determined in this work, 967 cm^{-1}, falls in the range generally accepted for the vanadium–oxygen stretch in five-coordinate oxovanadium(IV) complexes, 910–1035 cm^{-1}.[1,2] This is quite different from the value reported by Pasquali et al. for the V–O stretch. It is possible that although the crystal structure reported by Pasquali et al. was of a single crystal of the monomeric prism form, their IR spectrum was recorded on the unseparated mixture obtained after recrystallization, which contains mostly the needle form, with the assumption that the structure of the needles was the same as that of the crystal used to obtain the structural data. Since the needle form predominated, they observed the V–O stretch at 885 cm^{-1}. In this study, the V–O stretch of the needle form was observed at 888 cm^{-1}. A shift in the V–O stretching frequency to below 900 cm^{-1} has been considered an indication of oxygen-bridging, V–O–V polymerization.[7-10] Therefore it seems likely that the needle form of $V(O)L_2$ is such a polymer. In carbon disulfide the product shows a V–O stretch at 988 cm^{-1}, indicating that the complex is monomeric in solution.

Thus it seems that the suggestion of Mathew et al.[8] that a low-frequency V–O stretch serve as a diagnostic test for oxygen bridging in vanadyl complexes is valid, since Pasquali et al.[11] were mistaken in their assignment of a V–O stretch for a monomeric, five-coordinate complex at 885 cm^{-1}.

Acknowledgment. I thank Joanne Stewart of Hope College for drawing my attention to this problem.

Registry No. $V(O)L_2$, 32065-25-1; $[V(O)L_2]_x$, 132014-35-8.

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[13] In the presence of vanadium, carbon analyses may be depressed due to formation of vanadium carbide. Therefore this value is lower than the true value.

Contribution from the Department of Chemistry,
University of Missouri—Columbia, Columbia, Missouri 65211

Reaction of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ with Trimethylphosphine and Nitrosonium Tetrafluoroborate: Solid-State Structures of $[Rh_2(\mu\text{-}Cl_2)(NO)_2(\mu\text{-dppm})_2](BF_4)_2$ and $RhCl(PMe_3)(dppm)$

Yuan-Wen Ge and Paul R. Sharp*

Received April 27, 1990

Introduction

Bridging bis(diphenylphosphino)methane (dppm) and bis(dimethylphosphino)methane (dmpm) complexes of Rh and Ir constitute a large area of bimetallic chemistry. The entry points for most of this chemistry are the face-to-face complexes $M_2(CO)_2Cl_2(\mu\text{-}L_2)_2$ (M = Ir or Rh, L_2 = dppm or dmpm).[1] These complexes are versatile synthetic precursors and have been used to prepare a diverse range of complexes.[1,2]

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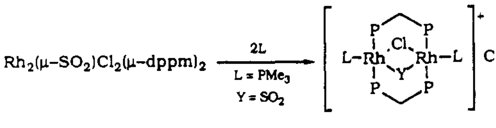
(1) Ir–dppm: (a) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637–1648. Rh–dppm: (b) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975–1981. Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119. Rh–dmpm: (c) Jenkins, J. A.; Ennett, J. P.; Cowie, M. *Organometallics* **1988**, *7*, 1845. (d) Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632–2640.

In this paper we report our attempts at preparing new Rh face-to-face complexes by the displacement of SO_2 from $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ (**1**)[3] by PMe_3 and NO^+.[4] Our interest in these complexes is as new starting materials for the preparation of CO-free analogues of the oxo,[5] imido, and amido[1d,6] complexes, which we have prepared from $M_2(CO)_2Cl_2(\mu\text{-}L_2)_2$.

Results

Reaction of 1 with PMe$_3$. Brown CH_2Cl_2 suspensions of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ (**1**) rapidly give deep purple solutions of $[Rh_2(\mu\text{-}SO_2)(\mu\text{-}Cl)L_2(\mu\text{-dppm})_2]Cl$ (**2**) when treated with 2 equiv of PMe_3 (eq 1, L = PMe_3) at −78 °C. Low-temperature ^{31}P and ^1H NMR spectroscopies of the reaction mixtures show **2** as the only product with signals characteristic of a symmetric *trans,trans*-dppm-bridged Rh dimer[1c,2b] with additional PMe_3 ligands. Conductivity measurements at −78 °C indicate a 1:1 electrolyte. FT-IR analysis of solid samples of **2**, obtained by removing the volatiles at low temperature, show SO_2 bands shifted to slightly lower energy from the parent complex **1**. Analysis of the volatiles show no free SO_2. This data is consistent with the structure shown in eq 1. The CO analogue of **2**, prepared in the same manner (CO addition of **1**), is believed to have the same ionic structure (L = CO).[3]



1 **2** (1)

Although solid samples of **2** are stable at room temperature, solutions of **2** are not stable above −30 °C. On being warmed above −30 °C, the purple solutions turn green and, at room temperature, brown. NMR spectra of the green solution suggest the formation of a single product with the same dppm to PMe_3 ratio as in **2** but with a much less symmetric structure. The same thermally unstable green product is obtained when 2 equiv of PMe_3 are added to THF solutions of **1** at −45 °C. The decomposed brown solutions contain, by ^{31}P NMR, the starting SO_2 complex **1** and small amounts of $OPMe_3$ as the only identifiable species.[7] Very broad, low-intensity signals are also observed.

In an alternate attempt to prepare the PMe_3 face-to-face complex $Rh_2Cl_2(PMe_3)_2(\mu\text{-dppm})_2$, dppm and PMe_3 were added to $[RhCl(COD)]_2$ (eq 2). The monomeric complex RhCl(PMe$_3$)(dppm) (**3**) was isolated. Complex **3** was characterized by an unexceptional X-ray crystal structure determination (supplementary material).

$$[\mathrm{RhCl(COD)}]_2 \xrightarrow[(2)\ 2\mathrm{PMe_3}]{(1)\ 2\mathrm{dppm}} \underset{\mathbf{3}}{2\mathrm{RhCl(PMe_3)(dppm)}} \qquad (2)$$

Table I. Crystallographic Data for $[Rh_2(\mu\text{-}Cl)_2(NO)_2(\mu\text{-dppm})_2](BF_4)_2\cdot 2CH_2Cl_2$ (**4**·$2CH_2Cl_2$)

formula	$C_{52}H_{48}B_2Cl_6F_8N_2O_2P_4Rh_2$
fw	1449.01
space group	$P2_1/n$ (No. 14)
a, Å	10.501 (5)
b, Å	19.092 (4)
c, Å	14.418 (7)
β, deg	90.69 (4)
V, Å^3	2890.4
Z	2
T, °C	−90
λ, Å	0.71069
d_{calc}, g·cm^{-3}	1.66
μ(Mo Kα), cm^{-1}	10.17
$R(F_o)$[a]	0.032
$R_w(F_0)$[b]	0.041

[a] $R(F_o) = (\sum||F_o| - |F_c||)/\sum F_o$. [b] $R_w(F_o) = [(\sum w(||F_o| - |F_c||)^2)/\sum wF_o^2]^{1/2}$; $w = 4F_o^2/(\sigma(F_o^2))^2$; p = 0.04.

Table II. Selected Positional Parameter for $[Rh_2(\mu\text{-}Cl)_2(NO)_2(\mu\text{-dppm})_2](BF_4)_2\cdot 2CH_2Cl_2$ (**4**·$2CH_2Cl_2$)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh	0.07549 (4)	0.02136 (2)	0.10813 (3)	1.100 (8)
P1	0.0119 (1)	−0.09189 (7)	0.15625 (9)	1.12 (3)
P2	−0.1436 (1)	−0.12421 (7)	−0.03360 (9)	1.08 (3)
Cl1	−0.1337 (1)	0.03821 (6)	0.03373 (9)	1.35 (3)
O	0.1295 (7)	0.0756 (3)	0.2902 (3)	6.0 (1)
N	0.1209 (5)	0.0514 (2)	0.2189 (3)	2.2 (1)
C1	−0.1297 (5)	−0.1236 (3)	0.0949 (3)	1.3 (1)

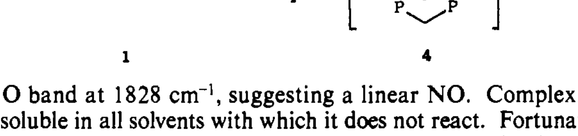
[a] Anisotropic thermal parameters are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Selected Intramolecular Distances (Å) and Angles (deg) for $[Rh_2(NO)_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2](BF_4)_2\cdot 2CH_2Cl_2$ (**4**·$2CH_2Cl_2$)[a]

Rh–Cl1	2.454 (1)	P1–C1	1.825 (5)
Rh–Cl1′	2.425 (1)	P2–C1′	1.856 (5)
Rh–P1	2.369 (1)	N–O	1.131 (6)
Rh–P2	2.354 (1)	Rh–Rh′	3.575 (1)
Rh–N	1.757 (4)		
Cl1–Rh–Cl1′	85.76 (4)	P1–Rh–N	96.1 (2)
Cl1–Rh–P1	89.63 (5)	P2–Rh–N	93.6 (2)
Cl1–Rh–P2	88.06 (5)	Rh–Cl1–Rh′	94.25 (5)
Cl1–Rh–N	125.9 (2)	Rh–P1–C1	113.1 (2)
Cl1′–Rh–P1	83.90 (5)	Rh–P2–C1′	115.5 (2)
Cl1′–Rh–P2	85.72 (5)	Rh–N–O	168.0 (5)
Cl1′–Rh–N	148.3 (2)	P1–C1–P2′	122.7 (3)
P1–Rh–P2	169.50 (5)		

[a] Primed and unprimed atoms are related by an inversion center.

Reaction of 1 with NOBF$_4$. Brown CH_2Cl_2 solutions of **1** rapidly precipitate brown $[Rh_2(\mu\text{-}Cl)_2(NO)_2(\mu\text{-dppm})_2](BF_4)_2$ (**4**) when treated with $NOBF_4$ (eq 3). The IR spectrum of **4** shows a single NO band at 1828 cm^{-1}, suggesting a linear NO. Complex **4** is insoluble in all solvents with which it does not react. Fortunately, crystals suitable for an X-ray crystal structure determination were obtained by an indirect route. Ethyl acetate was substituted for CH_2Cl_2 in the above reaction (eq 3). An unidentified pale brown powder with multiple NO bands in its IR spectrum was obtained (see Experimental Section). When this solid was dissolved in CH_2Cl_2, X-ray quality crystals of solvated **4** slowly deposited.



1 **4** (3)

An abbreviated summary of crystallographic and data collection parameters is given in Table I. Selected positional parameters

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(2) For examples and leading references, see: (a) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726–2732. (b) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *12*, 1632–1638. (c) Deraniyagala, S. P.; Grundy, K. R. *Organometallics* **1985**, *4*, 424–426. (d) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500–2507. (e) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chem.* **1985**, *24*, 50–56. (f) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796–1805. (g) Oro, L. A.; Carmona, D.; Perez, P. L.; Esteban, M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton, Trans.* **1985**, 973–979. (h) Boyd, D. C.; Rodman, G. S.; Mann, K. R. *J. Am. Chem. Soc.* **1986**, *108*, 1779. (i) Cotton, F. A.; Eagle, C. T.; Price, A. C. *Inorg. Chem.* **1988**, *27*, 4362–4368.

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(7) As suggested by a reviewer, $OPMe_3$ may result from a small amount of deoxygenation of SO_2. The reverse process, oxidation of coordinated S to SO and SO_2 has been observed. See: Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1988**, *27*, 3622–3628 and references cited therein.

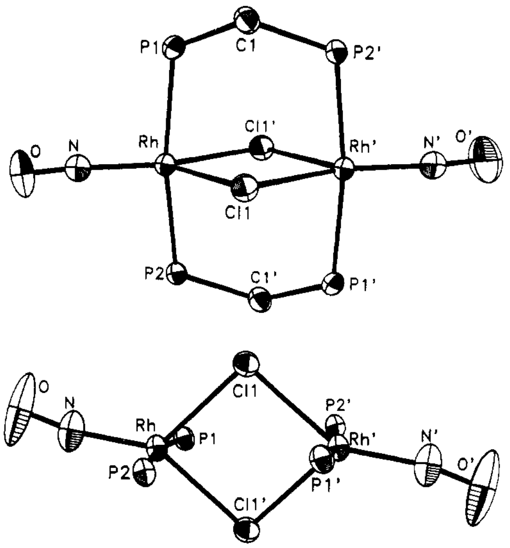

Figure 1. ORTEP diagrams of the cationic portion of $[Rh_2(NO)_2(Cl_2)(\mu\text{-dppm})_2](BF_4)_2{\cdot}2CH_2Cl_2$ ($4{\cdot}2CH_2Cl_2$): (a) "side" view; (b) "top" view (C1 and C1' omitted). 70% probability ellipsoids. Phenyl rings omitted for clarity. Primed and unprimed atoms are related by an inversion center at the center of the cation.

and interatomic distances and angles are given in Table II and III. The cationic portion of **4** (Figure 1) resides on an inversion center and contains 5-coordinate Rh centers with bridging chloride and dppm ligands and nearly linear (168°) NO ligands.

The geometry about the Rh atoms can be viewed as either square-pyramidal or trigonal-bipyramidal. In the square-pyramidal view one of the Cl ligands is apical (Cl1 for Rh, Figure 1b). This interpretation places the P atoms (P1 and P2), the other chloride (Cl1'), and the NO ligand in the basal plane. The greatest deviation from the idealized geometry is a bending away of the NO ligand from the apex (125.9° verses the ideal value of 90°). This is also seen in the 0.358 (5) Å deviation of the NO nitrogen from the least-squares plane containing Rh and the basal plane atoms. The alternative trigonal-bipyramidal view places the Cl ligands and the NO ligand in the trigonal plane (largest deviation is 0.010 Å) and the phosphines on the axis.

Discussion

Reactions. Sulfur dioxide displacement from $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ could be a versatile method for the preparation of new "face-to-face" complexes of Rh(I). However, our results and those reported for CO[3] suggest that for SO_2 displacement to occur the incoming ligand must be a π-acid. This is reasonable considering the π-acid character of the SO_2 ligand.[8] The addition of basic PMe_3 to the metal should strengthen the metal–SO_2 bonding while the addition of a π-acid such as CO or NO^+ should weaken the metal–SO_2 bonding. The "cutoff" for the π-acid strength needed for displacement of SO_2 has yet to be determined.

Structure. The trigonal-bipyramidal (TBP) description of the structure of **4** closely resembles that of the related monomeric Co complex $Co(NO)Cl_2(PMePh_2)_2$, although the NO ligand in the Co complex is further from linearity (164.5 (5)°).[9] The distortions in **4** from the ideal TBP geometry are similar to, though more severe than, those in the Co complex. These distortions are primarily in the trigonal plane and include a reduced Cl–M–Cl angle (108.4 (1)° for Co, 85.76(4)° for **4**) and an asymmetric placement of the NO ligand giving dissimilar Cl–M–NO angles (134.3 (2)° and 117.3 (2)° for Co, 148.3 (2)° and 125.9 (2)° for **4**). Trigonal-bipyramidal geometries with linear, basal plane NO ligands are also observed for two forms of $[IrH(NO)L_3]^+$ although the hydride ligand was not directly located in either structure.[10] The M–NO parameters are similar to those of **4**.

In contrast, the Rh and Ir complexes, $M(NO)Cl_2L_2$ (L = a phosphine),[11] and many related 5-coordinate complexes[12] are square-pyramidal with a strongly bent NO at the apex. As mentioned above, **4** can be viewed as square-pyramidal but with a basal, nearly linear NO. An apical NO is impossible for **4** since this would require trans Cl ligands, eliminating the possibility of Cl bridging.

The linear NO trigonal-bipyramidal geometry vs the bent NO square-pyramidal geometry has been considered both experimentally and theoretically.[11,12] The two geometries are apparently very close in energy, and the observation of two NO bands in the solution IR spectra of $Co(NO)Cl_2(PMePh_2)_2$ has lead to the suggestion that both geometries exist in solution.[9] An alternative explanation for the two bands involving different orientations of the NO ligand has also been proposed.[12a] Our observation that Rh can adopt the trigonal-bipyramidal geometry under the ligand constraints of **4** tends to support the two-geometry explanation.

A final comment on the structure of **4** involves the very large Rh–Rh separation of 3.575 (1) Å. For comparison, the separation in $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$ is only 3.2386 (5) Å.[3b] The large separation rules out the possibility of any Rh–Rh bonding and puts a strain on the dppm bridge (see Figure 1a), as indicated by the relatively large P–C–P angle of 122.7 (3)° and the nonlinear P–Rh–P angle of 169.50 (5)°. (Compare to the related values of 116.8 (2)° and 176.50 (2)° in $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$). The large Rh–Rh separation in **4** is presumably due to cation–cation repulsion of the two Rh centers and/or the angular requirements of the chloride bridges.

Experimental Section

General Procedures. All experiments were performed under a dinitrogen atmosphere in a VAC drybox or by Schlenk techniques. Solvents were dried under dinitrogen by recommended published techniques.[13] The petroleum ether used had a boiling range of 35–60 °C. $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$,[3] $[RhCl(COD)]_2$,[14] and PMe_3[15] were prepared according to literature procedures. $NOBF_4$ was sublimed prior to use, and dppm (Aldrich) was used as received. NMR shifts are reported in ppm, referenced to TMS for ^1H and to external H_3PO_4 for ^{31}P. Conductivity measurements were made with a Yellow Springs microcell using Et_4NCl as a standard. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Rh_2(SO_2)(PMe_3)_2(Cl)_2(\mu\text{-dppm})_2$ (2). Trimethylphosphine (3.5 μL, 0.037 mmol) was added by syringe to a stirred brown suspension of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ (20 mg, 0.018 mmol) in 2 mL of CH_2Cl_2 at -78 °C. A purple solution rapidly formed. After ca. 10 min the mixture was warmed to -45 °C and the volatiles were removed in vacuo, leaving a purple solid. The solid is stable, but solutions decompose if warmed above -30 °C.

Anal. Calcd (found) for $C_{56}H_{62}Cl_2O_2P_6Rh_2S{\cdot}0.5CH_2Cl_2$: C, 52.03 (51.71; H, 4.86 (4.62). (The CH_2Cl_2 in the isolated solid was confirmed by ^1H NMR analysis in $CDCl_3$.) ^1H NMR (90 MHz, CD_2Cl_2, -50 °C): 7.11–7.68 (m, 40 H, Ph), 4.28 and 3.31 (m, 2 × 2 H, PCH_2P), 0.80 (d, J_{HP} = 9 Hz, 18 H, PMe_3). ^{31}P NMR (36 MHz, CD_2Cl_2, -50 °C): 23.8 (dm, J_{PRh} = 115.2 Hz, 4 P, dppm), -11.9 (dt, J_{PRh} = 173.8 Hz, J_{PP} = 35.2 Hz, 2 P, PMe_3). IR (solid): $\nu(SO_2)$, 1152 (s) and 1037 cm^{-1}. Equivalent conductance (CH_2Cl_2, -78 °C, 5.3 × 10^{-4} M): 6.6 $cm^2\ \Omega^{-1}\ mol^{-1}$.

If THF is used as the solvent in the above reaction, or if CH_2Cl_2 solutions of **2** are warmed to above -30 °C, a green solution forms that is unstable at room temperature and has the following NMR properties.

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(8) For a recent review of sulfur oxide complexes, see: Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98–109.

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^{1}H NMR (90 MHz, CD_2Cl_2, −50 °C): 6.87–7.96 (m, 40 H, Ph), 4.64 and 2.85 (m, 2 × 2 H, PCH_2P), 0.63 (d, J_{HP} = 13 Hz, 18 H, PMe_3). ^{31}P NMR (36 MHz, CD_2Cl_2, −50 °C): 11.4–14.2 (m, 4 P, dppm), −22.9 to −28.7 (m, 2 P, PMe_3). IR (solid): $\nu(SO_2)$, 1153 (s) and 1042 cm^{-1}.

Preparation of $RhCl(PMe_3)$(dppm) (3). A solution of dppm (162 mg, 0.419 mmol) in toluene (2 mL) was added to a stirred solution of $[RhCl(COD)]_2$ (104 mg, 0.211 mmol) in 2 mL of toluene. PMe_3 (4.2 μL, 0.44 mmol) was injected into the rapidly stirred orange solution. A yellow precipitate formed which, after 0.5 h, was removed by filtration, washed with Et_2O, and dried in vacuo. Yield: 190 mg (75%). The product is slightly soluble in toluene, X-ray-quality crystals were grown from toluene/Et_2O.

^{1}H NMR (90 MHz, CD_2Cl_2): 7.36–8.51 (m, 20 H, Ph), 3.98 (t, J_{HP} = 13 Hz, 2 H, PCH_2P), 1.10 (d, J_{HP} = 7.6 Hz, 18 H, PMe_3). ^{31}P NMR (36 MHz, CD_2Cl_2, −50 °C): −4.1 to −19.7 (m, 2 P, dppm), −32.9 to −49.6 (m, 1 P, PMe_3). See the supplementary material for the structure determination.

Preparation of $[Rh_2(NO)_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2](BF_4)_2$ (4). Solid $NOBF_4$ (24 mg, 0.20 mmol) was added to a stirred brown solution of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ (102 mg, 0.092 mmol) in 3 mL of CH_2Cl_2. A brown precipitate formed. After ca. 4 h the reaction volume was reduced in vacuo to ca. 1 mL, and the brown product was isolated by filtration and drying in vacuo. Yield: 114 mg (97%).

Alternatively, the reaction may be done as above in ethyl acetate. However, the resulting pale brown product (IR (mineral oil): ν(NO), 1635 (s sh), 1624 (s), 1592 (s) cm^{-1}), isolated as described above, is not **4** and has not been identified. When this solid is dissolved in CH_2Cl_2, crystals of a CH_2Cl_2 solvate of **4** precipitate within a few minutes. Yield: 76%.

IR (mineral oil mull): ν(NO), 1828 (s) cm^{-1}. Complex **4** is insoluble in noncoordinating or weakly coordinating solvents (THF). It dissolves in MeCN to give a green product with the following spectroscopic properties. IR (mineral oil mull): ν(NO), 1653 (m br) cm^{-1} (no MeCN peak was detected). ^{1}H NMR (90 MHz, CD_3CN): 7.24 (br, 40 H, Ph), 4.39 (quintet, J_{HP} = 5 Hz, 4 H, PCH_2P). ^{31}P NMR (36 MHz, CD_3CN): 7.1 (d, J_{PRh} = 103.5 Hz).

Structure Analyses. An abbreviated summary of crystallographic and data collection parameters for **4** is given in Table I. A full table, including the structure of **3**, and details of the structure determinations may be found in the supplementary material.

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Supplementary Material Available: Figures showing ORTEP diagrams of **3** and **4**, tables listing crystallographic and data collection parameters, positional parameters, anisotropic thermal parameters, and bond distances and angles for **3** and **4** and least-squares planes for **4**, and a summary describing structure determinations for **3** and **4** (11 pages); listings of structure factors for **3** and **4** (33 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry
and Biochemistry, University of California,
Los Angeles, California 90024, and
Department of Chemistry, University of California,
Santa Barbara, California 93106

Metallo–Oxo Complex Formation from Photochemical Cleavage of Bis(cyclopentadienyl)molybdenum Carbonate

Maher Henary,[†] William C. Kaska,[*,‡] and Jeffrey I. Zink[*,†]

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Introduction

Photochemical carbon–oxygen bond cleavage of carbon dioxide or the carbonate ion requires high-energy vacuum UV irradiation.[1] However, complexation of these molecules to a transition-metal ion lowers the energy required for this cleavage to occur.[2-4] In the case of the coordinated carbonate ion, two simple cleavage reactions are possible: breaking one carbon–oxygen bond gives carbon dioxide and the oxide ion, while breaking two carbon–oxygen bonds gives carbon monoxide and the elements of the peroxide ion. Both the oxide and the peroxide ions can act as ligands for early transition metals in high oxidation states.[5] Thus, photolysis of transition-metal carbonato complexes offers the possibility of synthesizing metal–oxo or metal–peroxo complexes from stable precursors.[6] This is especially appealing because carbon dioxide and carbonate ion are in thermodynamic equilibrium with water:

$$CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-}$$

Photochemical synthesis of metal–oxo compounds is not well-known. Two recent examples from our laboratories include the photolysis of a dinuclear copper carbonato complex to produce a μ-oxo complex[7] and photolysis of a rhodium carbonato complex to produce a reactive oxo complex that further interacts with starting material to produce dimers.[6] An important goal is to produce a metal–oxo complex, which can be isolated, by photolysis of a carbonato complex. Ideally, the oxo complex should be stable enough to characterize and reactive enough to transfer oxygen to various substrates. We report here the synthesis and photochemical cleavage of bis(cyclopentadienyl)molybdenum carbonate to produce bis(cyclopentadienyl)molybdenum oxide and some further reactions to give oxygen gas.

Experimental Section

Materials. All of the reactions and photolyses were performed under purified argon. The photolyses were all performed in quartz cells, and the solutions or suspensions were stirred. The photolysis of the molybdenum carbonate also occurs in Pyrex vessels although the process takes longer. Tetrahydrofuran (THF) was distilled from benzophenone ketyl under argon[8] (THF must be used immediately after distillation or the photolysis will often not occur). An authentic sample of $(C_5H_5)_2Mo{=}O$ was prepared according to the literature.[9] Photolyses were performed only on samples of Cp_2MoCO_3 that were freshly prepared and stored below −10 °C in the refrigerator.

Preparation of $(C_5H_5)_2MoCO_3$. A degassed water solution of Na_2CO_3 (0.14 g, 1.32 mmol) was added to a degassed water solution of Cp_2MoBr_2 (Cp_2MoCl_2 can be used as well) (0.255 g, 0.66 mmol) (obtained by heating green Cp_2MoBr_2 in water until it dissolved), and the resulting mixture was stirred at room temperature until the green solution of molybdenum complex became burgundy colored. The resultant solution was filtered and concentrated by using a nitrogen stream or rotary evaporator. The product was purified by using $EtOH/H_2O$.[10] Anal. Calcd for $(C_5H_5)_2MoCO_3$: C, 46.16; H, 3.53. Found: C, 45.88; H, 3.33.

Physical Measurements. Electronic absorption spectra were obtained with a HP 8451 diode array spectrophotometer. The UV absorption spectrum of the molybdenum carbonate was obtained as a Nujol mull, whereas the UV spectrum of the reaction mixture, which included $Cp_2Mo{=}O$, was obtained in anhydrous THF in matched quartz cells at room temperature.

The photochemistry of the carbonate complex was studied by using a 200-W mercury lamp at 366 nm or an argon ion laser at 351.1 and 363.8 nm.

Infrared spectra were taken with the sample dispersed between AgCl plates, as Nujol mulls between CsI plates or in THF solution under argon

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[†] University of California, Los Angeles.

[‡] University of California, Santa Barbara.

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