Inorg. Chem. **1996,** *35,* 3073−3076 **3073**

Evaluation of Triflate Displacement by Water in CH_2Cl_2 Solution: Comparison of *trans*-$[Rh(CO)(PPh_3)_2(OSO_2CF_3)]$ and the Crystalline Salt *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$

Anna Svetlanova-Larsen and John L. Hubbard*

Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322-0300

Received October 5, 1995

Introduction

During the course of our studies of the organometallic chemistry of the electrophilic $[Cp^*Ru(NO)]^{2+}$ fragment, we have determined that dissociation of OTf^- from $Cp^*Ru(NO)(OTf)_2$ to give the corresponding solventocations is somewhat exothermic but entropically costly due to the solvent reorganization required for the formation of the product ion pairs ($Cp^* = \eta$-$C_5(CH_3)_5$; $OTf = OSO_2CF_3^-$).[1] Thus, we find that in a homogeneous H_2O-saturated CH_2Cl_2 solution of $Cp^*Ru(NO)(OTf)_2$, the major species in solution is the neutral ditriflate complex with only small amounts of $[Cp^*Ru(NO)(OTf)(OH_2)]^+$ and $[Cp^*Ru(NO)(OH_2)_2]^{2+}$ being present. In H_2O solution, OTf^- solvolysis is promoted by the considerable Lewis acidity of the $[Cp^*Ru(NO)]^{2+}$ fragment, leading to H_3O^+ and dinuclear μ-hydroxy complexes.[1b,2]

The nature of weakly coordinating ions is important in the discussion of coordination unsaturation and catalytic reactivity.[3,4] We continue to be interested in the equilibria of OTf^- displacement by coordinating solvents and weak ligands. In concert with our work on $Cp^*Ru(NO)(OTf)_2$, some previous work has shown OTf^- to be a "moderately strong" ligand.[5] For example, a kinetic study of the $M(CO)_5(OTf)$ complexes (M = Mn, Re) showed substitution of OTf^- by oxygen donor solvents in CH_2Cl_2 to occur for M = Mn but not for M = Re.[6] If one considers OTf^- to be a fairly good ligand, the report that *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ persists in solution with no detectable traces of the parent complex *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ would be counterintuitive[7] even though the dissociation of OTf^- in the "basic" d^8 Rh complexes might be expected to be more favorable than in electrophilic d^6 complexes like $Cp^*Ru(NO)(OTf)_2$.[7,8] Prompted by the rather sketchy analytical details reported for *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]\cdot H_2O$[9] and the importance of square planar rhodium complexes in catalytic reactions,[10] we embarked on a reinvestigation of this case to see if H_2O actually displaces the OTf^- ligand in CH_2Cl_2. The results of this study show that OTf^- is a better ligand than H_2O in CH_2Cl_2.

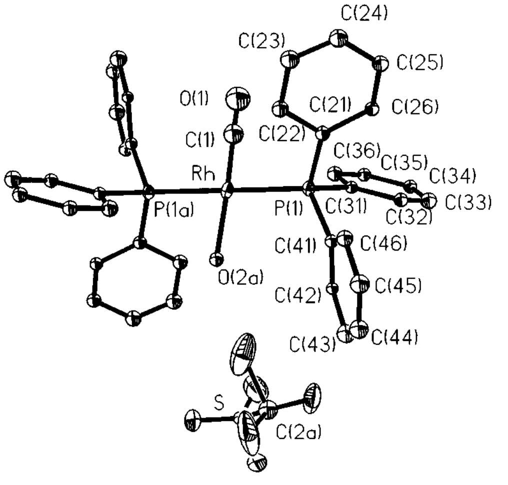

Figure 1. Molecular structure of *trans*-$[Rh(PPh_3)_2(CO)(OH_2)][OTf]$. Selected bond distances (Å): Rh−P(1), 2.333(4); Rh−C(1), 1.70(1); Rh−O(1), 2.00(1); P(1)−C(21), 1.81(2); P(1)−C(31), 1.84(1); P(1)−C(41), 1.81(2); C(1)−O(1), 1.05(1). Selected bond angles (deg): C(1)−Rh−P(1), 90(3); O(2)−Rh−P(1), 87.4(7); Rh−C(1)−O(1), 177(3).

Results

Characterization of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$. The combustion analysis for the crystalline material isolated from the reaction of *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$ with AgOTf in benzene agrees with the formula "$[Rh(CO)(PPh_3)_2(OTf)]\cdot H_2O$". The use of more than 1 equiv of AgOTf in the reaction leads to significant contamination of the product with AgOTf.[11] The presence of unreacted AgOTf in the product is easily detected by a broadening of the ^{19}F NMR signal, the depression of the melting point from 178 °C, and the reduction of the carbon content as determined by combustion analysis.

The single-crystal structure determination for crystals of "$[Rh(CO)(PPh_3)_2(OTf)]\cdot H_2O$" shows consistency with the analytical formulation. The calculated crystal density of 1.57 g/cm^3 is the same as the density determined by flotation in CCl_4/hexane. The molecular structure of the complex unambiguously shows a *trans*-arrangement of the PPh_3 ligands (Figure 1).

---

(1) (a) Burns, R. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9514. (b) Svetlanova-Larsen, A.; Zoch, C. R.; Hubbard, J. L. *Organometallics*, in press.

(2) Lewis acidic metal ions like Al^{3+} are noted for their reactivity in water to give acidic solutions containing polynuclear μ-OH complexes; see: Burgess, J. *Metal Ions in Solution;* John Wiley & Sons: New York, 1978.

(3) (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17 and references therein. (b) Beck, W.; Sünkel, K.; *Chem. Rev.* **1988**, *88*, 1405 and references therein. (c) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chem.* **1992**, *31*, 2376.

(4) Humphrey, R. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

(5) (a) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Organometallics* **1992**, *11*, 2645. (b) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464. (c) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070. (d) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293. (e) Odenkirk, W.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 6392. (f) Haggin, J. Aqueous Media Offer Promises And Problems In Organometallic Catalysis. *Chem. Eng. News Oct. 10*, 28−33. (g) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169; (h) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (i) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (j) Darensbourg, D. J.; Stafford, N. W.; Joo, F.; Reibenspies, J. H. *J. Organomet. Chem.* **1995**, *488*, 99. (k) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

(6) (a) Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972. (b) Trogler, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 6459.

(7) Branan, N. M.; Hoffman, N. W.; McElroy, E. A.; Prokopuk, N.; Salazar, A. B.; Robbins, M. J.; Hill, W. E.; Webb, T. R. *Inorg. Chem.* **1991**, *30*, 1200.

(8) (a) Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.

(9) Neither the work in ref 3 nor that in references therein reported the combustion analysis, mp, and solid-state IR ν_{CO} data for the Rh−OTf complex: Branan, D. M.; Hoffman, N. W.; McElroy, E. A.; Ramage, D. L.; Robbins, M. J; Eyler, J. R.; Watson, C. H.; deFur, P.; Leary, J. A. *Inorg. Chem.* **1990**, *29*, 1915.

(10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principals of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987; chapters 10−12 and references therein.

(11) This reaction can be successfully performed in fluorobenzene with 1 equiv of AgOTf according to the published procedure for the synthesis of $(PPh_3)_2Ir(CO)(OTf)$: Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

S0020-1669(95)01287-0 CCC: $12.00

Despite disorder of the CO and H_2O ligands, the molecular structure clearly shows the presence of an outersphere OTf^- ion (see Experimental Section). Henceforth, we will refer to this material as *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$.

The IR spectrum of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ in a Nujol mull shows a strong ν_{CO} absorption at 2008 cm^{-1}. A CH_2Cl_2 solution of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ shows a ν_{CO} absorption at 1996 cm^{-1}. The ^{19}F NMR spectrum of this CH_2Cl_2 solution shows a single sharp resonance at δ −78.5 and the ^{31}P NMR spectrum shows a doublet at δ 28.2 ($J = 125$ Hz). The presence of water in the homogeneous CH_2Cl_2 solutions does not alter the IR spectrum or the ^{19}F, ^{31}P, and ^1H NMR spectra. The molar conductivity of a 0.02 M solution of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ in CH_2Cl_2 is 2.0 (1) Ω^{-1} cm^{-1} mol^{-1}. For comparison, the molar conductivity of a 0.01 M solution of *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$ in CH_2Cl_2 is 1.5 (1) Ω^{-1} cm^{-1} mol^{-1}.

Isolation of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$. Analytically pure *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ is obtained by the azeotropic removal of water from a benzene solution prepared with *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ or by freeze-drying the benzene solution under high vacuum. The IR spectrum of microcrystalline *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in Nujol shows a ν_{CO} absorption at 1988 cm^{-1}, and the ν_{CO} absorption appears at 1996 cm^{-1} when the complex is dissolved both in rigorously dry CH_2Cl_2 and in H_2O-saturated CH_2Cl_2. The ^1H, ^{19}F, and ^{31}P NMR signals of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in rigorously dry CH_2Cl_2 are identical to those observed for *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ and do not change upon the addition of H_2O. The solid residue remaining after removal of the H_2O-saturated CH_2Cl_2 shows a ν_{CO} absorption at 2008 cm^{-1} in Nujol.

Reactivity of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$. Addition of $[Ph_3PNPPh_3]Cl$ to a CH_2Cl_2 solution of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ causes an immediate shift of the ^{19}F NMR resonance from δ −78.52 to δ −78.60. The appearance of a ν_{CO} IR absorption at 1976 cm^{-1} and a new doublet at δ 26.9 ($J = 127$ Hz) in the ^{31}P NMR spectrum of this solution corresponds to a complete conversion to *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$[12] and free OTf^-.

Addition of 1 equiv of pyridine to *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ dissolved in CH_2Cl_2 causes the initial δ −78.52 ^{19}F NMR resonance to shift to δ −78.60. This represents complete conversion to *trans*-$[Rh(CO)(PPh_3)_2(py)][OTf]$ as indicated by a new doublet in the ^{31}P NMR spectrum at δ 31.8 ($J = 129$ Hz) and a single ν_{CO} absorption at 2009 cm^{-1}.[13] Subsequent addition of 1 equiv of $[Ph_3PNPPh_3]Cl$ to this solution does not cause any change in ^{19}F NMR spectrum, but the presence of a mixture of *trans*-$[Rh(CO)(PPh_3)_2(py)][OTf]$ and *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$ is indicated by their characteristic ^{31}P signals and their ν_{CO} absorptions at 2009 and 1976 cm^{-1}.

Comparative Characteristics of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$. The CH_2Cl_2 solutions of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$[7] deteriorate rapidly at ambient temperature, necessitating their spectral evaluation within 1 h of preparation. In CH_2Cl_2, the ν_{CO} absorption for *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$ appears at 1999 cm^{-1} and the ^{31}P NMR spectrum shows a doublet at δ 31.1 ($J = 128$ Hz). Addition of pyridine results in the shift of the ^{31}P NMR resonance downfield to δ 31.8 ($J = 129$ Hz) and the appearance of a single ν_{CO} absorption at 2009 cm^{-1}. The molar conductance of 0.01 M solution of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$ in CH_2Cl_2 is 12 (1) Ω^{-1} cm^{-1} mol^{-1}.

Discussion

In contrast to an earlier report,[7] the results of our study show that *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ does not undergo OTf^- substitution by H_2O in CH_2Cl_2. The 20 cm^{-1} difference in the ν_{CO} absorptions for analytically pure *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ and *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ clearly illustrates the difference between cationic *trans*-$[Rh(CO)(PPh_3)_2(OH_2)]^+$ and neutral *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in the solid-state. However, the presence of a single carbonyl-containing species in CH_2Cl_2 in solutions prepared from either *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ or *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ is compelling evidence that *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ is the only detectable complex in solution. The H_2O is easily removed by azeotropic distillation in benzene. The ^{31}P NMR signals of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in CH_2Cl_2 shift to ca. 3 ppm to lower field upon the addition of pyridine, and identical ^{31}P NMR signals are generated when pyridine is added to *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$. This shows that pyridine displaces both H_2O and OTf^-, giving the *trans*-$[Rh(CO)(PPh_3)_2(py)]^+$ ion from two different starting points. The similarity of the ^{31}P NMR signals of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ and *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$ is consistent with these complexes being neutral species in solution. The similarity of the downfield ^{31}P NMR signals from CH_2Cl_2 solutions of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$ and *trans*-$[Rh(CO)(PPh_3)_2(py)][OTf]$ is consistent with the presence of the *trans*-$[Rh(CO)(PPh_3)_2(OH_2)]^+$ and *trans*-$[Rh(CO)(PPh_3)_2(py)]^+$ cations in solution. The conductivity measurements lead to the same conclusion as the ^{31}P NMR data. The low electrolytic character of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ and *trans*-$[Rh(CO)(PPh_3)_2(Cl)]$ suggests they dissolve in CH_2Cl_2 as neutral complexes whereas the significantly higher molar conductivity of *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][BF_4]$ shows the presence of the *trans*-$[Rh(CO)(PPh_3)_2(OH_2)]^+$ and $[BF_4]^-$ ions in the CH_2Cl_2 solution.

While ^{19}F NMR spectroscopy is especially important in the study of the $Cp^*Ru(NO)(OTf)_2$,[1] the small chemical shift difference between bound and free OTf^- precludes the application of ^{19}F NMR spectroscopy as a quantitative probe of the equilibria in the Rh cases.[14] Nevertheless, a measurable shift of the ^{19}F NMR signal occurs when Cl^- or pyridine is added to solutions of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in CH_2Cl_2. Since no shift in the ^{19}F NMR signal occurs when Cl^- is added to *trans*-$[Rh(CO)(PPh_3)_2(py)][OTf]$, this evidence supports OTf^- being bound to Rh when *trans*-$[Rh(CO)(PPh_3)_2(OH_2)][OTf]$ is dissolved in CH_2Cl_2.

The present study shows the previous assessment of the equilibria in eq 1 to be incorrect. Our inability to detect the presence of any cationic *trans*-$[Rh(CO)(PPh_3)_2(OH_2)]^+$ in CH_2Cl_2 leads to a K_{eq} of at least 10^2 based on a minimum detection limit of 1% in the NMR spectra.

$$K_{eq} \geq 10^2 \qquad (1)$$

$$trans\text{-}[Rh(CO)(PPh_3)_2(OH_2)]^+ + OTf^- \rightleftarrows trans\text{-}[Rh(CO)(PPh_3)_2(OTf)] + H_2O$$

It is important to note that the relatively high ν_{CO} absorption energy of *trans*-$[Rh(CO)(PPh_3)_2(OTf)]$ in CH_2Cl_2 might lead to the incorrect interpretation that a cationic complex is present

---

(12) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

(13) Reddy, G. K. N.; Ramesh, B. R. *J. Organomet. Chem.* **1975**, *87*, 347.

(14) Small differences between the ^{19}F NMR signals of bound and free OTf^- occur in related square planar complexes: (a) Stang, P. J.; Huang, Y. H.; Arif, A. M. *Organometallics* **1992**, *11*, 231. (b) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110. (c) Bennet, B. L.; Birnbaum, J.; Roddick, D. M. *Polyhedron* **1995**, *14*, 187.

Table 1. Crystallographic Data for *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf]

chem formula: $C_{38}H_{32}O_5F_3SP_2Rh$
fw = 822.6
$a = 23.401(8)$ Å
$b = 9.122(4)$ Å
$c = 17.047(6)$ Å
$\beta = 107.03(3)°$
$V = 3479(2)$ Å^3
$Z = 4$
space group: monoclinic, $C2/c$ (No. 15)
$T = 173$ K
$\lambda = 0.710\ 73$ Å (Mo Kα)
ρ(calcd) = 1.57 g/cm^3
ρ(obsd) = 1.57(2) g/cm^3
$\mu = 0.70$ mm^{-1}
$R(F^2)$ [$I > 2\sigma(I)$]: R1^a = 0.1057, wR2^b = 0.1740
$R(F^2)$ (all data): R1^a = 0.2126, wR2^b = 0.2308
GOF^c on F^2: 1.108

[a] $R1 = \sum||F_o| - |F_c||\sum|F_o|$. [b] $wR2 = |\sum[w(F_o^2 - F_c^2)]^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ where n = no. of reflections, p = no. of parameters refined; $w=1/[\sigma^2(F_o^2)+(0.0326P)^2 + 224.2319P]$ where $P = (F_o^2 + 2F_c^2)/3$.

in solution. As reported for several other cases, the ν_{NO} or ν_{CO} absorptions of OTf$^-$ complexes fall at 23−50 cm^{-1} *higher* energy than their Cl$^-$ analogues.[1,5] For example, the ν_{CO} absorptions for (η-C$_5$(CH$_3$)$_5$)Fe(CO)$_2$OTf are 23 cm^{-1} higher than for (η-C$_5$(CH$_3$)$_5$)Fe(CO)$_2$Cl.[15] The strongly electron-withdrawing SO$_2$CF$_3$ moiety on the OTf$^-$ donor O-atom likely reduces the π-donor ability of OTf$^-$ compared to Cl$^-$.

In summary, we have shown that solid *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf] precipitates preferentially from wet CH$_2$Cl$_2$ or benzene solutions rather than anhydrous *trans*-[Rh(CO)(PPh$_3$)$_2$(OTf)]. In CH$_2$Cl$_2$ solution, however, the OTf$^-$ ligand is a substantially better ligand than water, leading to *trans*-[Rh(CO)(PPh$_3$)$_2$(OTf)] as the only detectable species. Triflate displacement from Rh by H$_2$O does not occur to a significant extent in CH$_2$Cl$_2$ or benzene. Thus, the OTf$^-$ ion in these solvents cannot be classified as a weak ligand in the same category as BF$_4^-$.

Experimental Section

General Data. Standard Schlenk techniques were employed for routine experiments unless otherwise indicated. A Vacuum Atmospheres Dry-Lab glovebox with an N$_2$-atmosphere containing less than 1 ppm H$_2$O and 1 ppm O$_2$ was utilized for the preparation and handling of anhydrous materials. CH$_2$Cl$_2$ was rigorously dried using PbNa alloy and transferred in glassware that was dried in a 160 °C oven. The concentration of H$_2$O in homogeneous H$_2$O-saturated CH$_2$Cl$_2$ was determined to be 0.198 g/100 mL of CH$_2$Cl$_2$.[16] The nitrogen reaction atmosphere was purified by passing it through scavengers for water (Aquasorb, Mallinckrodt) and oxygen (Catalyst R3-11, Chemical Dynamics, So. Plainfield, NJ). Organic solvents were distilled under nitrogen over appropriate drying agents prior to use.[17] All other chemical reagents were used as received from Aldrich unless stated otherwise. Infrared spectra were recorded on a Mattson Polaris-Icon FT-spectrometer. The ^{31}P, ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker ARX-400 NMR spectrometer operating at 162 MHz (^{31}P), 400 MHz (^{1}H), and 376.2 MHz (^{19}F). The residual solvent peak of CDCl$_3$ was used as the internal NMR standard (^{1}H δ 7.24). ^{19}F chemical shifts were referenced externally to CCl$_3$F (δ 0.0)[17] or internally to 3,5-bis(trifluoromethyl)benzene (δ −63.20 in CDCl$_3$). ^{1}H NMR spectra in CH$_2$Cl$_2$ were measured using solvent presaturation techniques and were shimmed and referenced to the signals from CDCl$_3$ sealed inside a 1.5-mm capillary located concentrically inside the 5-mm NMR tube. The chemical shifts reported for the complexes in CH$_2$Cl$_2$ are identical to those in CD$_2$Cl$_2$. Conductivity measurements were performed on a YSI Model 31A conductivity bridge. For comparison purposes, a 0.02 M solution of [Ph$_3$PNPPh$_3$]Cl in CH$_2$Cl$_2$ has a molar conductance of 50(1) Ω^{-1} cm^{-1} mol^{-1}. Melting points were measured with a Mel-Temp device (Laboratory Devices) in open capillaries and are uncorrected. Combustion analyses were performed by Atlantic Microlab, Inc. <Norcross, GA.

Synthesis of *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf]. A mixture of *trans*-[Rh(CO)(PPh$_3$)$_2$(Cl)] (0.13 g, 0.20 mmol) and AgOTf (0.05 g, 0.20 mmol) in 10 mL of benzene (not rigorously dried) was stirred vigorously for 12 h. The reaction was deemed complete when the 1976 cm^{-1} signal of the starting chloride complex was no longer detectable by IR spectroscopy. The solution was filtered, taken to dryness *in vacuo* and the residue was redissolved in 5 mL of dichloromethane. Addition of 5 mL of hexane followed by storage at −70 °C for 12 h produced lemon-yellow crystalline *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf] (120 mg, 0.15 mmol, 79%). IR ν_{CO} (CH$_2$Cl$_2$, cm^{-1}): 1996 vs, (Nujol mull, cm^{-1}) 2008 vs. ^{1}H NMR (CH$_2$Cl$_2$): δ 7.45 (m, 10 H), δ 7.6 (m, 20 H). ^{31}P NMR (CDCl$_3$): δ 29.5 (d, J = 125 Hz), (CH$_2$Cl$_2$): δ 28.2 (J = 125 Hz). ^{19}F NMR (CH$_2$Cl$_2$): δ −78.52 Anal. Calcd for RhP$_2$C$_{38}$H$_{30}$O$_4$F$_3$S·H$_2$O: C, 55.48; H, 3.92. Found: C, 55.43; H, 3.98. Mp: 178−180 °C.

Synthesis of *trans*-[Rh(CO)(PPh$_3$)$_2$(OTf)]. A Schlenk-distillation apparatus was filled with a solution prepared from *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf] (0.150 g, 0.19 mmol) and 20 mL of rigorously dried benzene. Distillation resulted in the removal of H$_2$O in the early cloudy distillate fractions. After the distillate became clear, the remaining solvent was removed *in vacuo* to leave a quantitative yield of *trans*-[Rh(CO)(PPh$_3$)$_2$(OTf)] as a yellow powder. IR ν_{CO} (Nujol mull, cm^{-1}): 1988 vs. The IR and NMR spectral properties of Rh(CO)(PPh$_3$)$_2$(OTf) in CH$_2$Cl$_2$ solution are identical to those described above for *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf]. Anal. Calcd for RhP$_2$C$_{38}$H$_{30}$O$_4$F$_3$S: C, 56.72; H, 3.76. Found: C, 56.54; H, 3.95. Mp: 169−170 °C.

An alternative method of preparing *trans*-[Rh(CO)(PPh$_3$)$_2$(OTf)] was to freeze-dry the benzene solution of *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf] under high vacuum using a liquid-nitrogen trap. The residue that remained had an IR absorption at 1988 cm^{-1}.

X-ray Structural Analysis of *trans*-[Rh(CO)(PPh$_3$)$_2$(OH$_2$)][OTf]. A weakly diffracting, but acceptable, crystal was found after the examination of numerous candidates. The specimen selected was centered vertically at 173 K on a Siemens P4 Autodiffractometer. The computer centering of 25 random reflections revealed the monoclinic lattice with $a = 23.401(8)$ Å, $b = 9.1222(4)$ Å, $c = 17.047(6)$ Å; $\beta = 107.03(3)°$, and V = 3479(2) Å^3. Data collection of $0 \le h \le 26$, $0 \le k \le 10$, $-19 \le l \le 19$ for a primitive lattice showed a C-lattice by the systematic absences $h + k \neq 2n$. The presence of a c glide plane was indicated by the systematic absences $h0l$, $h00$, and $00l$ when $h \neq 2n$ and $l \neq 2n$. Solution and refinement of the structure was carried out on an IBM-compatible 486 personal computer using the SHELXS-86[18] and SHELXL-93[19] programs from Sheldrick.[20] Selection of the space group $C2/c$ and the use of Patterson methods led to the location of the Rh atom at the special position (0.5, 0.0, 0.0). The P atom and the C atoms of the phenyl rings were clearly visible in the first difference map. The unique PPh$_3$ group showed no sign of disorder. Three peaks of approximately equal weight were located along a vector that formed a ca. 90° angle to the Rh−P vector. These peaks were

---

(15) Hubbard, J. L.; McVicar, W. L. *J. Organomet. Chem.* **1992**, *429*, 369.
(16) Scheflan, L.; Jacobs, M. *The Handbook of Solvents*; Van Nostrand: New York, 1953; p 112.
(17) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; pp 25, 433.
(18) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.
(19) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation; SHELXL-93 scattering factors from: *International Tables for X-ray Crystallography* Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht: The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502, neutral atom scattering factors), 4.2.6.8 (pp 219−222, f',f''), and 4.2.4.2 (pp 193−199, absorption coefficients).
(20) SHELXL-93 is available from Siemens Analytical X-ray Instruments, 6300 Enterprise Lane, Madison, WI 53719, or directly from G. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammannstrasse 4, D-37077 Göttingen, Germany: gsheldr@shelx.uni-ac.gwdg.de.

successfully modeled isotropically as a 1:1 disorder of a CO ligand and an H_2O ligand.

After the Rh and P peaks, the next largest peak was located 5.5 Å from the Rh atom. This peak was situated in the center of three smaller peaks that formed a ca. 3-fold symmetric trigonal pyramid. Application of the crystal symmetry operations generated four symmetry-related peaks that, overall, formed a staggered ethane-like fragment that was assigned as an end-to-end disordered $SO_3CF_3^-$ moiety. Upon assigning the large peak as a S atom with a site-occupation factor = 0.5, the largest peak in the subsequent difference map was located 0.96 Å from the S position and just off the vector between S and the position of its symmetry equivalent S(a). Overall, the pattern appeared to be the partially resolved superposition of the C atom (from the CF_3 group) and the S atom (of the SO_3 group). Therefore, the best approximation of the disordered $SO_3CF_3^-$ resulted from a model where both the S and C(2) atoms where given site-occupation factors of 0.5 and the F(1), F(2), and F(3) atoms were assigned site-occupation factors of 1.0 each in order to approximately account for both the superposition of the F and O atoms.

Despite the disorder in the CO, H_2O, and $SO_3CF_3^-$ positions, refinement of the structure to 10.57% was possible. The density of the crystals was determined to be 1.57(2) g/cm^3 by flotation in a CCl_4/hexane mixture. The calculated density for 4 molecules of *trans*-[Rh(CO)$(PPh_3)_2(OH_2)$][OTf] per unit cell is 1.57 g/cm^3.

Acknowledgment. The support of the National Science Foundation (Grant CHE-9215872) to J.L.H. is gratefully acknowledged. We acknowledge the NSF and the Utah State University Research Office for jointly funding the purchase of the USU X-ray diffraction (Grant CHE-9002379) and NMR (Grant CHE-9311730) facilities.

Supporting Information Available: Tables of crystallographic data, collection parameters, atomic coordinates, and equivalent isotropic displacement parameters, complete listing of bond distances and bond angles, anisotropic displacement parameters, and H-atom coordinates (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

IC951287H

Additions and Corrections

1995, Volume 34

Anthony F. Lagalante, Brian N. Hansen, Thomas J. Bruno,* and Robert E. Sievers: Solubilities of Copper(II) and Chromium(III) β-Diketonates in Supercritical Carbon Dioxide.

Page 5785. Two sponsors were accidentally omitted from the Acknowledgment. The following should be added to this section: R.E.S. and A.F.L. acknowledge NSF Grant ATM-9115295 and EG&G Rocky Flats Contract ASC222874DB for providing partial support of this research.

IC960236X