

Evaluation of Triflate Displacement by Water in CH_2Cl_2 Solution: Comparison of *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OSO}_2\text{CF}_3)]$ and the Crystalline Salt *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OH}_2)][\text{OTf}]$

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Introduction

During the course of our studies of the organometallic chemistry of the electrophilic $[\text{Cp}^*\text{Ru}(\text{NO})]^{2+}$ fragment, we have determined that dissociation of OTf^- from $\text{Cp}^*\text{Ru}(\text{NO})(\text{OTf})_2$ 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 ($\text{Cp}^* = \eta\text{-C}_5(\text{CH}_3)_5$; $\text{OTf} = \text{OSO}_2\text{CF}_3^-$).¹ Thus, we find that in a homogeneous H_2O -saturated CH_2Cl_2 solution of $\text{Cp}^*\text{Ru}(\text{NO})(\text{OTf})_2$, the major species in solution is the neutral ditriflate complex with only small amounts of $[\text{Cp}^*\text{Ru}(\text{NO})(\text{OTf})(\text{OH}_2)]^+$ and $[\text{Cp}^*\text{Ru}(\text{NO})(\text{OH}_2)_2]^{2+}$ being present. In H_2O solution, OTf^- solvolysis is promoted by the considerable Lewis acidity of the $[\text{Cp}^*\text{Ru}(\text{NO})]^{2+}$ 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 $\text{Cp}^*\text{Ru}(\text{NO})(\text{OTf})_2$, some previous work has shown OTf^- to be a "moderately strong" ligand.⁵ For example, a kinetic study of the $\text{M}(\text{CO})_5(\text{OTf})$ complexes ($\text{M} = \text{Mn}, \text{Re}$) showed substitution of OTf^- by oxygen donor solvents in CH_2Cl_2 to occur for $\text{M} = \text{Mn}$ but not for $\text{M} = \text{Re}$.⁶ If one considers OTf^- to be a fairly good ligand, the report that *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OH}_2)][\text{OTf}]$ persists in solution with no detectable traces of the parent complex *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OTf})]$

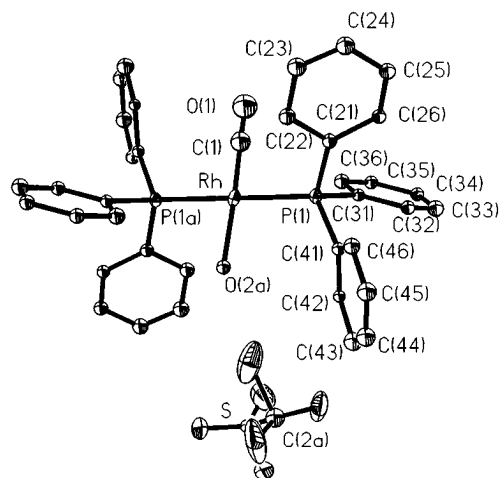


Figure 1. Molecular structure of *trans*- $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{OH}_2)][\text{OTf}]$. Selected bond distances (Å): Rh–P(1), 2.333(4); Rh–C(1), 1.70(1); Rh–O(1), 2.00(1); P(1)–C(21), 1.81(2); P(1)–C(31), 1.84(1); P(1)–C(41), 1.81(2); C(1)–O(1), 1.05(1). Selected bond angles (deg): C(1)–Rh–P(1), 90(3); O(2)–Rh–P(1), 87.4(7); Rh–C(1)–O(1), 177(3).

would be counterintuitive⁷ 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 $\text{Cp}^*\text{Ru}(\text{NO})(\text{OTf})_2$.^{7,8} Prompted by the rather sketchy analytical details reported for *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OH}_2)][\text{OTf}] \cdot \text{H}_2\text{O}$ 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 .

Results

Characterization of *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OH}_2)][\text{OTf}]$

The combustion analysis for the crystalline material isolated from the reaction of *trans*- $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Cl})]$ with AgOTf in benzene agrees with the formula $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OTf})] \cdot \text{H}_2\text{O}$. 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 $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OTf})] \cdot \text{H}_2\text{O}$ shows consistency with the analytical formulation. The calculated crystal density of 1.57 g/cm³ 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).

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Despite disorder of the CO and H₂O 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)(PPh₃)₂(OH₂)] [OTf].

The IR spectrum of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] in a Nujol mull shows a strong ν_{CO} absorption at 2008 cm^{−1}. A CH₂Cl₂ solution of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] shows a ν_{CO} absorption at 1996 cm^{−1}. The ¹⁹F NMR spectrum of this CH₂Cl₂ solution shows a single sharp resonance at δ −78.5 and the ³¹P NMR spectrum shows a doublet at δ 28.2 (*J* = 125 Hz). The presence of water in the homogeneous CH₂Cl₂ solutions does not alter the IR spectrum or the ¹⁹F, ³¹P, and ¹H NMR spectra. The molar conductivity of a 0.02 M solution of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] in CH₂Cl₂ 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)(PPh₃)₂(Cl)] in CH₂Cl₂ is 1.5 (1) Ω^{−1} cm^{−1} mol^{−1}.

Isolation of *trans*-[Rh(CO)(PPh₃)₂(OTf)]. Analytically pure *trans*-[Rh(CO)(PPh₃)₂(OTf)] is obtained by the azeotropic removal of water from a benzene solution prepared with *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] or by freeze-drying the benzene solution under high vacuum. The IR spectrum of microcrystalline *trans*-[Rh(CO)(PPh₃)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 CH₂Cl₂ and in H₂O-saturated CH₂Cl₂. The ¹H, ¹⁹F, and ³¹P NMR signals of *trans*-[Rh(CO)(PPh₃)₂(OTf)] in rigorously dry CH₂Cl₂ are identical to those observed for *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] and do not change upon the addition of H₂O. The solid residue remaining after removal of the H₂O-saturated CH₂Cl₂ shows a ν_{CO} absorption at 2008 cm^{−1} in Nujol.

Reactivity of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf]. Addition of [Ph₃PNPPh₃]Cl to a CH₂Cl₂ solution of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] causes an immediate shift of the ¹⁹F 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 ³¹P NMR spectrum of this solution corresponds to a complete conversion to *trans*-[Rh(CO)(PPh₃)₂(Cl)]¹² and free OTf[−].

Addition of 1 equiv of pyridine to *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] dissolved in CH₂Cl₂ causes the initial δ −78.52 ¹⁹F NMR resonance to shift to δ −78.60. This represents complete conversion to *trans*-[Rh(CO)(PPh₃)₂(py)] [OTf] as indicated by a new doublet in the ³¹P 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 [Ph₃PNPPh₃]Cl to this solution does not cause any change in ¹⁹F NMR spectrum, but the presence of a mixture of *trans*-[Rh(CO)(PPh₃)₂(py)] [OTf] and *trans*-[Rh(CO)(PPh₃)₂(Cl)] is indicated by their characteristic ³¹P signals and their ν_{CO} absorptions at 2009 and 1976 cm^{−1}.

Comparative Characteristics of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄]. The CH₂Cl₂ solutions of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄]⁷ deteriorate rapidly at ambient temperature, necessitating their spectral evaluation within 1 h of preparation. In CH₂Cl₂, the ν_{CO} absorption for *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄] appears at 1999 cm^{−1} and the ³¹P NMR spectrum shows a doublet at δ 31.1 (*J* = 128 Hz). Addition of pyridine results in the shift of the ³¹P 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)(PPh₃)₂(OH₂)] [BF₄] in CH₂Cl₂ is 12 (1) Ω^{−1} cm^{−1} mol^{−1}.

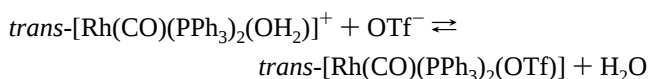
Discussion

In contrast to an earlier report,⁷ the results of our study show that *trans*-[Rh(CO)(PPh₃)₂(OTf)] does not undergo OTf[−] substitution by H₂O in CH₂Cl₂. The 20 cm^{−1} difference in the ν_{CO} absorptions for analytically pure *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] and *trans*-[Rh(CO)(PPh₃)₂(OTf)] clearly illustrates the difference between cationic *trans*-[Rh(CO)(PPh₃)₂(OH₂)]⁺ and neutral *trans*-[Rh(CO)(PPh₃)₂(OTf)] in the solid-state. However, the presence of a single carbonyl-containing species in CH₂Cl₂ in solutions prepared from either *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] or *trans*-[Rh(CO)(PPh₃)₂(OTf)] is compelling evidence that *trans*-[Rh(CO)(PPh₃)₂(OTf)] is the only detectable complex in solution. The H₂O is easily removed by azeotropic distillation in benzene. The ³¹P NMR signals of *trans*-[Rh(CO)(PPh₃)₂(OTf)] in CH₂Cl₂ shift to ca. 3 ppm to lower field upon the addition of pyridine, and identical ³¹P NMR signals are generated when pyridine is added to *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄]. This shows that pyridine displaces both H₂O and OTf[−], giving the *trans*-[Rh(CO)(PPh₃)₂(py)]⁺ ion from two different starting points. The similarity of the ³¹P NMR signals of *trans*-[Rh(CO)(PPh₃)₂(OTf)] and *trans*-[Rh(CO)(PPh₃)₂(Cl)] is consistent with these complexes being neutral species in solution. The similarity of the downfield ³¹P NMR signals from CH₂Cl₂ solutions of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄] and *trans*-[Rh(CO)(PPh₃)₂(py)] [OTf] is consistent with the presence of the *trans*-[Rh(CO)(PPh₃)₂(OH₂)]⁺ and *trans*-[Rh(CO)(PPh₃)₂(py)]⁺ cations in solution. The conductivity measurements lead to the same conclusion as the ³¹P NMR data. The low electrolytic character of *trans*-[Rh(CO)(PPh₃)₂(OTf)] and *trans*-[Rh(CO)(PPh₃)₂(Cl)] suggests they dissolve in CH₂Cl₂ as neutral complexes whereas the significantly higher molar conductivity of *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [BF₄] shows the presence of the *trans*-[Rh(CO)(PPh₃)₂(OH₂)]⁺ and [BF₄][−] ions in the CH₂Cl₂ solution.

While ¹⁹F 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 ¹⁹F NMR spectroscopy as a quantitative probe of the equilibria in the Rh cases.¹⁴ Nevertheless, a measurable shift of the ¹⁹F NMR signal occurs when Cl[−] or pyridine is added to solutions of *trans*-[Rh(CO)(PPh₃)₂(OTf)] in CH₂Cl₂. Since no shift in the ¹⁹F NMR signal occurs when Cl[−] is added to *trans*-[Rh(CO)(PPh₃)₂(py)] [OTf], this evidence supports OTf[−] being bound to Rh when *trans*-[Rh(CO)(PPh₃)₂(OH₂)] [OTf] is dissolved in CH₂Cl₂.

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)(PPh₃)₂(OH₂)]⁺ in CH₂Cl₂ leads to a *K*_{eq} of at least 10² based on a minimum detection limit of 1% in the NMR spectra.

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



It is important to note that the relatively high ν_{CO} absorption energy of *trans*-[Rh(CO)(PPh₃)₂(OTf)] in CH₂Cl₂ might lead to the incorrect interpretation that a cationic complex is present

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Table 1. Crystallographic Data for *trans*-[Rh(CO)(PPh₃)₂(OH₂)](OTf)

chem formula: C₃₈H₃₂O₅F₃SP₂Rh
 fw = 822.6
 a = 23.401(8) Å
 b = 9.122(4) Å
 c = 17.047(6) Å
 β = 107.03(3)°
 V = 3479(2) Å³
 Z = 4

space group: monoclinic, C2/c (No. 15)

T = 173 K
 λ = 0.710 73 Å (Mo Kα)
 ρ(calcd) = 1.57 g/cm³
 ρ(obsd) = 1.57(2) g/cm³
 μ = 0.70 mm⁻¹
 R(F²) [I > 2σ(I)]: R1^a = 0.1057, wR2^b = 0.1740
 R(F²) (all data): R1^a = 0.2126, wR2^b = 0.2308
 GOF^c on F²: 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-C₅(CH₃)₅)Fe(CO)₂OTf are 23 cm⁻¹ higher than for (η-C₅(CH₃)₅)Fe(CO)₂Cl.¹⁵ The strongly electron-withdrawing SO₂CF₃ 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)(PPh₃)₂(OH₂)](OTf) precipitates preferentially from wet CH₂-Cl₂ or benzene solutions rather than anhydrous *trans*-[Rh(CO)(PPh₃)₂(OTf)]. In CH₂Cl₂ solution, however, the OTf⁻ ligand is a substantially better ligand than water, leading to *trans*-[Rh(CO)(PPh₃)₂(OTf)] as the only detectable species. Triflate displacement from Rh by H₂O does not occur to a significant extent in CH₂Cl₂ or benzene. Thus, the OTf⁻ ion in these solvents cannot be classified as a weak ligand in the same category as BF₄⁻.

Experimental Section

General Data. Standard Schlenk techniques were employed for routine experiments unless otherwise indicated. A Vacuum Atmospheres Dry-Lab glovebox with an N₂-atmosphere containing less than 1 ppm H₂O and 1 ppm O₂ was utilized for the preparation and handling of anhydrous materials. CH₂Cl₂ was rigorously dried using PbNa alloy and transferred in glassware that was dried in a 160 °C oven. The concentration of H₂O in homogeneous H₂O-saturated CH₂Cl₂ was determined to be 0.198 g/100 mL of CH₂Cl₂.¹⁶ 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 ³¹P, ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker ARX-400 NMR spectrometer operating at 162 MHz (³¹P), 400 MHz (¹H), and 376.2 MHz (¹⁹F). The residual solvent peak of CDCl₃ was used as the internal NMR standard (¹H δ 7.24). ¹⁹F chemical shifts were referenced externally to CCl₃F (δ 0.0)¹⁷ or internally to 3,5-bis(trifluoromethyl)benzene (δ -63.20 in CDCl₃). ¹H NMR spectra in CH₂Cl₂ were measured using solvent presaturation techniques and were shimmed and referenced to the signals from CDCl₃ sealed inside a 1.5-mm capillary located concentrically inside the 5-mm NMR tube. The chemical shifts reported for the complexes in CH₂Cl₂ are identical to those in CD₂Cl₂. Conductivity measurements were performed on a YSI Model 31A conductivity bridge. For comparison purposes, a 0.02 M solution of [Ph₃PNPPh₃]Cl in CH₂Cl₂ 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)(PPh₃)₂(OH₂)](OTf). A mixture of *trans*-[Rh(CO)(PPh₃)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)(PPh₃)₂(OH₂)](OTf) (120 mg, 0.15 mmol, 79%). IR ν_{CO} (CH₂Cl₂, cm⁻¹): 1996 vs. (Nujol mull, cm⁻¹) 2008 vs. ¹H NMR (CH₂Cl₂): δ 7.45 (m, 10 H), δ 7.6 (m, 20 H). ³¹P NMR (CDCl₃): δ 29.5 (d, J = 125 Hz), (CH₂Cl₂): δ 28.2 (J = 125 Hz). ¹⁹F NMR (CH₂Cl₂): δ -78.52 Anal. Calcd for RhP₂C₃₈H₃₀O₄F₃S·H₂O: C, 55.48; H, 3.92. Found: C, 55.43; H, 3.98. Mp: 178–180 °C.

Synthesis of *trans*-[Rh(CO)(PPh₃)₂(OTf)]. A Schlenk-distillation apparatus was filled with a solution prepared from *trans*-[Rh(CO)(PPh₃)₂(OH₂)](OTf) (0.150 g, 0.19 mmol) and 20 mL of rigorously dried benzene. Distillation resulted in the removal of H₂O 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)(PPh₃)₂(OTf)] as a yellow powder. IR ν_{CO} (Nujol mull, cm⁻¹): 1988 vs. The IR and NMR spectral properties of Rh(CO)(PPh₃)₂(OTf) in CH₂Cl₂ solution are identical to those described above for *trans*-[Rh(CO)(PPh₃)₂(OH₂)](OTf). Anal. Calcd for RhP₂C₃₈H₃₀O₄F₃S: 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)(PPh₃)₂(OTf)] was to freeze-dry the benzene solution of *trans*-[Rh(CO)(PPh₃)₂(OH₂)](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)(PPh₃)₂(OH₂)](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 = 9.122(4) Å, c = 17.047(6) Å; β = 107.03(3)°, and V = 3479(2) Å³. Data collection of 0 ≤ h ≤ 26, 0 ≤ k ≤ 10, -19 ≤ l ≤ 19 for a primitive lattice showed a C-lattice by the systematic absences h + k ≠ 2n. The presence of a c glide plane was indicated by the systematic absences h0l, h00, and 00l when h ≠ 2n and l ≠ 2n. Solution and refinement of the structure was carried out on an IBM-compatible 486 personal computer using the SHELXS-86¹⁸ and SHELXL-93¹⁹ 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 PPh₃ 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

(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, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-37077 Göttingen, Germany: gsheldr@shelx.uni-ac.gwdg.de.

(15) Hubbard, J. L.; McVicar, W. L. *J. Organomet. Chem.* **1992**, 429, 369.

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successfully modeled isotropically as a 1:1 disorder of a CO ligand and an H₂O 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 SO₃CF₃⁻ 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 CF₃ group) and the S atom (of the SO₃ group). Therefore, the best approximation of the disordered SO₃CF₃⁻ resulted from a model where both the S and C(2) atoms were 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, H₂O, and SO₃CF₃⁻ positions, refinement of the structure to 10.57% was possible. The density of

the crystals was determined to be 1.57(2) g/cm³ by flotation in a CCl₄/hexane mixture. The calculated density for 4 molecules of *trans*-[Rh(CO)(PPh₃)₂(OH₂)](OTf) per unit cell is 1.57 g/cm³.

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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.

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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.

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