may be due to long-range couplings, as recently suggested by Tortorelli for the Rh_2^{4+} complexes $Rh_2(\mu\text{-}PPh_2Py)_2(CO)_2Cl_4$ and $[Rh_2(\mu\text{-}PPh_2Py)_2(t\text{-}BuNC)_2Cl_3]PF_6$.[17]

In order to obtain some evidence for the proposed solution structure, complexes **1** and **2** were allowed to react with $TlPF_6$. The products of the reaction of **1** and **2** with $TlPF_6$ are critically dependent on the solvent used. Complex **1** reacts with an excess of $TlPF_6$ in CH_3CN leading to the monocationic complex $[Rh_2(form)_2(\mu\text{-}O_2CCF_3)(\mu\text{-}PPh_2Py)]PF_6$ (**3**) whereas no reaction occurs when acetone is used as solvent. Complex **3** has been characterized by IR, ^{31}P NMR, and conductivity measurements. The solid-state IR spectrum of **3**, besides the ν(P–F) stretching, shows a single $\nu_{asym}(CO_2)$ at 1631 cm^{-1}, while the ^{31}P NMR spectrum exhibits the familiar double doublet, which is sharp both at 225 and 310 K. On the contrary, complex **2** reacts with $TlPF_6$ in acetone as solvent, affording the monocationic complex $[Rh_2(form)_2(\mu\text{-}PPh_2Py)_2(O_2CCF_3)]PF_6$ (**4**). The solid-state IR spectrum of **4** shows the expected ν(P–F) stretching as well as a band at 1684 cm^{-1}, indicating the presence of a monocoordinated carboxylate group. With a repeat of the synthesis in CH_3CN, the non-carboxylate compound $[Rh_2(form)_2(\mu\text{-}PPh_2Py)_2][PF_6]_2$ (**5**) was obtained, as shown by the IR spectrum, which does not show absorptions attributable to the ν(O–C–O) stretching frequency.

Both complexes **1** and **2** serve as convenient precursors to new Rh_2^{4+} complexes. They undergo metathetical exchange reactions in which one or both the monoligated trifluoroacetate groups are replaced by X^- ligands (X = Cl, Br, I). Treatment of **1** with an excess of KX (X = Cl, Br) produces the complexes $Rh_2(form)_2(\mu\text{-}O_2CCF_3)(\mu\text{-}PPh_2Py)X$ (X = Cl (**6**), Br (**7**)), while treatment of **2** with the same halides gives the complexes $Rh_2(form)_2(\mu\text{-}PPh_2Py)_2(O_2CCF_3)Cl$ (**8**) and $Rh_2(form)_2(\mu\text{-}PPh_2Py)_2I_2$ (**9**). Analytical data and IR spectroscopy provide excellent evidence of the displacement of the fluoro carboxylate groups. IR spectra of complexes **6** and **7** display $\nu(CO_2)$ absorptions at 1643 and 1634 cm^{-1}, strongly suggesting that only bridging or chelating trifluoroacetate groups are present, while in the spectra of **9** no bands attributable to the $\nu(CO_2)$ stretching are present.

Acknowledgment. We thank the Public Ministry of Education for financial support.

Supplementary Material Available: Tables SI–SVII, listing full crystal data, nonessential atomic distances and angles, hydrogen atom parameters, temperature factors, and complete positional parameters, and a figure showing a packing diagram (10 pages); a table of calculated and observed structure factors (59 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Carbonylbis(triphenylphosphine)rhodium(I) Complexes of Water and Weakly Coordinating Anions

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New complexes *trans*-$Rh(PPh_3)_2(CO)OPOF_2$ and $[trans\text{-}Rh(PPh_3)_2(CO)(OH_2)]Z{\cdot}nH_2O$ ($Z = SO_3CF_3$, $n = 1$; $Z = BF_4$, $n = 2$; $Z = ClO_4$, $n = 2$) were prepared and characterized. Syntheses of the four species entailed metathesis of the Rh(I) chloride with $AgPF_6$, $AgSO_3CF_3$, $AgBF_4$, and $AgClO_4$, respectively, in undried solvents. The water-free $OPOF_2$ complex arises from hydrolysis of a spectroscopically detected Rh(I) PF_6^- species. Metathesis studies with $[N(PPh_3)_2]^+$ salts and reactions with pyridine and CO showed the affinity of $[Rh(PPh_3)_2(CO)]^+$ in CH_2Cl_2 for ligands L to follow the trend L = $(O_2CCF_3)^- > (ONO_2)^- >$ pyridine $> (OPOF_2)^- \gg H_2O \gg (SO_3CF_3)^- \approx (BF_4)^- \approx (ClO_4)^-$. Monoolefins such as C_2H_4 and $PhCH{=}CH_2$ failed to displace the very weakly coordinating ligand H_2O from $[Rh(PPh_3)_2(CO)(OH_2)]SO_3CF_3{\cdot}H_2O$ in CH_2Cl_2. The crystal structure of $[Rh(PPh_3)_2(CO)(OH_2)][BF_4]{\cdot}{}^1/_2H_2O{\cdot}{}^1/_4C_6H_{12}$ has been determined. The crystal belongs to the triclinic crystal system, space group $P\bar{1}$, with lattice constants $a = 11.865$ (2) Å, $b = 17.235$ (6) Å, $c = 18.590$ (5) Å, $\alpha = 91.95$ (2)°, $\beta = 101.62$ (2)°, $\gamma = 101.83$ (2)°, and $Z = 4$.

Introduction

In the course of preparing a series of bis(triphenylphosphine)carbonylrhodium(I) complexes of uninegative ligands,[1,2] we became concerned about using $AgClO_4$ and the Rh(I) perchlorate complex[3] intermediate routinely.[4] We then tried readily available Ag^+ salts of several other weakly coordinating anions to effect similar metathesis of the chloride ligand to obtain a convenient synthon. Although we achieved the latter objective, we discovered that the actual products were not the results of the expected simple metathesis. Indeed, we found that the SO_3CF_3, BF_4, and ClO_4 complexes contained coordinated water (in addition to water of crystallization) rather than anionic ligand and the expected PF_6 complex had undergone hydrolysis in undried solvent to afford coordinated $(OPOF_2)^-$. [The synthesis of $Rh(PPh_3)_2(CO)(OSO_2CF_3)$ was reported while this study was in progress.[5]] To expand the ligand affinity data for $[Rh(PPh_3)_2(CO)]^+$ gathered earlier, we included the known nitrate and trifluoroacetate complexes (since $(O_2CCF_3)^-$ and $(ONO_2)^-$ are considered borderline weakly coordinating anions) along with the new difluorophosphate complex and the aqua cation in equilibrium studies of ligand substitution employing $[N(PPh_3)_2]^+$ salts and pyridine. We also studied the degree of displacement of anion or aqua ligand for the series with CO at 1 atm and for the aqua–$(SO_3CF_3)^-$ species with a set of alkenes.

Transition-metal complexes of weakly coordinating anions are of considerable interest as Lewis acid reagents,[6] and numerous

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examples of low-valent complexes containing coordinated anions such as $(OSO_2CF_3)^-$,[7a,b] $(OSO_2C_4F_9)^-$,[7a] $(OSO_2F)^-$,[7c] $(FBF_3)^-$,[7a,d,e] $(OHBF_3)^-$,[7e] $(OClO_3)^-$,[7f,g] $(OPOF_2)^-$,[7f,g] $(OTeF_5)^-$,[7h] $[B(OTeF_5)_4]^-$,[7i] $(FPF_5)^-$,[7j–l] $(FAsF_5)^-$,[7j–l] and $(FSbF_5)^-$[7j–l] have been synthesized. Several reviews on complexes of some of these anions have appeared.[8] Our results described herein provide affinities of a soft d^8 metal moiety for four of the weakly coordinating anions listed above, as well as for the borderline anions $(O_2CCF_3)^-$ and $(ONO_2)^-$ and the neutral ligands water and pyridine.

To facilitate discussion of syntheses and reactions of the rhodium(I) complexes, the formula $Rh(PPh_3)_2(CO)L$ will be abbreviated as {Rh}L (where L is either a neutral or uninegative ligand). C_6H_5 is abbreviated as Ph and $[N(PPh_3)_2]Y$ as (PPN)Y.

Experimental Section

Spectra. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer equipped with Model 3600 data station. Data were processed on a PC in a custom multivariate-analysis program in BASIC.[9] ^{31}P NMR spectra of {Rh}L solutions in toluene, toluene/CH_2Cl_2, or $CDCl_3$ were recorded on a Bruker AM400 spectrometer operating at 162 MHz. ^{19}F NMR spectra of CH_2Cl_2 solutions of $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ and $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ + pyridine (ca. 1:2) were recorded on the same spectrometer at 376 MHz, using CCl_3F as internal standard.

Commercially Available Reagents. All solvents were commercial reagent grade (CH_2Cl_2, 1,2-$C_2H_4Cl_2$, benzene, diethyl ether, heptane, cyclohexane). (PPN)Cl and (PPN)NO_3 were used as received from Strem. Pyridine (J. T. Baker reagent) was dried over molecular sieves. CO (Air Products CP grade) was used as received. The silver(I) salts were used as purchased: $AgSO_3CF_3$ (Alfa or Aesar), $AgPF_6$ (Aldrich or Strem), $AgClO_4$ (Strem), and $AgBF_4$ (Aesar). Olefins were used as received (liquids in only microliter amounts): ethylene (Air Products, CP grade), cyclohexene (Fisher reagent), cyclooctene (Aldrich, 95%), styrene (Aldrich, Gold Label), and dimethyl maleate (Aldrich, 96%).

Synthesis of (PPN)SO_3CF_3. A mixture of (PPN)Cl (5.00 g, 8.71 mmol) and excess $AgSO_3CF_3$ (2.91 g, 11.3 mmol) was stirred 16 h in 200 mL of CH_2Cl_2 in a Schlenk flask protected from light. It was then filtered through Celite on a sintered-glass funnel, and the residue was washed with two 25-mL portions of CH_2Cl_2. The filtrate volume was reduced to ca. 25 mL, and the desired product was precipitated as white crystals by slow addition of 200 mL of diethyl ether. These were filtered and washed with two 20-mL portions of cold ether to afford a first crop of 4.09 g; a second crop (0.76 g) was obtained by concentrating the filtrate to ca. 25 mL, adding another 100 mL of ether to the concentrate, refrigerating the resulting mixture overnight, and filtering as for the first crop. The total yield was 81.0% after drying at 90 °C/10 mTorr; mp 207 °C. Anal. Calcd for $C_{37}H_{30}F_3NO_3P_2S$: C, 64.63; H, 4.40. Found: C, 64.53; H, 4.40.

$(PPN)^+$ salts of $(O_2CCF_3)^-$, $(BF_4)^-$, and $(ClO_4)^-$ were prepared in a similar manner for qualitative use in recording IR spectra of these anions in uncoordinated form.

Preparation of New Rhodium(I) Complexes. The preparation of $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ illustrates the technique used for all four new Rh(I) compounds. Although all solvents used were stored over molecular sieves, glassware was not oven-dried and most synthetic manipulations described here were carried out in bench-top fashion with only partial protection from the atmosphere; i.e., no care was taken to maintain a strictly anhydrous or anaerobic environment. To a mixture of solid {Rh}Cl[10] (2.513 g, 3.637 mmol) and $AgSO_3CF_3$ (1.210 g, 4.709 mmol; stored in a Schlenk tube under nitrogen and weighed with only an extremely brief exposure to air) in a 500-mL Schlenk flask shielded from light were added 300 mL of benzene and a magnetic stir bar; the resulting yellow suspension was stirred 16 h. [Such reactions with silver(I) salts were generally run overnight to ensure complete conversion of the chloro complex to the desired metathesis product, even though the times actually required were likely much shorter.] A nitrogen gas blanket was used to limit exposure to water over this period. Then the mixture was filtered through Celite on a sintered-glass funnel, and the resulting yellow-orange solution was concentrated to a volume of about 25 mL. [Reducing the volume further often resulted in formation of a brown tar upon addition of heptane in the next step.] To the concentrate was slowly added first 10 mL of diethyl ether and then 120 mL of heptane; the resulting yellow crystals were filtered, washed with two 20-mL portions of heptane, and dried at reduced pressure to afford a first crop of 1.938 g. Concentrating the filtrate on a rotary evaporator to preferentially remove ether and benzene and then adding more heptane and refrigerating overnight afforded a second crop (0.468 g) of yellow crystals. A third crop (0.134 g) was obtained similarly. The total yield corresponded to 83.1% of that expected for complete conversion to $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$.

The two other $[\{Rh\}(OH_2)]Z$ complexes were prepared in a similar fashion as dihydrates in 78.1% (Z = BF_4) and 91.3% (Z = ClO_4) yield. Their waters of hydration were retained even after drying at 90 °C/10 mTorr. Anal. Calcd for $C_{37}H_{36}BF_4O_4P_2Rh$ (Z = BF_4): C, 55.81; H, 4.56; F, 9.81. Found: C, 55.94; H, 4.53; F, 9.70. Anal. Calcd for $C_{37}H_{36}ClO_8P_2Rh$ (Z = ClO_4): C, 54.93; H, 4.48. Found: C, 55.21; H, 4.30. The {Rh}$OPOF_2$ species was obtained without waters of hydration in 79.6% yield by an analogous procedure (via the in situ hydrolysis). Anal. Calcd for $C_{37}H_{30}F_2O_3P_3Rh$: C, 58.75; H, 4.00. Found: C, 58.56; H, 4.09.

In one experiment, a mixture initially containing {Rh}Cl and $AgPF_6$ in benzene was sampled after only 0.25 h. The suspension withdrawn was stripped to a solid that was extracted with CH_2Cl_2; IR analysis of that extract showed the carbonyl band to be centered at 1998 cm^{-1} (where those for $[\{Rh\}(OH_2)]^+$ were observed), not at 1988 cm^{-1} where dichloromethane solutions of isolated {Rh}$OPOF_2$ absorbed. Attempts to isolate a pure rhodium(I) hexafluorophosphate species by processing reaction mixtures after short stirring periods afforded what appeared to be mixtures of {Rh}$OPOF_2$ and the initially observed species.

{Rh}$OPOF_2$ and $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ complexes were also characterized by FAB and LD mass spectrometry.[2]

Preparation of Previously Synthesized Rhodium(I) Complexes. Syntheses of the complexes {Rh}ONO_2 and {Rh}O_2CCF_3 were carried out as described previously.[1] Their purities were checked by infrared spectroscopy and thin-layer chromatography on silica.

PPN Salt Ligand Substitution Equilibria Studies.[11] These experiments were conducted anhydrously, using CH_2Cl_2 dried thoroughly over molecular sieve 4A,[1] glassware hot from an oven at 150 °C blanketed with nitrogen gas before it could cool sufficiently to adsorb water from the atmosphere, and sampling for infrared analysis under nitrogen.

The reaction of {Rh}O_2CCF_3 with (PPN)NO_3 provides a typical example. A 27.0-mg amount of {Rh}O_2CCF_3 (0.0414 mmol) and 31.7-mg amount of (PPN)NO_3 (0.0528 mmol) were placed into an oven-dried Schlenk tube under nitrogen. A 20.0-mL aliquot of anhydrous CH_2Cl_2 was withdrawn under nitrogen from a solvent Schlenk flask (fitted with a single-hole rubber stopper into which a previously oven-dried volumetric pipet had been inserted) and added to the reactants to form a pale yellow solution. A rubber septum was inserted into the Schlenk tube. After 0.2 h, a well-flushed oven-dried Hamilton gas-tight syringe was inserted through the septum, and about 0.8 mL of the solution was withdrawn and transferred under nitrogen into a CaF_2 infrared cell (2.5-mm path length). A spectrum was recorded (at 21 °C) over the range 2400–1700 cm^{-1}, and the small absorbances due to the presence of PPN^+ were subtracted. The portion of 1999–1960 cm^{-1} was used for calculation of equilibrium concentrations of {Rh}O_2CCF_3 and {Rh}ONO_2 (vide infra). To check the influence of small amounts of H_2O on the equilibria, 20 μL thereof was injected into the mixtures and samples were analyzed by IR after another 0.2 h of stirring. In separate experiments, the molar absorptivities of the respective {Rh}L species were determined for 2.00 mM solutions (ca. 15 mg weighed to ±0.2 mg in 10.0 mL) for use in the multivariate-analysis program.

Related experiments were conduced on a similar scale for the following {Rh}L/(PPN)Y combinations at the ratios indicated: (a) {Rh}ONO_2/(PPN)SO_3CF_3 (1:4.00), (b) {Rh}$OPOF_2$/(PPN)NO_3 (1:1.05), (c) {Rh}$OPOF_2$/(PPN)SO_3CF_3 (1:4.00), (d) $[\{Rh\}(OH_2)][ClO_4]\cdot 2H_2O$/(PPN)$SO_3CF_3$ (1:4.00), and (e) $[\{Rh\}(OH_2)][BF_4]\cdot 2H_2O$/(PPN)$SO_3CF_3$ (1:4.00). The slight discontinuity in all experiments at 2000 cm^{-1} due to the instrumental grating change prompted us to use no data

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Table I. Infrared Spectroscopic Data for $Rh(PPh_3)_2(CO)L$ Complexes

compound	$\nu(CO)$, cm^{-1} $(\epsilon)^a$	anion bands in CH_2Cl_2,^{b,c} cm^{-1}	intensity^c in Nujol
$[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$	1998 (0.112 ± 0.005)	1322 (s), 1209 (s), 1188 (ms), 1168 (m), 1024 (s)	1278 (s), 1245 (s), 1223 (m), 1172 (ms), 1161 (ms), 1029 (s)
$[\{Rh\}(OH_2)][ClO_4]\cdot 2H_2O$	1998 (0.063 ± 0.003)	1200–990 (br, s)	1200–990 (br, m)
$[\{Rh\}(OH_2)][BF_4]\cdot 2H_2O$	1998 (0.059 ± 0.003)	1200–900 (br, s)	1200–900 (br, m)
$[\{Rh\}(C_5H_5N)][SO_3CF_3]$	2004 (0.142 ± 0.006)	1214 (ms), 1156 (s), 1027 (s)	1280 (sh), 1263 (ms), 1223 (m), 1146 (s), 1029 (ms)
$[\{Rh\}(CH_3CN)][SO_3CF_3]$	2012^d	1219 (m), 1156 (s), 1030 (s)	
$(PPN)SO_3CF_3$		1157 (ms), 1030 (s)	1281 (ms), 1263 (s), 1223 (m), 1031 (s)
$\{Rh\}NO_3$	1984 (0.111 ± 0.005)		1280 (ms), 997 (mw)
$\{Rh\}O_2CCF_3$	1982 (0.088 ± 0.004)	1685 (m)	
$\{Rh\}O_2PF_2$	1988 (0.091 ± 0.004)		1307 (s), 1119 (ms), 874 (m), 841 (m)

^{a} In CH_2Cl_2. ^{b} Region 1325–1200 partially obscured by solvent bands. ^{c} Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad. ^{d} Prepared in situ from $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ and CH_3CN in ca. 1:2 ratio.

above 1999 cm^{-1} in numerical data analysis.

Ligand Replacement Equilibria with Pyridine. These equilibria in 1,2-dichloroethane were also studied under anhydrous conditions. A stock solution of pyridine (4.32 mM) was prepared under nitrogen by transferring 79.1 mg of pyridine via a gas-tight syringe into an oven-dried 100-mL volumetric flask fitted with a septum and then adding 1,2-$C_2H_4Cl_2$ by cannula to the mark. The stock solution was transferred by cannula into a Schlenk flask for more convenient handling under nitrogen. The 20.0-mL aliquots of stock solution were transferred via pipet as described above into Schlenk flasks containing weighed amounts of the respective $\{Rh\}L$; e.g., for $\{Rh\}ONO_2$, two samples of 34.4 mg and 62.0 mg afforded solutions of respective total $[\{Rh\}]$ of 2.40 and 4.33 mM, with nominal respective $[py]/[\{Rh\}ONO_2]$ ratios of 1.80 and 0.998. The resulting pale yellow solutions were stirred for 0.2 h at 21 °C and sampled for infrared analysis as in the $\{Rh\}L/(PPN)Y$ studies. Data were recorded every cm^{-1} over the range 2030–1960 cm^{-1}. A sample of $[Rh(PPh_3)_2(CO)(C_5H_5N)][SO_3CF_3]$ (the cation is termed $[\{Rh\}py]^+$ hereafter)[12] isolated from an equimolar mixture of pyridine and $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ in CH_2Cl_2 was used to prepare a 2.00 mM solution in 1,2-$C_2H_4Cl_2$ for determination of the molar absorptivity of $[\{Rh\}py]^+$. A multivariate-analysis program in BASIC was used to calculate equilibrium concentrations of the respective Rh(I) species in solution and their equilibrium constants.[9] [The slight instrumental grating discontinuity appeared to cause little problem in data analysis here.] The influence of small amounts of H_2O on the equilibria was checked as described for the anion-metathesis experiments.

Anion Displacement Equilibria with CO. These experiments were conducted anhydrously at 21 °C in 1,2-$C_2H_4Cl_2$ under 1.01 atm of CO. Samples of mass of roughly 8 mg (0.012 mol) of $\{Rh\}L$ were weighed to the nearest 0.2 mg; each was transferred into an oven-dried Schlenk tube containing a magnetic stir-bar under nitrogen. A 6.0-mL aliquot of dry solvent was added by pipet, and the head-space was purged quickly with CO; the pale yellow solution was stirred rapidly for 2.0 h to ensure solution saturation with CO. A mineral oil bubbler kept CO pressure essentially constant at 1.01 atm. The solution was sampled under CO via use of an oven-heated gas-tight syringe and an infrared sample cell connected to a CO line. The Teflon Luer stoppers gave air-tight fits for the analysis. Infrared spectra were recorded over the range 2400–1700 cm^{-1}. A broad new band at 2025 cm^{-1} with a shoulder at 2036 cm^{-1} was observed to have grown in.

Reactions of $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ with Alkenes. To solutions of $[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ (2.0 mM) in dry CH_2Cl_2 were added those liquid alkenes whose amounts are indicated by the alkene/$[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$ ratios in the Results section, and samples were withdrawn for IR analysis under nitrogen after stirring for 0.3 h. The reaction with ethylene was conducted at 1.01 atm in a manner analogous to that described for reaction with CO above.

Crystal Structure of $[Rh(PPh_3)_2(CO)(OH_2)][BF_4]\cdot{}^1/_2H_2O\cdot{}^1/_4C_6H_{12}$. Cyclohexane vapor was allowed to slowly diffuse into a solution of 100 mg of $[\{Rh\}(OH_2)][BF_4]\cdot 2H_2O$ in a minimum amount of benzene (ca. 10 mL). A suitable crystal was isolated and mounted in a glass fiber. [There were so few crystals as to preclude spectroscopic characterization and elemental analysis.] Autoindexing on 18 reflections centered from a rotation photograph indicated a triclinic cell (Table V); attempted lattice transformation did not locate a higher symmetry cell. A hemisphere of data ($+h,\pm k,\pm l$) was collected ($\theta/2\theta$ scans, 1–50° in 2θ); collection details are described in Table S-I in the supplementary material. The merging *R* for equivalent reflections was 0.0357. The data were subjected to Lorentz and polarization corrections and to an empirical absorption correction.[13] A general extinction correction was not applied; however, three low-angle reflections that appeared to be seriously affected by extinction were removed from the data set for the final refinement.

The space group $P\bar{1}$ was chosen for refinement on the basis of intensity statistics; the asymmetric unit contains two independent $[Rh(PPh_3)_2(CO)(OH_2)]^+$, two $(BF_4)^-$, a lattice water, and half a cyclohexane molecule (see below). The rhodium and phosphorus atoms were recovered from the Patterson map; the remaining non-hydrogen atoms appeared in subsequent difference maps. The phenyl rings (12 per asymmetric unit) were refined as rigid groups of D_{6h} symmetry (d_{C-C} = 1.395 Å, d_{C-H} = 0.960 Å) with individual isotropic temperature factors for the phenyl carbons. It was immediately apparent that the complex contains coordinated water instead of tetrafluoroborate anion and that the $(BF_4)^-$ counterions are not entirely "well-behaved". Around B(1), F(11) is apparently ordered. However, small peaks around F(12), F(13), and F(14) suggested that the ion exists in one major and two minor rotational orientations about the local C_3 axis defined by the B(1)–F(11) bond. The other $(BF_4)^-$ shows similar behavior; we did not refine this disorder. Finally, we observed a cluster of peaks that form a nonplanar six-membered ring about the inversion points $^1/_2$, $^1/_2$, $^1/_2$, which we have assigned as cyclohexane based on the history of the crystal. The large temperature factors on the unique carbons C(3), C(4), and C(5), as well as relatively poor C–C distances, suggest the possibility of disorder or partial occupancy of these atoms. A total of 6479 reflections was used in the refinement of 379 variables. Water hydrogens were not unequivocally located.

Final positional parameters, temperature factors, and bond distances and angles are given in Tables VI–IX. The final electron density map showed a number of peaks of electron density ca. 0.75 $e^-/Å^3$. These peaks, all associated with the phenyl rings, reflect some anisotropic motion of the phenyl carbons that was not adequately described by the rigid-body refinement of these atoms. Further refinement without the rigid-group restrictions on the phenyl carbons did not result in location of the water hydrogens or resolution of the disorder/occupancy problems with the BF_4^- ions and the cyclohexane molecule.

Results

Although silver(I)-promoted metathesis of the chloro ligand in the well-known Vaska complex by weakly coordinating anions proceeded smoothly, formation of the anticipated $[Rh(PPh_3)_2(CO)]^+$ complexes of $(SO_4CF_3)^-$, $(BF_4)^-$, $(ClO_4)^-$, and $(PF_6)^-$ was prevented by the presence of small amounts of water. For the first three cases, water is apparently a stronger ligand than the respective weakly coordinating anions, and samples of aqua complexes with additional water of crystallization were isolated in high yield. Solid samples of the respective aqua complexes hold their water of crystallization tightly (up to at least 90 °C/10 mTorr). The anticipated complex of $(PF_6)^-$ was found to be a complex of its hydrolysis product, containing coordinated $(OPOF_2)^-$ and no water of crystallization. IR analysis of a $\{Rh\}Cl/AgPF_6$ reaction mixture after only a short contact time detected a carbonyl stretching band at 1998 cm^{-1}, a position corresponding to that of the aqua cation, $[\{Rh\}(OH_2)]^+$, or (less likely) a $\{Rh\}FPF_5$ species; however, attempts to isolate a pure rhodium(I) hexafluorophosphate species by processing reaction mixtures after

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[12] Reddy, G. K. N.; Ramesh, B. R. *J. Organomet. Chem.* **1975**, *87*, 347.

[13] All calculations were carried out with the SHELXTL-PLUS system (Siemens Analytical X-Ray Instruments, Madison, WI).

Table II. ^{31}P NMR Data for $Rh(PPh_3)_2(CO)L$ Complexes

complex	$\delta(^{31}P)$, ppm[a]	J(Rh–P), Hz
$[\{Rh\}(OH_2)][SO_3CF_3]\cdot H_2O$[b]	+29.5	125
$[\{Rh\}(OH_2)][ClO_4]\cdot 2H_2O$[c]	+29.8	126
$[\{Rh\}(OH_2)][BF_4]\cdot 2H_2O$[d]	+30.9	123
$\{Rh\}NO_3$[c]	+30.8	134
$\{Rh\}O_2CCF_3$[d]	+31.5	137
$\{Rh\}OPOF_2$[c,e]	+29.5	125

[a] Doublet, relative to external H_3PO_4 (85%). [b] In $CDCl_3$. [c] In toluene. [d] In CH_2Cl_2/toluene. [e] O*P*OF$_2$: $\delta(^{31}P) = -17.4$ ppm; J(P–F) = 955 Hz.

short stirring periods afforded what appeared to be mixtures of $\{Rh\}OPOF_2$ and the initially observed species. Synthesis of $\{Rh\}ONO_2$ and $\{Rh\}O_2CCF_3$ via the aqua complexes and the respective sodium salts in methanol/water afforded solid samples containing no waters of crystallization. Spectroscopic properties of the complexes are listed in Tables I and II.

We have assigned coordinated status to the anions $(ONO_2)^-$, $(O_2CCF_3)^-$, and $(OPOF_2)^-$ in their $[Rh(PPh_3)_2(CO)]^+$ complexes on the basis of their respective infrared spectra and elemental analyses showing the absence of water in crystalline samples isolated. The nitrate complex exhibits bands at 1280 (strong) and 997 cm^{-1} (medium weak) characteristic of monodentate nitrate; a shoulder at 1480 cm^{-1} on a strong Nujol band at 1460 cm^{-1} apparently corresponds to the nearly concealed $\nu_{asym}(NO_2)$ absorption. Our spectrum is very similar those of PPh_3-substituted rhenium(I)-nitrate complexes[14] and *cis*-$Pt(NH_3)_2(ONO_2)_2$.[15] Characteristic bands for monodentate difluorophosphate ligand were observed for $\{Rh\}OPOF_2$ in Nujol at 1307, 1119, 874, and 841 cm^{-1}, at positions very close to those reported for Re(I)[7g] and hydridoiridium(III)[16] difluorophosphate species. Comparison of IR spectra of CH_2Cl_2 solutions and Nujol mulls of $\{Rh\}O_2CCF_3$ and $(PPN)O_2CCF_3$ showed the former to exhibit a medium-intensity carboxylate C=O stretch at 1685 cm^{-1} and the latter a carboxylate C=O stretch of strong intensity at 1690 cm^{-1} (similar to other monodentate trifluoroacetate complexes[17]).

IR spectra of the tetrafluoroborate and perchlorate species in both CH_2Cl_2 and Nujol resembled spectra of complexes containing the respective uncoordinated anions[8,18] and the spectra of their respective $(PPN)^+$ salts.[11] Elemental analyses showing the presence of three waters per rhodium for both species and the crystal structure of the cyclohexane-solvated aqua tetrafluoroborate complex indicate that H_2O rather than the anion appears in the inner coordination sphere. An IR spectrum of the BF_4 form of the aqua cation in Nujol showed broad bands (weak or medium) at 1119, 1054, and 977 cm^{-1} (not present in a spectrum of $\{Rh\}Cl$ in Nujol) superimposed on the general broad pattern in the 1200–900-cm^{-1} B–F stretching region (consistent[19] with hydrogen bonding to $(BF_4)^-$; vide infra). Also present in the ν(O–H) region were broad weak bands at 3599 and 3355 cm^{-1}. The carbonyl stretches of the Rh(I) aqua complexes containing counterions $(ClO_4)^-$ and $(BF_4)^-$ appeared at the same frequency (1988 cm^{-1}) and had molar absorptivities identical within experimental error (0.059 and 0.063, both ±0.003). The trifluoromethanesulfonate species also had the identical carbonyl stretching frequency; however, the molar absorptivity of the latter absorption was dramatically different: 0.112 ± 0.005. Since one would not usually expect such a large difference between the molar absorptivities of the same complex cation in substances having only different counterions, the ^{19}F NMR spectra of "$Rh(PPh_3)_2(CO)(SO_3CF_3)\cdot 2H_2O$" and of a known Rh(I) cation with $(SO_3CF_3)^-$ as uncoordinated counterion, $[\{Rh\}py][SO_3CF_3]$, were recorded. Both spectra showed sharp singlets at −78.7 ppm relative to CCl_3F in CH_2Cl_2, so it appears unlikely that the former species contained coordinated $(SO_3CF_3)^-$. Further evidence for that point was provided in similarities in the 1350–900-cm^{-1} ranges of the infrared spectra of "$Rh(PPh_3)_2(CO)(SO_3CF_3)\cdot 2H_2O$", $[\{Rh\}py][SO_3CF_3]$, $[\{Rh\}(CH_3CN)][SO_3CF_3]$, and $(PPN)SO_3CF_3$. Assignments of individual vibrations for the trifluoromethanesulfonate anion are quite difficult[20] compared with those for simpler anionic ligands such as nitrate and perchlorate. The bands reported by Trogler et al.[7b] for $[Mn(CO)_5(PBu_3)][SO_3CF_3]$ in CH_2Cl_2 for ν(SO) at 1161 and 1031 cm^{-1} were, however, similar in intensity and frequency to those at 1168 and 1024 cm^{-1} for "$Rh(PPh_3)_2(CO)(SO_3CF_3)\cdot 2H_2O$" (and those of the other uncoordinated trifluoromethanesulfonate species listed above as well); moreover, the IR spectrum reported for $Re(CO)_5OSO_2CF_3$ in this particular region was dissimilar to those for the known ionic SO_3CF_3 species above and for "$Rh(PPh_3)_2(CO)(SO_3CF_3)\cdot 2H_2O$".

Table III. Equilibrium Data[a,b] for $\{Rh\}L + Y^- = \{Rh\}Y + L$

L	Y^-	K_c	$X_{\{Rh\}Y}$[b]
$O_2CCF_3^-$	ONO_2^-	$<10^{-4}$	<0.01
$OPOF_2^-$	ONO_2^-	78 ± 32	0.90 ± 0.03
$OPOF_2^-$	$OSO_2CF_3^-$	$<10^{-4}$	<0.01
$OH_2(ClO_4^-)$	$OSO_2CF_3^-$	$<10^{-4}$	<0.01
$OH_2(BF_4^-)$	$OSO_2CF_3^-$	$<10^{-4}$	<0.01
ONO_2^-	$OSO_2CF_3^-$	$<10^{-4}$	<0.01

[a] In CH_2Cl_2 at 21 °C. [b] Anions present as ion-paired $(PPN^+)Y^-$. [c] $X_{\{Rh\}Y}$ represents the fraction of Rh(I) complexes present as $\{Rh\}Y$ for initial $[(PPN)Y]/[\{Rh\}L] = 1$.

Table IV. Equilibrium Data[a,b] for $\{Rh\}L + py = \{Rh\}py^+ + L$

L	K_c	$X_{\{Rh\}py}$[c]
$O_2CCF_3^-$	$<10^{-4}$	<0.01
ONO_2^-	0.35 ± 0.16	0.37 ± 0.07
$OPOF_2^-$	3.2 ± 1.6	0.4 ± 0.06
$OH_2(ClO_4^-)$	$>10^4$	>0.99
$OH_2(FBF_3^-)$	$>10^4$	>0.99
$OH_2(SO_3CF_3^-)$	$>10^4$	>0.99

[a] In $1,2-C_2H_4Cl_2$ at 21 °C. [b] Anions present as ion-paired $(PPN^+)Y^-$. [c] $X_{\{Rh\}py}$ represents the fraction of Rh(I) complexes present as $\{Rh\}py^+$ for initial $[py]/[\{Rh\}L] = 1$.

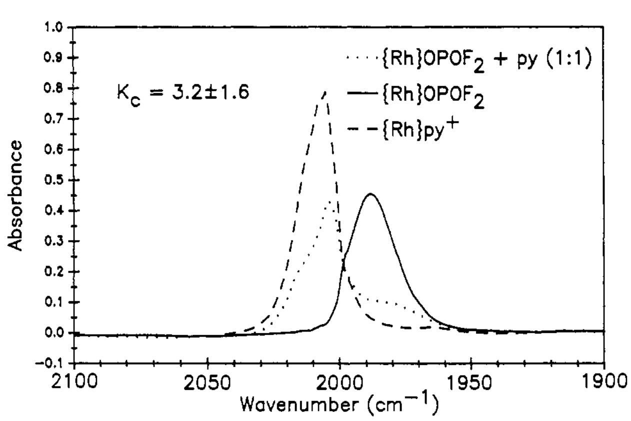

Figure 1. IR spectrum of $Rh(PPh_3)_2(CO)OPOF_2$ + pyridine (1:1). $[\{Rh\}OPOF_2 + py = \{Rh\}py^+ + OPOF_2^-.]$

Equilibrium Studies on Ligand Displacement. Using $(PPN)SO_3CF_3$ and $(PPN)NO_3$, we directly measured the degree of displacement of neutral and uninegative ligands, L, as shown by the equilibrium in eq 1. Pertinent data are listed in Table III.

$$Rh(PPh_3)_2(CO)L + Y^- = Rh(PPh_3)_2(CO)Y + L \quad (1)$$

Experiments in which the aqua complex in perchlorate and tetrafluoroborate forms was treated with 4 equiv of $(PPN)SO_3CF_3$ afforded spectra in which essentially no change in the starting spectrum of the $[\{Rh\}(OH_2)]^+$ species had occurred. [Even though

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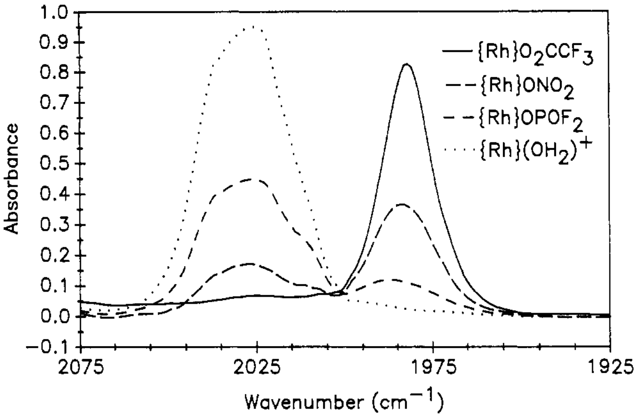

Figure 2. IR spectra of Rh(PPh$_3$)$_2$(CO)L under 1 atm of CO.

the carbonyl stretching frequency maximum is the same (1998 cm^{-1}) for the three aqua cation species, the molar absorptivity of the SO$_3$CF$_3$ form differs sufficiently from that of the ClO$_4$ and BF$_4$ forms to allow acceptable quantitative analyses of the two mixtures.] Addition of small amounts of water to the solutions of the experiments afforded essentially no perturbation of the equilibrium positions initially measured.

Data for the displacement of ligand L from {Rh}L by pyridine (py) in 1,2-dichloroethane (eq 2) are presented in Table IV.

$$\mathrm{Rh(PPh_3)_2(CO)L + py = [Rh(PPh_3)_2(CO)py]^+ + L} \quad (2)$$

Pyridine fails to appreciably replace (O$_2$CCF$_3$)$^-$ at 1:1 initial [py]/[{Rh}L]; however, at this reactant ratio it displaces the anion to a considerable extent in {Rh}ONO$_2$ and {Rh}OPOF$_2$ (see reaction spectra for {Rh}OPOF$_2$ in Figure 1) and the aqua ligand essentially completely in all three anionic forms. [These results parallel those from the set of experiments for ligand displacement by monoanions, even though 1,2-C$_2$H$_4$Cl$_2$ appears to stabilize the cations somewhat less than does CH$_2$Cl$_2$.[21]] Addition of small amounts of water to the solutions of the experiment afforded essentially no perturbation of the equilibrium positions initially measured.

Qualitatively similar results were observed for the reaction of {Rh}L with CO in 1,2-C$_2$H$_4$Cl$_2$ at 1 atm (eq 3). The aqua ligand

$$\mathrm{Rh(PPh_3)_2(CO)L + 2CO = [Rh(PPh_3)_2(CO)_3]^+ + L} \quad (3)$$

(in SO$_3$CF$_3$, BF$_4$, and ClO$_4$ forms) was essentially completely displaced under these conditions, affording a broad new carbonyl band at 2025 cm^{-1} with a high-energy shoulder at 2036 cm^{-1}. Spectra containing both sets of bands were obtained for solutions of {Rh}OPOF$_2$, {Rh}ONO$_2$, and {Rh}O$_2$CCF$_3$ under CO at 21 °C, with the series above showing increasingly lower respective fractions of {Rh}L present. The influence of anion upon this system is displayed in Figure 2. Our spectra appear consistent with the formation of [Rh(PPh$_3$)$_2$(CO)$_3$]$^+$, reported by Schrock and Osborn[22] upon stirring a solution of [Rh(PPh$_3$)$_2$(1,5-cyclooctadiene)]$^+$ under 1 atm of CO. Again, addition of small amounts of water to the solutions of the experiment afforded essentially no perturbation of the equilibrium positions initially measured.

Treating the aqua cation with moderate excesses of several monoolefins in CH$_2$Cl$_2$ afforded no displacement of coordinated water. Stirring a solution of [{Rh}(OH$_2$)][SO$_3$CF$_3$]·H$_2$O in CH$_2$Cl$_2$ at 20 °C under 1 atm of ethylene produced no change in position or intensity of the initial carbonyl stretching band at 1998 cm^{-1}. The following alkenes, with alkene/[{Rh}(OH$_2$)]-[SO$_3$CF$_3$]·H$_2$O molar ratios in parentheses, also generated no change in position or intensity of the initial IR carbonyl stretching band: norbornene (5), styrene (5), dimethyl maleate (30), cyclohexene (100), and cyclooctene (100). C$_2$H$_4$, generally considered a weaker ligand than CO,[24] apparently does not stabilize a bis(ethylene)-substituted analogue of [Rh(PPh$_3$)$_2$(CO)$_3$]$^+$, [Rh(PPh$_3$)$_2$(CO)(C$_2$H$_4$)$_2$]$^+$.

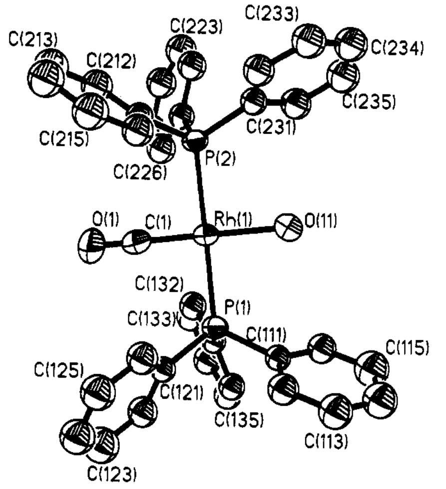

Figure 3. View of Rh(1) of [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][BF$_4$]·$^1/_2$H$_2$O·$^1/_4$C$_6$H$_{12}$. Thermal ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity, along with atom labels for some of the phenyl carbons.

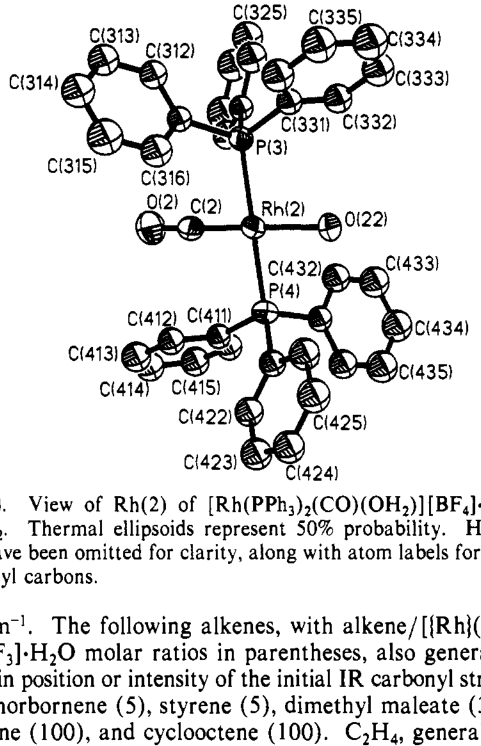

Figure 4. View of Rh(2) of [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][BF$_4$]·$^1/_2$H$_2$O·$^1/_4$C$_6$H$_{12}$. Thermal ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity, along with atom labels for some of the phenyl carbons.

Crystal Structure of [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][BF$_4$]·$^1/_2$H$_2$O·$^1/_4$C$_6$H$_{12}$. The isolation of a cation in which a water molecule rather than (BF$_4$)$^-$ is coordinated was demonstrated by X-ray structural analysis (alone, since so little material was obtained that no spectroscopic characterization or elemental analysis could be performed). Views of the two independent cations in the unit cell are displayed in Figures 3 and 4. Coordination about the central rhodium atom showed little deviation from square-planar geometry, and the Rh–P and Rh–C bond lengths are close to those observed for a variety of trans (bis)phosphine derivatives.[25-30] The

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(21) The extent of replacement of anionic L by several neutral ligands is significantly greater in CH$_2$Cl$_2$ than in 1,2-C$_2$H$_4$Cl$_2$: Branan, D. M.; Hoffman, N. W.; McElroy, A. E.; Prokopuk, N.; Robbins, M. J. Unpublished results.

(22) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. The reaction of Rh(PPh$_3$)$_2$(CO)Cl with AlCl$_3$ under CO was earlier proposed to yield [*trans*-Rh(PPh$_3$)$_2$(CO)$_2$]$^+$,[23] rather than the tricarbonyl cation reported by these authors. The correct formula appears that of the tricarbonyl.

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Table V. Crystallographic Data[a]

empirical formula	$C_{37}H_{32}BO_2F_4PRh(H_2O)_{1/2}(C_6H_{12})_{1/4}$
space group	triclinic, $P\bar{1}$
a	11.865 (2) Å
b	17.235 (6) Å
c	18.590 (5) Å
α	91.95 (2)°
β	101.62 (2)°
γ	101.83 (2)°
V	3633 (2) Å^3
Z	4
fw	790.4
density (calc)	1.45 g/cm^3
λ	0.71073 Å
T	22 °C
μ	6.0 cm^{-1}
$R_1(F_o)$	5.75%
$R_2(F_o)$	5.70%

[a] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $R_2 = [[\sum w(|F_o| - |F_c|)^2]/\sum(wF_o^2)]^{1/2}$.

$Rh-OH_2$ bond distance is remarkably close to that observed by Alcock et al. for *trans*-$[Rh[Ph_2P(CH_2)_2(OCH_2CH_2)_3PPh_2](CO)(OH_2)]^+$, in which the coordinated water is strongly hydrogen-bonded to O(1) and O(3) in the ether backbone.[28,30] Since hydrogens were not located, our structural data do not provide major insight into the type of hydrogen bonding that may be present in the complex. Data are presented in Tables V–IX.

Discussion

Although generation of the expected rhodium(I) Vaska complexes of coordinated $(SO_3CF_3)^-$, $(BF_4)^-$, $(ClO_4)^-$, and $(PF_6)^-$ was prevented by the small quantities of water present under aerobic conditions, the aqua cation formed with the first three anions above still proved a reagent useful for making a range of neutral and monocationic {Rh}L species. That water should prove a stronger ligand than $(SO_3CF_3)^-$, $(BF_4)^-$, and $(ClO_4)^-$ for $\{Rh\}^+$ is not totally unexpected, given the number of examples in the literature of low-valent transition-metal aqua complexes generated via displacement of weakly binding anions from the inner coordination sphere by H_2O[8] (e.g., preference of Pt(II)[19] in $[(R_3P)_2PtCl]^+$ for H_2O over $(BF_4)^-$ and the facile replacement[31] of coordinated $(BF_4)^-$ and $(PF_6)^-$ (as Y^-) in the d^4 series $CpM(CO)_2(L)Y$ by H_2O). The preference of Re(II)[31] for coordinating the extremely poor ligand CH_2Cl_2 rather than $(BF_4)^-$ in $[CpRe(NO)(PPh_3)(CH_2Cl_2)][BF_4]$ further illustrates the weakness with which this set of anions binds. [It should be noted, however, that coordinated $(SO_3CF_3)^-$ in $Re(CO)_5OSO_2CF_3$ is not replaced by H_2O in CH_2Cl_2.[7b]]

Treating the aqua complex in perchlorate and tetrafluoroborate forms with 4 equiv of $(PPN)SO_3CF_3$ afforded spectra in which essentially no change in the starting spectrum of the $[\{Rh\}(OH_2)]^+$ species had occurred; this observation suggests a reason why even though the carbonyl stretching frequency maximum is the same (1988 cm^{-1}) for the three aqua cation species, the molar absorptivity of the SO_3CF_3 form differs markedly from that of the ClO_4 and BF_4 forms (0.112 ± 0.005 for the first; 0.059 and 0.063, both ± 0.003, for the last two). Those results imply that the aqua cation forms considerably stronger ion pairs in CH_2Cl_2 with $(ClO_4)^-$ and $(BF_4)^-$ (via hydrogen bonding between the aqua ligand hydrogens and the counterions) than with $(SO_3CF_3)^-$; such interactions might change the degree of polarization of the $Rh-OH_2$ bond and consequently also that of the trans CO bond to afford the lower molar absorptivities for the carbonyl stretch of the ClO_4 and BF_4 forms. The number of potential hydrogen bonding sites (four for $(ClO_4)^-$ and $(BF_4)^-$, versus three in $(SO_3CF_3)^-$, numbers which may have some relationship to the number of waters of crystallization found in their respective complexes) may play some role in such a pattern. The resistance of the water of crystallization to removal (no loss up to 90 °C at 10 mTorr for all three anionic forms of $[\{Rh\}(OH_2)]^+$) implies the existence of strong hydrogen bonding between these anions and H_2O.

The IR spectrum of $[\{Rh\}(OH_2)][BF_4]$ is quite similar to those of other low-valent aqua complexes[16,32,33] in which unligated counterion $(BF_4)^-$ is hydrogen-bonded to coordinated H_2O. [Hydrogen bonding between the aqua ligand and $(BF_4)^-$ or related anions[34] seems characteristic of such complexes.[8]] Weak to medium bands at 1119, 1054, and 977 cm^{-1} are consistent with the lowering of symmetry for totally free $(BF_4)^-$ to hydrogen-bonded $(BF_4)^-$ (from T_d to most likely a C_{2v} bridging structure[19]). The two weak bands in the ν(O–H) region at 3599 and 3355 cm^{-1} likely correspond to absorptions by waters of crystallization and the aqua ligand, respectively. The lower frequency was assigned to Rh(I)-bound H_2O, since coordination to a transition-metal moiety weakens the O–H bonds, which are further weakened by hydrogen bonding of the hydrogens to fluorine atoms in the counterion,[19] and ν(O–H) absorptions for similar transition-metal aqua cations hydrogen-bonded to unligated $(BF_4)^-$ have been observed at similar wavenumbers.[16,32,33] Considerably lower energy ν(O–H) absorptions (3200–3050-cm^{-1} range) were observed for three $[(R_3P)_2PtCl(OH)_2][BF_4]$ species, perhaps because the latter contain no strong π-back-bonding ligand.

The isolation of $\{Rh\}OPOF_2$ rather than $\{Rh\}FPF_5$ from the reaction mixture of {Rh}Cl and $AgPF_6$ has some precedent, for several other low-valent transition-metal hexafluorophosphate species have been shown to undergo relatively facile hydrolysis to generate difluorophosphate complexes.[7f,g] A coproduct of hydrolysis of the hexafluorophosphate ligand must be HF (2 mol/mol of $(PF_6)^-$). One might expect its conjugate base F^- (a much stronger ligand for $[Rh(PPh_3)_2(CO)]^+$ than is $(OPOF_2)^-$)[35] to replace the $(OPOF_2)^-$ ligand; that such a phenomenon did not occur may be rationalized in terms of the considerably greater affinity of H^+ for F^- (a much stronger Bronsted–Lowry base than $(OPOF_2)^-$) and possible consumption of the HF by reaction with the glass vessel walls.

$Rh(PPh_3)_2(CO)OClO_3$ was first prepared by Peone and Vaska,[3] who showed it to be a convenient intermediate for preparing a wide range of related rhodium(I) complexes via displacement of the coordinated perchlorate ligand. When we used the conditions described for one version of the perchlorate complex synthesis[3b] (employing aerobic precipitation and filtration of the microcrystalline product), the sample we isolated was shown by elemental analysis to contain three waters per Rh and not have $(ClO_4)^-$ in the inner coordination sphere. Several studies excluding air and water using $Rh(PPh_3)_2(CO)OClO_3$ and its Ir(I) analogue prepared via the earlier anaerobic/anhydrous route[3a] have been reported.[36] A recent paper by the same group[37] reports a kinetic study for displacement of coordinated perchlorate from the Rh(I) complex by CH_3CN and small unsaturated nitriles in which the nitrile ligand samples used were not pretreated as done earlier to rigorously remove water; the results reported, however, appear to show no pernicious effect of any small amounts of water that might have been present upon the kinetics data.

The three sets of equilibria studied (displacement of L in {Rh}L by X^-, pyridine, and CO) showed a clear trend in relative affinity of $[Rh(PPh_3)_2(CO)]^+$ for this set of neutral ligands and weakly coordinating anions: L = $(O_2CCF_3)^- > (ONO_2)^- >$ pyridine >

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Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Rh(1)	1743 (1)	1747 (1)	2855 (1)	42 (1)	C(312)	7048	8083	1463	53 (2)
C(1)	922 (8)	943 (6)	2184 (6)	62 (4)	C(313)	7812	8829	1570	62 (3)
O(1)	413 (6)	436 (4)	1751 (4)	96 (4)	C(314)	7686	9406	2075	69 (3)
O(11)	2710 (5)	2763 (3)	3549 (3)	58 (2)	C(315)	6796	9237	2472	79 (3)
P(1)	−44 (2)	2025 (1)	3025 (1)	41 (1)	C(316)	6033	8492	2364	65 (3)
P(2)	3491 (2)	1356 (1)	2756 (1)	44 (1)	C(321)	5184 (5)	6540 (3)	827 (3)	45 (2)
C(111)	65 (5)	3026 (2)	3433 (3)	40 (2)	C(322)	4328	6641	224	66 (3)
C(112)	−212	3635	3002	57 (2)	C(323)	4402	6402	−487	89 (3)
C(113)	−59	4401	3329	71 (3)	C(324)	5391	6062	−594	83 (3)
C(114)	370	4557	4086	77 (3)	C(325)	6187	5961	9	76 (3)
C(115)	647	3948	4518	79 (3)	C(326)	6113	6200	719	68 (3)
C(116)	494	3182	4191	57 (2)	C(331)	5895 (5)	6343 (3)	2365 (3)	43 (2)
C(121)	−1178 (4)	1906 (3)	2183 (2)	40 (2)	C(332)	5479	5520	2280	55 (2)
C(122)	−2356	1571	2172	59 (2)	C(333)	6039	5036	2751	70 (3)
C(123)	−3200	1495	1517	81 (3)	C(334)	7014	5375	3306	77 (3)
C(124)	−2864	1754	873	72 (3)	C(335)	7430	6198	3390	76 (3)
C(125)	−1686	2090	884	70 (3)	C(336)	6870	6682	2920	63 (3)
C(126)	−842	2165	1539	60 (3)	C(411)	553 (5)	7600 (3)	1125 (3)	44 (2)
C(131)	−713 (4)	1370 (3)	3650 (3)	41 (2)	C(412)	990	8421	1196	54 (2)
C(132)	−383	644	3761	57 (2)	C(413)	532	8894	667	67 (3)
C(133)	−921	114	4205	64 (3)	C(414)	−363	8546	68	69 (3)
C(134)	−1789	311	4538	64 (3)	C(415)	−800	7725	−3	70 (3)
C(135)	−2119	1037	4428	61 (3)	C(416)	−342	7252	525	56 (2)
C(136)	−1581	1566	3984	50 (2)	C(421)	821 (5)	7310 (3)	2659 (2)	46 (2)
C(211)	3576 (5)	1150 (3)	1804 (2)	44 (2)	C(422)	12	7794	2663	57 (2)
C(212)	3743	421	1545	61 (3)	C(423)	−284	8000	3322	63 (3)
C(213)	3800	294	809	74 (3)	C(424)	229	7723	3978	62 (3)
C(214)	3690	894	333	75 (3)	C(425)	1038	7239	3974	71 (3)
C(215)	3523	1623	591	70 (3)	C(426)	1334	7033	3315	64 (3)
C(216)	3466	1750	1327	56 (2)	C(431)	300 (5)	6008 (3)	1564 (3)	47 (2)
C(221)	3672 (5)	453 (3)	3201 (3)	46 (2)	C(432)	700	5464	1160	62 (3)
C(222)	4791	294	3426	60 (3)	C(433)	2	4704	943	76 (3)
C(223)	4919	−406	3758	73 (3)	C(434)	−1095	4489	1130	80 (3)
C(224)	3929	−947	3864	71 (3)	C(435)	−1494	5033	1535	80 (3)
C(225)	2810	−788	3639	76 (3)	C(436)	−796	5792	1751	63 (3)
C(226)	2681	−87	3308	62 (3)	B(1)	2981 (13)	2000 (8)	5296 (9)	75 (6)
C(231)	4845 (4)	2073 (3)	3182 (3)	44 (2)	F(11)	3094 (7)	2727 (4)	5020 (3)	115 (4)
C(232)	5570	2522	2774	57 (2)	F(12)	2879 (7)	1426 (4)	4756 (4)	136 (4)
C(233)	6571	3078	3133	67 (3)	F(13)	3969 (8)	2036 (5)	5803 (5)	164 (5)
C(234)	6848	3185	3900	68 (3)	F(14)	2090 (8)	1850 (5)	5621 (5)	169 (5)
C(235)	6123	2735	4309	73 (3)	B(2)	2646 (12)	3903 (8)	2045 (9)	78 (6)
C(236)	5122	2179	3949	60 (3)	F(21)	3636 (6)	3607 (4)	2134 (4)	127 (4)
Rh(2)	3216 (1)	7001 (1)	1850 (1)	40 (1)	F(22)	2812 (6)	4585 (4)	1695 (4)	116 (4)
C(2)	3383 (7)	7844 (6)	1326 (5)	54 (4)	F(23)	2572 (9)	4111 (6)	2749 (5)	184 (6)
O(2)	3529 (6)	8394 (4)	999 (4)	88 (4)	F(24)	1721 (7)	3373 (4)	1730 (5)	165 (5)
O(22)	3060 (5)	6043 (3)	2544 (3)	57 (2)	O(3)	4344 (8)	6513 (5)	3873 (4)	125 (5)
P(3)	5135 (2)	6947 (1)	1740 (1)	42 (1)	C(3)	3786 (14)	4709 (9)	4668 (11)	162 (11)
P(4)	1216 (2)	6998 (1)	1804 (1)	43 (1)	C(4)	4798 (18)	4517 (9)	4437 (9)	156 (10)
C(311)	6158 (4)	7914 (3)	1860 (3)	41 (2)	C(5)	5952 (13)	4621 (8)	5024 (7)	94 (7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$(OPOF_2)^- \gg H_2O \gg (SO_3CF_3)^- \approx (BF_4)^- \approx (ClO_4)^-$. For complexes of $[Rh(PPh_3)_2(CO)]^+$, $(O_2CCF_3)^-$ cannot be considered weakly coordinating, and $(ONO_2)^-$ is only marginally so. $(OPOF_2)^-$ has much lower affinity for the parent cation (but still higher than that of H_2O); the poorly coordinating H_2O ligand is in turn considerably more tightly held than by the truly weakly coordinating anions $(BF_4)^-$, $(SO_3CF_3)^-$, $(ClO_4)^-$.

Research by Songstad's group[38] suggests that all $[PPN]^+$ salts are strongly associated in CH_2Cl_2 as ion pairs having large association constants essentially independent of anion nature; thus there should exist in eq 1 for uninegative L little thermodynamic preference in formation of monoanion L relative to X^-. If so, the equilibrium positions observed (represented in Table III best by the mole fraction $X_{\{Rh\}Y}$) provide reasonable estimates of relative stabilities of {Rh}L and {Rh}Y in solution. The ligand affinity trend determined fails to correlate with our spectroscopic data for the complexes: wavenumber or molar absorptivity of the IR carbonyl stretching band or chemical shift or coupling constant with ^{103}Rh of the ^{31}P nuclei. A similar lack of correlation between the affinity trend for more strongly ligating anions and various parameters was noted earlier.[1]

Failure to observe complexes of $[trans\text{-}Rh(PPh_3)_2(CO)(ol)]^+$, where ol = monoolefin, is best rationalized in terms of π-bonding effects, for numerous Rh(I) monoolefin complexes have been prepared. Competition for electron density from the filled Rh(I) d orbitals between the extremely strong π-acceptor CO and the ligand trans to it in the square-planar complex apparently has a major role in determining the stability of the Vaska-type species. [Such an argument nicely explains the relative affinities of $[trans\text{-}Rh(PPh_3)_2(CO)]^+$ for the halides, $X^- = F^- > Cl^- > Br^- > I^-$, since only F^- of the halides has no appropriate d orbitals available for π back-bonding.[35]] Thus we might expect both $[trans\text{-}Rh(PPh_3)_2(CO)(C_2H_4)]^+$ and $[trans\text{-}Rh(PPh_3)_2(CO)_2]^+$ to be unstable due to the respective trans CO/C_2H_4 and CO/CO interactions. This system is markedly different from the d^6 and d^4 BF_4 complexes studied by Beck's group[7d,e] from which $(BF_4)^-$ is facilely replaced by olefins in CH_2Cl_2 solutions; it is, however, similar to the d^6 system $W(NO)(CO)_2(PPh_3)_2OClO_3$ in which the weakly coordinating perchlorate ligand trans to the very potent π-acid nitrosyl group is facilely replaced by halides and pseudohalides but not by CO at 1000 psi.[39]

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Table VII. Anisotropic Displacement Parameters ($Å^2 \times 10^3$)[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	33 (1)	47 (1)	49 (1)	0 (1)	10 (1)	13 (1)
C(1)	45 (6)	70 (7)	76 (7)	-13 (6)	17 (5)	18 (5)
O(1)	73 (5)	92 (6)	109 (6)	-54 (5)	11 (5)	6 (4)
O(11)	45 (4)	61 (4)	65 (4)	-8 (3)	6 (3)	12 (3)
P(1)	36 (1)	47 (1)	44 (1)	5 (1)	9 (1)	15 (1)
P(2)	35 (1)	42 (1)	57 (2)	1 (1)	13 (1)	13 (1)
Rh(2)	39 (1)	44 (1)	40 (1)	4 (1)	8 (1)	14 (1)
C(2)	39 (5)	57 (6)	70 (7)	16 (5)	11 (5)	16 (5)
O(2)	95 (6)	83 (5)	100 (6)	47 (5)	32 (5)	37 (5)
O(22)	57 (4)	50 (4)	72 (4)	25 (3)	21 (3)	19 (3)
P(3)	42 (1)	42 (1)	42 (1)	0 (1)	10 (1)	11 (1)
P(4)	41 (1)	50 (1)	39 (1)	1 (1)	8 (1)	14 (1)
B(1)	90 (11)	58 (9)	96 (11)	12 (8)	48 (9)	27 (8)
F(11)	169 (7)	77 (4)	97 (5)	14 (4)	12 (5)	36 (5)
F(12)	211 (8)	79 (5)	125 (6)	-14 (4)	92 (6)	0 (5)
F(13)	141 (7)	184 (8)	167 (8)	35 (6)	-21 (6)	88 (7)
F(14)	159 (8)	144 (7)	233 (10)	-17 (6)	142 (8)	1 (6)
B(2)	70 (9)	50 (8)	112 (12)	5 (8)	13 (9)	17 (7)
F(21)	118 (6)	99 (5)	178 (7)	28 (5)	31 (5)	49 (5)
F(22)	99 (5)	79 (5)	168 (7)	47 (5)	21 (5)	17 (4)
F(23)	219 (10)	201 (9)	143 (7)	-46 (7)	102 (7)	18 (7)
F(24)	114 (6)	87 (5)	241 (10)	-2 (6)	-29 (6)	-29 (5)
O(3)	140 (8)	152 (8)	75 (6)	8 (5)	1 (5)	38 (6)
C(3)	130 (14)	103 (13)	272 (23)	-29 (13)	124 (15)	-8 (11)
C(4)	183 (19)	128 (14)	142 (15)	-3 (11)	40 (16)	-6 (14)
C(5)	137 (13)	69 (9)	92 (10)	-4 (7)	49 (9)	38 (9)

[a] The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

Table VIII. Bond Lengths (Å)

Rh(1)-C(1)	1.807 (9)	Rh(2)-C(2)	1.776 (10)
Rh(1)-O(11)	2.115 (5)	Rh(2)-O(22)	2.130 (6)
Rh(1)-P(1)	2.346 (3)	Rh(2)-P(3)	2.347 (3)
Rh(1)-P(2)	2.346 (3)	Rh(2)-P(4)	2.357 (3)
C(1)-O(1)	1.146 (11)	C(2)-O(2)	1.145 (12)
P(1)-C(111)	1.830 (5)	P(3)-C(311)	1.826 (5)
P(1)-C(121)	1.822 (5)	P(3)-C(321)	1.831 (6)
P(1)-C(131)	1.830 (6)	P(3)-C(331)	1.815 (6)
P(2)-C(211)	1.821 (5)	P(4)-C(411)	1.820 (6)
P(2)-C(221)	1.818 (5)	P(4)-C(421)	1.839 (6)
P(2)-C(231)	1.827 (4)	P(4)-C(431)	1.813 (5)
B(1)-F(11)	1.362 (15)	B(2)-F(21)	1.357 (17)
B(1)-F(12)	1.355 (16)	B(2)-F(22)	1.361 (16)
B(1)-F(13)	1.337 (17)	B(2)-F(23)	1.370 (19)
B(1)-F(14)	1.306 (20)	B(2)-F(24)	1.294 (14)
C(3)-C(4)	1.447 (29)	C(3)-C(5A)	1.223 (20)
C(4)-C(5)	1.543 (22)		

Conclusions

The aqua cation [*trans*-$Rh(PPh_3)_2(CO)(OH_2)]^+$ with the very weakly coordinating counteranions $(SO_3CF_3)^-$, $(BF_4)^-$, and $(ClO_4)^-$ can be prepared conveniently via Ag^+-assisted metathesis of the rhodium(I) chloride under aerobic conditions for use as a synthetic intermediate for making a wide range of the PPh_3 rhodium Vaska complexes. When $AgPF_6$ is used, hydrolysis of $(PF_6)^-$ affords a species containing coordinated $(OPOF_2)^-$ instead of H_2O. A crystal structure of the aqua cation in tetrafluoroborate form showed it to have typically square-planar geometry around rhodium; the $Rh-OH_2$ bond distance was very similar to that observed in another Vaska-type aqua cation. A study of ligand exchange equilibria showed the following relative affinities of L for $[Rh(PPh_3)_2(CO)]^+$ to form $Rh(PPh_3)_2(CO)L$: L = $(O_2CCF_3)^- > (ONO_2)^- >$ pyridine $> (OPOF_2)^- \gg H_2O \gg (SO_3CF_3)^- \approx (BF_4)^- \approx (ClO_4)^-$. $(O_2CCF_3)^-$ is held fairly strongly, and only $(SO_3CF_3)^-$, $(BF_4)^-$, $(ClO_4)^-$, and H_2O can be described for $[Rh(PPh_3)_2(CO)]^+$ as truly weakly coordinating, with $(OPOF_2)^-$ being borderline; all of the latter are relatively facilely displaced in weakly polar solvents such as 1,2-$C_2H_4Cl_2$ by pyridine to form $[Rh(PPh_3)_2(CO)(C_5H_5N)]^+$ and by CO to form $[Rh(PPh_3)_2(CO)_3]^+$. Monoolefins, however, fail to displace even the weakest ligands of the set.

Table IX. Bond Angles (deg)

C(1)-Rh(1)-O(11)	174.1 (4)	C(2)-Rh(2)-O(22)	176.1 (3)
C(1)-Rh(1)-P(1)	89.1 (3)	C(2)-Rh(2)-P(3)	85.8 (3)
O(11)-Rh(1)-P(1)	91.1 (2)	O(22)-Rh(2)-P(3)	94.3 (2)
C(1)-Rh(1)-P(2)	89.4 (3)	C(2)-Rh(2)-P(4)	92.0 (3)
O(11)-Rh(1)-P(2)	90.9 (2)	O(22)-Rh(2)-P(4)	88.4 (2)
P(1)-Rh(1)-P(2)	174.1 (1)	P(3)-Rh(2)-P(4)	172.9 (1)
Rh(1)-C(1)-O(1)	178.9 (10)	Rh(2)-C(2)-O(2)	177.8 (8)
Rh(1)-P(1)-C(111)	115.0 (2)	Rh(2)-P(3)-C(311)	114.4 (2)
Rh(1)-P(1)-C(121)	114.1 (2)	Rh(2)-P(3)-C(321)	112.5 (2)
C(111)-P(1)-C(121)	105.5 (3)	C(311)-P(3)-C(321)	104.0 (3)
Rh(1)-P(1)-C(131)	112.4 (2)	Rh(2)-P(3)-C(331)	116.7 (2)
C(111)-P(1)-C(131)	104.0 (3)	C(311)-P(3)-C(331)	104.2 (2)
C(121)-P(1)-C(131)	104.8 (2)	C(321)-P(3)-C(331)	103.6 (3)
Rh(1)-P(2)-C(211)	112.5 (2)	Rh(2)-P(4)-C(411)	115.7 (2)
Rh(1)-P(2)-C(221)	113.6 (2)	Rh(2)-P(4)-C(421)	117.3 (2)
C(211)-P(2)-C(221)	105.2 (3)	C(411)-P(4)-C(421)	103.8 (3)
Rh(1)-P(2)-C(231)	114.9 (2)	Rh(2)-P(4)-C(431)	111.3 (2)
C(211)-P(2)-C(231)	106.5 (3)	C(411)-P(4)-C(431)	104.1 (2)
C(221)-P(2)-C(231)	103.2 (2)	C(421)-P(4)-C(431)	103.1 (3)
P(1)-C(111)-C(112)	121.7 (2)	P(3)-C(311)-C(312)	121.8 (2)
P(1)-C(111)-C(116)	118.2 (2)	P(3)-C(311)-C(316)	118.2 (2)
P(1)-C(121)-C(122)	121.7 (2)	P(3)-C(321)-C(322)	118.6 (2)
P(1)-C(121)-C(126)	118.3 (2)	P(3)-C(321)-C(326)	121.1 (2)
P(1)-C(131)-C(132)	118.7 (2)	P(3)-C(331)-C(332)	118.4 (2)
P(1)-C(131)-C(136)	121.2 (2)	P(3)-C(331)-C(336)	121.6 (2)
P(2)-C(211)-C(212)	122.3 (2)	P(4)-C(411)-C(412)	118.7 (2)
P(2)-C(211)-C(216)	117.7 (2)	P(4)-C(411)-C(416)	121.2 (2)
P(2)-C(221)-C(222)	120.4 (2)	P(4)-C(421)-C(422)	121.9 (2)
P(2)-C(221)-C(226)	119.6 (2)	P(4)-C(421)-C(426)	118.1 (2)
P(2)-C(231)-C(232)	122.9 (2)	P(4)-C(431)-C(432)	118.3 (2)
P(2)-C(231)-C(232)	122.9 (2)	P(4)-C(431)-C(432)	118.3 (2)
P(2)-C(231)-C(236)	117.1 (2)	P(4)-C(431)-C(436)	121.6 (2)
F(11)-B(1)-F(12)	110.4 (12)	F(21)-B(2)-F(22)	109.3 (11)
F(11)-B(1)-F(13)	105.7 (10)	F(21)-B(2)-F(23)	104.0 (11)
F(12)-B(1)-F(13)	109.9 (13)	F(22)-B(2)-F(23)	107.1 (11)
F(11)-B(1)-F(14)	111.5 (13)	F(21)-B(2)-F(24)	111.5 (11)
F(12)-B(1)-F(14)	110.9 (10)	F(22)-B(2)-F(24)	114.3 (12)
F(13)-B(1)-F(14)	108.3 (12)	F(23)-B(2)-F(24)	110.0 (13)
C(4)-C(3)-C(5A)	110.1 (14)	C(3)-C(4)-C(5)	117.6 (14)
C(4)-C(5)-C(3A)	110.1 (14)		

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Supplementary Material Available: Stereoviews of the unit cell, a complete structure determination summary (Table S-I), and H atom coordinates and isotropic displacement parameters (Table S-III) (6 pages); observed and calculated structure factors (Table S-II) (46 pages). Ordering information is given on any current masthead page.

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