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Formation and characterization of simple, stable, coordinated water complexes of rhodium and iridium. The crystal structure of *trans*-$[Rh(PPh_3)_2(CO)(H_2O)]^+CF_3SO_3^-$

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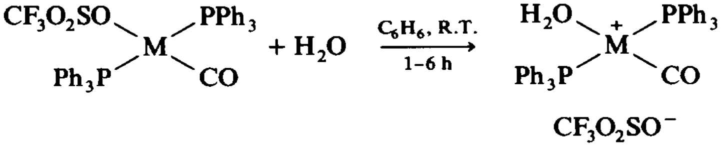
Abstract

Reaction of *trans*-$(Ph_3P)_2Rh(CO)(OSO_2CF_3)$ and *trans*-$(Ph_3P)_2Ir(CO)(OSO_2CF_3)$ with water in benzene results in the formation of stable *trans*-$[(Ph_3P)_2Rh(CO)(H_2O)]^+ CF_3SO_3^-$ and *trans*-$[(Ph_3P)_2Ir(CO)(H_2O)]^+ CF_3SO_3^-$, respectively. The crystal structure of the Rh-complex is reported.

Transition metal complexes of weakly coordinating ligands [1] play a paramount role in homogeneous catalytic processes. In most of these systems a solvent molecule (such as CH_3CN, THF, ether, H_2O, etc.) is generally assumed to temporarily occupy the vacant coordination site; in solution, the site is subsequently filled by the desired substrate of the coordinatively unsaturated "active" catalytic complex. Hence, such solvent complexes are of considerable interest [2] but are seldom of sufficient stability to be fully characterized, let alone isolated. In this paper we report the formation and characterization, including a single X-ray crystal structure, of *stable* simple 16-electron cationic water complexes of rhodium and iridium.

Reaction of *trans*-$(Ph_3P)_2Ir(CO)(CF_3SO_3)$ [3*], **1a**, in slightly moist benzene gave *trans*-$[(Ph_3P)_2Ir(CO)(H_2O)]^+CF_3SO_3^-$, **2a**, (eq. 1) in 62% isolated yield as a microcrystalline yellow solid. Likewise, reaction of the corresponding Rh-complex [4] gave the analogous Rh-water complex **2b** in 87% isolated yield.



(1)

1a: M = Ir
1b: M = Rh

2a: M = Ir
2b: M = Rh

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* A reference number with an asterisk indicates a note in the list of references.

Table 1

Physical and spectroscopic properties of **2**

Complex	m.p., °C	IR, cm^{-1}		^{1}H NMR, δ	^{31}P{^{1}H} NMR, δ	^{19}F NMR, δ
2a	149–153	3373 br, OH	1176	7.83–7.74 (m, 12H)	30.28 (s) ^{b,c}	−78.7 (s) ^{b,d}
	(dec.)	3133	1165	7.66–7.55 (m, 18H)		
		3058	1097	2.42 (br s, 2H) ^{a,b}		
		2000 s, CO	1073			
		1482	1029			
		1436	999			
		1336	744			
		1281	709			
		1243	693			
		1225	635			
		1203				
2b	148–151	3300 br, OH	1163	7.80–7.60 (m, 12H)	29.43 (d,	−77.7 (s) ^{d,e}
	(dec.)	3059	1097	7.57–7.39 (m, 18H)	J(Rh–P) =	
		2009 s, CO	1029	2.38 (br s, 2H) ^{a,e}	124.0 Hz) ^{c,e}	
		1481	744			
		1435	708			
		1278	694			
		1246	637			
		1174				

[a] Referenced to internal $(CH_3)_4Si$. [b] In CD_3NO_2. [c] Referenced to external 85% H_3PO_4. [d] Referenced to external $CFCl_3$. [e] In $CDCl_3$.

The physical [5*] and spectral properties of complexes **2** are summarized in Table 1. The identity of these simple water-complexes follows from their spectral data and in particular the OH signals in the IR, and the ^{1}H NMR. The single ^{31}P signal establishes the *trans* geometry of **2** and the presence of the CO and CF_3SO_3 groups is confirmed by the IR and ^{19}F NMR data, respectively.

A definitive structural assignment for **2b** was established by X-ray crystallography. An ORTEP diagram of **2b** is given in Fig. 1. Selected bond lengths and bond angles are summarized in Table 2. The X-ray data clearly demonstrate a square-

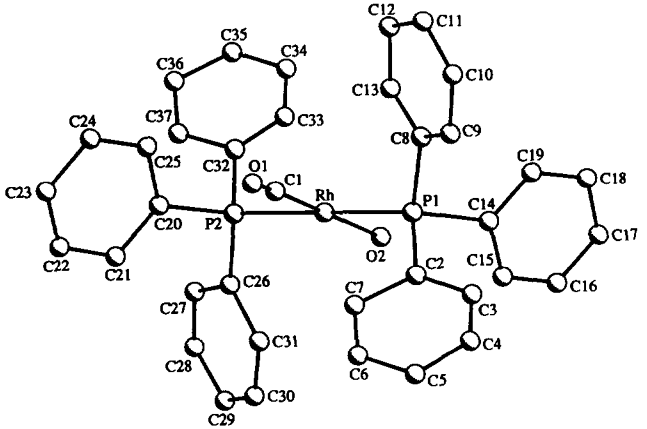

Fig. 1. An ORTEP diagram of the cation of **2b**. The triflate anion and hydrogen atoms are omitted for clarity.

Table 2

Selected bond distances (Å) and bond angles (deg) for complex **2b** (estimated standard deviations are in parentheses)

Rh–P1	2.311(4)	P2–Rh–P1	178.5(2)
Rh–P2	2.350(4)	O2–Rh–P1	93.3(3)
Rh–O2	2.316(12)	O2–Rh–P2	86.6(2)
Rh–C1	1.777(5)	C1–Rh–P1	90.6(5)
C1–O1	1.099(5)	C1–Rh–P2	89.4(5)
		C1–Rh–O2	175.0(6)

planar arrangement around the central Rh with the four bond angles in the range 86.6–93.3°. The Rh–O bond distance of 2.316 Å is somewhat longer than the Rh–O of about 2.20–2.28 Å of more complex Rh-water complexes [6]. The remainder of the structural features of **2b** are within normal range and unexceptional.

Although a few complexes of rhodium with coordinated water are known [6] they generally contain complex ligands and to our knowledge only a single iridium complex with coordinated water has been reported [2d].

Both the Rh and Ir complexes **2** rapidly and reversibly exchange H_2O for D_2O, as monitored by ^1H NMR spectroscopy. However, in the absence of appropriate labeling it is not possible to tell if this "exchange" represents replacement of only the hydrogens or the entire coordinated water molecule.

In summary, interaction of water with the square planar triflate complexes **1** results in the formation of the corresponding 16-electron square planar cationic water complexes **2** that are stable in both solution and the solid state. The formation of other possible solvent complexes as well as the chemistry of these novel, simple "solvent"-complexes will be the subject of future reports.

Experimental

General. All reactions were performed in an atmosphere of nitrogen by using standard Schlenk techniques. Benzene was distilled from CaH_2 and degassed prior to use. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. NMR spectra were recorded on a Varian XL-300 spectrometer. X-ray data were collected on a CAD-4 diffractometer. Elemental analyses were conducted by Atlantic Microlab.

Preparation of trans-$[(Ph_3P)_2Ir(CO)(H_2O)]^+CF_3SO_3^-$ *(2a).* A 100-mL Schlenk flask was charged with **1a** (0.120 g, 0.134 mmol), benzene (ca. 5.0 mL) and a magnetic stir bar. The flask was capped with a rubber septum. The resulting solution was stirred under nitrogen and H_2O (ca. 100 μL) was added by syringe. The reaction mixture was allowed to stir at room temperature for ca. 6 h, during which time a pale yellow powder formed. Ether (ca. 50 mL) was added with stirring to effect further precipitation. The powder was collected by filtration on a fine frit sintered glass funnel, washed with benzene (ca. 5.0 mL), ether (ca. 5.0 mL), and dried under vacuum to give **2a** (0.076 g, 0.083 mmol, 62%).

Preparation of trans-$[(Ph_3P)_2Rh(CO)(H_2O)]^+CF_3SO_3^-$ *(2b).* This compound was prepared from **1b** (0.118 g, 0.147 mmol), benzene (ca. 3.0 mL) and H_2O (ca. 100 μL) in a manner identical to **2a**. After 1 h, identical workup gave **2b** as a pale yellow powder (0.105 g, 0.128 mmol, 87%).

Supplemental material. Experimental details of the X-ray of complex **2b**, including tables of crystallographic data, atomic position and thermal parameters, and selected intramolecular distances and angles are available from the authors.

Acknowledgements

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5 Elemental Analyses: **2a**: Found: C, 50.14; H, 3.59. $C_{38}H_{32}F_3IrO_5P_2S$ calcd.: C, 50.05; H, 3.54%. **2b**: Found: C, 55.59; H, 3.95. $C_{38}H_{32}F_3O_5P_2RhS$ calcd.: C, 55.48; H, 3.92%.

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