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trans-$RuCl_2(PEt_3)_2(CO)(H_2O)$, an Aquo Carbonyl Complex of Ruthenium: Synthesis, Structural Characterization, and Reactivity

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Water is relatively rare as a ligand in 18e organometallic complexes because the hard oxygen atom binds only weakly to many transition metal atoms.[1] Moreover, coordinated water may be activated toward proton transfer to other ligands, limiting the range of aquo complexes which can be isolated and characterized. These properties of lability and reactivity render organometallic aquo complexes extremely useful in synthesis[2,3] and catalysis.[1,4,5] Coordinated water has long been known to play an important role in catalytic acetylene hydration[6] and more recently was implicated in hydroformylation reactions[7].

We report herein the synthesis and characterization of *trans*-$RuCl_2(PEt_3)_2(CO)(H_2O)$ (**1**), an aquo carbonyl complex of ruthenium(II). Although a number of related organometallic aquo complexes have been described,[8,9,10a–d] very few have been structurally characterized. An accurate X-ray structural analysis of **1** at low temperatures has revealed an interesting pattern of hydrogen bonds in which intermolecular O–H···Cl interactions provide lattice stabilization of the aquo complex.

Experimental Section

All syntheses and reactions were performed under a nitrogen atmosphere. MeOH solvent was distilled over CaH_2 before use. Infrared spectra were taken in NaCl cells in CH_2Cl_2 using a Nicolet 520 FT-IR spectrometer. The aquo compound for NMR studies was purified by recrystallization from hexane and dried in vacuo. NMR spectra were recorded on Bruker AC 200 and AM 250 spectrometers. Shifts are reported with respect to TMS (^1H, ^{13}C) or 85% external H_3PO_4 (^{31}P). Microanalyses were carried out by M-H-W Laboratories, Phoenix, AZ.

Synthesis of $RuCl_2(PEt_3)_2(CO)(H_2O)$ (1). The *all-trans* complex $RuCl_2(PEt_3)_2(CO)_2$ (**2**) (150 mg, 0.323 mmol), prepared as previously described,[11] in 10 mL of MeOH was refluxed for 1 h. At this stage, most of the starting material was converted to the monocarbonyl solvate species $Ru(CO)(solv)Cl_2(PEt_3)_2$ (ν(CO) in MeOH, 1941 cm^{-1}), with a minor amount of the thermally more stable isomer *cis,cis,trans*-$Ru(CO)_2Cl_2(PEt_3)_2$ (**3**) formed. Refluxing **2** in dry hexane at similar temperatures led to no reaction other than an isomerization to the *cis*-dicarbonyl complex **3**. The solvent was then removed in vacuo. Extraction with wet hexane (3 × 10 mL) followed by crystallization at 263 K afforded 75 mg (51%) of the pure carbonyl aquo compound **1**. IR (CH_2Cl_2), cm^{-1}: ν(CO) 1939 (broad). $^{31}P\{^1H\}$ NMR (($(CD_3)_2CO$), δ (ppm): T = 223 K, 24.0 (s, *trans* PEt_3); T = 303 K, 23.1 (s, *trans* PEt_3); T = 313 K, four isomers, 23.0 (s, *trans* PEt_3), 22.0 (s, *trans* PEt_3), 21.5 (s, *trans* PEt_3), 45.2, 42.6 (dd, $^2J_{PP}$ = 30.4 Hz, *cis* PEt_3). After 3 h with the solution maintained at 313 K, the ratio of the four isomers was approximately 4:3:3:4. ^1H NMR ($CDCl_3$), δ (ppm): T = 298 K, 2.7 (very broad, exchange of coordinated and free H_2O). ^1H NMR (CD_2Cl_2), δ (ppm): T = 200 K, 3.99 (s, coordinated H_2O), 2.70 (s, free H_2O); T = 290 K, 2.79 (broad, exchange of coordinated and free H_2O), 1.94 (m, CH_2), 1.16 (m, CH_3). Anal. Calcd for $RuC_{13}H_{32}O_2Cl_2P_2$: C, 34.37; H, 7.10; P, 13.63. Found: C, 34.44; H, 7.25; P, 13.74.

Reaction of 1 with CO. Carbon monoxide was bubbled through a solution of $RuCl_2(PEt_3)_2(CO)(H_2O)$ (**1**) in CH_2Cl_2 at room temperature and at 1-atm pressure for 5 min. IR measurements indicated quantitative formation of the known dicarbonyl compound *all-trans*-$RuCl_2(PEt_3)_2(CO)_2$ (**2**). ν(CO) (CH_2Cl_2) cm^{-1}, 1993 (s).

Reaction of 1 with $PMePh_2$. A mixture of **1** with 4 equiv of $PMePh_2$ in CH_2Cl_2 was stirred at room temperature. The reaction was complete within 5 min as monitored by FT-IR spectroscopy. IR (CH_2Cl_2): ν(CO) 1961 cm^{-1} (broad). A ^{31}P NMR spectrum of the product solution indicated the presence of two isomers in a 7:1 ratio which were not further separated. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ (ppm): isomer I (minor), 8.69 (d, PEt_3, $^2J_{PP}$ = 37 Hz), –3.61 (t, $PMePh_2$, $^2J_{PP}$ = 37 Hz); isomer II (major), 6.34 (d, PEt_3, $^2J_{PP}$ = 35 Hz), –18.28(t, $PMePh_2$, $^2J_{PP}$ = 35 Hz).

X-ray Crystallography: Data Collection and Refinement. An orange polyhedral crystal was mounted in epoxy at the end of a glass fiber. Indexing, cell refinement, and data collection were performed on a Nicolet Siemens R3m/V diffractometer with Mo Kα radiation at 200 K. The unit cell parameters were determined and refined from a set of 25 general reflections (23° < 2θ < 32°) well distributed in reciprocal space. Data were collected through ω scans over the range 4° < 2θ < 50° with variable scan speeds (2.93–29.30°/min). Two standard reflections were measured after every 100 reflections and showed no significant loss in intensity during data acquisition. Data were corrected for Lorentz and polarization effects and for absorption by a face-indexed numerical procedure. Of 3562 independent reflections collected, 3322 ($F > 6.0\sigma(F)$) were considered observed and used in the structure solution and refinement. The minimum and maximum transmission factors through the crystal were calculated to be 0.5870 and 0.6660, respectively. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques using the Siemens SHELXTL PLUS software. Anisotropic refinement of all non-hydrogen atoms revealed the positions of all of the hydrogen atoms. In the final cycles of refinement, hydrogen atoms were included in their found positions and refined isotropically. Scattering factors for non-hydrogen atoms were taken from ref 12a. For hydrogen atoms the data of Stewart et al.[12b] were used. Full details of cell constants, data collection and final refinement are given in Table I. Atomic coordinates and equivalent isotropic displacement coefficient are compiled in Table II, and selected bond distances and angles are listed in Table III.

Results and Discussion

The readily accessible compound *all-trans*-$RuCl_2(PEt_3)_2(CO)_2$ (**2**), which has been used as a starting material for the synthesis of a series of Ru(II) bis(acetylides) and bis(diacetylides),[11] appears to be a useful source of the formally unsaturated but solvent-stabilized fragment $RuCl_2(PEt_3)_2(CO)$ in solution. As monitored by FT-IR spectroscopy, refluxing **2** in methanol solution leads to the displacement of one carbonyl group, affording a species with a single ν(CO) band at 1939 cm^{-1} (CH_2Cl_2), presumably *trans*-$RuCl_2(PEt_3)_2(CO)(MeOH)$. Addition of wet hexane and cooling

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Table I. Structure Determination Summary for **1**

formula	$C_{13}H_{32}Cl_2O_2P_2Ru$	fw	454.3
ρ(calcd)	1.497 Mg/m^3	space group	$P2_1/n$ (No. 14)
a	8.221(2) Å	*T*	200 K
b	20.173(5) Å	λ	0.710 73 Å
c	12.162(3) Å	μ	12.0 cm^{-1}
β	91.62(2)°	transm coeff.	0.5870–0.6660
V	2016.3(7) Å^3	*R*	1.93%
Z	4	R_w	2.65%

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
Ru(1)	2420.9(2)	5880.5(1)	1249.0(1)	18.7(1)
Cl(1)	5096.5(7)	5995.1(3)	555.4(5)	29.5(2)
Cl(2)	−241.9(6)	5555.9(3)	1802.2(4)	29.4(2)
P(1)	3452.5(7)	5161.6(3)	2659.8(4)	22.9(2)
P(2)	1365.8(7)	6583.9(3)	−183.3(4)	22.6(2)
O(1)	2701(2)	7070.6(8)	2664(1)	44.3(6)
O(2)	2265(2)	5022.3(8)	149(1)	27.7(5)
C(1)	2586(3)	6599(1)	2132(2)	26.4(7)
C(2)	3362(3)	4291(1)	2244(2)	30.6(7)
C(3)	3880(4)	3770(1)	3084(2)	46(1)
C(4)	2332(4)	5139(1)	3949(2)	41.8(9)
C(5)	1839(5)	5791(2)	4448(3)	56(1)
C(6)	5598(3)	5263(1)	3078(2)	36.1(8)
C(7)	6088(4)	5953(1)	3473(3)	42.9(9)
C(8)	2180(3)	7431(1)	−239(2)	37.2(8)
C(9)	3931(4)	7510(2)	−543(4)	70(1)
C(10)	1672(3)	6252(1)	−1562(2)	34.6(8)
C(11)	1108(4)	6680(2)	−2528(2)	49(1)
C(12)	−825(3)	6749(1)	−156(2)	30.7(7)
C(13)	−1337(3)	7158(1)	834(3)	44(1)
H(21)	3113(34)	4900(14)	−50(22)	41(9)
H(22)	1597(37)	4941(15)	−354(24)	61(10)

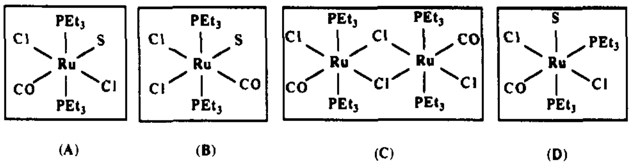
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) and Angles (deg) for **1**

Ru(1)–Cl(1)	2.389(1)	Ru(1)–Cl(2)	2.399(1)
Ru(1)–P(1)	2.384(1)	Ru(1)–P(2)	2.391(1)
Ru(1)–O(2)	2.189(2)	Ru(1)–C(1)	1.807(2)
P(1)–C(2)	1.829(2)	P(1)–C(4)	1.842(3)
P(1)–C(6)	1.833(3)	P(2)–C(8)	1.837(3)
P(2)–C(10)	1.829(2)	P(2)–C(12)	1.833(2)
O(1)–C(1)	1.153(3)	C(2)–C(3)	1.518(4)
C(4)–C(5)	1.510(5)	C(6)–C(7)	1.522(4)
C(8)–C(9)	1.505(5)	C(10)–C(11)	1.519(4)
C(12)–C(13)	1.528(4)	O(2)–H(21)	0.79(3)
O(2)–H(22)	0.83(3)		
Hydrogen Bonds			
H(22)···Cl(2a)	2.29(3)	H(21)···Cl(1b)	2.42(3)
Cl(1)–Ru(1)–Cl(2)	169.1(1)	Cl(1)–Ru(1)–P(1)	90.0(1)
Cl(2)–Ru(1)–P(1)	86.6(1)	Cl(1)–Ru(1)–P(2)	90.2(1)
Cl(2)–Ru(1)–P(2)	92.9(1)	P(1)–Ru(1)–P(2)	178.9(1)
Cl(1)–Ru(1)–O(2)	84.2(1)	Cl(2)–Ru(1)–O(2)	85.3(1)
P(1)–Ru(1)–O(2)	88.4(1)	P(2)–Ru(1)–O(2)	90.6(1)
Cl(1)–Ru(1)–C(1)	94.5(1)	Cl(2)–Ru(1)–C(1)	96.1(1)
P(1)–Ru(1)–C(1)	92.4(1)	P(2)–Ru(1)–C(1)	88.6(1)
O(2)–Ru(1)–C(1)	178.5(1)	Ru(1)–P(1)–C(2)	112.0(1)
Ru(1)–P(1)–C(4)	116.8(1)	C(2)–P(1)–C(4)	101.2(1)
Ru(1)–P(1)–C(6)	116.8(1)	C(2)–P(1)–C(6)	102.5(1)
C(4)–P(1)–C(6)	105.5(1)	Ru(1)–P(2)–C(8)	117.0(1)
Ru(1)–P(2)–C(10)	113.2(1)	C(8)–P(2)–C(10)	104.3(1)
Ru(1)–P(2)–C(12)	115.5(1)	C(8)–P(2)–C(12)	101.0(1)
C(10)–P(2)–C(12)	104.1(1)	Ru(1)–C(1)–O(1)	177.7(2)
P(1)–C(2)–C(3)	118.0(2)	P(1)–C(4)–C(5)	117.8(2)
P(1)–C(6)–C(7)	115.7(2)	P(2)–C(8)–C(9)	117.4(2)
P(2)–C(10)–C(11)	117.0(2)	P(2)–C(12)–C(13)	113.9(2)
H(21)–O(2)–H(22)	106(3)		
Hydrogen Bond Angles			
O(2)–H(22)···Cl(2a)	163(2)	O(2)–H(21)···Cl(1b)	150(2)

to 263 K afforded orange-yellow crystals of the *trans*-carbonylaquo complex $RuCl_2(PEt_3)_2(CO)(H_2O)$ (**1**) in good yields. Crystals of **1** are stable in air in the solid state, very soluble in methylene chloride, acetone, and other polar organic solvents, but sparingly soluble in hexane.

Chart I. Possible Structures for **1** in Solution (s = Solvent)



The aquo complex was characterized by FT-IR and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and by a low temperature single-crystal X-ray diffraction study. The ν(CO) frequency of **1** (1939 cm^{-1}) is significantly lower than that of **2** (1993 cm^{-1}), reflecting the substitution of a strong π-acid by an electron donor ligand H_2O. The ^1H NMR spectrum in $CDCl_3$ at room temperature displays a very broad H_2O resonance, indicating a rapid exchange of coordinated and free water molecules. Similar observations of exchange-broadened ^1H (H_2O) resonances were recently reported for $OsH(H_2O)(CO)_2(PR_3)_2$[9] and $Ru(CO)(H_2O)(F)(Cyttp)$[13] (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$). When solutions of **1** were cooled to 200 K in CD_2Cl_2, separate resonances for coordinated and free water were observed at δ = 3.99 and 2.70 ppm, respectively. Deeming and co-workers have likewise noted the slowing of metal-water exchange processes at low temperatures for Rh(III) and Ir(III) aquo complexes,[14] with similar chemical shifts (cf. $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$, δ 4.56 ppm for coordinated water and 2.73 ppm for free H_2O). The lability of the coordinated water molecule in **1** is further demonstrated by the temperature dependence of the $^{31}P\{^1H\}$ NMR chemical shifts of **1**. Thus over the temperature range 223–313 K, a singlet ^{31}P resonance at δ 24.0–23.1ppm corresponding to the *trans* isomer A of **1** (Chart I) was observed in $(CD_3)_2CO$. At 313 K, resonances from four different isomers, three with *trans* PEt_3 ligands and one with *cis* PEt_3 ligands, were evident. The isomerization reactions in $(CD_3)_2CO$ took place at a moderate rate and were irreversible. Although a precise identification of the species present in these solutions cannot be made, the four isomers in Chart I, *trans*-A, -**B**, and -C and *cis*-**D**, are all possible and fit the observed spectra.

In the solid state as shown by X-ray diffraction, the molecules of **1** have the *trans* geometry, i.e. isomer A. The excellent diffraction characteristics of the crystal combined with low temperature data collection enabled us to locate all hydrogen atoms of the ligands in a Fourier map. A perspective view of the molecular structure is shown in Figure 1. The ruthenium atom is surrounded by six ligands in a slightly distorted octahedron coordination environment. The geometry of the oxygen atom in the H_2O ligand is best described as pyramidal with H(21)–O(2)–H(22), H(21)–O(2)–Ru(1), and H(22)–O(2)–Ru(1) angles of 106, 114, and 129°, respectively. The Ru(1)–O(2) bonding distance to the coordinated water molecule (2.189(2) Å) is, as found in several transition metal aquo complexes,[10a–d] significantly longer than the sum of the covalent radii (1.99 Å) given by Pauling[10e] for oxygen (0.66 Å) and ruthenium (1.33 Å). The value for the covalent radius of ruthenium (1.41 Å) calculated from the compilation of Ru–C distances in Orpen's tabulation[10f] gives a benchmark Ru–O value of 2.07 Å. The Ru(1)–O(2) bond in **1** (2.189(2)Å) is even longer than this, reflecting the weak nature of the metal–water bonding. Two chlorine ligands are clearly bent toward the H_2O site, with the angle Cl(1)–Ru–Cl(2) being 169.1(1)°. This large deviation from the ideal angle between *trans* ligands in an octahedron is due principally to the occurrence of strong intermolecular hydrogen bonding as illustrated in Figure 2.

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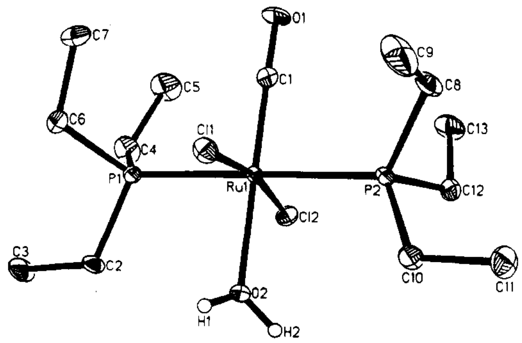

Figure 1. Molecular structure diagram of **1**.

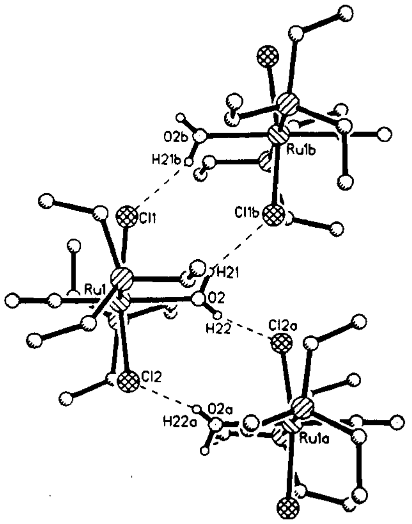

Figure 2. Hydrogen bonding of **1**. Hydrogen atoms on Et groups have been omitted for clarity. $a = -x, 1-y, -z$; $b = 1-x, 1-y, -z$. Cl(2)···O(2a) = 3.09 Å, Cl(1)···O(2b) = 3.12 Å.

The H_2O molecule is a weakly nucleophilic "hard" donor ligand and, therefore, as mentioned earlier, is not strongly attached to most low-valent transition metals.[1] Hydrogen bonding plays an important role in stabilizing the crystal structures of almost all organometallic aquo complexes, and indeed, the hydrogen atoms of the water molecule are almost always involved in hydrogen bonding in such compounds. The most common transition metal aquo compounds are ionic, where the coordinated H_2O is stabilized both by the formal positive charge on the metal cations and through strong hydrogen bonding with the counterions such as ClO_4^-, SO_4^{2-} and BF_4^-.[2,10b,13,15] In most neutral species on the other hand, a coligand bearing uncoordinated electronegative atoms, for instance, monodentate RSO_3^- or $RCOO^-$, is often present, and as a result, effective intramolecular hydrogen bonding is formed.[10c,16] Solvent molecules crystallized in the lattice can also provide a hydrogen-bond acceptor site, as has been observed in the $Ru(CO)_3Cl_2(H_2O)$·diglyme structure where the ether "diglyme" was the solvent used for the crystallization.[10d] The neutral title compound **1** represents one of very few examples where the stabilizing forces are the intermolecular hydrogen bonds between a water molecule and Cl ligands as shown in Figure 2. The two hydrogen atoms in each H_2O ligand are hydrogen bonded to two chlorine atoms coordinated to different adjacent molecules (a and b), and the distances shown in Figure 2 and in Table III are within the normal range for hydrogen bond lengths. The small O--H···Cl (163 and 150°) angles are not unusual when Cl is the acceptor in a hydrogen bond.[17] It is interesting to note the quasi one dimensional linkage through hydrogen bonding in the lattice (Figure 3).

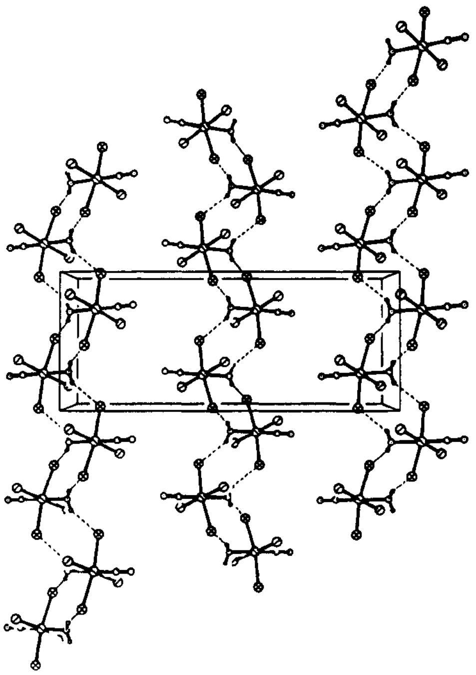

Figure 3. Crystal packing of **1** (projection on *xy* plane). Et groups on PEt_3 ligands have been omitted for clarity.

Preliminary results show that compound **1** is chemically labile and the lightly bound water molecule is readily displaced by other ligands. Thus reaction with CO at ambient temperatures converted the aquo compound **1** to the *all-trans*-dicarbonyl starting material **2** immediately and quantitatively (eq 1).

$$\mathrm{RuCl_2(PEt_3)_2(CO)_2} \underset{\text{(ii)}}{\overset{\text{(i)}}{\rightleftharpoons}} \mathrm{RuCl_2(PEt_3)_2(CO)(H_2O)} \tag{1}$$

(i) MeOH, refluxing, recrystallizing from wet solvent

(ii) CO, R.T.

Reaction with diphenylmethylphosphine also led to the rapid displacement of the water ligand and the formation of tris(phosphine) complexes of ruthenium(II), albeit as a mixture of two isomers. Attempts to separate the isomers by silica-gel chromatography were not successful. The ease of preparation of **1** and the facility with which the weakly bound H_2O molecule can be displaced suggest that **1** may have considerable synthetic and catalytic potential as an effective source of the electronically and coordinatively unsaturated fragment $RuCl_2(CO)(PEt_3)_2$. We are currently exploring these possibilities.

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Supplementary Material Available: Tables S1–S3, listing parameters for X-ray data collection, reduction, and refinement, anisotropic thermal parameters, and hydrogen atom positional and thermal parameters for **1** (5 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors (13 pages) are available upon request from the authors.

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