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trans-Aquacarbonylbis(triphenylarsine)-rhodium(I) Tetrafluoroborate Dichloromethane Solvate (1/1)

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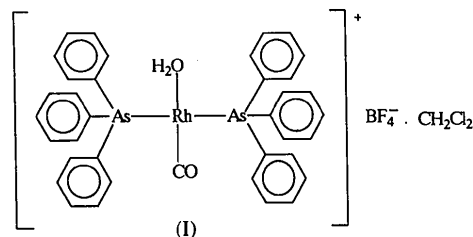
Abstract

The crystal structure of the title compound, $[Rh(C_{18}H_{15}As)_2(CO)(H_2O)]BF_4 \cdot CH_2Cl_2$, consists of $[Rh(AsPh_3)_2(CO)(H_2O)]^+$ cations, BF_4^- anions and CH_2Cl_2 solvate molecules held together by hydrogen bonds and van der Waals forces. The cationic complex has a slightly distorted square-planar geometry at the Rh atom, with the two $AsPh_3$ ligands mutually *trans*. The Rh—As (average), Rh—C(CO) and Rh—O(H_2O) bond distances are 2.4256 (5), 1.787 (4) and 2.118 (3) Å, respectively. The coordinated water molecule is involved in hydrogen bonding with the BF_4^- anion.

Comment

Most homogeneous catalytic cycles involve transition metal compounds interacting with weakly coordinating ligands. Often, it is postulated that the solvent coordinates to the transition metal and stabilizes intermediate species (Collman, Hegedus, Norton & Finke, 1987). Recently, there have been two reports of crystal structures

of four-coordinate rhodium(I) cationic compounds in which a water molecule is coordinated to the metal centre. Branan *et al.* (1991) reported the isolation and crystal structure of *trans*- $[Rh(PPh_3)_2(CO)(H_2O)]BF_4$, (II), and Stang, Song, Huang & Arif (1991) prepared and characterized the analogous $(CH_3SO_3)^-$ salt, (III). In the present paper, we report the crystal structure of the related triphenylarsine compound (I), which was obtained as described by Evans, Howlader & Atlay (1994).



The structure, together with atom labelling, is shown in Fig. 1. The geometry around the Rh centre is essentially square-planar with the four bond angles in the range 87.9 (1)–93.7 (1)°, in agreement with the geometry of the analogous phosphine compounds. The Rh—C bond length [1.787 (4) Å] is also similar to those found in the phosphine compounds, while the C=O bond is slightly longer [1.162 (5) Å, *cf.* 1.099 and 1.145 (11) Å for the corresponding $CF_3SO_3^-$ and BF_4^- triphenylphosphine compounds, respectively]. This difference is not statistically significant but appears to be consistent with the reduced back-bonding ability of the triphenylarsine ligands compared with phosphines, between the metal and the carbonyl group. This effect is also consistent with the lowering of the carbonyl stretching frequency to 1990 cm^{-1} [*cf.* 2009 and 1998 cm^{-1} in (II) and (III), respectively].

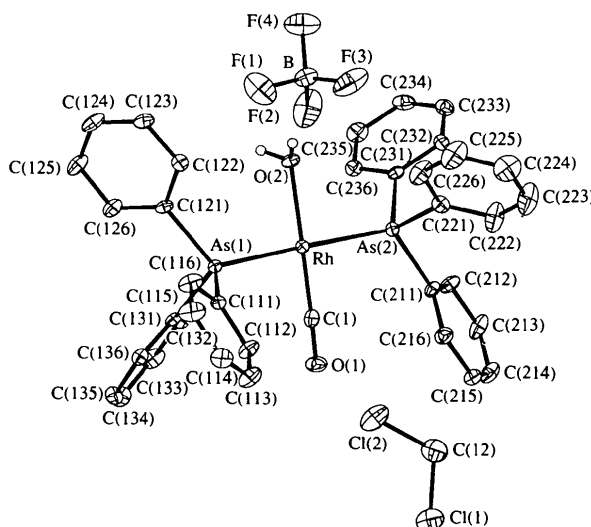


Fig. 1. Structure of (1) showing the atom-numbering scheme. H atoms (except those of the water molecule) have been omitted for clarity. Displacement ellipsoids are plotted at the 40% probability level.

Rh—As bond lengths are within the expected range (Clark, Hempleman, Dawes, Hursthouse & Flint, 1985), as are the As—C bond lengths. The Rh—O bond distance of 2.118 (3) Å is in close agreement with that found by Branan *et al.* (1991) for the corresponding triphenylphosphine compound, which exists in two forms [Rh—O 2.115 (5) and 2.130 (6) Å]. These authors reported that the phosphine compound exhibits weak-to-medium IR bands at 1119, 1054 and 977 cm⁻¹, which were ascribed to the counterion, BF₄⁻, and were lowered in frequency due to hydrogen-bonding to the coordinated water ligand. The triphenylarsine compound exhibits similarly lowered BF₄⁻ bands at 1118, 1020 and 996 cm⁻¹. The crystal structure determination supports the presence of hydrogen-bonding between the coordinated water and the anion. The bond lengths and angles of possible hydrogen bonds are given in Table 3. The two closest O...F distances of 2.647 (7) and 2.679 (7) Å are in good agreement with those recently reported in other species in which hydrogen-bonding is believed to occur. For example, Scheidt, Geiger, Lee, Gans & Marchon (1992) reported O...F distances of 2.68 and 2.79 Å in [Fe(TPP)(EtOH)₂]BF₄ (where TPP is tetraphenylphosphinate), and Mootz & Steffen (1981) found distances of 2.702 and 2.753 Å in [(CH₃OH)₂H]BF₄.

The geometric parameters associated with the BF₄⁻ anion and CH₂Cl₂ solvate are as expected.

Experimental

The title compound was obtained as described by Evans, Howlader & Atlay (1994). Single crystals for X-ray work were grown by slow diffusion of hexane into a solution of dichloromethane under argon.

Crystal data

[Rh(C ₁₈ H ₁₅ As) ₂ (CO)(H ₂ O)]·BF ₄ ·CH ₂ Cl ₂	Mo Kα radiation
<i>M_r</i> = 933.11	λ = 0.71069 Å
Triclinic	Cell parameters from 250 reflections
<i>P</i> $\bar{1}$	θ = 2.26–30.11°
<i>a</i> = 12.069 (1) Å	μ = 2.328 mm ⁻¹
<i>b</i> = 12.600 (2) Å	<i>T</i> = 150.0 (2) K
<i>c</i> = 13.556 (2) Å	Parallelepiped
α = 87.97 (1)°	0.20 × 0.12 × 0.10 mm
β = 67.36 (1)°	Yellow
γ = 80.19 (1)°	
<i>V</i> = 1873.8 (4) Å ³	
<i>Z</i> = 2	
<i>D_x</i> = 1.654 Mg m ⁻³	

Data collection

FAST area detector with rotating anode generator (Darr, Drake, Hursthouse & Malik, 1993)	3677 observed reflections
Absorption correction: none	[<i>I</i> > 2σ(<i>I</i>)]
9155 measured reflections	<i>R</i> _{int} = 0.0357
8208 independent reflections	θ _{max} = 30.11°
	<i>h</i> = -16 → 16
	<i>k</i> = -12 → 16
	<i>l</i> = -16 → 18

Refinement

Refinement on *F*²
R [*F* > 4σ(*F*)] = 0.0287
wR (*F*²) = 0.0724
S = 0.302
 8208 reflections
 491 parameters
w = 1/σ²(*F*²)
 (Δ/σ)_{max} = -0.325

Δρ_{max} = 0.67 e Å⁻³
 Δρ_{min} = -0.56 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

*U*_{iso} for H atoms; *U*_{eq} = (1/3)Σ_{*i*}Σ_{*j*}*U*_{*ij*}*a*_{*i*}^{*}*a*_{*j*}^{*} for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> _{iso}
Rh	0.00012 (2)	0.23932 (2)	0.25550 (2)	0.01609 (7)
As1	0.20087 (3)	0.13619 (3)	0.15800 (3)	0.01506 (9)
As2	-0.19352 (3)	0.35248 (3)	0.35430 (3)	0.01826 (9)
C1	0.0213 (3)	0.3239 (3)	0.1433 (3)	0.0237 (8)
O1	0.0349 (3)	0.3759 (3)	0.0683 (3)	0.0362 (8)
O2	-0.0400 (2)	0.1331 (2)	0.3845 (2)	0.0248 (6)
C111	0.3336 (3)	0.2126 (3)	0.1400 (3)	0.0181 (7)
C112	0.3315 (4)	0.3135 (3)	0.0957 (4)	0.0281 (9)
C113	0.4275 (4)	0.3684 (4)	0.0766 (4)	0.0365 (11)
C114	0.5248 (4)	0.3236 (4)	0.1031 (4)	0.0310 (10)
C115	0.5266 (4)	0.2244 (4)	0.1479 (4)	0.0374 (11)
C116	0.4309 (4)	0.1690 (4)	0.1680 (4)	0.0311 (10)
C121	0.2498 (3)	-0.0009 (3)	0.2107 (3)	0.0194 (8)
C122	0.2466 (3)	-0.0065 (4)	0.3145 (3)	0.0255 (9)
C123	0.2804 (4)	-0.1046 (4)	0.3537 (3)	0.0284 (9)
C124	0.3166 (4)	-0.1971 (4)	0.2894 (4)	0.0362 (11)
C125	0.3208 (4)	-0.1918 (4)	0.1868 (4)	0.0345 (10)
C126	0.2875 (4)	-0.0943 (3)	0.1462 (3)	0.0263 (9)
C131	0.2315 (3)	0.1043 (3)	0.0101 (3)	0.0156 (7)
C132	0.1331 (4)	0.0888 (3)	-0.0138 (3)	0.0250 (9)
C133	0.1489 (4)	0.0713 (4)	-0.1196 (3)	0.0289 (9)
C134	0.2608 (4)	0.0719 (4)	-0.2013 (4)	0.0317 (10)
C135	0.3594 (4)	0.0857 (4)	-0.1771 (3)	0.0290 (9)
C136	0.3452 (4)	0.1020 (3)	-0.0714 (3)	0.0233 (8)
C211	-0.2626 (4)	0.4631 (3)	0.2800 (3)	0.0234 (8)
C212	-0.3759 (4)	0.4611 (3)	0.2772 (3)	0.0264 (9)
C213	-0.4248 (4)	0.5416 (4)	0.2244 (4)	0.0349 (11)
C214	-0.3596 (5)	0.6229 (4)	0.1757 (4)	0.0372 (11)
C215	-0.2471 (4)	0.6246 (4)	0.1793 (4)	0.0391 (12)
C216	-0.1980 (4)	0.5450 (4)	0.2315 (4)	0.0334 (10)
C221	-0.1908 (4)	0.4332 (4)	0.4716 (3)	0.0261 (9)
C222	-0.2578 (5)	0.5347 (4)	0.5043 (5)	0.0481 (14)
C223	-0.2532 (6)	0.5901 (5)	0.5881 (5)	0.057 (2)
C224	-0.1797 (5)	0.5441 (5)	0.6396 (4)	0.0514 (14)
C225	-0.1135 (6)	0.4431 (5)	0.6090 (5)	0.053 (2)
C226	-0.1186 (5)	0.3875 (4)	0.5252 (4)	0.0410 (12)
C231	-0.3272 (3)	0.2742 (3)	0.4200 (3)	0.0205 (8)
C232	-0.4247 (3)	0.3133 (4)	0.5129 (3)	0.0261 (9)
C233	-0.5235 (4)	0.2605 (4)	0.5532 (4)	0.0327 (10)
C234	-0.5278 (4)	0.1703 (4)	0.5018 (4)	0.0342 (11)
C235	-0.4295 (4)	0.1296 (4)	0.4086 (4)	0.0376 (11)
C236	-0.3284 (4)	0.1825 (3)	0.3676 (4)	0.0267 (9)
C11	0.15965 (11)	0.77781 (13)	-0.02152 (13)	0.0531 (4)
C12	0.1766 (2)	0.58367 (13)	0.0977 (2)	0.0717 (5)
C12	0.0912 (5)	0.7090 (5)	0.0945 (5)	0.060 (2)
B	0.0945 (5)	0.1339 (5)	0.6112 (4)	0.0329 (11)
F1	0.2130 (3)	0.0850 (4)	0.5617 (3)	0.0744 (12)
F2	0.0426 (4)	0.1482 (3)	0.5373 (3)	0.0844 (13)
F3	0.0867 (4)	0.2266 (3)	0.6639 (3)	0.0781 (12)
F4	0.0362 (3)	0.0637 (3)	0.6867 (3)	0.0653 (10)
H2A	-0.040 (4)	0.0629 (14)	0.362 (4)	0.045 (15)
H2B	-0.0020 (18)	0.134 (4)	0.4340 (15)	0.054 (17)

Table 2. Selected geometric parameters (Å, °)

Rh—C1	1.787 (4)	As2—C231	1.934 (4)
Rh—O2	2.118 (3)	As2—C211	1.951 (4)
Rh—As2	2.4245 (6)	C1—O1	1.162 (5)
Rh—As1	2.4268 (6)	B—F1	1.366 (6)

As1—C121	1.932 (4)	B—F3	1.362 (6)
As1—C131	1.937 (3)	B—F2	1.364 (6)
As1—C111	1.939 (4)	B—F4	1.385 (6)
As2—C221	1.931 (4)		
C1—Rh—O2	173.73 (14)	C111—As1—Rh	114.07 (11)
C1—Rh—As2	90.05 (12)	C221—As2—C231	104.3 (2)
O2—Rh—As2	87.95 (8)	C221—As2—C211	102.7 (2)
C1—Rh—As1	88.68 (12)	C231—As2—C211	101.5 (2)
O2—Rh—As1	93.71 (8)	C221—As2—Rh	112.88 (12)
As2—Rh—As1	176.00 (2)	C231—As2—Rh	114.22 (12)
C121—As1—C131	104.1 (2)	C211—As2—Rh	119.39 (12)
C121—As1—C111	103.0 (2)	O1—C1—Rh	177.6 (4)
C131—As1—C111	100.58 (15)	Rh—O2—H2A	111 (3)
C121—As1—Rh	119.39 (11)	Rh—O2—H2B	120 (3)
C131—As1—Rh	113.47 (10)	H2A—O2—H2B	114 (4)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2B...F2	0.95	1.71 (2)	2.647 (7)	170 (3)
O2—H2A...F4 ⁱ	0.95	1.73 (2)	2.679 (7)	177 (3)
C226—H226...F2	0.93	2.48 (2)	3.335 (7)	153 (3)
C234—H234...F1 ⁱⁱ	0.93	2.38 (2)	3.276 (7)	163 (3)
C12—H12B...F3 ⁱⁱⁱ	0.97	2.48 (2)	3.189 (7)	130 (3)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x-1, y, z$; (iii) $-x, 1-y, 1-z$.

The unit-cell and intensity data were recorded at 150 K on a FAST area detector diffractometer using MADNES software (Pflugrath & Messerschmidt, 1989); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). All calculations were performed on a 486DX2/66 personal computer. The two H atoms bonded to the water molecule were located experimentally and refined with O—H distances constrained to 0.95 Å; other H atoms were included in idealized positions (C—H = 0.93 Å); U_{iso} 's for all H atoms were freely refined.

Data collection: MADNES MADONL (Pflugrath & Messerschmidt, 1989). Cell refinement: MADNES REFINE. Data reduction: MADNES ABSURD. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SNOOPI (Davies, 1983). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene- κ^2N^2, N^6)mercury(II) Tetrakis(trifluoroacetato)mercury(II) Dichloromethane Solvate

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Abstract

The title compound, [Hg(C₂₃H₂₃N₃)₂][Hg(C₂F₃O₂)₄].0.7CH₂Cl₂, is ionic with Hg forming complex anions and cations. The cation contains two neutral ligand ($L = 4\text{-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene}$) molecules giving Hg L_2^{2+} , and the anion incorporates four trifluoroacetate ions giving Hg(tfa)₄²⁻. Coordination around Hg in the cation is elongated tetrahedral with Hg—N 2.20 (2), 2.24 (3), 2.22 (2) and 2.30 (3) Å; the bite angles to the two bidentate ligands (L) are 84.9 (9) and 82.3 (9)°. In the anion, the shortest Hg—O contacts to the four tfa groups are 2.41 (2), 2.33 (4), 2.22 (2) and 2.38 (4) Å; the coordination is irregular and can only be described as approximately tetrahedral. The solvent molecule, dichloromethane, occupies a cavity in the structure.

Comment

The preparation of the ligand 4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene, L , and the crystal structure of the product of the reaction of L with copper(II) acetate have been described previously (Breuer & Small, 1991). It was of interest to examine the product of the