Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Carbonyl(ferrocenyldiphenylphosphine)(tropolonato)-rhodium(I)

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Received 12 June 2001
Accepted 9 July 2001
Online 13 July 2001

The square-planar Rh^I complex, $[Rh(trop)(PFcPh_2)(CO)]$ (tropH = 2-hydroxy-2,4,6-cycloheptatrienone, $C_7H_6O_2$, and $PFcPh_2$ = ferrocenyldiphenylphosphine, $C_{22}H_{19}FeP$), contains a five-membered chelate ring. The most important bond lengths and angles include Rh—O 2.0838 (14) Å (*trans* to P) and Rh—O 2.0487 (14) Å (*trans* to CO), Rh—P 2.2395 (5) Å, Rh—C 1.803 (2) Å, and O—Rh—O 77.56 (6)° and P—Rh—C 89.73 (7)°.

Key indicators

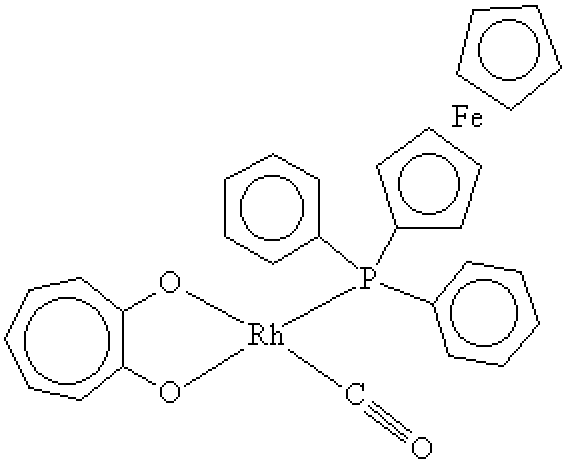
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.062
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A large number of rhodium(I) complexes are known, of which many involve π-bonding ligands such as CO, phosphines and arenes. A subset of these compounds includes β-diketonate and tropolonate. In this paper, we report the structure of $[Rh(trop)(CO)(PFcPh_2)]$, (I), as another complex in this series containing a ferrocenyl-functionalized tertiary phosphine.

The title compound crystallizes as a distorted square-planar moiety (Fig. 1) with the most important bond distances and angles given in Table 1. The efficient packing in the crystal structure is illustrated by the closest intermolecular contact of 2.91 Å between the rhodium centre and H43B($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$).



(I)

The Rh—P bond of 2.2395 (5) Å is comparable with that found in the corresponding $[Rh(trop)(CO)(PPh_3)]$ and $[Rh(cupf)(CO)(PPh_3)]$ (cupf = N-hydroxy-N-nitrosobenzeneaminato-O,O') complexes, see Table 2. The Rh—O2 bond is significantly longer than the Rh—O3 bond due to the larger *trans* influence of $PFcPh_2$ compared with CO. The small steric demand of the tropolonate ligand is illustrated by the small

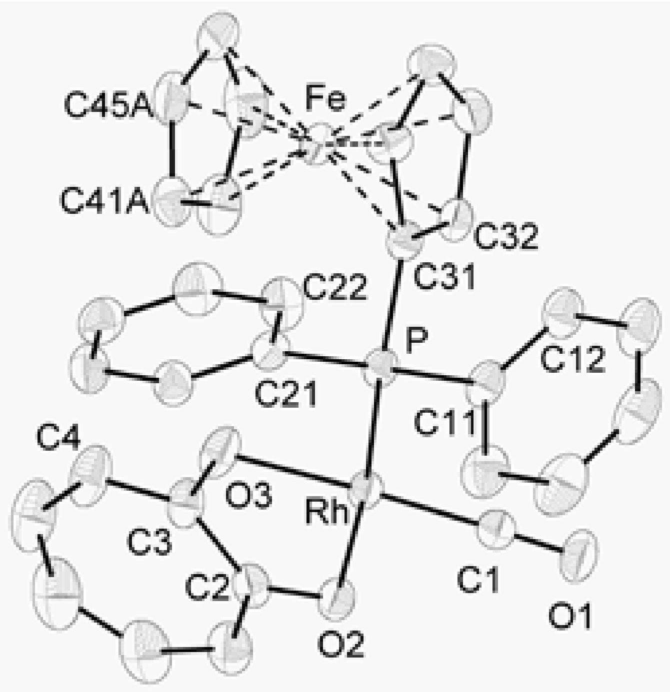


Figure 1
The structure of (I) showing the numbering scheme and displacement ellipsoids (30% probability; Brandenburg & Berndt, 1999). The first digit refers to the number of the ring and the second to the number of the C atom in the ring. H atoms have been omitted for clarity.

O2—Rh—O3 bite angle of 77.56 (6)° and the consequent O3—Rh—P, O2—Rh—C1 and P—Rh—C1 coordination angles of 96.75 (4), 95.98 (8) and 89.73 (7)°, respectively. To date, [Rh(cupf)(CO)(PPh_3)] is the only analogous complex, containing a five-membered *O,O*-chelate, for which a smaller O—Rh—O bite angle has been reported (Basson *et al.*, 1986), see Table 2. A slight elongation is observed in the Rh—O2 and Rh—O3 bonds compared with similar complexes. The Rh^I centre is only slightly displaced by a distance of 0.0308 (8) Å from the plane defined by the four donor atoms of the respective ligands.

The variation in electron density of the Rh^I centre as a function of the substituent X on the tertiary aryl phosphine PX_3 is illustrated by the slight decrease of the carbonyl stretching frequency. This arises as an increase in the electron density on the rhodium centre results in increased back donation to the carbonyl C atom which in turn lowers ν(CO). This is illustrated for both the solid-state and liquid-state data presented in Table 3, which are in agreement with the trend in basicity of the tertiary phospines as reflected in the respective pK_a values.

It was reported by Steyn *et al.* (1997) and extended to a wider range by Roodt & Steyn (2000) that the first order Rh–P coupling constants, ^1J(Rh–P), in rhodium–phosphine complexes, determined from ^{31}P NMR, enable good estimates of the Rh—P bond strength. Although small, a tendency is observed in Table 3, indicating $PFcPh_2$ to be better electron donating than PPh_3, and comparable to P(p-CH_3-Ph)$_3$.

The torsion angles of −72.3 (2) and −63.5 (6)° for Rh—P—C31—C41*A* and Rh—P—C31—C41*B* illustrate the different orientations of the ferrocenyl moiety (see *Experimental*), and is also related to the solid-state steric demand of the $PFcPh_2$ ligand (Otto *et al.*, 2000). In this regard, effective (using the actual Rh—P bond distance) and Tolman cone-angles (using a Rh—P bond distance of 2.28 Å; Tolman, 1977) of 171.2 and 169.8° for orientation β_1, and 167.4 and 166.1° for orientation β_2, were calculated.

Experimental

[Rh(trop)$(CO)_2$] (Leipoldt *et al.*, 1980) (10 mg, 0.036 mmol) was dissolved in warm acetone (*ca* 4 ml, 313 K), $PFcPh_2$ (Sollott *et al.*, 1963) (10 mg, 0.027 mmol) was added as solid, and the solution was filtered. Cooling to room temperature and slow evaporation of the solvent yielded crystals suitable for X-ray analysis. Yield: quantitative based on the phosphine. Spectral data, IR (KBr): ν(CO) 1965 cm^{-1}, (CH_2Cl_2) ν(CO) 1974 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.43 (q, 4H), 4.22 (s, 5H), 7.3 (m, 15H). ^{31}P NMR ($CDCl_3$, 121.497 MHz): 41.21 (d), ^1J(Rh–P) 174 Hz.

Crystal data

[Rh($C_7H_5O_2$)($C_{22}H_{19}FeP$)(CO)]
$M_r = 622.22$
Monoclinic, $P2_1/n$
$a = 11.3122$ (7) Å
$b = 16.2035$ (9) Å
$c = 14.2663$ (8) Å
$\beta = 104.046$ (10)°
$V = 2536.8$ (3) Å^3
$Z = 4$
$D_x = 1.629$ Mg m^{-3}
$D_m = 1.630$ Mg m^{-3}
D_m measured by flotation in aqueous KI
Mo $K\alpha$ radiation
Cell parameters from 6239 reflections
$\theta = 2.8$–28.3°
$\mu = 1.32$ mm^{-1}
$T = 293$ (2) K
Prism, orange
0.30 × 0.26 × 0.20 mm

Data collection

Siemens SMART CCD 1K diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.694$, $T_{max} = 0.779$
27 848 measured reflections
6239 independent reflections
5239 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 28.3$°
$h = -15 \rightarrow 15$
$k = -21 \rightarrow 21$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.08$
6239 reflections
373 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.9003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.035$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh—C1	1.803 (2)	Rh—P	2.2395 (5)
Rh—O3	2.0487 (14)	C1—O1	1.141 (2)
Rh—O2	2.0838 (14)		
C1—Rh—O3	172.71 (8)	O3—Rh—P	96.75 (4)
C1—Rh—O2	95.98 (8)	O2—Rh—P	174.29 (4)
O3—Rh—O2	77.56 (6)	O1—C1—Rh	177.0 (2)
C1—Rh—P	89.73 (7)		
Rh—P—C31—C41*A*	−72.3 (2)	Rh—P—C31—C41*B*	−63.5 (6)

Table 2
Comparative X-ray data for [Rh(*O*,*O*-Bid^a)(CO)(*L*)] complexes.

Complex	Rh–O3^b	Rh–O2^b	Rh–P	O3–Rh–O2
[Rh(trop)(CO)(PFcPh$_2$)]^d	2.0487 (14)	2.0838 (14)	2.2395 (5)	77.56 (6)
[Rh(trop)(CO)(PPh$_3$)]^e	2.034 (7)	2.081 (7)	2.232 (2)	77.8 (3)
[Rh(cupf)(CO)(PPh$_3$)]^f	2.024 (6)	2.063 (6)	2.232 (3)	76.6 (3)

Notes: (*a*) bidentate oxygen ligand forming five-membered chelate; (*b*) O atom *trans* to the carbonyl; (*c*) O atom *trans* to the phosphine; (*d*) present study; (*e*) Leipoldt *et al.* (1980); (*f*) Basson *et al.* (1986).

Table 3
Comparative spectroscopic data for [Rh(trop)(CO)(*L*)] complexes.

L	ν(CO) (KBr/cm^{-1})	ν(CO) (CH$_2$Cl$_2$/cm^{-1})	^1J(Rh–P) (Hz)	pK_a^{a}
P(*p*-CH$_3$-Ph)$_3$	1966	1973	175	3.84
PFcPh$_2$	1965	1974	174	
PPh$_3$	1974	1975	173	2.73
P(*p*-F-Ph)$_3$	1975	1976	172	1.97

Notes: (*a*) Wilkinson (1987).

Some disorder was identified in the β-cyclopentadienyl ring (β_1: C41*A*–C45*A*; β_2: C41*B*–C45*B*). Statistical averaging and similar displacement parameters for each paired set of C atoms resolved the disorder of the system, significantly decreasing the reliability index, *R*, from 0.058 to 0.036. H atoms were placed in idealized positions using a riding model and thermal movement was refined using an overall equivalent isotropic displacement parameter.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL*97.

Financial assistance of the South African NRF and the Research Fund of the University of the Free State is gratefully acknowledged.

References

Basson, S. S., Leipoldt, J. G., Roodt, A. & Venter, J. A. (1986). *Inorg. Chim. Acta*, **118**, L45–47.
Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Release 2.1*c*. Crystal Impact GbR, Bonn, Germany.
Leipoldt, J. G., Bok, L. D. C., Basson, S. S. & Meyer, H. (1980). *Inorg. Chim. Acta*, **42**, 105–108.
Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
Roodt, A. & Steyn, G. J. J. (2000). *Recent Research Developments in Inorganic Chemistry*, Vol. 2, edited by S. G. Pandalai, pp. 1–23. Trivandrum, India: Transworld Research Network.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sollott, G. P., Mertwoy, H. E., Portmoy, S. & Snead, J. L. (1963). *J. Org. Chem.* **28**, 1090–1092.
Steyn, G. J. J., Roodt, A., Poletaeva, I. & Varshavsky, Y. (1997). *J. Organomet. Chem.* **536**, 197–205.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 3, 313–348.
Wilkinson, G. (1987). *Comprehensive Coordination Chemistry*, Vol. 2, pp. 51–75. New York: Pergamon Press.