spots. With an image-plate detector of diameter 180 mm, only reflections with $\theta < 20.9°$ could be observed.

Data collection: *EXPOSE* in *Stoe IPDS* (Stoe & Cie, 1997). Cell refinement: *SELECT* in *Stoe IPDS*. Data reduction: *INTEGRATE* in *Stoe IPDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON*98 (Spek, 1990) and *ATOMS* (Dowty, 1997). Software used to prepare material for publication: *PLATON*98.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1037). Services for accessing these data are described at the back of the journal.

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trans-Carbonylchlorobis(tri-*p*-tolylphosphine)rhodium(I)

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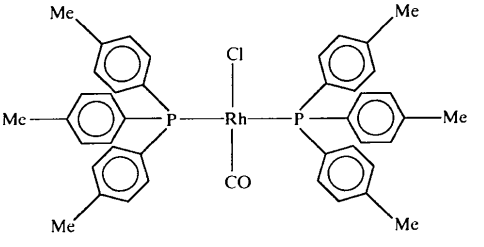
Abstract

The crystal structure of the square-planar title compound, $[RhCl(C_{21}H_{21}P)_2(CO)]$, describes another of the Vaska-type complexes. It is isomorphous with selected Ir^{I} and even Pt^{II} structures. Important bond lengths include Rh—P1 2.3344 (11), Rh—P2 2.3305 (11), Rh—Cl 2.3581 (12), Rh—C1 1.798 (5) and C1—O1 1.139 (6) Å.

Comment

The original Vaska complex, $[Ir(CO)(Cl)(PPh_3)_2]$, was first reported in 1959 (Angoletta, 1959), but was later correctly formulated by Vaska in 1961 (Vaska & Di Luzio, 1961). Complexes of this type have since been established as catalysts in a variety of processes and have been extensively studied within this context (Douek & Wilkinson, 1969; Vastag *et al.*, 1979; Rankin *et al.*, 1997).

In this paper, we report the rhodium analogue, (I), with tri-*p*-tolylphosphine as another complex in this range. The compound is one of the few crystallographic examples of these complexes which does not show disorder along the carbonyl/chloro axis. A further interesting feature is the P—Rh—P bond angle of 175.67 (4)°, which is significantly smaller than 180°.



(I)

The rhodium Vaska analogue, $[Rh(CO)(Cl)(PPh_3)_2]$, is only slightly soluble in solvents such as acetone, but by incorporating the *p*-CH_3 substituents on the phenyl rings, this problem was overcome, enabling a wider range of solution studies (Table 2).

The compound crystallizes as well defined square-planar moieties with the bulky phosphine ligands in a *trans* orientation. All bond distances are within normal ranges and are very similar to those in the analogous PPh_3 complex. It was shown recently (Steyn *et al.*, 1997) that the first order Rh–P coupling constants in rhodium–phosphine complexes, determined from ^{31}P NMR, enable quite good estimates of the Rh—P bond distances and are therefore also indicative of the *trans* influence being exerted on them. In the current study, the smaller $^1J_{RhP}$ value compared with the PPh_3 analogue can be attributed to a larger *trans* influence being exerted by the more electron-donating tri-*p*-tolylphosphine ligands [Brønsted pK_a (protonated forms) of PPh_3 = 2.73 and of P(*p*-tolyl)$_3$ = 3.84]. This effect is also evident from the lower carbonyl stretching frequency (Table 2) as an increase in the electron density on the rhodium center results in increased back donation to the carbonyl C atom and thus lowers ν(CO).

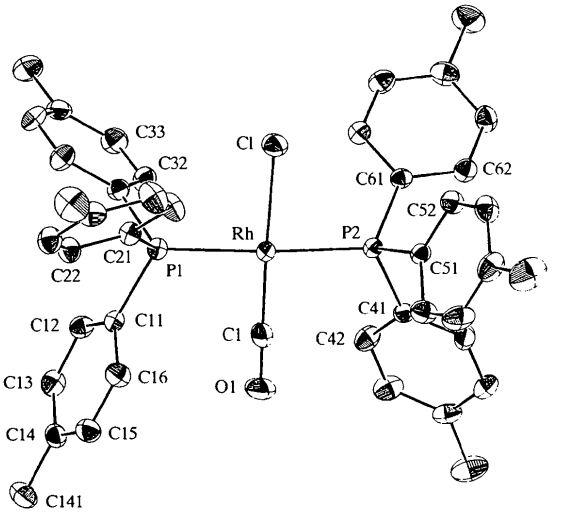


Fig. 1. The structure of (I) showing the numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

This crystallographic study further presents a rare example of isomorphism through a series of complexes containing different metal centers (along the group as well as down the triad) and different ligands in the coordination polyhedron (P and As as donor atoms in the bulky ligands, and combinations of CO, Cl and CH_3 *trans* to each other). It was found to be isomorphous with the Ir^I complexes *trans*-[Ir(CO)(CH_3){P(*p*-$C_6H_4CH_3$)$_3$}$_2$] (Janik *et al.*, 1992) and *trans*-[Ir(CO)(Cl){P(*p*-$C_6H_4CH_3$)$_3$}$_2$] (Churchill *et al.*, 1987), and indeed even with the Pt^{II} complex *trans*-[Pt(CH_3)(Cl){As(*p*-$C_6H_4CH_3$)$_3$}$_2$] (Otto & Roodt, 1996). This kind of behavior was noted previously (however not to the same extent) for complexes containing very bulky ligands, but it is not very common (Bachechi *et al.*, 1977).

Experimental

[Rh(CO)$_2$(μ-Cl)]$_2$ (20 mg, 0.051 mmol) was dissolved in 5 ml acetone and tri-*p*-tolylphosphine (78 mg, 0.257 mmol) was added as the solid, resulting in slight effervescence as CO gas was liberated from the starting compound. Slow evaporation of the solvent gave yellow crystals of the desired product in yields > 85%. Spectral data: IR (KBr) ν(CO) = 1968 cm^{-1}, (CH_2Cl_2) ν(CO) = 1976 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, $CHCl_3$ = 7.24 p.p.m.): 2.33 (*s*, 18H), 7.13 (*d*, 12H), 7.57 (*q*, 12H); ^{31}P NMR ($CDCl_3$, 121.497 MHz, 85% H_3PO_4 = 0 p.p.m.): 27.2 (doublet due to 100% ^{103}Rh), $^1J_{RhP}$ = 118 Hz.

Crystal data

[RhCl(C$_{21}$H$_{21}$P)$_2$(CO)]
M_r = 775.07
Orthorhombic
$Pna2_1$
a = 21.479 (4) Å
b = 10.569 (2) Å
c = 16.807 (3) Å
V = 3815.4 (12) Å^3
Z = 4
D_x = 1.349 Mg m^{-3}
D_m = 1.313 Mg m^{-3}
D_m measured by flotation in NaI/H_2O
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 17–22°
μ = 0.633 mm^{-1}
T = 293 (2) K
Prism
0.36 × 0.34 × 0.32 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4205 measured reflections
3872 independent reflections
3410 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.97°
h = 0 → 26
k = 0 → 13
l = 0 → 20
3 standard reflections
frequency: 60 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.065
S = 1.163
3872 reflections
440 parameters
H atoms treated by a mixture of independent and constrained refinement
w = $1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.4240P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.314 e Å^{-3}
$\Delta\rho_{min}$ = −0.262 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (3)

Table 1. *Selected geometric parameters (Å, °)*

Rh—C1	1.798 (5)	P1—C11	1.825 (4)
Rh—P2	2.3305 (11)	P2—C51	1.808 (5)
Rh—P1	2.3344 (11)	P2—C61	1.827 (4)
Rh—Cl	2.3581 (12)	P2—C41	1.831 (4)
P1—C31	1.821 (4)	O1—C1	1.139 (6)
P1—C21	1.822 (4)		
C1—Rh—P2	91.77 (15)	P2—Rh—Cl	88.19 (4)
C1—Rh—P1	90.64 (15)	P1—Rh—Cl	89.84 (4)
P2—Rh—P1	175.67 (4)	O1—C1—Rh	176.5 (6)
C1—Rh—Cl	173.11 (19)		

Table 2. *Comparative X-ray, NMR and IR data for [Rh(CO)(Cl)L_2] complexes*

L	Rh—P (Å)	$^1J_{RhP}$ (Hz)†	ν(CO) (cm^{-1})‡
PPh_3§	2.331 (7)	129	1979
$P(p\text{-}C_6H_4F)_3$	Not determined	129	1983
$P(p\text{-}C_6H_4Cl)_3$	Not determined	127	1983
$P(p\text{-}C_6H_4OCH_3)_3$	Not determined	121	1975
$P(p\text{-}C_6H_4CH_3)_3$	2.3325 (11)	118	1976

† *ca* 7 m*M* in $CDCl_3$. ‡ 2.5 m*M* in CH_2Cl_2. § Kemp *et al.* (1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1000). Services for accessing these data are described at the back of the journal.

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