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The crystal structure of carbonyl-[4-(2,4-dichlorophenylamino)pent-3-en-2-onato-κ²*N*,*O*]-(triphenylphosphine-κ*P*)rhodium(I), $RhC_{30}H_{25}Cl_2NO_2P$

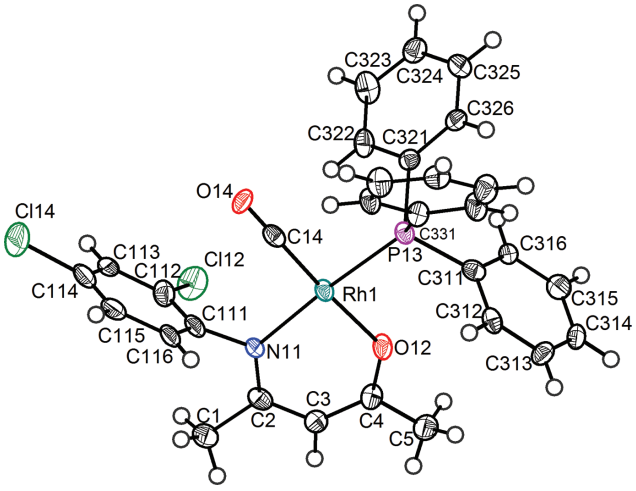

Table 1: Data collection and handling.

Crystal:	Vuboid, colourless
Size:	0.22 × 0.15 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.93 mm^{-1}
Diffractometer, scan mode:	X8 ApexII Kappa CCD, φ and ω-scans
$2\theta_{max}$, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9906, 6127, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4921
$N(param)_{refined}$:	330
Programs:	Bruker programs [12, 13], via SIR2014 [14], DIAMOND [15], WinGX, ORTEP [16], SHELX [17]

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Abstract

$RhC_{30}H_{25}Cl_2NO_2P$, orthorhombic $P2_12_12_1$ (no. 19), $a = 7.6656(5)$ Å, $b = 16.6097(11)$ Å, $c = 20.9423(14)$ Å, $V = 2666.4(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0649$, $wR_{ref}(F^2) = 0.1632$, T = 100 K.

CCDC no.: 1575207

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a 5 mL acetone solution of [Rh(2,4-Cl_2-Phony)$(CO)_2$] (0.0207 g, 51.49 µmol) was added PPh_3 (0.0137 g, 52.23 µmol) resulting in the immediate evolution of gas. The solution was left to crystallize. Crystals suitable for X-ray diffraction were obtained in quantitative yield (0.0328 g, 100%). **IR** (KBr): ν_{CO} 1963.4 (s) cm^{-1}. **UV/Vis:** $\lambda_{max} = 328$ nm, $\epsilon = 12678\ M^{-1}{\cdot}cm^{-1}$.

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^{1}H NMR (600.28 MHz, CD_2Cl_2, 25 °C): 1.34 (s, 5H), 1.98 (s, 1H), 4.98 (s, 3H), 6.26 (d, 116H), 6.62 (dd, 115H), 7.02 (m, Arom), 7.71 (d, 113H). **^{13}C NMR** (150.96 MHz, CD_2Cl_2, 25 °C): 19.15 (s, 1C), 29.22 (s, 5C), 99.17 (s, 3C), 127.18 (s, 111C), 127.21 (s, 116C), 128.07 (s, Arom), 128.31 (s, Arom), 128.44 (s, 115C), 129.91 (s, 112C), 130.59 (s, 114C), 152.25 (s, 113C), 165.99 (s, 2C), 180.30 (s, 4C), 188.20(d, 14C). **^{31}P NMR** (242.99 MHz, CD_2Cl_2, H_3PO_4, 25 °C): 43.52 (d, $J_{Rh\text{-}P}$ 161.35 Hz).

Experimental details

The methyl groups were generated to fit the difference electron density and the groups were then refined as rigid rotors, while the aromatic and methine H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. C—H = 0.98 Å and 0.95 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(C)$, respectively. During the structure refinement it became apparent to constrain the U_{ij} parameters of the atoms C111 and C116 using the EADP command of the SHELX system.

Discussion

Rhodium(I) dicarbonyl complexes of the type [Rh(*L*,*L*′)$(CO)_2$] containing chelating mono-anionic bidentate (*L*,*L*′) ligands coordinated to rhodium *via* (O,O) donor atoms have been studied as catalyst precursors [1–3]. The title complex forms part of a study which investigates complexes containing

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Rh1	0.86210(7)	0.18073(3)	0.28939(2)	0.01997(14)
N11	0.7378(8)	0.2079(4)	0.3749(3)	0.0215(13)
O12	1.0336(7)	0.2713(3)	0.3076(2)	0.0290(13)
O14	0.6362(8)	0.0407(3)	0.2629(2)	0.0284(11)
P13	1.0094(2)	0.15912(11)	0.19709(8)	0.0199(4)
Cl12	0.8431(3)	0.07631(14)	0.46271(12)	0.0446(6)
Cl14	0.1983(4)	−0.03765(17)	0.43525(14)	0.0603(8)
C1	0.6752(11)	0.2786(5)	0.4747(4)	0.0316(18)
H1A	0.5511	0.2776	0.4635	0.047*
H1B	0.7044	0.3308	0.4936	0.047*
H1C	0.7	0.2356	0.5054	0.047*
C2	0.7824(10)	0.2659(5)	0.4157(3)	0.0259(16)
C3	0.9233(9)	0.3188(5)	0.4052(3)	0.0226(14)
H3	0.9411	0.3587	0.437	0.027*
C4	1.0375(9)	0.3201(5)	0.3552(3)	0.0233(14)
C5	1.1822(11)	0.3806(5)	0.3536(4)	0.0333(19)
H5A	1.2948	0.3527	0.3554	0.05*
H5B	1.1716	0.4169	0.3903	0.05*
H5C	1.1751	0.4119	0.314	0.05*
C14	0.7209(10)	0.0951(5)	0.2721(3)	0.0226(16)
C111	0.6021(10)	0.1525(5)	0.3937(4)	0.0306(13)
C112	0.6404(11)	0.0879(5)	0.4315(3)	0.0291(16)
C113	0.5154(13)	0.0288(5)	0.4454(4)	0.038(2)
H113	0.5434	−0.0166	0.471	0.046*
C114	0.3462(13)	0.0393(6)	0.4197(4)	0.041(2)
C115	0.3043(11)	0.1034(5)	0.3835(4)	0.036(2)
H115	0.1891	0.1088	0.3673	0.043*
C116	0.4319(10)	0.1630(5)	0.3693(4)	0.0306(13)
H116	0.4032	0.2087	0.3441	0.037*
C311	1.1696(10)	0.2372(4)	0.1843(3)	0.0237(16)
C312	1.1152(9)	0.3145(5)	0.1688(3)	0.0249(15)
H312	0.9944	0.3241	0.1623	0.03*
C313	1.2307(10)	0.3778(5)	0.1623(4)	0.0272(17)
H313	1.1894	0.4298	0.1509	0.033*
C314	1.4076(10)	0.3651(5)	0.1725(3)	0.0253(17)
H314	1.4879	0.4083	0.1684	0.03*
C315	1.4661(10)	0.2888(5)	0.1888(4)	0.0286(17)
H315	1.5867	0.2798	0.1964	0.034*
C316	1.3484(10)	0.2252(4)	0.1939(3)	0.0259(16)
H316	1.3902	0.1729	0.2041	0.031*
C321	1.1351(10)	0.0655(4)	0.1931(3)	0.0203(14)
C322	1.1317(10)	0.0130(5)	0.2454(4)	0.0281(16)
H322	1.0644	0.0258	0.2821	0.034*
C323	1.2276(10)	−0.0583(5)	0.2433(4)	0.034(2)
H323	1.2237	−0.0946	0.2783	0.041*
C324	1.3266(10)	−0.0760(5)	0.1914(4)	0.0296(18)
H324	1.3935	−0.1241	0.1908	0.036*
C325	1.3307(11)	−0.0249(5)	0.1398(4)	0.0307(18)
H325	1.4017	−0.0374	0.104	0.037*
C326	1.2314(10)	0.0449(4)	0.1399(4)	0.0237(16)
H326	1.2298	0.0787	0.1033	0.028*
C331	0.8886(9)	0.1600(4)	0.1207(3)	0.0212(15)
C332	0.7241(10)	0.1266(5)	0.1168(4)	0.0262(17)
H332	0.6693	0.1069	0.1543	0.031*
C333	0.6376(11)	0.1213(5)	0.0588(4)	0.0326(18)
H333	0.525	0.0976	0.0571	0.039*
C334	0.7131(10)	0.1502(5)	0.0038(4)	0.0273(17)
H334	0.6518	0.1475	−0.0356	0.033*
C335	0.8783(11)	0.1831(5)	0.0061(3)	0.0351(18)
H335	0.9311	0.2034	−0.0316	0.042*
C336	0.9688(11)	0.1865(6)	0.0650(3)	0.0312(18)
H336	1.0846	0.2068	0.0664	0.037*

bidentate β-enaminoketonato ligands, starting with 4-(phenylamino)pent-3-en-2-onato (PhonyH [4]) coordinated to rhodium *via* (N,O) donor atoms. The proposal that only one CO-group in a [Rh(N,O-bid)$(CO)_2$]-type complex will be substituted by triphenyl phosphine, with the product being one of two possible isomers [5], has been confirmed [6–8]. In each case the CO-group *trans* to the N-atom will be substituted, attributed to the larger *trans*-influence of the N-donor atom over the O-atom. This is also evident in the title compound, where [Rh(2,4-diCl-Phony)(CO)(PPh_3)] is formed by the substitution of the carbonyl ligand in the dicarbonyl rhodium(I) complex [Rh(2,4-diCl-Phony)$(CO)_2$] [9] by PPh_3. Rh1 is displaced from the plane formed by N11, O12, P13 and C14 by 0.01 Å. It may appear that a C—O$\cdots\pi$ interaction might be possible between the carbonyl oxygen, O14, and the delocalized electrons of the phenyl ring of the bidentate ligand, with the distance from O14 to the centroid of the phenyl moiety of the bidentate N,O-ligand being 3.393(5) Å. However, the angle between a line between the O14 atom to the centroid and a plane through the phenyl ring is 75.0°, and this angle, in conjunction with the C14—O14$\cdots$centroid angle of 81.2° refutes this possibility. A similar observation may be made concerning a Cl$\cdots$Cl interaction. At first glance a Type II [10] close intermolecular Cl$\cdots$Cl interaction appears to be present, with a Cl$\cdots$Cl distance of 3.367(4) Å; the C—Cl$\cdots$Cl angles of 137.5(4)° and 98.5(4)° once more refute the possibility. Bond distances and angles involving rhodium in the complex do not differ significantly from those in the related complex [Rh(2,6-diCl-Phony)(CO)(PPh_3)] [8], with the exception of the Rh—N and Rh—C distances. These distances of 2.076(6) Å and 1.825(8) Å, respectively, are in turn shorter and significantly longer than in [Rh(2,6-diCl-Phony)(CO)(PPh_3)], illustrating the effect of the position of the second chloride atom on the phenyl ring on the electronic effect of the ligand. The effective cone angle, θ_E, [11] of 155.80(9)° is similar to the angles in the related compounds.

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