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Crystal structure of monocarbonyl(*N*-nitroso-*N*-oxido-phenylamine- $\kappa^2 O, O'$) (tricyclohexylphosphine- κP)rhodium(I), $C_{25}H_{39}N_2O_3PRh$

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Abstract

$C_{25}H_{39}N_2O_3PRh$, triclinic, $P2_1/n$ (no. 14), $a = 13.505(5)$ Å, $b = 14.266(5)$ Å, $c = 13.405(4)$ Å, $\beta = 91.280(3)^\circ$, $V = 2574.8(15)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0399$, $wR_{ref}(F^2) = 0.1026$, $T = 100$ K.

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Table 1: Data collection and handling.

Crystal:	Orange plate
Size:	$0.24 \times 0.19 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.75 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.0° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	31,008, 6189, 0.070
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5256
$N(\text{param})_{\text{refined}}$:	289
Programs:	Bruker [1], SIR97 [2], WinGX [3], SHELX [4], Diamond [5]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The synthesis of the title complex started with refluxing of hydrated $RhCl_3$ in DMF for 30 min [6]. After cooling, an equivalent amount of the ammonium salt of *N*-nitrosophenylhydroxylamine (cupferron) was added to the DMF solution [7], whereupon $[Rh(\text{cupf})(CO)_2]$ was precipitated by the addition of ice-water. $[Rh(\text{cupf})(CO)(PCy_3)]$ was prepared by adding an equivalent amount of tricyclohexylphosphine to an acetone solution of $[Rh(\text{cupf})(CO)_2]$ and precipitated with the addition of ice-water. Orange single crystals of $[Rh(\text{cupf})(CO)(PCy_3)]$ suitable for data collection were obtained after recrystallization from a 1:1 dichloromethane acetonitrile mixture.

Experimental details

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $C-H = 0.95$ and 0.98 Å and $U_{\text{iso}}(H) = 1.5$ and $1.2 U_{\text{eq}}(C)$,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Rh1	0.27045 (2)	0.23037 (2)	0.40595 (2)	0.02524 (8)
P1	0.22497 (5)	0.36301 (5)	0.32757 (5)	0.02454 (15)
O1	0.08193 (18)	0.22858 (19)	0.5150 (2)	0.0480 (6)
O2	0.40484 (15)	0.22150 (14)	0.33833 (16)	0.0312 (4)
O3	0.33146 (15)	0.10746 (15)	0.46387 (16)	0.0328 (5)
N1	0.41959 (18)	0.08689 (18)	0.4324 (2)	0.0315 (5)
N2	0.45498 (17)	0.14612 (16)	0.37090 (18)	0.0279 (5)
C1	0.1568 (3)	0.2303 (2)	0.4703 (2)	0.0352 (7)
C11	0.3319 (2)	0.4031 (2)	0.2527 (2)	0.0284 (6)
H11	0.360617	0.344279	0.224364	0.034*
C12	0.4162 (2)	0.4465 (2)	0.3171 (2)	0.0323 (6)
H12A	0.393850	0.507222	0.344712	0.039*
H12B	0.432213	0.404030	0.373754	0.039*
C13	0.5095 (2)	0.4623 (3)	0.2558 (3)	0.0406 (7)
H13A	0.560806	0.493642	0.297887	0.049*
H13B	0.536006	0.400923	0.234188	0.049*
C14	0.4859 (3)	0.5229 (3)	0.1645 (3)	0.0420 (8)
H14A	0.467057	0.586771	0.186359	0.050*
H14B	0.545735	0.528427	0.123590	0.050*
C15	0.4019 (2)	0.4808 (2)	0.1016 (2)	0.0387 (7)
H15A	0.423637	0.419790	0.074103	0.046*
H15B	0.386418	0.523222	0.044876	0.046*
C16	0.3085(2)	0.4657(2)	0.1619 (2)	0.0324 (6)
H16A	0.256715	0.435616	0.119336	0.039*
H16B	0.282879	0.527128	0.184603	0.039*
C21	0.1807 (2)	0.45819 (19)	0.4090 (2)	0.0279 (6)
H21	0.115301	0.435915	0.433321	0.034*
C22	0.2449 (2)	0.4734 (2)	0.5041 (2)	0.0348 (6)
H22A	0.255241	0.412602	0.538606	0.042*
H22B	0.310472	0.498307	0.485712	0.042*
C23	0.1948 (3)	0.5423 (2)	0.5738 (3)	0.0412 (7)
H23A	0.132411	0.514342	0.597393	0.049*
H23B	0.238596	0.553662	0.632839	0.049*
C24	0.1723 (3)	0.6350 (2)	0.5224 (3)	0.0422 (8)
H24A	0.235272	0.666357	0.505729	0.051*
H24B	0.136455	0.676504	0.568655	0.051*
C25	0.1100 (3)	0.6214 (2)	0.4276 (3)	0.0406 (7)
H25A	0.101242	0.682708	0.393582	0.049*
H25B	0.043711	0.597780	0.445138	0.049*
C26	0.1586 (2)	0.5519 (2)	0.3565 (2)	0.0349 (7)
H26A	0.220998	0.579132	0.332124	0.042*
H26B	0.113892	0.540805	0.298178	0.042*
C31	0.1233 (2)	0.3461 (2)	0.2333 (2)	0.0269 (6)
H31	0.120302	0.403498	0.190231	0.032*
C32	0.0204 (2)	0.3325 (2)	0.2789 (2)	0.0345 (7)
H32A	0.022178	0.277505	0.324251	0.041*
H32B	0.003460	0.388608	0.318756	0.041*
C33	−0.0597 (2)	0.3171 (3)	0.1971 (3)	0.0416 (8)
H33A	−0.124296	0.305873	0.228553	0.050*
H33B	−0.065864	0.374514	0.155708	0.050*
C34	−0.0352 (2)	0.2342 (2)	0.1309 (3)	0.0403 (8)
H34A	−0.085601	0.229181	0.076344	0.048*
H34B	−0.037070	0.175544	0.170485	0.048*
C35	0.0674 (3)	0.2457 (3)	0.0863 (3)	0.0413 (8)
H35A	0.066306	0.299467	0.039428	0.050*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H35B	0.083766	0.188436	0.048047	0.050*
C36	0.1480 (2)	0.2623 (2)	0.1669 (2)	0.0319 (6)
H36A	0.155116	0.205194	0.208727	0.038*
H36B	0.212108	0.273756	0.134643	0.038*
C41	0.5559 (2)	0.1349 (2)	0.3381 (2)	0.0279 (6)
C42	0.5885(2)	0.1907 (2)	0.2613 (2)	0.0355 (7)
H42	0.544764	0.233238	0.228065	0.043*
C43	0.6869 (2)	0.1833(3)	0.2334 (3)	0.0428 (8)
H43	0.710497	0.221407	0.180847	0.051*
C44	0.7504 (2)	0.1214 (3)	0.2813 (3)	0.0438 (8)
H44	0.817658	0.117649	0.262491	0.053*
C45	0.7161 (3)	0.0647 (3)	0.3567 (3)	0.0458 (8)
H45	0.759559	0.020912	0.388487	0.055*
C46	0.6180 (2)	0.0714 (2)	0.3865 (3)	0.0381 (7)
H46	0.594376	0.033162	0.438986	0.046*

respectively. The highest peak is 2.06 e Å^{−3} and deepest hole is −1.05 e Å^{−3}.

Comment

The use of tertiary phosphine mono-dentate ligands in the chemistry of [Rh(*L,L*-Bid)(CO)]₂ (where *L,L*-Bid = mono-anionic bidentate ligands) to yield [Rh(*L,L*-Bid)(CO)(PR₃)] has been extensively studied as potential catalysts precursors [8–11]. Tertiary phosphines are known to increase electron density on the metal centre. As a result, it has the potential to alter the chemistry thereof, depending on the PR₃ [10, 12, 13]. Moreover, the introduction of tertiary phosphines not only effect the electronic properties of these systems, but it also brings additional stability to these complexes [10].

More often than not, in square planar complexes of [Rh(*L,L*-Bid)(CO)]₂, substitution of tertiary phosphines tends to form two isomers as only one phosphine substitutes a carbonyl. Carbonyls extend the possibilities during the oxidative addition of alkyl iodides since they allow the formation of acyl adducts *via* migratory insertion into the metal alkyl bonds formed. The major isomer of the substitution product becomes quite predominant when the incoming PR₃ ligand is positioned *trans* to the stronger donor atom of the bidentate ligand. However, in cases where both donors have comparable donor capabilities the isomers will therefore form in comparable ratios [14]. The title structure consists of an *O,O*-donor bidentate ligand (cupferrate), a carbonyl and PCy₃ tertiary phosphine *trans* to the nitroso group. This substitution pattern in [Rh(cupf)(CO)(PCy₃)] is identical to what was

found in $[Rh(cupf)(CO)(PPh_3)]$ [11] and the related $[Rh(neocupf)(CO)(PPh_3)]$ [15]. Substitution of the carbonyl *trans* to the nitroso group shows that the nitroso oxygen (O3) has a greater *trans* influence than O2.

The geometric coordination is that of a square planar one. However, the square planar geometric orientation around the rhodium atom is significantly distorted from the ideal geometry, mainly caused by the small O2–Rh–O3 bite angle ($76.45(8)^\circ$) of the cupferrate ligand. This angular distortion is also indicated by the C1–Rh–O2 angle of $175.52(11)^\circ$. The respective Rh–O bond lengths are 2.075(2) and 2.051(6) Å which is in agreement with other rhodium(I) complexes with O,O-donor atoms [11, 14–16].

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