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Crystal Structure of Carbonyl(*N*-hydroxy-*N*-nitrosobenzenaminato-*O*,*O*′)-triphenylphosphinerhodium(I)

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We have recently reported on the oxidative addition mechanism of iodomethane to [Rh(β-dik)(CO)(L)] (β-dik = 2,4-pentanedionato, trifluoroacetylacetonato or hexafluoroacetylacetonato anions, L = phosphine) complexes [1, 2]. These results strongly suggested the ionic S_N2 two-step mechanistic route [3] but the presumably *trans* geometry of addition could not be established due to complicating equilibria. The use of cupferron instead of a β-diketone as ligand, offered a substantial smaller bite angle in the [Rh(cupf)(CO)(PPh$_3$)] complex which could favour an asymmetric concerted addition step during the oxidative addition of an alkyl halide. The scope of ths structure analysis was thus to determine the geometry of the specific isomer isolated from reaction (1). Since we are currently also concerned with the

$$[\mathrm{Rh(cupf)(CO)_2}] + \mathrm{PPh_3} \longrightarrow [\mathrm{Rh(cupf)(CO)(PPh_3)}] + \mathrm{CO} \qquad (1)$$

structural analysis of the oxidative addition product [Rh(cupf)(CO)(CH$_3$)(I)(PPh$_3$)], the nett result of these structures will aid the interpretation of the stereochemical path for the oxidative addition of CH$_3$I to the Rh(I) complex.

Experimental

The ammonium salt of *N*-nitrosophenylhydroxylamine (cupferron) was precipitated with hexane from a 1:1 acetone/methanol solution prior to use. [Rh(cupf)(CO)$_2$] was isolated from a DMF refluxed solution of hydrated RhCl$_3$ [4]. [Rh(cupf)(CO)(PPh$_3$)] was prepared in acetone solution according to reaction (1). Single crystals were grown from a concentrated 1:1 acetone/methanol solution, containing some water to initiate crystal growth.

Crystal Data

$\mathrm{RhC_{25}H_{20}N_2O_3P}$, molecular weight 530.3, space group $P\bar{1}$, $a = 9.223(2)$, $b = 10.081(7)$, $c = 13.292(3)$ Å, $\alpha = 100.31(5)$, $\beta = 108.86(2)$, $\gamma = 92.79(5)^\circ$, $Z = 2$, $V = 1143.1$ Å^3, $D_m = 1.52$ g cm^{-3}, μ(Mo Kα) = 8.2 cm^{-1}. Mo(K$\bar{\alpha}$) radiation (graphite monochromator) $\lambda = 0.71073$ Å, $3 \leqslant \theta \leqslant 25^\circ$, crystal dimensions 0.07 × 0.12 × 0.50 mm was used for intensity data collection. Final R and R_w values were 0.059 and 0.061 respectively for 2658 observed reflections [$I > 3\sigma(I)$] of 3827 independent reflections measured on an Enraf-Nonius CAD4F diffractometer. The intensity data were corrected for Lorentz, polarization effects and crystal decay.

The structure was solved by the heavy atom method and anisotropic refinement performed on all non-hydrogen atoms by least-squares methods using the X-Ray 72 system of programs. Atomic scattering factors were those tabulated by Cromer and Mann [5]. Atomic co-ordinates and thermal parameters are listed in Table I. See also 'Supplementary Material'.

TABLE I. Atomic Coordinates (×10^4) and Thermal Parameters (×10^3) for [Rh(cupf)(CO)(PPh$_3$)]. Estimated Standard Deviations given in Parentheses

Atom	x	y	z	*U_{eq}^{a}
Rh	150.7(8)	5029.4(6)	2739.6(6)	44(1)
N(1)	2148(10)	7239(8)	4340(7)	63(5)
N(2)	3015(8)	6449(7)	4010(6)	49(4)
O(1)	−3209(8)	5105(9)	1940(7)	85(6)
O(2)	2484(6)	5283(6)	3295(5)	47(3)
O(3)	686(8)	6812(6)	3892(6)	63(4)
P	−138(2)	3027(2)	1619(2)	37(1)
C(1)	−1887(11)	5029(9)	2251(8)	57(6)
C(11)	1629(9)	2708(7)	1310(8)	47(5)
C(12)	1657(11)	2589(9)	261(8)	57(6)
C(13)	3075(13)	2382(10)	98(10)	71(7)
C(14)	4397(12)	2330(10)	956(11)	74(8)
C(15)	4347(12)	2436(10)	2003(10)	68(7)
C(16)	2945(10)	2650(9)	2192(9)	55(6)
C(21)	−524(9)	1589(8)	2197(7)	41(4)
C(22)	134(11)	362(8)	2001(7)	52(5)
C(23)	−195(12)	−702(9)	2478(8)	57(6)
C(24)	−1139(13)	−582(11)	3082(9)	69(7)
C(25)	−1809(13)	625(11)	3269(10)	71(7)
C(26)	−1458(10)	1697(9)	2821(8)	53(5)
C(31)	−1635(9)	2757(8)	309(7)	42(4)
C(32)	−2435(11)	1465(8)	−225(7)	51(5)
C(33)	−3620(12)	1310(10)	−1229(8)	61(6)
C(34)	−3996(13)	2446(11)	−1712(9)	68(7)
C(35)	−3192(12)	3699(10)	−1194(9)	63(6)
C(36)	−2028(11)	3863(9)	−190(8)	58(6)
C(41)	4655(11)	6847(10)	4401(7)	53(5)
C(42)	5215(15)	8197(12)	4957(9)	80(8)
C(43)	6805(19)	8538(17)	5289(12)	102(11)
C(44)	7778(15)	7612(20)	5063(11)	96(10)
C(45)	7196(13)	6270(17)	4530(10)	89(9)
C(46)	5600(12)	5882(13)	4167(8)	70(7)

^{a}Anisotropic refinement, $U_{eq} = 1/3\Sigma_i\Sigma_j[U_{ij}(a_i^* a_j^*)(\bar{a}_i\bar{a}_j)]$

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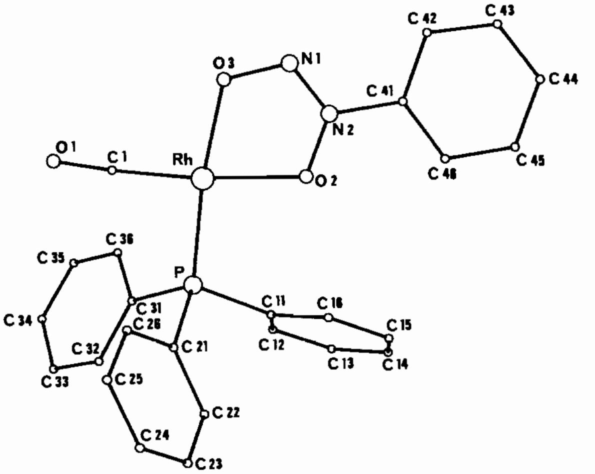

Fig. 1. Perspective view of the [Rh(cupf)(CO)(PPh_3)] molecule.

TABLE II. Selected Bond Distances (Å) and Angles (°) in [Rh(cupf)(CO)(PPh_3)]. Estimated Standard Deviations given in Parentheses

(a) Distances			
Rh–C(1)	1.78(1)	P–C(31)	1.804(7)
Rh–O(2)	2.024(6)	C(1)–O(1)	1.17(1)
Rh–O(3)	2.063(6)	O(3)–N(1)	1.30(1)
Rh–P	2.232(3)	O(2)–N(2)	1.329(8)
P–C(11)	1.83(1)	N(1)–N(2)	1.28(1)
P–C(21)	1.829(9)	N(2)–C(41)	1.44(1)
(b) Angles			
C(1)–Rh–P	88.7(3)	Rh–P–C(21)	113.2(3)
O(2)–Rh–P	96.8(2)	Rh–P–C(11)	111.5(2)
O(2)–Rh–O(3)	76.6(3)	O(2)–N(2)–N(1)	123.5(7)
C(1)–Rh–O(3)	98.1(4)	N(2)–N(1)–O(3)	113.6(7)
Rh–C(1)–O(1)	176.3(9)	N(1)–O(3)–Rh	115.4(6)
O(3)–Rh–P	172.6(2)	N(2)–O(2)–Rh	110.7(5)
O(2)–Rh–C(1)	172.8(3)	N(1)–N(2)–C(41)	119.0(7)
Rh–P–C(31)	117.5(3)	O(2)–N(2)–C(41)	117.5(7)

Results and Discussion

A perspective view and atom labeling of [Rh(cupf)(CO)(PPh_3)] are presented in Fig 1, whilst Table II gives some selected bond distances and angles. The rhodium atom is displaced by 0.01 Å from the O(2), O(3), C(1), P plane and the co-ordination polyhedrons are thus planar The plane of the chelate ring atoms are tilted 5.2° from the latter plane. The phenyl rings are all planar and their C–C bond distances range from 1.37(1) to 1.42(1) Å with an average of 1.40(2) Å. The limited bite angle (76.6(3)°) of the cupferrate ligand is responsible for the angular distortion from the normal expected square planar array in Rh(I) complexes. As a result of this, the O(3)–Rh–P, O(2)–Rh–C(1), O(3)–Rh–C(1) and O(2)–Rh–P angles deviate significantly from the normal expected values.

The Rh–P and Rh–CO bond distances are in good agreement with those of similar complexes, for example, [Rh(TFDMAA)(CO)(PPh_3)] [6] and [Rh(acac)(CO)(PPh_3)] [7]. The significant longer Rh–O(3) bond, compared to Rh–O(2), is due to the large *trans* influence of the PPh_3 ligand usually observed in complexes of the latter type. The O–N N–N and C–N bond distances of the cupferrate ligand agree, within experimental error, very well with those of Zr($cupf)_4$ [8], Fe($cupf)_3$ [9], Cu($cupf)_2$ [10] and Cu(cupf)($PPh_3)_2$ [11]. The O–N and N–N bond distances, being roughly equalized within experimental error, show that delocalization of π electrons took place. The N–N distance using Pauling's criteria [12], as well as the linear relationship between N–N bond distances and bond order calculated by the HMO method [13], indicate an 80% double bond character. Taking the N–O single and double bond distances as 1.44 and 1.20 Å respectively [12], it is evident that the N(1)–O(3) and N(2)–O(2) bonds have 58 and 45% double bond character respectively. This is also in agreement with experimental bond distance to bond order relationships for nitroso compounds [14].

The fact that only one CO group of the parent complex [Rh(cupf)($CO)_2$] could be replaced by PPh_3, makes it possible to compare the relative *trans* influence of the cupferrate oxygen atoms with those results of similar formulated complexes, [Rh(LL')(CO)(PPh_3)] (LL' = ligands such as β-diketones, thioacetylacetone, 8-hydroxyquinoline and 2-picolinic acid) [15]. The order of *trans* influence, according to Rh–P bond distances in the above complexes, was found to be $S > N > O$. The Rh–P distance for the present structure indicates a *trans* influence for the nitroso oxygen comparable to those of the β-diketone ligands. The fact that the CO group *trans* to the nitroso group in [Rh(cupf)($CO)_2$] was substituted by PPh_3, shows that the nitroso oxygen of the cupferrate's ligand atoms has the greater *trans* influence. If the same parallelism exists with regard to β-diketone ligands [16], it implies that O(2), compared to O(3), is more electron deficient (due to the electron withdrawing capacity of the phenyl group) resulting in a weaker Rh–O bond and thus exerting a smaller *trans* influence.

Crystallization studies on the product of reaction (1) indicated the formation of only the present isomer. Addition of excess PPh_3 instead of the equimolar reactant quantities required by reaction (1), does not lead to substitution of the remaining CO group of the present compound. A new compound, however, containing two PPh_3 groups and probably 5-coordinate, was isolated and is now structurally investigated.

Supplementary Material

A list of observed and calculated structure factors can be obtained from the authors.

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