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LETTER

A Dinuclear Rhodium(III) Complex with the *N,N'*-Ethylenebis(salicylideneiminato) (salen) Ligand in a Bridging Bis-bidentate Mode of Coordination. Crystal Structure of [{Rh(η^2-(C_6H_4)PPh_2)(η^2-P(*o*-ClC_6H_4)Ph_2)}$_2$(salen)](SbF_6)$_2$

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The literature on Schiff-base transition metal complexes has been extensively reviewed [1]. *N,N'*-Ethylenebis(salicylideneiminato) (salen) is the best-known potentially tetradentate ONNO-donor ligand that alternatively can act as a bridging bis-bidentate NO-donor ligand. However, only a limited number of complexes with salen acting as a bis-bidentate ligand have been described, [$(CO)_2Rh]_2$(salen) and [(cod)Rh]$_2$(salen) [2] (cod = 1,5-cyclooctadiene) being the only examples of complexes of this type known for rhodium. A related complex [(cod)Rh]$_2$(salophen) [3] has also been structurally characterized. In this communication we describe the synthesis and crystal structure of the complex [{Rh(η^2-(C_6H_4)PPh_2)(η^2-P(*o*-ClC_6H_4)Ph_2)}$_2$(salen)](SbF_6)$_2$, showing the bridging configuration of the salen ligand.

Experimental

Reagents and Solvent

Chemical reactions were carried out under dry argon by Schlenck-line procedures. All solvents were reagent grade and were dried and distilled before use. The complex $RhCl_2$(η^2-(C_6H_4)PPh_2)(η^2-P(*o*-ClC_6H_4)Ph_2) was obtained by the literature procedure [4].

Synthesis of [{Rh(η^2-(C_6H_4)PPh_2)(η^2-P(o-ClC_6H_4)Ph_2)}$_2$(salen)](SbF_6)$_2$ (1)

The salt $AgSbF_6$ (0.132 g, 0.384 mmol) was added to a dichloromethane solution (20 cm^3) of $RhCl_2$(η^2-(C_6H_4)PPh_2)(η^2-P(*o*-ClC_6H_4)Ph_2) (0.140 g, 0.192 mmol) and H_2salen (0.052 g, 0.192 mmol). The mixture was stirred at room temperature. After 12 h, a white precipitate of AgCl was filtered off. The resulting orange solution was concentrated to half the initial volume under vacuum. Addition of 10 cm^3 of n-hexane produced an orange oil which was washed with three portions of 10 cm^3 of n-hexane and dried under vacuum. Dissolution of the complex in dichloromethane:ethanol (10:1) and slow diffusion of n-hexane gave, after 2 days, orange crystals suitable for X-ray diffraction methods; yield 0.122 g, 62%. *Anal.* Found: C, 47.0; H, 3.29; N, 1.34. Calc. for ($C_{88}H_{70}Rh_2N_2O_2P_4Cl_2$)($SbF_6$)$_2$·$2Cl_2CH_2$: C, 48.4; H, 3.30; N, 1.26%.

Physical Techniques

The ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer, operating at 81.015 MHz, with 85% H_3PO_4 as external reference. The electrochemical experiments were carried out in a three-electrode cell under an inert atmosphere. The working and auxiliary electrodes were platinum; the reference electrode was a saturated Calomel electrode, electrically connected to the non-aqueous solution by a salt bridge containing the non-aqueous solvent (THF, freshly distilled from sodium benzophenone) and the supporting electrolyte ([NBu^n_4][PF_6], recrystallized from ethanol and dried at 80 °C under vacuum for 48 h). Cyclic voltammograms were obtained with a 305 HQ instrument, the programming function generator of which was connected to a 552 Amel potentiostate, and recorded with a Riken-Denshi F35 XY recorder. Controlled-potential electrolysis was performed in a three-compartment cell separated by glass frits. Working and auxiliary electrodes were of platinum mesh. The transferred charge was calculated by recording intensity versus time and carrying out a further integration. The system was calibrated against cobaltocene, [Co(η-C_5H_5)$_2$].

Crystal Data

($C_{88}H_{70}Rh_2N_2O_2P_4Cl_2$)($SbF_6$)$_2$, $M = 2059.6$; triclinic, space group $P\bar{1}$; $a = 15.2822(1)$, $b = 14.0461(2)$, $c = 10.4334(2)$ Å; $\alpha = 90.613(1)$, $\beta = 72.318(1)$, $\gamma = 100.344(1)°$; $V = 2096.80(5)$ Å^3, $Z = 1$, $D_x = 1.63$ g cm^{-3}; Mo Kα radiation (graphite crystal monochromator), $\lambda = 0.71073$ Å, μ(Mo Kα) = 12.35 cm^{-1}; $F(000) = 1022$, $T = 293$ K. Orange air-stable crystals were formed, 0.5 × 0.1 × 0.07 mm in size.

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Data Collection and Processing

Diffraction data for complex **1** were collected on a Nonius CAD4 single-crystal diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined from the angular settings of 25 reflections with $20 \leqslant \theta \leqslant 25$. A total of 8974 reflections were measured, *hkl* range (−18, −16, 0) to (18, 16, 12), theta limits ($0° < \theta < 25°$), using the $\omega-2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections were between 0.98 and 1.04. On all reflections, profile analysis was performed [5,6]; empirical absorption correction was applied using ψ scans [7], μ(Mo Kα) = 12.35 cm^{-1} (correction factors were in the range 0.80 to 1.00). Some double-measured reflections were averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma(I) = 0.036$, resulting in 7387 unique reflections of which only 2977 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data reduced to $|F_o|$ values.

Structure Analysis and Refinement

The structure was solved by Patterson interpretation using the program SHELX86 [8] which allowed us to locate Rh and Sb atoms. The remaining non-hydrogen atoms were located from successive Fourier syntheses. The structure was refined by least-squares using SHELX76 [9]; because of the size, a block-matrix refinement was used. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of some hydrogen atoms.

During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. Hydrogen atoms were included in their geometrically ideal positions and refined riding on the parent atom with a common isotropic temperature factor. Final conventional agreement factors were $R = 0.060$ and $R_w = 0.059$ for the 2971 observed reflections and 518 variables. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, $w = 1/(\sigma^2(F_o) + 0.00090(F_o)^2)$ with $\sigma^2(F_o)$ from counting statistics. The maximum shift over error ratio in the last full matrix least-squares cycle was less than 0.10. The final difference Fourier map showed no peaks higher than 1.15 e Å^{-3} nor deeper than −0.73 e Å^{-3}. The maximum residual electron density was located near to the Rh atom. Atomic scattering factors and corrections for anomalous dispersion for the Rh and Sb atoms were taken from the International Tables for X-ray Crystallography [10]. Geometrical calculations were made with PARST [11].

Results and Discussion

Molecular Structure of Complex 1

Figure 1 shows [12] a perspective view of the molecule with the atomic numbering scheme. Selected bond distances and bond angles are given in Table 1. The structure consists of a dinuclear dicationic unit with the salen bis-bidentate NO ligand

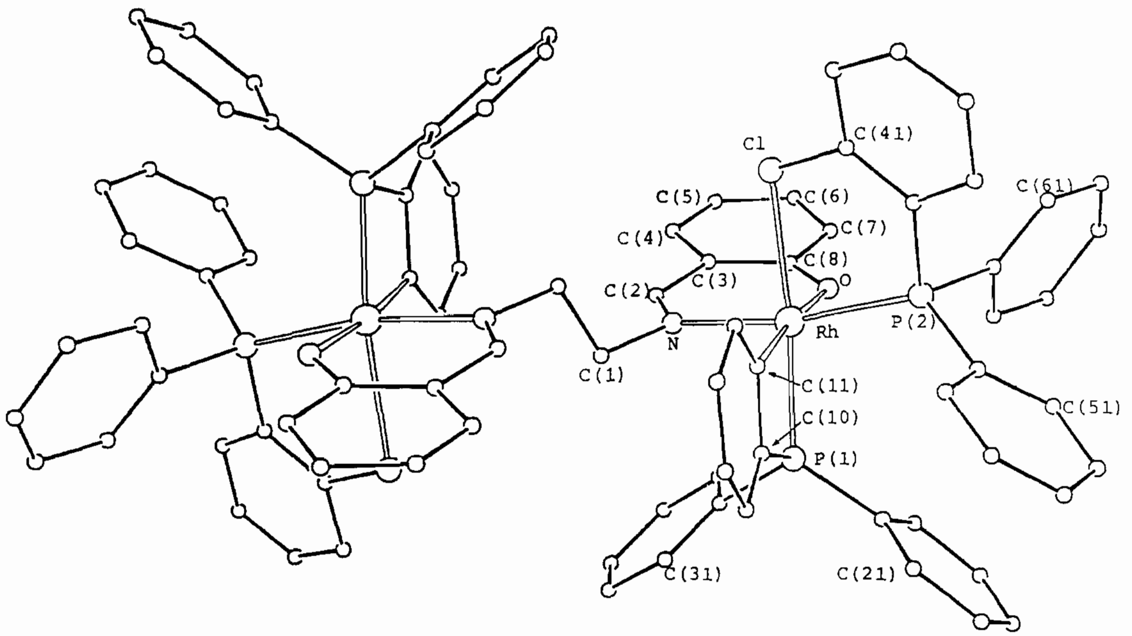

Fig. 1. Molecular structure of 1 showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to phosphorus and increases sequentially around the ring.

TABLE 1. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Bond lengths			
Rh–P(1)	2.231(3)	Rh–N	2.111(10)
Rh–O	2.075(11)	Rh–C(11)	2.020(14)
Rh–Cl	2.527(3)	Rh–P(2)	2.298(3)
P(1)–C(10)	1.776(13)	P(1)–C(20)	1.783(11)
P(1)–C(30)	1.805(13)	N–C(1)	1.481(19)
N–C(2)	1.284(18)	O–C(8)	1.270(17)
C(2)–C(3)	1.43(2)	C(3)–C(8)	1.403(19)
C(10)–C(11)	1.397(16)	Cl–C(41)	1.752(16)
P(2)–C(40)	1.791(12)	P(2)–C(50)	1.785(12)
P(2)–C(60)	1.810(16)	C(40)–C(41)	1.335(18)
Bond angles			
Cl–Rh–P(2)	83.0(1)	C(11)–Rh–P(2)	88.6(4)
C(11)–Rh–Cl	97.2(3)	O–Rh–P(2)	89.4(3)
O–Rh–Cl	88.1(3)	O–Rh–C(11)	174.0(4)
N–Rh–P(2)	169.3(3)	N–Rh–Cl	86.4(3)
N–Rh–C(11)	94.1(5)	N–Rh–O	88.9(4)
P(1)–Rh–P(2)	97.7(1)	P(1)–Rh–Cl	165.9(2)
P(1)–Rh–C(11)	68.8(3)	P(1)–Rh–O	106.0(3)
P(1)–Rh–N	92.9(3)	Rh–P(1)–C(30)	112.8(4)
Rh–P(1)–C(20)	126.5(5)	Rh–P(1)–C(10)	86.6(4)
Rh–N–C(2)	122.7(10)	Rh–N–C(1)	121.9(8)
C(1)–N–C(2)	115.4(11)	Rh–O–C(8)	127.5(10)
N–C(2)–C(3)	128.6(12)	C(2)–C(3)–C(8)	124.8(12)
C(2)–C(3)–C(4)	115.1(13)	O–C(8)–C(7)	116.9(13)
O–C(8)–C(3)	124.9(15)	P(1)–C(10)–C(15)	139.6(9)
P(1)–C(10)–C(11)	98.0(10)	C(11)–C(10)–C(15)	122.3(11)
Rh–C(11)–C(10)	106.7(9)	Rh–C(11)–C(12)	134.2(9)
Rh–Cl–C(41)	100.7(5)	Rh–P(2)–C(60)	113.9(4)
Rh–P(2)–C(50)	122.1(5)	Rh–P(2)–C(40)	104.4(5)
P(2)–C(40)–C(41)	122.9(12)	Cl–C(41)–C(40)	120.7(11)

bridging two rhodium(III) centres. The octahedral coordination around the rhodium atoms Rh(O–N)-(P–C)(P–Cl) is completed by one *ortho*-metallated phosphine and one P(o-ClC$_6$H$_4$)Ph$_2$ group acting as a chelating P, Cl ligand with the two phosphorus atoms in a *cis* arrangement. It should be noticed that the three chelating ligands create around each rhodium atom a four-, a five- and a six-membered ring, respectively, creating a rather irregular octahedral environment around the metal atoms. The four-membered ring, related to the *ortho*-metallated phosphine, gives a very acute P(1)–Rh–C(11) bond angle of 68.3(3)°, and substantial strains can be noticed in the metallated ring. The P(2)–Rh–Cl (83.0(1)°) and O–Rh–N (88.9(4)°) bond angles are related respectively to the five-membered ring (chelating phosphine) and the six-membered ring (salen ligand). The *ortho*-metallated four-membered Rh–P(1)–C(10)–C(11) ring is planar to within ±0.0018 Å, whereas for the five- and six-membered rings deviation from planarity is significant; the Rh atom lies at 0.82 Å and 0.32 Å respectively from the least-square planes defined by the Cl, C(41), C(40), P(2) and N, C(2), C(3), C(8), O atoms.

The bond distances around the rhodium in the Rh(P–C)(P–Cl) fragment fall within the range found in other related structures [4]. The Rh–N (2.111(10) Å) and Rh–O (2.075(11) Å) distances are in good agreement with the distance found in the complex [(cod)Rh]$_2$(salophen) [3].

The molecular packing consists of one dinuclear unit and two SbF$_6$ molecules in the unit cell. The large anisotropy of the thermal parameters for the F atoms suggest a slight disorder in the SbF$_6^-$ group.

The two halves of the salen ligand are related centrosymmetrically. This configuration, also observed in the cobalt(III) complex Co$_2$[3-MeO-(salen)]$_3$ [13], is the result of a fitting rotation around the CH$_2$–CH$_2$ bond in order to lessen the important sterical factors due to the presence of two octahedral metal centres attached to the same ligand.

NMR Spectra

The ^{31}P NMR spectrum of this complex (Cl$_3$CH solution) consists of two groups of signals; the one centred at about −29 ppm is assigned to the phosphorus of the metallated phosphine, whereas the low field set of signals (δ 41 ppm) corresponds to the phosphorus of the $P(o\text{-}ClC_6H_4)Ph_2$ ligand. Each set of signals contains three doublets of doublets of different intensities with coupling constant values ^1J(Rh–P) of 118 Hz for the chelating phosphine and 123 Hz for the metallated phosphine and ^2J(P–P′) 25 Hz, which are normal for Rh(III) complexes containing two phosphorus atoms in a mutually *cis* arrangement. Bearing in mind the small difference in the chemical shifts and coupling constants between the three sets of signals, we assign them to three different geometric isomers present in solution.

Electrochemical Study

Electrochemical measurements in THF (0.2 M $NBu^n{}_4PF_6$) at room temperature show that $[\{Rh(\eta^2\text{-}(C_6H_4)PPh_2)(\eta^2\text{-}P(o\text{-}ClC_6H_4)Ph_2)\}_2(salen)](SbF_6)_2$ undergoes a facile, partially reversible, electron reduction at −0.80 ($\Delta E_p = E_p{}^c - E_p{}^a \approx 90$ mV; ΔE_p under similar experimental conditions for $[Co(\eta\text{-}C_5H_5)_2]$ was ≈65 mV). Controlled-potential electrolysis and coulometry were carried out. No well-defined oxidation or reduction processes were detected upon electrochemical reduction of the complex ($E_{applied} = -0.9$ V), after passage of 4 F per mole of complex, indicating the reduction to Rh(I) species with decomposition. This decomposition is likely to be related to the breaking of the Rh–C bond of the four-membered ring. We have already observed in other complexes containing this type of metallocycle that it is very sensitive to the excess of electron density produced by chemical or electrochemical reduction [14].

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