Inorganica Chimica Acta, 156 (1989) 99–105

Reactions of $Rh_2(O_2CCH_3)_2\{Ph_2P(C_6H_4)\}_2$ with Monothiocarboxylic Acids: Facile Synthesis of $Rh_2(OSCR)_4 \cdot 2PPh_3$ Molecules and X-ray Crystal Structure of $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$

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(Received June 23, 1988)

Abstract

The reaction of $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2THF$ with an excess of the monothio acids HOSCR ($R = CH_3$, C_6H_5, $-C(CH_3)_3$) gives a series of products $Rh_2(OSCR)_4 \cdot 2PPh_3$ in which the initially bridging orthometallated triphenylphosphine ligands have been protonated and are now coordinated as neutral ligands to the rhodium(II) ions. In addition the two bridging acetate groups are displaced and the rhodium-to-rhodium bond is bridged by four monothiocarboxylate groups in the final product. The reaction products were characterized by elemental analyses, infrared and ^1H NMR spectroscopy. The structure of $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$ was unequivocally established by a single crystal X-ray diffraction experiment. This compound crystallizes in the monoclinic space group $P2_1/n$ with one half of the dimer constituting the asymmetric unit. The cell dimensions are: $a = 12.508(8)$, $b = 12.976(7)$, $c = 17.582(5)$ Å, $\beta = 92.31(3)°$, $V = 2851(2)$ Å^3 and $Z = 2$. The structure was refined to $R = 0.086$ ($R' = 0.070$). The Rh–Rh distance is 2.584(1) Å and the Rh–P distance 2.475(2) Å. The length of this metal–metal bond is appreciably greater than that observed for $Rh_2(OSCCH_3)_4 \cdot 2HOSCCH_3$ (2.550(3) Å), the only other tetramonothiocarboxylato complex of rhodium(II) to have been structurally characterized. The electron transfer behaviour of these compounds has been studied by cyclic voltammetry in several solvents. The potential at which the dinuclear molecule undergoes oxidation was found to be dependent on the identity of the substituent group on the monothiocarboxylate ligands, with the oxidation becoming easier as the electron-donating power of the substituent group was increased.

Introduction

Many dinuclear compounds of rhodium(II) have been reported in the literature [1–3]. However, the most extensively studied have undoubtedly been the dirhodium tetracarboxylate molecules. Both the mono- and diadducts of the $Rh_2(carboxylate)_4$ core have been prepared and characterized by X-ray crystallography. Spectroscopic results and theoretical calculations done on these tetracarboxylate molecules show [4–11] the metal–metal bond order to be 1.0 with the ground state electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$. The Rh–Rh bond lengths lie in the range 2.37–2.49 Å. The length of this metal-to-metal bond is dependent on both the type of bridging carboxylate and the identity of the axial ligands. If the axial ligand is an ambidentate one then its mode of coordination is dependent on the nature of R of the bridging $RCOO^-$ [12, 13].

Much current interest is focused on the redox properties of these molecules and the tetracarboxylates have been subjected to extensive investigation [14–20]. Wilson and Taube studied the aqueous oxidation of $Rh_2(O_2CCH_3)_4$ with ceric ion potentiometrically [14, 15]. They observed that the dirhodium complex could be reversibly oxidized in a single electron transfer. The potential of that oxidation reaction was dependent on the pH of the medium. Bear *et al.* have studied the electrooxidation and electroreduction reactions of ten $Rh_2(O_2CR)_4$ compounds in a wide range of solvents [18]. They observed that the mid-point potentials depended upon the identity of both the bridging carboxylate ligands and the electrochemical solvent. The potential for the $[Rh_2]^{4+/5+}$ couple was sensitive to the electron-donating or electron-withdrawing power of the substituent group, R, on the 3-atom bridge and an approximately linear relationship was observed between that potential and the Taft inductive parameters for the variously substituted carboxylates. For a given carboxylate complex it was found that the oxidation potential was inversely related to the solvents' donor ability, plots of E^0 *versus* Gurmann's Donor Number being approximately linear. Drago *et al.* [19] have investigated the electro-oxidation of a group of 1:1 and 1:2 adducts of $Rh_2(O_2CC_3H_7)_4$ in dichloromethane. They observed that the 1:2 adducts

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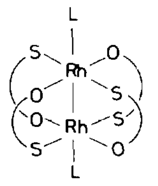
were more easily oxidized than the 1:1 adducts. Recently similar observations have been made by Bottomley and Hallberg [20].

Surprisingly, although the carboxylate complexes $Rh_2(O_2CR)_4$ have been studied extensively, the closely related monothiocarboxylates, $Rh_2(OSCR)_4$, have remained relatively neglected [21–24]. Indeed although more than thirty $Rh_2(O_2CR)_4L_n$ ($n = 0, 1, 2$) [1–3] have been structurally characterized, to the best of our knowledge only a single dirhodium tetramonothiocarboxylate, $Rh_2(OSCCH_3)_4 \cdot 2CH_3CSOH$, has been examined by X-ray crystallography [24]. In an attempt to remedy this situation we set out to develop a new synthetic route to $Rh_2(OSCR)_4 \cdot L_n$ molecules, and to investigate the redox chemistry of these species.

Since the discovery of the unusual dirhodium(II) molecules $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2L$ [25, 26] several reports of closely related compounds have appeared [27, 28]. In addition a number of studies into the reactivity of these new species have been published [29, 30]. Use of the reagent trimethylsilylchloride removes one or more of the bridging carboxylate ligands and a number of other species can then bind to one or both of the coordinatively unsaturated rhodium(II) ions [29, 30]. We have explored the reactions of $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2THF$ with a number of monothiocarboxylic acids. These reactions give a good yield of the $Rh_2(OSCR)_4 \cdot 2PPh_3$ molecules which have been characterized by spectroscopic, crystallographic and electrochemical techniques.

Results and Discussion

The previously reported syntheses of dirhodium tetramonothiocarboxylate molecules [27, 28] involved the treatment of $Rh_2(O_2CH)_4 \cdot 2H_2O$ with the appropriate monothiocarboxylic acid at elevated temperatures. Unfortunately the synthesis of $Rh_2(O_2CH)_4 \cdot 2H_2O$ from $M_2[RhCl_6]$ (M = Na, K) and aqueous formic acid is a low yield one [31]. In contrast the reaction between $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2$ and the monothiocarboxylic acids RCOSH ($R = CH_3$, C_6H_5, $C(CH_3)_3$) proceeds immediately to completion upon the intimate mixing of the two reagents in methanol. The ^1H NMR spectra of the orange powders obtained in these reactions indicate a ratio of monothiocarboxylate:phosphine ligands of 2:1 (see 'Experimental'). The infrared spectra of each compound contain bands at *ca.* 1550–1580 cm^{-1} which can be assigned to $\nu_{as}(CO)$ and further bands at *ca.* 1480 cm^{-1}, assigned to $\nu_s(CO)$. Each of the spectra contains a strong band at *ca.* 1180 cm^{-1} which may be due to $\nu(CS)$. The orthometallated starting material contained a band at 1540 cm^{-1} which had tentatively been assigned to the orthometallated phosphine ligands [26, 32]. This band is absent from the spectra of our products. These spectroscopic data, together with the results of microanalysis (C, H, S, P) are consistent with a molecular formula of $Rh_2(OSCR)_4 \cdot 2PPh_3$ for these products. To establish unequivocally the identity of these compounds one, $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$, was selected for an X-ray structural analysis. This showed that during reaction the dinuclear structure was retained and that the Rh–Rh bond was bridged by four monothiocarboxylate ligands. The phosphine ligands were now observed to occupy the sites *trans* to the rhodium-to-rhodium bond. Although four geometrically distinguishable isomers are possible in principle (I–IV) in any compound of this type in which the metal–metal bond is bridged by four asymmetric ligands, it is the most common isomer, isomer II, which is observed in this study [33–37].



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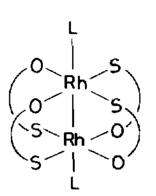

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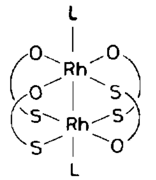

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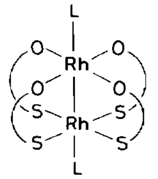

IV

Details of the solution of the structure are given in 'Experimental'. Selected bond distances and angles are presented in Tables 1 and 2 respectively The structure of $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$ is shown in Fig. 1. The molecule is a dimer lying on a crystallographic inversion centre with each rhodium atom exhibiting distorted octahedral coordination, with angles in the range 87–93°. The rhodium-to-rhodium bond is bridged by four monothiopivalate ligands in a cisoid arrangement. The site on each rhodium *trans* to the metal–metal bond is occupied by a triphenylphosphine molecule. The rhodium–rhodium distance at 2.584(1) Å is significantly greater than that found in $Rh_2(OSCCH_3)_4 \cdot 2HOSCCH_3$, which was observed to be 2.550(3) Å [24]. This increase in bond length reflects the relative donor power of the axial triphenylphosphine and monothioacetate ligands rather than any effect of changing the substituent on the bridging thiocarboxylate ligands, since the replacement of a methyl substituent by a t-butyl one is observed, in the rhodium tetracarboxylates, to lead to a shortening of the metal–metal bond [1, 12, 38].

TABLE 1. Bond Lengths (Å)

Rh(1*)–Rh(1)	2.584 (1)	Rh(1)–P(1)	2.475 (2)
Rh(1)–S(1)	2.268 (2)	Rh(1)–S(2)	2.277 (3)
Rh(1)–O(1)	2.078 (6)	Rh(1)–O(2)	2.099 (6)
P(1)–C(1)	1.828 (9)	P(1)–C(7)	1.838 (10)
P(1)–C(13)	1.830 (9)	S(1)–C(30)	1.691 (9)
S(2)–C(20)	1.690 (9)	C(1)–C(2)	1.417 (13)
C(1)–C(6)	1.407 (13)	C(2)–C(3)	1.408 (13)
C(3)–C(4)	1.399 (15)	C(4)–C(5)	1.393 (15)
C(5)–C(6)	1.389 (14)	C(7)–C(8)	1.423 (14)
C(7)–C(12)	1.377 (14)	C(8)–C(9)	1.410 (15)
C(9)–C(10)	1.400 (19)	C(10)–C(11)	1.400 (19)
C(11)–C(12)	1.430 (16)	C(13)–C(14)	1.385 (13)
C(13)–C(18)	1.419 (13)	C(14)–C(15)	1.411 (14)
C(15)–C(16)	1.355 (17)	C(16)–C(17)	1.407 (18)
C(17)–C(18)	1.406 (15)	C(20)–C(21)	1.525 (12)
C(21)–C(23)	1.524 (15)	C(21)–C(22)	1.545 (16)
C(21)–C(24)	1.517 (15)	C(30)–C(31)	1.566 (13)
C(31)–C(32)	1.485 (16)	C(31)–C(33)	1.441 (17)
C(31)–C(34)	1.587 (22)		

Asterisk represents the atom related by $\bar{x}$, $\bar{y}$, $\bar{z}$.

Useful comparisons might also be made with the structure of Rh$_2$(O$_2$CCH$_3$)$_4$·2PPh$_3$ [39]. The rhodium–rhodium bond length in this carboxylate compound is 2.4505(2) Å, more than one-tenth of

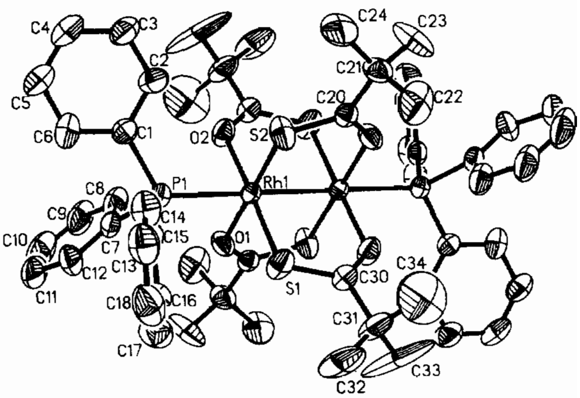

Fig. 1. The molecular structure of Rh$_2$(OSCC(CH$_3$)$_3$)$_4$·2PPh$_3$. Atoms are represented by thermal ellipsoids at the 50% level and the atomic labelling scheme is defined.

TABLE 2. Bond Angles (°)

P(1)–Rh(1)–Rh(1*)	178.4(1)	S(1)–Rh(1)–Rh(1*)	89.1(1)
S(1)–Rh(1)–P(1)	92.2(1)	S(2)–Rh(1)–Rh(1*)	89.3(1)
S(2)–Rh(1)–P(1)	91.6(1)	S(2)–Rh(1)–S(1)	90.7(1)
O(1)–Rh(1)–Rh(1*)	91.2(2)	O(1)–Rh(1)–P(1)	87.8(2)
O(1)–Rh(1)–S(1)	89.0(2)	O(1)–Rh(1)–S(2)	179.4(2)
O(2)–Rh(1)–Rh(1*)	91.0(2)	O(2)–Rh(1)–P(1)	87.7(2)
O(2)–Rh(1)–S(1)	177.6(2)	O(2)–Rh(1)–S(2)	91.7(2)
O(2)–Rh(1)–O(1)	88.6(3)	C(1)–P(1)–Rh(1)	119.3(3)
C(7)–P(1)–Rh(1)	113.6(3)	C(7)–P(1)–C(1)	98.6(4)
C(13)–P(1)–Rh(1)	115.1(3)	C(13)–P(1)–C(1)	103.2(4)
C(13)–P(1)–C(7)	104.8(4)	C(30)–S(1)–Rh(1)	110.0(3)
C(20)–S(2)–Rh(1)	110.2(3)	C(2)–C(1)–P(1)	119.6(7)
C(6)–C(1)–P(1)	119.8(8)	C(6)–C(1)–C(2)	120.4(9)
C(3)–C(2)–C(1)	119.0(10)	C(4)–C(3)–C(2)	119.5(10)
C(5)–C(4)–C(3)	121.2(10)	C(6)–C(5)–C(4)	120.0(10)
C(5)–C(6)–C(1)	119.8(11)	C(8)–C(7)–P(1)	113.1(7)
C(12)–C(7)–P(1)	123.9(9)	C(12)–C(7)–C(8)	122.7(10)
C(9)–C(8)–C(7)	119.6(11)	C(10)–C(9)–C(8)	118.1(12)
C(11)–C(10)–C(9)	121.9(12)	C(12)–C(11)–C(10)	120.5(13)
C(11)–C(12)–C(7)	117.2(12)	C(14)–C(13)–P(1)	120.2(8)
C(18)–C(13)–P(1)	118.7(8)	C(18)–C(13)–C(14)	120.9(9)
C(15)–C(14)–C(13)	118.9(10)	C(16)–C(15)–C(14)	119.8(11)
C(17)–C(16)–C(15)	123.3(11)	C(18)–C(17)–C(16)	117.2(11)
C(17)–C(18)–C(13)	119.9(11)	C(21)–C(20)–S(2)	119.0(7)
C(23)–C(21)–C(20)	108.5(8)	C(22)–C(21)–C(20)	105.4(8)
C(22)–C(21)–C(23)	109.9(10)	C(24)–C(21)–C(20)	113.2(9)
C(24)–C(21)–C(23)	110.0(10)	C(24)–C(21)–C(22)	109.8(10)
C(31)–C(30)–S(1)	117.6(7)	C(32)–C(31)–C(30)	115.5(10)
C(33)–C(31)–C(30)	108.9(10)	C(33)–C(31)–C(32)	109.8(12)
C(34)–C(31)–C(30)	103.8(10)	C(34)–C(31)–C(32)	104.7(12)
C(34)–C(31)–C(33)	114.2(16)		

Asterisk represents the atom related by $\bar{x}$, $\bar{y}$, $\bar{z}$.

an angstrom less than that reported here, yet surprisingly the rhodium phosphorus bond lengths are indistinguishable, at 2.475(2) and 2.477(1) Å respectively. The Rh–O bond distances, 2.078(6) and 2.099(6) Å, and the Rh–S bond distances, 2.268(2) and 2.277(3) Å, are closely similar to those reported for $Rh_2(OSCCH_3)_4$ [24]. There is no significant twisting about the rhodium–rhodium bond, the ligating atoms on the metals being virtually eclipsed (O(2)–Rh(1)–Rh(1*)–S(1*) = 2.4°, O(1)–Rh(1)–Rh(1*)–S(2*) = 0.3°).

Each of the complexes $Rh_2(OSCR)_4 \cdot 2PPh_3$ (R = –Ph, –Me, –CMe$_3$) was investigated by using cyclic voltammetry at 25 °C at a platinum electrode in dichloromethane and methanol using 0.1 M $(NBu_4)BF_4$ as supporting electrolyte. The maximum potential range investigated was +1.8 to –1.8 V in solvent CH_2Cl_2. Experiments were carried out both on purified samples of each compound and on solutions of $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2THF$ to which the appropriate thiocarboxylic acid had been added. In each experiment a single reversible or quasireversible oxidation to the Rh(2.5+) radical cation was observed. In addition a further irreversible oxidation was observed at more positive potentials. A highly irreversible reduction was observed at extreme negative potentials. Such features are frequently observed in cyclic voltammograms of dinuclear rhodium(II) compounds and are usually attributed to irreversible decomposition of the molecule coupled to the electron transfer reaction [18, 26]. The reversible oxidation potentials observed and the peak-to-peak separations ($\Delta E_p = E_{p,a} - E_{p,c}$) are summarized in Table 3.

The electrooxidation of each of the three compounds produced a single oxidation peak, at a potential of less than +1.0 volts, on the forward scan and a coupled reduction peak on the backward sweep. The substantial peak-to-peak separations and the observation that these separations increased with increasing scan rate was diagnostic of the quasireversible character of the electron transfer reactions. However, the ratio of cathodic to anodic current $i_{p,c}/i_{p,a}$ was close to unity at all scan rates, consistent with the absence of coupled chemical reactions [40, 41]. In addition plots of $i_p/\nu^{1/2}$ were approximately constant over sweep rates of 50–400 mV s^{-1}, indicating diffusion control. The potential for the electrooxidation of $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2THF$ measured under identical experimental conditions was +0.91 volts. If monothiopivalic or monothioacetic acid were added in excess to the electrochemical cell containing the orthometallated compound the wave at +0.91 was rapidly lost and a new wave observed at a potential closely similar to that which we observed for pure samples of the appropriate $Rh_2(OSCR)_4 \cdot 2PPh_3$ compound. In neither experiment were any electrochemical waves which could be attributed to intermediate species observed. However, a further irreversible wave at a potential of *ca.* –1.0 volts was observed in each case. This irreversible process could be attributed to the reduction of the proton associated with the carboxylic acid molecules displaced from the parent complex [26].

TABLE 3. Electrode Potentials (V) and ΔE_p (mV) for the Oxidation of $Rh_2(OSCR)_4 \cdot 2PPh_3$ Molecules[a]

Compound	Solvent	
	CH_2Cl_2	MeOH
$Rh_2(OSCPh)_4 \cdot 2PPh_3$	0.99 (170)	0.99 (190)
$Rh_2(OSCMe)_4 \cdot 2PPh_3$	0.65 (120)	0.64 (110)
$Rh_2(OSCCMe_3)_4 \cdot 2PPh_3$	0.56 (90)	0.55 (80)

[a] Peak potentials were measured at a scan rate of 100 mV s^{-1}.

Previous studies have attempted to correlate the potential for the electro-oxidation of $Rh_2(O_2CR)_4$ molecules with the electron-donating or electron-withdrawing ability of the substituent, R, on the bridging carboxylate ligands [18]. Although we have not collected an extensive set of data the same general trends are observed in this study. Returning to Table 3, we see that the oxidation process becomes more favourable as the electron-donating power of the substituent groups on the monothiocarboxylate ligands is increased. These electron-donating groups will help stabilize the higher oxidation state of the metal by increasing the energy of the highest occupied molecular orbital, most probably the π^* MO. Thus there is a more cathodic oxidation potential as the net electron density in the metal-metal bond is increased.

Experimental

Materials

The compound $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2CH_3CO_2H$ was prepared from rhodium(II) acetate [42] by a literature method [26]. All other reagents were obtained from normal commercial suppliers.

Preparation of $Rh_2(OSCCH_3)_4 \cdot 2PPh_3$

$Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2CH_3CO_2H$ (0.062 g, 0.07 mmol) was stirred in freshly distilled tetrahydrofuran (10 cm^3) until a homogeneous blue solution was obtained. The solvent was then removed under reduced pressure and the residue of $Rh_2(O_2CCH_3)_2(Ph_2P(C_6H_4))_2 \cdot 2THF$ redissolved in methanol (10 cm^3). An excess of CH_3COSH (0.5 cm^3) was added dropwise to this solution and an orange precipitate formed within 5 min. The precipitate was filtered off, washed with diethyl ether and air dried. Yield 0.037 g (54%).

Anal. Found: C, 50.9; H, 4.2; P, 6.1. Calc. for $C_{44}H_{42}O_4P_2S_4Rh_2$: C, 51.3; H, 4.1; P, 6.0%. ^1H NMR spectrum (CD_2Cl_2): δ 1.25 (s, 12H), δ 7.2–7.6 (m, 30H). Infrared spectrum (KBr disc): 3195(w), 3051(w), 1679(m), 1562(m), 1481(m), 1432(s), 1413(m), 1359(m), 1301(m), 1238(w), 1159(s), 1090(m), 1017(w), 1000(w), 735(s), 690(s), 597(w), 537(s), 493(m) cm^{-1}.

Preparation of $Rh_2(OSCPh)_4 \cdot 2PPh_3$

The compound was prepared in a manner closely analogous to that described above. Yield 63%.

Anal. Found: C, 58.8; H, 4.0; P, 4.6; S, 9.5. Calc. for $C_{46}H_{50}O_4P_2S_4Rh_2$: C, 60.1; H, 4.0; P, 4.8; S, 10.0%. ^1H NMR spectrum ($CDCl_3$): δ 7.03–7.55 (m) and δ 7.78–7.85 (m). Infrared spectrum (KBr disc): 3051(w), 1675(w), 1576(m), 1563(w), 1481(m), 1431(m), 1413(m), 1322(m), 1285(m), 1218(m), 1176(s), 1091(m), 974(s), 771(m), 743(m), 721(w), 686(s), 536(m), 494(m) cm^{-1}.

Preparation of $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$

This compound was prepared as described above. Yield 50%.

Anal. Found: C, 55.8; H, 5.5; P, 5.3; S, 9.9. Calc. for $C_{56}H_{66}O_4P_2S_4Rh_2$: C, 56.1; H, 5.6; P, 5.2; S, 10.7%. ^1H NMR spectrum ($CDCl_3$): δ 0.91 (s, 36H), δ 7.2–7.65 (m, 30H). Infrared spectrum (KBr disc): 3049(w), 3016(w), 2955(m), 2922(m), 2895(w), 1586(w), 1521(s), 1481(m), 1452(w), 1432(m), 1387(w), 1358(m), 1224(w), 1091(m), 1048(m), 1000(s), 740(m), 692(s), 551(w), 512(s), 485(m), 416(m) cm^{-1}.

Measurements

The elemental analyses were by University College London Department of Chemistry. The infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^1H NMR measurements were obtained on a Varian XL200 spectrometer. Chemical shifts are quoted to high field of tetramethylsilane. Voltammetric studies employed a Metrohm E506 potentiostat interfaced with a Metrohm E505 cell-stand utilizing a 3-electrode geometry. The working electrode was a platinum wire electrode (Metrohm EA285). A non-aqueous Ag, AgCl/Cl^-, CH_2Cl_2 electrode was used as a reference electrode (Metrohm EA441/5) and a platinum wire as an auxiliary electrode. The reference electrode was separated from the bulk solution by a fritted salt-bridge. Cyclic voltammetric measurements also employed a Metrohm E612 VA Scanner in conjunction with a Hewlett Packard 7035B X-Y recorder. Measurements were made in several solvents (see Table 3) containing 0.1 mol dm^{-1} of $[NBu_4][BF_4]$ as inert supporting electrolyte. De-aeration of the solution was performed before commencing each experiment and a stream of nitrogen was passed throughout. All potentials are reported with respect to the Ag/AgCl reference electrode (against which ferrocene is oxidized at +0.60 V).

X-ray Crystallographic Procedures

The molecular structure of $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$ was obtained by general procedures described before [43]. A detailed description is given below. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 4.

A red crystal of approximate size 0.2 × 0.25 × 0.5 mm was mounted on a glass fibre. All geometric and intensity data were taken from this crystal by using an automated four circle diffractometer (Nicolet R3m/V) equipped with graphite monochromated Mo Kα radiation. The crystal orientation matrix and unit cell parameters were obtained from a least-squares fit to the goniometer setting of 19 accurately located reflections in the range $9° < 2\theta < 27°$. Data scans, which employed a ω–2θ motion were made for 6595 reflections in the range $5° < 2\theta < 50°$. Three standard reflections were remeasured every 97 scans and showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarization effects. There were 4096 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. From the systematically absent data the space group was $P2_1/n$.

TABLE 4. Crystallographic Data for $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$

Formula	$Rh_2P_2S_4O_4C_{56}H_{66}$
Formula weight	1199.22
Space group	$P2_1/n$
a (Å)	12.508(8)
b (Å)	12.976(7)
c (Å)	17.582(5)
α (°)	90.0
β (°)	92.31(3)
γ (°)	90.0
V (Å^3)	2851(2)
Z	2
F(000)	1236
D_{calc} (g/cm^3)	1.40
Crystal size (mm)	0.2 × 0.25 × 0.5
μ (Mo Kα) (cm^{-1})	7.74
Data collection instrument	R3m/V
Radiation	Mo Kα (λ = 0.71073)
Orientation reflections no.; range (2θ)	19, $9 < 2\theta < 27$
Temperature (°C)	22
No. unique data	6595
total with $F_o^2 > 3\sigma(F_o^2)$	4096
No. parameters	307
R [a]	0.086
R' [b]	0.070
Weighting scheme	$w^{-1} = \sigma^2F + 0.000051F^2$
Largest shift/e.s.d., final cycle	0.001
Largest peak (e/Å^3)	0.873

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R' = \Sigma[(|F_o| - |F_c|)\cdot w^{1/2}]/\Sigma|F_o|w^{1/2}$.

TABLE 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$

	x	y	z	U_{eq}[a]
Rh(1)	402(1)	426(1)	611(1)	28(1)
P(1)	1175(2)	1286(2)	1764(1)	35(1)
S(1)	−733(2)	−521(2)	1303(1)	54(1)
S(2)	1652(2)	−849(2)	699(2)	54(1)
O(1)	−737(5)	1591(5)	544(3)	46(2)
O(2)	1404(5)	1352(5)	−32(4)	48(2)
C(1)	2615(7)	1527(7)	1841(5)	38(3)
C(2)	3284(8)	1136(9)	1278(6)	52(4)
C(3)	4378(9)	1395(10)	1311(6)	65(4)
C(4)	4777(9)	2047(9)	1889(6)	60(4)
C(5)	4119(8)	2421(9)	2446(7)	56(4)
C(6)	3038(9)	2173(8)	2422(6)	54(4)
C(7)	704(8)	2616(7)	1881(6)	45(3)
C(8)	751(9)	3213(8)	1205(7)	57(4)
C(9)	484(10)	4268(9)	1221(8)	72(5)
C(10)	210(11)	4697(10)	1917(10)	91(6)
C(11)	183(10)	4106(10)	2582(9)	83(6)
C(12)	418(9)	3028(9)	2566(7)	63(4)
C(13)	904(8)	649(7)	2664(5)	42(3)
C(14)	1702(9)	94(8)	3049(6)	55(4)
C(15)	1449(10)	−453(10)	3712(6)	63(4)
C(16)	439(12)	−420(10)	3964(6)	75(5)
C(17)	−400(10)	122(9)	3587(7)	69(5)
C(18)	−155(8)	662(9)	2923(6)	57(4)
C(20)	1500(7)	−1660(7)	−49(5)	34(3)
C(21)	2288(8)	−2548(8)	−123(6)	50(3)
C(23)	2432(12)	−2753(11)	−967(7)	88(6)
C(22)	1749(11)	−3486(9)	244(8)	83(5)
C(24)	3365(10)	−2344(12)	275(9)	96(6)
C(30)	−1474(7)	−1305(7)	722(5)	37(3)
C(31)	−2273(9)	−2058(10)	1099(6)	65(5)
C(32)	−2380(10)	−1927(13)	1932(7)	94(6)
C(33)	−3307(11)	−1963(21)	714(9)	190(13)
C(34)	−1733(19)	−3157(13)	1013(12)	159(11)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The position of the unique rhodium atom was derived from a three-dimensional Patterson map. The remaining non-hydrogen atoms were found by iterative application of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were successfully refined anisotropically, although the isotropic equivalent temperature factors for the t-butyl carbon atoms are higher than those of the other carbon atoms in the structure, as might have been expected. The final least-squares refinement included 307 parameters for 4096 variables. The last cycle gave $R = 0.086$, $R' = 0.070$, and did not shift any parameters by more than 0.001 times its estimated standard deviation. The final difference-Fourier was featureless, the highest peak being 0.87 $e/Å^3$.

The fractional atomic coordinates and equivalent isotropic thermal vibrational parameters for $Rh_2(OSCC(CH_3)_3)_4 \cdot 2PPh_3$ are listed in Table 5. Important bond distances and angles are listed in Tables 1 and 2 respectively. Crystallographic calculations used the SHELXTL PLUS program package [44].

Supplementary Material

Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

Acknowledgements

We wish to thank Johnson Matthey plc for generous loans of rhodium trichloride and the SERC for financial support (E.C.M.) and for provision of the X-ray equipment.

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