

## Reactions of Tetra-acetatodirrhodium(II) with Arenesulphinates

By Joe G. Norman, jun.,\* and Edmond O. Fey, Department of Chemistry, University of Washington, Seattle, Washington 98195, U.S.A.

The reactions of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  with  $\text{RSO}_2\text{H}$  and  $\text{RSO}_2^-$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-}p$ ) have been investigated to determine whether the products formed contain *S*-bonded sulphinato-ligands or *OO'*-bonded bridging sulphinato-ligands and Rh–Rh bonds. With  $\text{RSO}_2\text{H}$ ,  $[\text{Rh}(\text{O}_2\text{SR})_3]$  or a solvate thereof is always obtained. With  $\text{RSO}_2^-$ , the initial product is  $[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{O}_2\text{SR})_2]^{2-}$  and the final product is  $[\text{Rh}_2(\text{OH})_2(\text{OH}_2)_2(\text{O}_2\text{SR})_6]^{2-}$ . In all cases the sulphinato-ligands are *S* bonded. The preference of rhodium for *S* rather than *O* co-ordination of sulphinato-ligands thus appears more important as a structure-determining factor than formation of Rh–Rh bonds.

A VARIETY of transition-metal complexes containing sulphinato-ligands,  $\text{RSO}_2^-$ , bound through one or both oxygen atoms or through sulphur, is now known.<sup>1,2</sup> The structural analogy between  $\text{RSO}_2^-$  and  $\text{RCO}_2^-$  suggests the possible existence of strongly metal–metal bonded dimers  $[\text{M}_2(\text{O}_2\text{SR})_4]$  containing bridging *OO'*-bonded sulphinates for the metals ( $\text{Mo}^{\text{II}}$ ,  $\text{Re}^{\text{III}}$ ,  $\text{Rh}^{\text{II}}$ , etc.) known to form analogous carboxylates.<sup>3</sup> However, it is not clear whether the preference of these metals for the binuclear structure outweighs their expected preference<sup>1</sup> for *S*- rather than *O*-co-ordinated sulphinates. We have tested the relative importance of these two factors by investigating the reactions of molybdenum(II) and rhodium(II) acetate dimers with arenesulphinic acids and their sodium salts. The results of the rhodium reactions are discussed below; they clearly demonstrate that, for rhodium, the preference for bonding to sulphur rather than oxygen is the dominant factor. No well defined molybdenum sulphinates have been isolated; oxidation of  $\text{Mo}^{\text{II}}$  by the ligand appears to be the important reaction.

### EXPERIMENTAL

All reactions were made under dry nitrogen. Solvents were heated under reflux and saturated with nitrogen while

cooling. The salts  $\text{Na}[\text{O}_2\text{SPh}] \cdot 2\text{H}_2\text{O}$  and  $\text{Na}[\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p] \cdot 2\text{H}_2\text{O}$  were purchased from J. T. Baker Chemical Co. Benzenesulphinic acid was prepared by neutralization of aqueous  $1.5 \text{ mol dm}^{-3}$   $\text{Na}[\text{O}_2\text{SPh}] \cdot 2\text{H}_2\text{O}$  with  $6 \text{ mol dm}^{-3}$   $\text{HCl}$  and drying of the resulting white crystalline precipitate over  $\text{P}_4\text{O}_{10}$ . I.r. spectra were recorded on a Beckman IR-10 instrument in Fluorolube and mineral-oil mulls from 400 to  $4000 \text{ cm}^{-1}$ . Elemental analyses were by Spang Micro-analytical Laboratory, Ann Arbor, Michigan, and Chemalytics, Tempe, Arizona (rhodium being determined there by atomic absorption).

*Tri(arenesulphinato)rhodium(III)*,  $[\text{Rh}(\text{O}_2\text{SR})_3]$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-}p$ ).—The complex  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  (0.10 g)<sup>4</sup> was dissolved in a solution of  $\text{PhSO}_2\text{H}$  (2.0 g) in tetrahydrofuran (thf) ( $10 \text{ cm}^3$ ). The solution was heated under reflux for 4 h during which time a yellow precipitate formed. The mixture was filtered in air and the powdery solid was washed with thf and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ , yield 0.24 g (100%). The complex is insoluble in all common solvents. I.r. spectrum:  $3065\text{w}$ ;  $1480\text{w}$ ;  $1450\text{m}$ ;  $1220\text{s}$ ;  $1180\text{m}$ ;  $1085\text{m}$ ;  $1030\text{m}$ ;  $1005\text{s}$ ;  $985\text{s}$ ;  $755\text{m}$ ;  $710\text{m}$ ;  $685\text{s}$ ;  $585\text{s}$ ;  $535\text{s}$ ; and  $450\text{m cm}^{-1}$  (Found: C, 41.05; H, 3.30; Rh, 19.6; S, 18.3. Calc. for  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{RhS}_3$ : C, 41.05; H, 2.85; Rh, 19.55; S, 18.3%). The same product was obtained in methanol, and an analogous product was prepared from  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{H}$ .

*Disodium Tetra-acetatodi(arenesulphinato)dirrhodate(II)–Water* (1/2),  $\text{Na}_2[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{O}_2\text{SR})_2] \cdot 2\text{H}_2\text{O}$  ( $\text{R} = \text{Ph}$  or

<sup>1</sup> G. Vitzthum and E. Lindner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 315.

<sup>2</sup> A. Wojcicki, *Adv. Organometallic Chem.*, 1974, **12**, 32.

<sup>3</sup> F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27.

<sup>4</sup> G. A. Rempel, P. Legzdins, H. Smith, and G. Wilkinson, *Inorg. Synth.*, 1972, **13**, 90.

$\text{C}_6\text{H}_4\text{Me-}p$ ).—The salt  $\text{Na}[\text{O}_2\text{SPh}]\cdot 2\text{H}_2\text{O}$  (0.9 g), recrystallized from water–acetone, was dissolved in a solution of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  (0.2 g) in methanol (125  $\text{cm}^3$ ); the colour changed from blue-green to violet. The solution was concentrated *in vacuo* until a precipitate appeared; during concentration the colour of the solution changed to red-orange. The mixture was filtered and the filtrate allowed to stand overnight at room temperature. The resulting orange crystalline solid was filtered off and washed with a solution of  $\text{Na}[\text{O}_2\text{SPh}]\cdot 2\text{H}_2\text{O}$  (0.38 g) in methanol (40  $\text{cm}^3$ ) (to remove excess of ligand; pure methanol decomposes the adduct to  $[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{MeOH})_2]$ ), then with acetone, and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ , yield 0.23 g (63%). The complex dissolves in water, MeOH, and *NN*-dimethylformamide (dmf) (blue solutions), pyridine (red solution), and dimethyl sulphoxide (dmsO) (orange solution); it is insoluble in acetone and  $\text{CH}_2\text{Cl}_2$ . The same colours were obtained by dissolving pure  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  in these solvents<sup>5</sup> and hence replacement of the axial sulphinates by solvent molecules is indicated. I.r. spectrum: 3 440s; 3 050w; 1 650m; 1 580s; 1 440s; 1 410s; 1 350m; 1 310w; 1 175w; 1 090s; 1 070m; 1 050m; 1 025m; 1 010s; 985s; 755m; 705s; 630m; 620m; 590s; 510m; and 390  $\text{cm}^{-1}$  (Found: C, 29.9; H, 3.15; Na, 5.55; Rh, 25.3; S, 7.95. Calc. for  $\text{C}_{20}\text{H}_{26}\text{Na}_2\text{O}_{14}\text{Rh}_2\text{S}_2$ : C, 29.8; H, 3.25; Na, 5.70; Rh, 25.5; S, 7.95%). An analogous product was obtained from  $\text{Na}[\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p]\cdot 2\text{H}_2\text{O}$ .

*Disodium Diaquadihydroxohexa(toluene-*p*-sulphinato)-dirhodium(III)-Water* (1/4),  $\text{Na}_2[\text{Rh}_2(\text{OH})_2(\text{OH}_2)_2(\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p)_4]\cdot 4\text{H}_2\text{O}$ .—The complex  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  (0.4 g) was dissolved in a solution of  $\text{Na}[\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p]\cdot 2\text{H}_2\text{O}$  (2.4 g) in water (100  $\text{cm}^3$ ) at 80 °C to give an orange-red solution. The solution was kept at 80 °C for 2 h, during which time an orange precipitate formed and an oily film appeared on the surface; the solution was then cooled to room temperature. The orange solid was pipetted out to minimize contamination with the film, and washed in air with diethyl ether. It was reprecipitated from ethanol by careful addition of a solution of  $\text{Na}[\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p]\cdot 2\text{H}_2\text{O}$  (0.5 g) in water (25  $\text{cm}^3$ ) at 75 °C until a precipitate began to form, followed by slow cooling to room temperature and isolation as before with minimum washing with water. Small amounts of the film were found in the product despite the above precautions, but their presence did not appear to appreciably affect the analytical results obtained; the film possibly represents a polymeric form of the complex. The solid was dried *in vacuo* over  $\text{P}_4\text{O}_{10}$  at 65 °C, yield 0.59 g (49%). The complex is soluble in water, MeOH, thf, acetone, and  $\text{CH}_2\text{Cl}_2$  giving orange solutions. I.r. spectrum: 3 460s; 1 630m; 1 595m; 1 490m; 1 180s; 1 090m; 1 040s; 1 025s; 1 005s; 810m; 705m; 640s; 580s; 510m; and 480  $\text{cm}^{-1}$ . Conductivity (in MeOH,  $10^{-3}\text{ mol dm}^{-3}$ ):  $\Lambda = 43 \pm 3\text{ S cm}^2\text{ mol}^{-1}$ ; gradient of plot of  $\Lambda$  against  $c^{1/2} = 500 \pm 50$  (Found: C, 38.35; H, 3.65; Na, 3.80; Rh, 15.6; S, 14.4%; *M* (methanol) 1 270—1 330. Calc. for  $\text{C}_{42}\text{H}_{56}\text{Na}_2\text{O}_{20}\text{Rh}_2\text{S}_6$ : C, 38.05; H, 4.25; Na, 3.45; Rh, 15.55; S, 14.5%; *M* 1 325).

## RESULTS AND DISCUSSION

Reaction of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  with  $\text{RSO}_2\text{H}$  in refluxing thf or methanol produced highly insoluble yellow powders which analyzed as  $[\text{Rh}(\text{O}_2\text{SR})_3]$ . The yield was quantita-

tive, consistent with (though not confirming) the simple reaction  $[\text{Rh}_2(\text{O}_2\text{CMe})_4] + 6\text{RSO}_2\text{H} \longrightarrow 2[\text{Rh}(\text{O}_2\text{SR})_3] + 4\text{MeCO}_2\text{H} + \text{H}_2$ . We find that trisulphinatorhodium(III) complexes of this type are invariably formed from  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  if acid is present, whether as  $\text{RSO}_2\text{H}$  or other acids such as  $\text{HBF}_4$ . The related hydrated complexes  $[\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SR})_3]$  have been previously prepared from  $\text{RhCl}_3\cdot x\text{H}_2\text{O}$  and  $\text{Na}[\text{O}_2\text{SR}]$  in water.<sup>6</sup> We find that they may be converted into our complexes on heating *in vacuo*.

Appearance of  $\nu_{\text{asym}}(\text{SO}_2)$  at ca. 1 220  $\text{cm}^{-1}$  in both  $[\text{Rh}(\text{O}_2\text{SR})_3]$  and  $[\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SR})_3]$  indicates S co-ordination of sulphinates to the metal.<sup>1</sup> The extreme insolubility of both complexes implies strong intermolecular interactions. These probably arise from hydrogen bonding in the hydrate; in  $[\text{Rh}(\text{O}_2\text{SR})_3]$  the three now-vacant co-ordination sites around each rhodium are probably filled by oxygen atoms of sulphinato-ligands whose sulphurs are co-ordinated to other rhodium atoms. Consistently,  $\nu_{\text{sym}}(\text{SO}_2)$  shifts from 1 050  $\text{cm}^{-1}$  in the hydrate to 985  $\text{cm}^{-1}$  in the anhydrous complex.

Addition of  $\text{Na}[\text{O}_2\text{SR}]$  to the blue-green solution of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  in methanol leads to immediate formation of the orange adducts  $\text{Na}_2[\text{Rh}_2(\text{O}_2\text{CMe})_4(\text{O}_2\text{SR})_2]$  with the sulphinates apparently co-ordinated *trans* to the Rh–Rh bond.<sup>7</sup> Their i.r. spectra are superpositions of that of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  and bands assignable to  $\text{RSO}_2^-$ , the positions of the latter indicating S-co-ordinated sulphinates.<sup>8</sup> The orange colour is also consistent with sulphur bonding since known O-bonded adducts are blue-green and the S-bonded dmsO adduct is orange.<sup>5</sup>

Prolonged heating under reflux of methanol solutions of  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  and excess of  $\text{Na}[\text{O}_2\text{SR}]$  led only to complexes still containing acetate. However, complete substitution was achieved, together with oxidation to  $\text{Rh}^{\text{III}}$ , by treating  $[\text{Rh}_2(\text{O}_2\text{CMe})_4]$  with  $\text{Na}[\text{O}_2\text{SC}_6\text{H}_4\text{Me-}p]$  at 80 °C in water (pH 7), or in basic solution initially adjusted to pH 11 with NaOH, in which case the mother liquor after reaction was at pH 5. The complex obtained differs from the simple trisulphinatorhodium(III) complexes obtained in acid in being orange, ionic, and soluble in polar organic solvents. Conductivity measurements are consistent with a 2 : 1 electrolyte where one ion has very low mobility.<sup>9,10</sup> These observations, together with analytical and molecular-weight data, suggest the formula  $\text{Na}_2[\text{Rh}_2(\text{OH})_2(\text{OH}_2)_2(\text{O}_2\text{SR})_6]\cdot 4\text{H}_2\text{O}$ . The presence of  $[\text{OH}]^-$  is further supported by the fact that, when the solution was adjusted to pH 1 with  $\text{HBF}_4$  the orange complex did not form and  $[\text{Rh}(\text{OH}_2)_3(\text{O}_2\text{SR})_3]$  was obtained instead. Two structures for the anion consistent with the i.r. spectrum and other data are shown below (any geometric isomer is of course also possible). Here  $\text{R} = \text{C}_6\text{H}_4\text{Me-}p$ . Hydroxo-bridged metal complexes are well known, and indeed  $[\text{Rh}(\text{OH}_2)_6]^{3+}$

<sup>7</sup> F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *Acta Cryst.*, 1971, **B27**, 1664.

<sup>8</sup> J. Chatt and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1969, 1770.

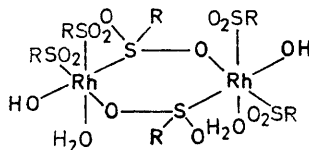
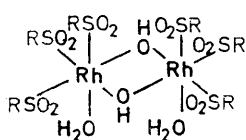
<sup>9</sup> W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

<sup>10</sup> R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

<sup>5</sup> S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, 1963, **5**, 960.

<sup>6</sup> E. Lindner and I. P. Lorenz, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 979.

is acidic ( $pK_a$  3.3).<sup>11</sup> There are only a few examples of OS-bridging sulphinates known.<sup>12</sup> However, we are unable to confirm either structure, or choose between



them, in the absence of X-ray structural information. We do not expect to obtain such information, as we have never obtained the complex in a suitable crystalline form. Experiments designed to differentiate between hydroxo-

<sup>11</sup> F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley-Interscience, New York, 1972, p. 1024.

and sulphinato-bridging, such as the spectra of deuteriated samples, have proved inconclusive.

Thus complete substitution of RSO<sub>2</sub><sup>-</sup> for MeCO<sub>2</sub><sup>-</sup> ligands in [Rh<sub>2</sub>(O<sub>2</sub>CMe)<sub>4</sub>] is apparently always accompanied by oxidation to Rh<sup>III</sup>. Under no conditions were products containing Rh-Rh bonds and OO'-bridging sulphinato-ligands isolated.

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support.

[5/1336 Received, 7th July, 1975]

<sup>12</sup> I. P. Lorenz, E. Lindner, and W. Reuther, *Angew. Chem. Internat. Edn.*, 1975, **14**, 256. However, note that our complexes [Rh(O<sub>2</sub>SR)<sub>3</sub>] probably have an analogous structure to those reported in this reference.