A Thiolate-bridged Diruthenium–Disodium Complex

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The tetranuclear complex $[(CO)_4(PPh_3)_2Ru_2(\mu_2\text{-}SEt)_4(\mu_3\text{-}SEt)_2Na_2(thf)_2]$ (thf = tetrahydrofuran) has been synthesized; the two ruthenium centres are linked by a network consisting of four doubly- and two triply-bridging thiolate ligands and two sodium atoms.

Thiolate complexes of the type $Ru(SR)_2(CO)_2(PPh_3)_2$ can be made by oxidative addition of diaryl disulphide to $Ru(CO)_2(PPh_3)_3$ in thf,[1] or by the metathesis reaction of metal thiolates with species such as $RuCl(CO)_2(PPh_3)_2$ in acetone.[2]† Attempts to synthesize corresponding alkyl thiolate species by such methods usually give mixtures‡ or intractable oils, but an unusual thiolate-bridged diruthenium–disodium complex $[(CO)_4(PPh_3)_2Ru_2(\mu_2\text{-}SEt)_4(\mu_3\text{-}SEt)_2Na_2(thf)_2]$ **1** has been isolated in 55% yield from a metathesis reaction in thf.

A thf (100 ml) suspension of *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$ (0.52 g, 0.70 mmol) and NaSEt (1.4 g, 17 mmol) was stirred under Ar for 1 h at room temperature, and then filtered; the yellow filtrate was evaporated to dryness, and the residue dissolved in thf (10 ml) and reprecipitated by addition of hexane (100 ml). A crystal of **1** was prepared by diffusion of hexane into a concentrated thf solution of the complex under Ar in the dark, and the structure determined by X-ray analysis (Fig. 1).§

The complex has a crystallographic centre of symmetry, and thus only half of the atoms are labelled in Fig. 1. The two Ru atoms are connected to each other by a network of six bridging

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† For example, we have made the *p*-thiocresolate complex *cis,cis,trans*-$Ru(SC_6H_4pMe)_2(CO)_2(PPh_3)_2$ **2** by both routes, and fully characterized the species spectroscopically and crystallographically (to be published).

‡ These include *cis,cis,trans*-$Ru(SEt)_2(CO)_2(PPh_3)_2$ **3** and -$RuCl(SEt)(CO)_2(PPh_3)_2$ **4**. NMR data (δ; *J*/Hz) are measured in C_6D_6 under Ar at room temperature; ^{31}P shifts are reported relative to 85% H_3PO_4, downfield shifts being positive. For **3**: ^1H NMR: δ 1.16 (t, 6H, $^3J_{HH}$ 7.4, Me), 1.97 (q, 4H, $^3J_{HH}$ 7.4, CH_2), 7.04 (m, 18H, *m*-/*p*-Ph), 8.22 (m, 12H, *o*-Ph). $^{31}P\{^1H\}$ NMR: δ 11.18 (s); IR (Nujol): ν(CO) 2022, 1963 cm^{-1}. For **4**: ^1H NMR: δ 1.13 (t, 3H, $^3J_{HH}$ 7.4, Me), 1.92 (q, 2H, $^3J_{HH}$ 7.3, CH_2), 7.0 (m, 18H, *m*-/*p*-Ph), 8.25 (m, 12H, *o*-Ph). $^{31}P\{^1H\}$ NMR: δ 14.54 (s); IR (Nujol): ν(CO) 2042, 1988 cm^{-1}. Mass spectrometry *m*/*z* 778 $(M)^+$, 750 $(M - CO)^+$, 722 $(M - 2CO)^+$.

§ *Crystal data*: $C_{60}H_{76}Na_2O_6P_2Ru_2S_6$, $M = 1395.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.189(3)$, $b = 13.124(3)$, $c = 12.032(4)$ Å, $\alpha = 99.70(2)$, $\beta = 110.61(2)$, $\gamma = 67.95(2)°$, $V = 1668.4(8)$ Å^3, $Z = 1$, $D_c = 1.389$ g cm^{-3}. Data were collected on a Rigaku AFC6S diffractometer at 294 K. The final unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with $2\theta = 20.0$–$26.5°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed uniformly by 12%. The structure was solved by conventional heavy-atom methods, the coordinates of the Ru, P and S atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from the subsequent difference Fourier syntheses. Calculations were performed using TEXSAN.[3] The final values of R and R_w were 0.039 and 0.043, respectively, for 4252 reflections with $I \geq 3.00\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

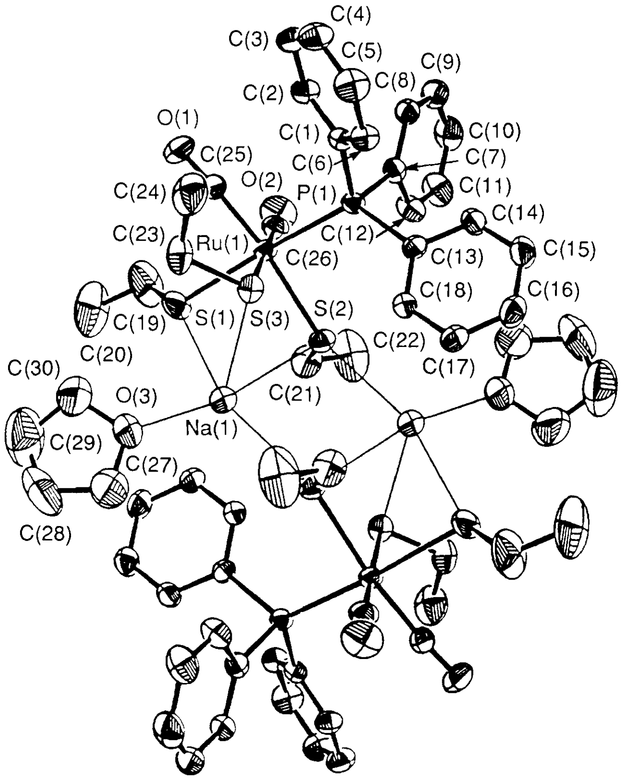

Fig. 1 The structure of **1** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)–S(1) 2.434(2), Ru(1)–S(2) 2.474(1), Ru(1)–S(3) 2.467(1), Ru(1)–P(1) 2.375(1), Ru(1)–C(25) 1.865(5), Ru(1)–C(26) 1.877(5), Na(1)–O(3) 2.365(5), Na(1)–S(1) 2.824(2), Na(1)–S(2) 3.019(2), Na(1)–S(3) 2.821(2), S(2)–Na(1)* 2.839(2); S(1)–Ru(1)–S(2) 88.46(5), S(2)–Ru(1)–S(3) 88.47(5), S(1)–Ru(1)–S(3) 84.69(5), S(1)–Ru(1)–P(1) 170.79(5), C(25)–Ru(1)–C(26) 90.5(2), S(1)–Na(1)–S(2) 71.64(6), S(1)–Na(1)–O(3) 95.3(1), S(1)–Na(1)–S(3) 71.50(6), S(2)–Na(1)–S(2)* 85.79(7). * Denotes symmetry operation: $1 - x, -y, -z$.

thiolate ligands and two sodium atoms; four thiolates [S(1),S(3),S(1)* and S(3)*] bridge one Ru and one Na, and two thiolates [S(2) and S(2)*] bridge one Ru and two Na atoms. Such triple bridging between transition metal and alkali metal ions is unprecedented. The recently reported anionic species $[Na\{Ru(CO)_2(Se_4)_2\}_2]^{3-}$ contains Se atoms (of Se_4^{2-} ligands) bridging Ru and Na atoms,[4] while examples of alkyl thiolate ligands bridging three Ru atoms are known.[5] More generally, there are few examples of transition metal complexes containing alkali metal cations 'trapped' *via* bridging thiolate ligands: (Nb–Na),[6] (Lu–Li)[7] and (U–Li),[8] although there are numerous examples within bridged alkoxide systems, including mixed doubly- and triply-bridged species.[9]

In complex **1**, the Na has distorted square-pyramidal geometry, the available sixth site [*trans* to S(3)] being blocked by a phenyl group of PPh_3; the Na–S bond lengths within the μ_2-thiolate moieties are comparable to that found in NaSMe (2.8 Å),[10] while the Na–S(2) distance involving the μ_3-thiolate is 0.2 Å longer. The geometry at Ru is essentially octahedral. The lengths of the Ru–C bonds, and the Ru–S bonds *trans* to them, are the same as in the corresponding bonds within *cis,cis,trans*-$Ru(SC_6H_4pMe)_2(CO)_2(PPh_3)_2$, **2**;† the Ru–S(1) bond in **1** is ~0.04 Å shorter than these Ru–S bonds, and the Ru–P(1) bond is 0.07 Å shorter than the Ru–P bonds in **2**, the differences being rationalized in terms of relative *trans* influences.

The room temperature solution structure of **1** differs from that in the solid state. Lack of conductivity in fresh thf solutions (up to 1 mmol dm^{-3}) shows that there is no significant dissociation into ions, but the ^1H NMR spectrum (in C_6D_6) shows that two of the thiolate groups at each Ru centre are magnetically equivalent. These are labelled (*a*) in the spectroscopic data¶ and are presumably the S(2) and S(3) thiolates *trans* to the carbonyls; (*b*) refers to the thiolate *trans* to the phosphine. The (*a*) thiolate groups could become equivalent *via* fluxionality within the dimer, or be present as such within a monomeric species containing only μ_2-thiolates between Ru and Na. Selective decoupling of the ^1H NMR spectrum at δ 1.41 [the Me(*a*) resonance] yields an AX pattern for the inequivalent $CH_2(a)$ protons, and decoupling at δ 1.59 [the Me(*b*) resonances] reveals a non-first-order AB pattern produced by the $CH_2(b)$ protons, which are inequivalent because of chirality at S(1); the inversion process at S(1) is clearly slow on the NMR time-scale. Unfortunately, we have been unable to determine the solution molecular weight of **1**, because of limitations in solubility and insufficient stability in solution.

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References

1 C.-L. Lee, J. Chisholm, B. R. James, D. A. Nelson and M. A. Lilga, *Inorg. Chim. Acta*, 1986, **121**, L7.
2 R. M. Catala, D. Cruz-Garritz, H. Torrens and R. L. Richard, *J. Organomet. Chem.*, 1988, **354**, 123.
3 TEXSAN/TEXRAY structural analysis package which includes versions of the following: DIRDIF, direct methods for difference structures by P. T. Beurskens; ORFLS, full-matrix least-squares analysis, and ORFFE, function and errors, by W. R. Busing, K. O. Martin and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.
4 M. Draganjac, S. Dhingra, S.-P. Huang and M. G. Kanatzidis, *Inorg. Chem.*, 1990, **29**, 590.
5 T. A. Creswell, J. A. K. Howard, F. G. Kennedy, S. A. R. Knox and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1981, 2220; M. I. Bruce, O. B. Shawkataly and B. K. Nicholson, *J. Organomet. Chem.*, 1985, **286**, 427.
6 S.-M. Koo, R. Bergero, A. Salifoglou and D. Coucouvanis, *Inorg. Chem.*, 1990, **29**, 4844.
7 H. Schumann, I. Albrecht and E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 985; H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Muchmore and J. Pickardt, *J. Organomet. Chem.*, 1988, **349**, 103.
8 K. Tatsumi, Y. Matsubara, Y. Inoue, A. Nakamura, R. E. Cramer, G. J. Tagoshi, J. A. Golen and J. W. Gilje, *Inorg. Chem.*, 1990, **29**, 4928.
9 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
10 E. Weiss and U. Joergens, *Chem. Ber.*, 1972, 481.

¶ Spectroscopy for **1**: ^1H NMR: δ 1.41 [t, 12H, $^3J_{HH}$ 7.6 Hz, Me(*a*)], 1.41 (m, 8H, β-CH_2 of thf), 1.59 [t, 6H, $^3J_{HH}$ 7.3 Hz, Me(*b*)], 2.71 [dq, 8H, $^2J_{HH}$ 9.0 Hz, $^3J_{HH}$ 7.3 Hz, $CH_2(a)$], 2.95 [dq, 8H, $^2J_{HH}$ 9.0 Hz, $^3J_{HH}$ 7.5 Hz, $CH_2(a)$], 2.97 [dq, 4H, $^2J_{HH}$ 9.0 Hz, $^3J_{HH}$ 7.3 Hz, $CH_2(b)$], 2.98 [dq, 4H, $^2J_{HH}$ 9.0 Hz, $^3J_{HH}$ 7.5 Hz, $CH_2(b)$], 3.57 (m, 8H, α-CH_2 of thf), 7.06 (m, 6H, *p*-Ph), 7.15 (t, 12H, $^3J_{HH}$ 7.0 Hz, *m*-Ph), 7.96 (t, 12H, $^3J_{HH}$ 8.8 Hz, *o*-Ph). $^{13}C\{^1H\}$ NMR: δ 20.73 [s, Me(*b*)], 20.89 [s, Me(*a*)], 25.16 [s, $CH_2(a)$], 25.71 (s, β-C of thf), 26.62 [s, $CH_2(b)$], 67.85 (s, α-C of thf), 128.16 (s, *p*-Ph), 130.22 (s, *m*-Ph), 134.50 (d, $^2J_{PC}$ 9.4 Hz, *o*-Ph), 135.28 (d, $^1J_{PC}$ 41.9 Hz, P–C), 197.48 (s, CO). $^{31}P\{^1H\}$ NMR: δ 25.05 (bs). IR (Nujol): ν(CO) 2014, 1952 cm^{-1}. Mass spectrometry *m/z* 1324 ± 5 $(M - thf)^+$. The ^1H and ^{13}C NMR spectral assignments were made with the help of COSY and HETCOR experiments.