Structure and Dynamics of $[Rh_4(CO)_9(\overline{SCH_2SCH_2SC}H_2)]$: a Fluxional Butterfly

Robert J. Crowte, John Evans, and Michael Webster
Department of Chemistry, The University, Southampton SO9 5NH, U.K.

$[Rh_4(CO)_9(\overline{SCH_2SCH_2SC}H_2)]$ adopts a 'butterfly' rhodium skeleton with a CO bridging the wing-tip atoms in the crystal and in solution; at ambient temperature in solution, the rhodium skeleton is non-rigid with the inter wing-tip vector exchanging between three adjacent positions.

Stabilisation of clusters by 'tripod' phosphorus and arsenic donor ligands has received much recent attention.[1,2] After observing the close steric match of 1,3,5-trithiacyclohexane (**1**) with a triangle of second transition series metals, we investigated the substitution reaction of (**1**) with $[Rh_4(CO)_{12}]$ (**2**). We report that the product of this reaction, $[Rh_4(CO)_9(\overline{SCH_2SCH_2SC}H_2)]$ (**3**), adopts an unexpected 'butterfly' metal skeleton which is fluxional in solution above −100 °C.

The molecular structure of complex (**3**) was identified by *X*-ray diffraction.† Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. 3556 Unique reflections were recorded from a crystal at room temperature ($1.5° \leq \theta \leq 25.0°$), 2261 [where $F > 5\sigma(F)$] of which were used in structure analysis. The heavy atom skeleton (Rh and S) was located by direct methods and the model developed by standard means.[3] Disorder was encountered with the sites of one rhodium atom [Rh(4)], and two carbonyl groups (7 and 9). Pairs of sites labelled A and B were identified (60.8 and 39.2% occupancy respectively) giving a final $R = 0.044$ ($R_w = 0.053$).

The molecular structure of complex (**3**) is shown in Figure 1 (the more dominant sites A are shown). The rhodium atoms define a 'butterfly,' rather than the expected tetrahedron of the parent $[Rh_4(CO)_{12}]$ (**2**),[4] in a structure similar to that reported for $[Rh_4(\mu\text{-}CO)_4(\mu\text{-}SO_2)_3\{P(OPh)_3\}_4]$.[5] The long Rh···Rh distance [3.016 Å for Rh(1)–Rh(4A) and 3.113 Å Rh(2)–Rh(4B)] is apparently compensated by relatively short metal–metal bonds to Rh(4) (2.515—2.681 Å), which are comparable with the 2.550 Å considered to be consistent with a Rh=Rh double bond in $[Rh(\mu\text{-}Bu^t_2P)(CO)(PMe_3)]_2$.[6] However all these distances are larger than the 'single' bonds observed in Rh_2^{4+} derivatives.[7]

The second notable feature of the structure is the bridging carbonyl group (symmetric within a tolerance of 3σ for the Rh–C distances) between the non-bonded wing-tip rhodium atoms, in contrast to the previously discussed condition[8] for the occurrence of bridging sites. Such groups have been observed in the 'A-frame' dimers $[M_2Cl_2(\mu\text{-}CO)\{\mu\text{-}(EPh_2)_2CH_2\}_2]$ (M = Pd, E = As; M = Pt, E = P),[9] in which the structure is also supported by bidentate group 5 donor ligands. The occurrence of this site between metal atoms within a cluster on an edge which is otherwise unsupported remains unusual.

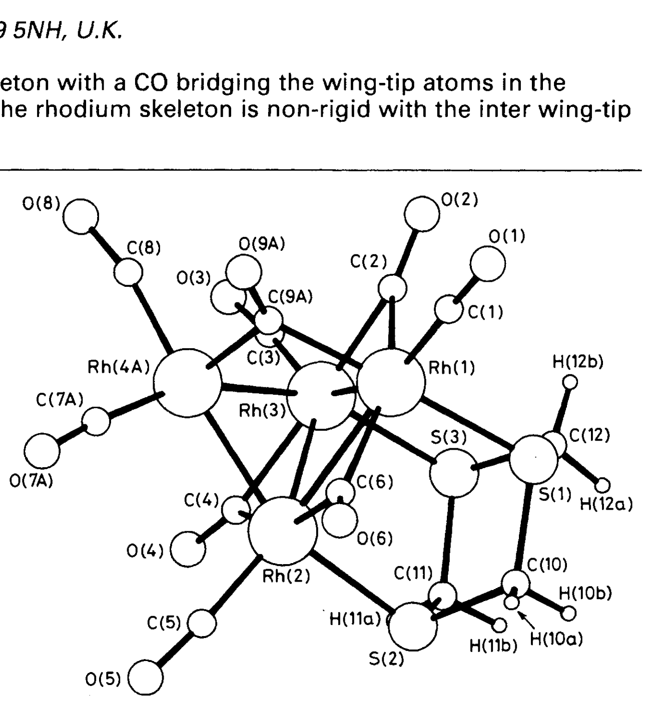

Figure 1. The molecular structure of $[Rh_4(CO)_9(\overline{SCH_2SCH_2SC}H_2)]$ (**3**). Important bond lengths (Å): Rh(1)–Rh(2) 2.733(1), Rh(2)–Rh(3) 2.705(1), Rh(3)–Rh(1) 2.716(1), Rh(1)–Rh(4A) 3.016(2), Rh(2)–Rh(4A) 2.515(2), Rh(3)–Rh(4A), 2.592(2), Rh(1)–Rh(4B) 2.537(2), Rh(2)–Rh(4B) 3.113(3), Rh(3)–Rh(4B) 2.681(2), Rh(1)–S(1) 2.410(3), Rh(2)–S(2) 2.415(3), Rh(3)–S(3) 2.405(3), C(9A)–Rh(4A) 1.99(2), C(9A)–Rh(1) 2.04(2), C(9B)–Rh(4B) 2.02(4), and C(9B)–Rh(2) 2.13(4). Interplane angles: Rh(1),Rh(2),Rh(3)/S(1),S(2),S(3) 0.41°; Rh(1),Rh(2),Rh(3)/Rh(1),Rh(3),Rh(4B) 85.5°; Rh(1),Rh(2),Rh(3)/Rh(2),Rh(3),Rh(4A) 83.3°.

The i.r. spectrum of complex (**3**) in CH_2Cl_2 solution exhibits four bands in the bridging ν(CO) region, suggesting that the structure in the crystal is maintained in solution with idealised C_s symmetry. This is clearly demonstrated in the ^{13}C n.m.r. spectrum of a 15% ^{13}CO enriched sample of (**3**) recorded at −100 °C.‡ A single exchange process was evident on monitoring both ^{13}C and ^{1}H n.m.r. spectra between −100 and 39 °C which generates an apparent 3-fold axis through Rh(4). The nature of this process is evident from the ^{13}C n.m.r. spectrum of the carbonyl region at 39 °C.‡ At this temperature, averaging of the bridging carbonyl group across the wing-tips of the 'butterfly' with the two terminal carbonyl groups on Rh(4) generates a doublet of quartets. Hence these three groups remain attached to Rh(4) but visit each of the three basal atoms in a 'semi-localised' exchange process, with only one end of the bridging unit opening. This can readily be achieved by the intermediacy of the tetrahedral structure of (**3**) (Figure 2). As a consequence of the switch from a pseudo-eclipsed geometry between the carbonyl bonds to Rh(4) and the metal–metal vectors to the staggered prefer-

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† *Crystal data:* $C_{12}H_6O_9Rh_4S_3$ (**3**), $M = 801.99$, monoclinic, $a = 8.451(3)$, $b = 16.032(2)$, $c = 15.349(3)$ Å, $\beta = 103.23(2)°$, $U = 2024.4$ Å^3, $F(000) = 1512$, D_m (flotation) $= 2.60(3)$ g cm^{-3}, $Z = 4$, $D_c = 2.630$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 34.6$ cm^{-1}, space group $P2_1/n$ (No. 14) from systematic absences.

The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ I.r., ν(CO) in CH_2Cl_2: 2067s, 2034sh, 2019vs, 1993m, 1883m, 1855m, 1815m, and 1803sh cm^{-1}; ^{13}C n.m.r. at 90.53 MHz in $CHFCl_2$–CD_2Cl_2 at −100 °C using labels in Figure 2 for assignments (*J* in Hz): δ 258.08 (t, *J* 36, CO_a), 240.73 (distorted t, *J* 32, $CO_{a'}$), 201.30 [dd, $J(Rh^4\text{–}C)$ 20, $J(Rh^1\text{–}C)$ 48, CO_c], 189.05 (d, *J* 81, $CO_{b'}$), 186.85 (d, *J* 81, CO_b), and 184.33 (d, *J* 72.5, $CO_{c'}$). In $[^2H_8]$-toluene at 39 °C with calculated values from −100 °C in parentheses: δ 242.13 (246.51) [t, *J* 34(33), CO_a and $CO_{a'}$], 188.46 (189.99) [d of q, $J(Rh^4\text{–}C)$ 57 (55), $J(Rh^{1,2,3}\text{–}C)$ 5 (5), CO_c and $CO_{c'}$], and 188.10 (188.32) [dd, $J(Rh^{1,2,\text{ or }3}\text{–}C)$ 81 (81), $^2J(Rh^4\text{–}C)$ 2, CO_b and $CO_{b'}$].

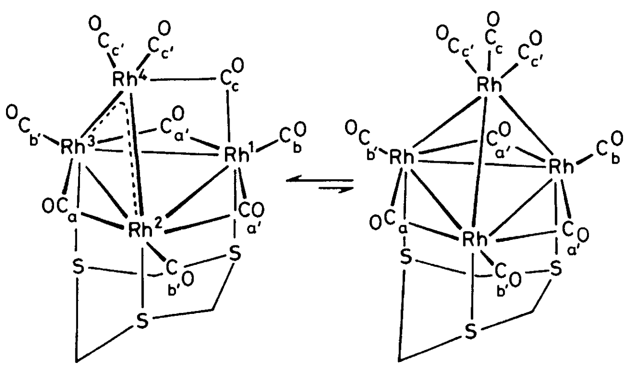

Figure 2. Proposed exchange mechanism for (3).

ence in a structure derived from $[Rh_4(CO)_{12}]$, these three carbonyl groups (c and c′ in Figure 2) will visit the three basal rhodium atoms after repetitions of this structural switch. A necessary corollary is that the position of the non-bonded separation within the 'butterfly' cycles between the three adjacent sites.

Clearly the tridentate sulphur donor does not stabilise the tetrahedral cluster. Complex (**3**) does not exhibit the increased stability reported for $[Rh_4(CO)_9\{CH(PPh_2)_3\}]$.[1] Although the skeletal non-rigidity of (**3**) demonstrates that the tetrahedral form is close in energy to the 'butterfly,' it is evident that the substitution has favoured the 'butterfly' form. Apparently as a consequence of the breaking of one Rh–Rh bond, the remaining metal–metal distances to the apical atom are short; from structural and electron counting criteria this may be considered as a delocalised double bond as depicted in Figure 2. Steric reasons appear unimportant. The ligand is less bulky than the tripod phosphine and arsine previously studied, and appears to adopt a normal chair conformation. There is only a negligible dihedral angle between the plane of the sulphur atoms and the basal trirhodium plane (0.41°). One possible reason for the structural preference may arise from *too close* a matching of the ligand and rhodium triangles. The mean Rh_{basal}–Rh_{basal}–C bond angle in (**2**) is 107°,[4] whereas the corresponding Rh–Rh–S bond angles in (**3**) average at 94.2°. These axial carbonyl groups in (**2**) approach colinearity with the Rh_{basal}–Rh_{apical} vector (mean Rh_{apical}–Rh_{basal}–C_{axial} 165°) indicating that the orientation of the carbonyl groups on the basal metal atoms optimises the overlap of a metal fragment orbital with the apical metal. The constraint imposed by the tridentate ligand in complex (**3**) effectively rotates the co-ordination sphere of these units so the fragment orbitals from the metal base are splayed out. The observed distortion allows a distorted pentagonal bipyramid co-ordination geometry of these basal metal atoms with mean S–Rh_{basal}–Rh_{apical} and S–Rh_{basal}–C(9) angles of 153 and 177° respectively. Design of ligands for cluster stabilisation should therefore take account not only of the size of the face to be capped but also of the preferred orientations for maximum metal overlaps with *remote* metal atoms.

The exchange process identified for complex (**3**) is novel. It may, however, occur in other systems where the equilibrium favours the $[Rh_4(CO)_{12}]$-derived structure. In this respect, we note the magnetic equivalence of the three carbonyl ^{13}C nuclei bound to the apical metal atom in $[M_4(CO)_9\{CH(PPh_2)_3\}]$ (M = Rh and HRu).[1]

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