Synthesis and Characterisation (by *X*-Ray Crystallography) of Di-azido- and Di-*S*-thiocyanato-di-μ-methylene-bis(pentamethylcyclopentadienyl) dirhodium and Related Molecules

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cis and *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CH_3)_2]$ react with HCl to give *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2Cl_2]$ which gives *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2X_2]$ with NaX, *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2Et_2]$ with Et_3Al, and *cis*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(O_2CMe)]^+$ with NaOAc; *X*-ray determinations of $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2X_2]$ (X = N_3 and SCN) confirm the structures.

The recently discovered *cis*- and *trans*-dimethyl-di-μ-methylene-bis(pentamethylcyclopentadienyl)dirhodium complexes (**1a**, **b**) both react readily with HCl in pentane to give the dichloro-di-μ-methylene-dirhodium complex (**2**) in 86% yield.† The μ-CH_2 ligands are retained in (**2**), as indicated by the ^{1}H n.m.r. spectrum which also shows the geometry of the complex to be *trans*[1] {δ 1.63 (s, C_5Me_5) and 10.25 [t, *J*(Rh–H) 2.3 Hz, μ-CH_2]}. The stability of the $Rh_2(\mu\text{-}CH_2)_2$ bridge unit in these complexes, at least to low acid concentrations, may be contrasted with the high reactivity towards acids shown by other Rh–μ–CH_2–Rh bridges.[2]

Both (**1a**) and (**1b**) also react with acetic or trifluoroacetic acid to give the μ-carboxylato-di-μ-methylene complexes (**3**) (in 20—50% yield). These complexes were conveniently characterised as their PF_6^- salts. The ^{1}H n.m.r. spectra showed them to have the *cis*-geometry with inequivalent methylene hydrogens.[1] {For example, (**3**, R = CF_3; X = PF_6) shows δ 1.73 (s, 15H, C_5Me_5), 9.07 (d, 2H, *J* 0.4 Hz), and 9.60 [dt, 2H, *J*(H–H) 0.4, *J*(Rh–H) 2.2 Hz], μ-CH_2.}

Metathesis reactions on complex (**2**) gave the purple dibromo , the blue-purple di-iodo-, the light-red di-azido-, and the pink di-thiocyanato-complexes (**4**)—(**7**) in 89—97% yields. Their ^{1}H n.m.r. spectra showed all to have the *trans*-configuration. This was confirmed by *X*-ray structure determinations of the di-azido-complex (**6**) and of the isomorphous and isostructural dithiocyanato-complex (**7**).

Crystal data for (**6**): $C_{22}H_{34}N_6Rh_2$, *M* = 588.4, monoclinic, *a* = 18.97(3), *b* = 13.10(2), *c* = 9.18(2) Å, β = 86.4(1)°, *U* = 2277 Å^3, *Z* = 4, D_c = 1.72, D_m = 1.68 g cm^{-1}, *F*(000) = 1192, μ(Mo-K_α) = 14.8 cm^{-1}, space group *C*2/*c* (C^6_{2h}, No. 15) (from systematic absences). Current *R* 0.074 for 1200 reflections [$6.5° < 2\theta < 50°$, $I > 3\sigma(I)$, Mo-K_α, λ = 0.71069 Å].‡

Crystal data for (**7**): $C_{24}H_{34}N_2Rh_2S_2$, *M* = 620.5, monoclinic, *a* = 19.09(4), *b* = 13.76(3), *c* = 9.47(7) Å, β = 86.7(1)°, *U* = 2482 Å^3, *Z* = 4, D_c = 1.66, D_m = 1.65 g cm^{-3}, *F*(000) = 1256, μ(Mo-K_α) = 14.9 cm^{-1}, space group *C*2/*c* (C^6_{2h}, No. 15) (from systematic absences). Current *R* 0.087 for 1498 reflections [$6.5° < 2\theta < 50°$, $I > 3\sigma(I)$, Mo-K_α, λ = 0.71069 Å].‡

Both complexes (**6**) and (**7**) are centrosymmetric; each rhodium is η^5-bonded to a C_5Me_5 ring, and joined to the other by two methylene bridges. In (**6**) each rhodium is also bonded to a terminal azide [∠Rh–N–N 114(1)°], while in (**7**) each

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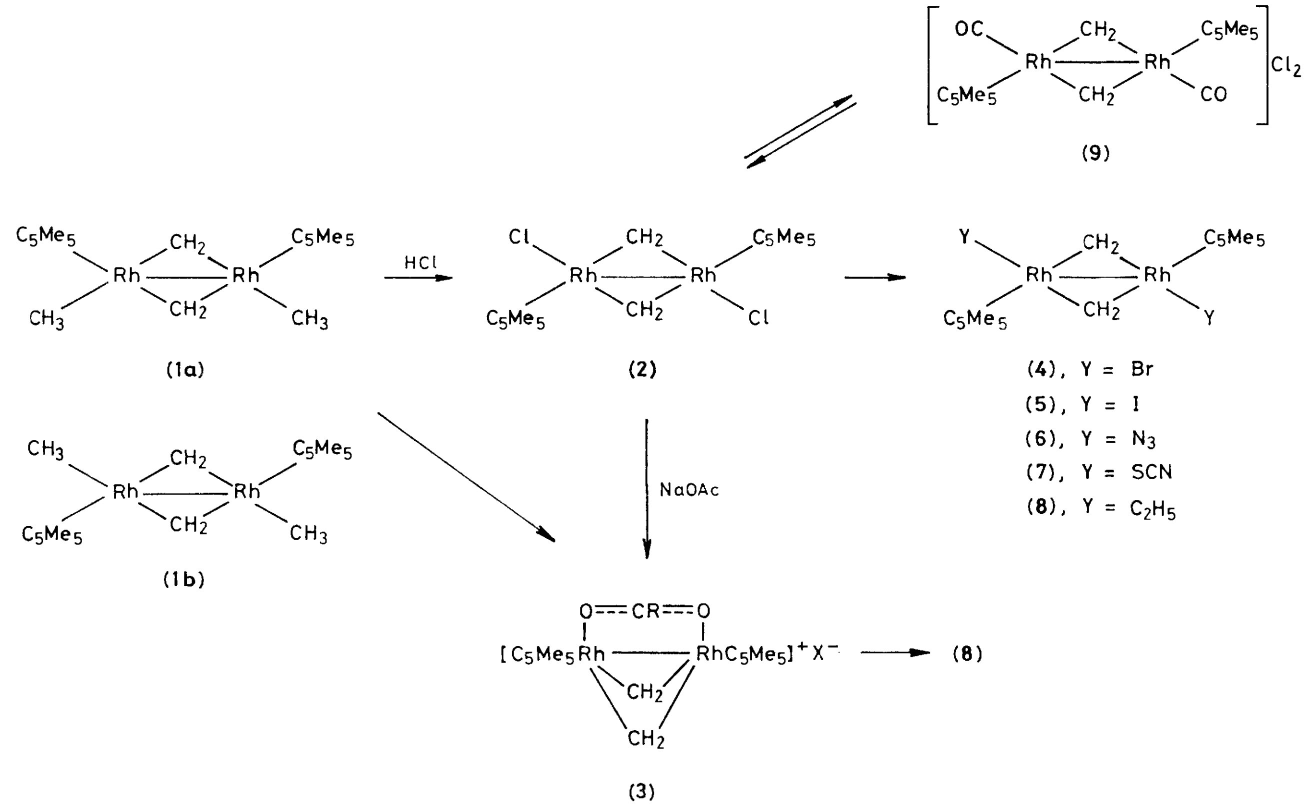
† All new complexes gave satisfactory analyses and mass spectra.

‡ The atomic co-ordinates for this work 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.



rhodium is S-bonded to thiocyanate [∠Rh–S–C 104(1)°]. The two rhodium atoms are very close together[3] in both complexes.§ Formally each Rh in complexes (**1**)—(**8**) is in the (+IV) oxidation state, d^5. The diamagnetism observed for these complexes is therefore explained by the presence of a Rh–Rh bond.

The complexes (**2**)—(**7**) are reasonably robust, for example, *trans-* (**2**) reacts with sodium acetate in methanol to give *cis-* (**3**, X = OAc). This reaction also shows that the $Rh_2(\mu\text{-}CH_2)_2$ bridge is quite flexible. The metatheses probably proceed by S_N1-type (D) reactions and we note, for example, that (**2**) reacts reversibly with CO in methanol to give the unstable dicationic dicarbonyl (**9**) [ν(CO) 1960 and 2060 vs cm^{-1}].

The dichloro-complex (**2**) also reacted with triethylaluminium to give the crimson diethyl complex (**8**) (42%), which was also obtained (47%) from the trifluoroacetate (**3**). On pyrolysis (**8**) gave significant amounts of C_4 (as well as C_1—C_3) hydrocarbons; this reaction corresponds to the formation of propene on pyrolysis of (**1a**) or (**1b**).[1]

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§ Bond lengths (a) of *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(SCN)_2]$ (**7**): Rh–Rh, 2.657(2); Rh–S, 2.393(6); Rh–CH_2, 2.06, 2.04(2); Rh–C (C_5Me_5, mean), 2.23(2) Å, and (b) of *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(N_3)_2]$ (**6**); Rh–Rh, 2.635(2); Rh–N, 2.150(15); Rh–CH_2, 2.011, 2.024(17); Rh–C (C_5Me_5, mean), 2.227(17) Å.