Synthesis and *X*-Ray Crystal Structure of Trimesitylrhodium(III)

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The first neutral homoleptic aryl of rhodium(III), $Rh(2,4,6\text{-}Me_3C_6H_2)_3$, has been made by interaction of $RhCl_3(C_4H_8S)_3$ and mesitylmagnesium bromide; the *X*-ray crystal structure suggests that there is 'agostic' interaction between Rh and an *ortho*-CH_3 group in a distorted *fac*-octahedral geometry, but solution spectroscopic data show no evidence for agostic hydrogen bonding; ^1H NMR spectra over a temperature range indicate synchronized rotation of the mesityl group about the Rh–C bond for which $\Delta G^\ddagger$ is *ca.* 63 kJ mol^{-1}.

Neutral homoleptic alkyls and aryls of the platinum group metals are known only for ruthenium and osmium;[1] the redox chemistry[2a] of $M(2\text{-}MeC_6H_4)_4$ (M = Ru, Os) and reactions of $Os(2\text{-}MeC_6H_4)_4$ with Lewis bases[2b] have been described.

We have now made $Rh(2,4,6\text{-}Me_3C_6H_2)_3$ (**1**) as orange crystals air stable both as solid and in solution by interaction of mesitylmagnesium bromide with $RhCl_3(C_4H_6S)_3$ in tetrahydrofuran (thf)–Et_2O followed by solvent removal, extraction with hexane and crystallisation in *ca.* 40% yield.† The solid state structure, as determined by *X*-ray crystallography, is quite remarkable.‡ The Rh–C_3 fragment is pyramidal, with C–Rh–C angles of 103.8(3)—105.8(3)°. The molecule has approximate three-fold symmetry and the three ligands are tilted such that one methyl carbon on each is similarly distant from the metal atom at *ca.* 2.80 Å. More importantly, one hydrogen on each of these methyls is oriented to make a very close contact of *ca.* 2.2 Å with the metal. The angles between the three Rh ··· H contacts lie between 90 and 93° and the metal geometry can thus be described as distorted *fac*-octahedral C_3RhH_3. This structure contrasts strongly with that of the Mn(mes)$_3$ unit (mes = mesityl) in [Li(thf)$_4$][Mn(mes)$_3$][3] in which the anion is essentially trigonal planar.

Spectroscopic criteria for identification of agostic interactions in solution have been described.[4] Sometimes there may be lowered C–H stretching frequencies in IR spectra around 2700—2350 cm^{-1}; in NMR spectra the bridging H-atom of a M ··· H–C moiety can result in a high field shift of the averaged ^1H signal of a methyl group involved in agostic interaction while the ^{13}C–^1H coupling constant also may be lowered for the agostic H atom. None of these effects are observed for (**1**) in either IR or NMR spectra.§ In some agostic systems the C–H ··· groups can be considered as weak ligands, displaceable by other ligands; no thf adduct is obtained even on refluxing (**1**) in the solvent.

Variable temperature ^1H NMR spectra (−30 to 85 °C) show that each mesityl group rotates about the Rh–C bond in a synchronised fashion. The activation parameter was calculated using equation (1),[5] where Δν is the separation (in Hz) between the two 2-methyl resonances (80.02 Hz) or the two aromatic 3,5-hydrogen atoms (200.05 Hz) at 243 K and T_c is the coalescence temperature (308 and 328 K, respectively).

$$\Delta G^\ddagger = -RT_c \ln \pi\, \Delta\nu\, h(2)^{-\frac{1}{2}}(kT_c)^{-1} \qquad (1)$$

For the CH_3 groups, $\Delta G^\ddagger$ = 62.6 kJ mol^{-1} and for the H atoms, 64.0 kJ mol^{-1}. The agreement indicates that only a single process is involved. These values are similar to those[6] for rotation about the M–C bond of mesityl groups in other compounds, *e.g.*, Nb(mes)$_2$Cl$_3$, $\Delta G^\ddagger$ = 61.9 kJ mol^{-1}.

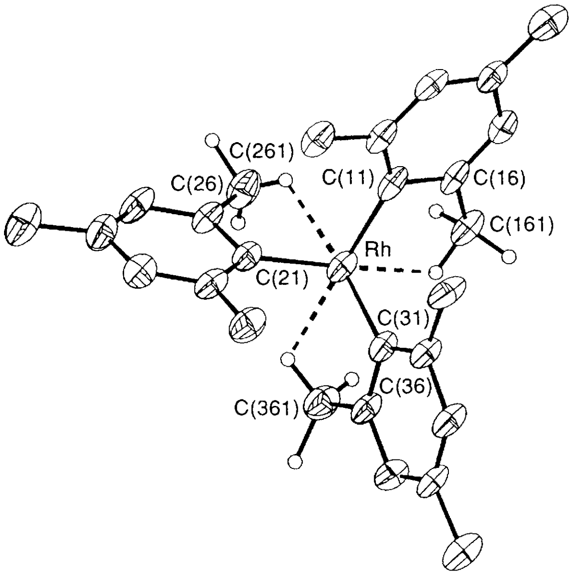
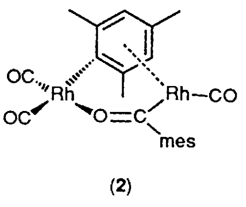


Figure 1. The structure of $Rh(2,4,6\text{-}Me_3C_6H_2)_3$ (**1**). Selected bond lengths (Å) and angles (°) are: Rh–C(*nl*) 1.964(7), 1.960(7), 1.977(7); Rh ··· H(*n6l*) 2.25(2), 2.30(2), 2.37(2); C(*n6l*)–Rh–C(*n′l*) 105.8(3), 103.8(3), 104.5(3),; H(*n6l*)–Rh–H(*n′6l*) 90.5(6), 90.5(6), 92.4(7); Rh–C(*nl*)–C(*n6*) 106.9(4), 106.8(4), 106.3(4).



(**2**)

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† Decomp. >172 °C. Found (required): C, 70.2 (70.4); H, 7.3 (7.2)%.

‡ *Crystal data* for (**1**): $C_{27}H_{33}Rh$, *M* = 460.465, triclinic, $P\bar{1}$, *Z* = 2, *a* = 7.377(5), *b* = 12.988(3), *c* = 13.149(6) Å, α = 114.45(3), β = 90.70(4), γ = 93.46(3)°, *U* = 1143.9 Å, D_c = 1.337 g cm^{-3}, *F*(000) = 480, μ(Mo-K_α) = 6.73 cm^{-1}. The structure was solved *via* the heavy atom method and refined by least squares using 3373 observed data [$F_o > 3\sigma(F_o)$] out of a total of 4173 measured using an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) and an ω/2θ scan. The final *R*, R_w values were 0.050 and 0.052 for 385 parameters, and unit weights. Hydrogens on the *ortho*-methyls involved in close metal interactions and on the phenyl rings were located and refined normally. The other methyl hydrogens were included with suitable constraints to achieve stable refinement. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *NMR data* for (**1**) (25 °C, C_6D_6) ^1H: δ 1.91 (br. s, 3H *o*-Me), 2.05 (br. s, 3H, *o*-Me), 2.16 (s, 3H, *p*-Me), 6.25 (br. s, 1H, aromatic H), 6.63 (br. s, 1H, aromatic H). $^{13}C\{^1H\}$: δ 17.2 (br. q, J_{C-H} 129.07 Hz, *o*-CH_3), 20.56 (q, J_{C-H} 125.78 Hz, 't,' $J_{C-H'}$ 4.5 Hz, *p*-CH_3), 25.06 (br. q, J_{C-H} 129.60 Hz, *o*-CH_3), 127.15 [d, J_{C-H} 140.91 Hz, C(3) or C(5)], 134.44 [q, J_{C-H} 5.6 Hz, C(4)], 135.78 [s, C(2) or C(6)], 137.01 [d, J_{Rh-C} 55.8 Hz, C(1)], 145.99 [s, C(2) or C(6)].

The reactions of (**1**) will be discussed later; carbon monoxide gives the unusual bridged complex (**2**) whose *X*-ray structure has been determined, together with dimesitylketone.

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