Novel Five-co-ordinate Diorganorhodium Compounds. *X*-Ray Structure of Bis-*ortho*-chelated $[Rh^{III}(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ †

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Compounds of the type $[Rh^{III}(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ have been synthesized by (*i*) oxidative addition of MeI (80% yield) or EtI (minor product) to $[Rh^{I}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(cod)]$ (cod = cyclo-octa-1,5-diene); (*ii*) reaction of $[Rh^{III}Cl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (acac = acetylacetonate) with either $AlMe_3$, $AlEt_3$, or LiMe–LiI; (*iii*) metathesis of $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (R = Me or Et, X = Cl or I) with $Ag(O_2CMe)$ or $Ag(O_3SCF_3)$. The solid-state structure of $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ was determined by an *X*-ray diffraction study. Crystals are orthorhombic, space group *Pbca*, with lattice parameters a = 14.899(3), b = 15.744(3), c = 13.191(2) Å, U = 3 094(2) Å^3, Z = 8, D_c = 1.87 g cm^{-3}, R = 0.055. The structure has a square-pyramidal five-co-ordinate rhodium centre. One C and two N atoms of the chelating aryl moiety together with the I atom define the basal plane, and the methyl group lies at the apex [Rh–C(aryl) 1.940(8), Rh–C(methyl) 2.029(11) Å]. ^{103}Rh N.m.r. studies of the novel five-co-ordinate diorganorhodium(III) compounds have been carried out.

Rhodium–alkyl complexes are thought to be key intermediates in important catalytic processes like hydrogenation and hydroformylation.[1] Much effort has gone into the elucidation of conditions and mechanisms for these processes and numerous model compounds have been developed to study the intimate steps in these reactions. Isolation of such rhodium–alkyl intermediates as stable complexes is only possible when ligands are present that have specific electronic and steric properties. Because of their chelating capability, terdentate ligands like neutral $PhP(CH_2CH_2PPh_2)_2$[2,3] and monoanionic $N(SiMe_2CH_2PPh_2)_2^-$ used by Fryzuk *et al.*,[4–8] the bis-*ortho*-substituted aryl diphosphine ligands used by Shaw and co-workers,[9–16] Kaska and co-workers,[17,18] and Rimml and Venanzi,[19,20] and the nitrogen analogues used by Van Koten and co-workers[21–39] and Canty *et al.*[40,41] have proven to be very suitable ligands in this field. In particular, platinum complexes of the monoanionic ligand $C_6H_3(CH_2NMe_2)_2$-2,6 have been used in our laboratory to study and 'trap', otherwise transient, intermediates in important electron-transfer processes like oxidative addition and reductive elimination.[21–39]

For example, reaction of $[PtX\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ with excess MeY (X, Y = halide) leads to formation of $[PtY\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ and MeX [equation (1)].[34] In contrast, reaction of methyl iodide with the cation $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$ yields a unique 'arenonium' complex, that can be thought of as a 'frozen' intermediate in a reductive C–C coupling at the platinum centre [equation (2)].[26]

In both these cases it is believed that the product precursor is a methyl–platinum(IV) species, $[Pt(Me)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$, which in the latter case affords the arenonium product *via* a 1,2-methyl shift from Pt to the metal-bonded C(aryl) atom. Although there was strong evidence for the intermediacy of $[Pt(Me)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$, a complex of this type was never observed or isolated. However, Puddephatt and Scott[42] have characterized a related, cationic intermediate, *fac*-$[Pt^{IV}Me_3(SMe_2)_2(NCCD_3)]^+I^-$, during the oxidative addition of methyl iodide to *cis*-$[Pt^{II}Me_2(SMe_2)_2]$, that eventually leads to *fac*-$[Pt^{IV}IMe_3(SMe_2)_2]$.

In two other papers we reported on rhodium-(I)[37] and -(III)[38] complexes bearing the $C_6H_3(CH_2NMe_2)_2$-2,6 ligand. In this paper we describe the synthesis and properties of new, five-co-ordinate diorganorhodium(III) compounds, $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, which are the neutral, isoelectronic analogues of the aforementioned $[Pt(Me)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$ intermediate.

Experimental

$[Rh\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(cod)]$ (cod = cyclo-octa-1,5-diene)[37] and $[RhCl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (acac = acetylacetonate)[38] were synthesized according to published methods. Solvents were carefully dried and distilled in a nitrogen atmosphere prior to use. Reactions were carried out in an atmosphere of dry nitrogen at room temperature unless stated otherwise. Elemental analyses were carried out by the Analytical Department of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. Field desorption (f.d.) mass spectra were obtained with a Varian MAT711 double-focussing mass spectrometer and were performed by the Organic Department of the University of Amsterdam (Professor N. M. M. Nibbering). ^{1}H N.m.r. spectra were recorded either on a Bruker AC100 or on a Bruker WM250 spectrometer; the latter was also used for the ^{13}C n.m.r. spectra measurements.

Rhodium-103 *N.M.R. Measurements.*—The ^{103}Rh n.m.r. experiments were performed on a Bruker AC100 spectrometer equipped with a 10-mm ^{103}Rh-$\{^{31}$P, ^{1}H$\}$ probe, a second PTS 160 synthesizer provided with a 90° phase shifter, a B-SV 3 heteronucleus decoupling unit with a selective ^{103}Rh amplifier

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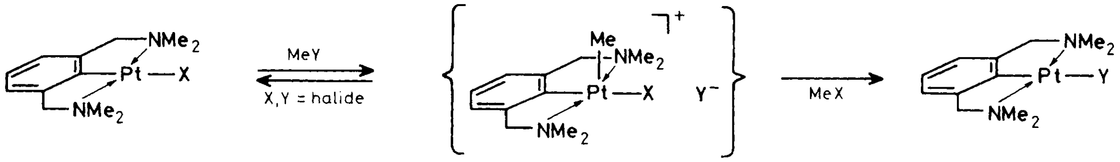
† {2,6-Bis[(dimethylamino)methyl]phenyl-*C,N,N'*}iodomethylrhodium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



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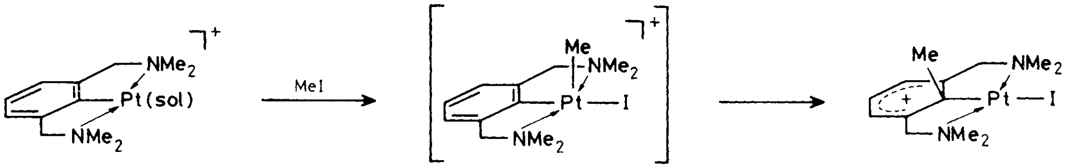


(2)

for ^{103}Rh decoupling[43] and a B-VT 1000 temperature control unit (± 1 °C). All measurements were carried out in 10-mm tubes with *ca.* 0.02 mol dm^{-3} solutions in C_6D_6 at 295 K.

Since direct detection of ^{103}Rh is not possible at 2.3 T, ^{103}Rh n.m.r. signals were obtained indirectly by using the REVERSE–INEPT technique.[44,45] The ^{103}Rh resonance frequency range was first measured by means of the echo-type pulse sequence: 90°(^{1}H)–τ–180°(^{1}H), 180°(^{103}Rh)–τ–f.i.d.(^{1}H) with $\tau = [2J(\text{RhH})]^{-1} = 0.16$ s (f.i.d. = free induction decay). When the 180° Rh pulse is applied close to or on resonance, inversion of the ^{1}H signals that couple with ^{103}Rh [Rh–CH_3 or Rh–CH_2CH$_3$ and Rh–N–CH(benzylic)] occurs while the rest of the spectrum remains unchanged. The exact ^{103}Rh chemical shift was determined by REVERSE 2D,^{1}H–^{103}Rh spectra, using the pulse sequence:[44,45] 90°(^{1}H)–τ–90°(^{103}Rh)–$t_{\frac{1}{2}}$–180°(^{1}H)–$t_{\frac{1}{2}}$–90°(^{103}Rh)–f.i.d.(^{1}H). The preparation time was 2 s, two dummy scans were used, and the 90° pulses used were 20 μs for ^{1}H and 30 μs for ^{103}Rh. Employment of a 16-step phase cycling rejects protons that are not coupled to ^{103}Rh and gives quadrature detection in the F1 dimension. Distribution of 64 t_1 increments over a spectral width of 5 000 Hz posed no problems in detecting the cross peaks. The total measurement time was typically less than 1 h.

In order to determine the ^{103}Rh chemical shift more accurately and to ascertain that the cross peaks were not folded in, the experiment was repeated using a smaller spectral width in the F1 dimension (1 000 Hz, 128 t_1 increments) and a change of the carrier frequency. This resulted in a transform matrix 256 X 1K f.i.d. The matrix was zero-filled in the F1 dimension and processed in the usual manner. The ^{103}Rh chemical shift is obtained in the F1 dimension [accuracy ± 1 p.p.m., determined by the temperature dependence, $\Delta\delta(^{103}\text{Rh}) = 1$ p.p.m. K^{-1}] and $\delta(^1\text{H})$ and J(RhH) are obtained in the F2 dimension. Calculation of $\delta(^{103}\text{Rh})$ was carried out by determining the absolute ^{103}Rh frequency of the cross peak and relating it to the arbitrary reference frequency ($\Xi = 3.16$ MHz) scaled for the operating field (^{1}H, 100,131,316 Hz) to ν(ref.) = 3 164 196 Hz. Signals at higher frequency are taken as positive chemical shifts.

Synthesis of [Rh(Me)I{$C_6H_3(CH_2NMe_2)_2$-2,6}].—(*a*) To a stirred solution of [Rh{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)], prepared from [{RhCl(cod)}$_2$] (0.99 g, 2.01 mmol) and an equimolar amount of $Li_2[C_6H_3(CH_2NMe_2)_2\text{-}2,6]_2$ in diethyl ether (30 cm^3), was quickly added at room temperature methyl iodide (0.9 cm^3, *ca.* 4 mol equiv.). A yellow solid formed instantly; the solvent was then removed *in vacuo* and the residue extracted with benzene (4 × 10 cm^3). The red coloured benzene extract was evaporated to dryness and the resultant bright orange *solid* thoroughly washed with pentane (3 × 40 cm^3). Drying *in vacuo* yielded 1.40 g (3.22 mmol, 80%) of [Rh(Me)I{$C_6H_3(CH_2NMe_2)_2$-2,6}] (Found: C, 37.2; H, 5.5; I, 28.2; N, 6.0%; M^+, 436. $C_{13}H_{22}IN_2Rh$ requires C, 35.8; H, 5.1; I, 29.1; N, 6.4%; M, 436). Crystals of this compound, suitable for *X*-ray diffraction work, were grown by slow evaporation of a saturated benzene solution.

(*b*) To a stirred solution of [RhCl(acac){$C_6H_3(CH_2NMe_2)_2$-2,6}] (65 mg, 0.17 mmol) in tetrahydrofuran (thf) (5 cm^3) at −35 °C was quickly added a solution of LiMe–LiI (1:1) in diethyl ether (0.1 cm^3, 1.6 mol dm^{-3}). The reaction mixture was then slowly warmed to room temperature and after 1 h all volatiles were removed *in vacuo*. The residue was extracted with benzene and the extracts filtered over Celite. The filtrate was evaporated to dryness and the resulting solid washed several times with pentane to afford pure [Rh(Me)I{$C_6H_3(CH_2NMe_2)_2$-2,6}] in 85% yield.

Reaction of [Rh{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)] *with Ethyl Iodide.*—A stirred solution of [Rh{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)] (0.23 g, 0.58 mmol) and ethyl iodide (0.2 cm^3, *ca.* 5 mol equiv.) in benzene (10 cm^3) was refluxed for 1 h. After cooling, the dark orange solution was filtered and the filtrate evaporated to dryness. The residue was washed with pentane (2 × 15 cm^3) yielding 0.22 g of a yellow solid. Two of the various products present in this substance were identified by ^{1}H n.m.r. and f.d. mass spectroscopy as [Rh(Et)I{$C_6H_3(CH_2NMe_2)_2$-2,6}] [Found: m/z 450 (M^+)] and [{RhI(cod)}$_2$] [Found: m/z 676 (M^+)].

Synthesis of [Rh(Me)(O_2CMe){$C_6H_3(CH_2NMe_2)_2$-2,6}].—Solid Ag(O_2CMe) (45 mg, 0.27 mmol) was added to a solution of [Rh(Me)I{$C_6H_3(CH_2NMe_2)_2$-2,6}] (113 mg, 0.26 mmol) in benzene (5 cm^3) and stirred for 3 d. The reaction mixture was filtered over Celite and the bright yellow filtrate concentrated *in vacuo* to an orange oil. Shaking this oil overnight with pentane (10 cm^3) yielded, after filtration and drying, the light yellow *solid* [Rh(Me)(O_2CMe){$C_6H_3(CH_2NMe_2)_2$-2,6}] (63 mg, 0.17 mmol, 75%) (Found: C, 47.8; H, 7.1; N, 7.4; O, 10.8%; M^+, 368. $C_{15}H_{25}N_2O_2Rh$ requires C, 48.9; H, 6.9; N, 7.6; O, 8.7%; M, 368).

Synthesis of [Rh(Me)(O_3SCF_3){$C_6H_3(CH_2NMe_2)_2$-2,6}].—The procedure used was analogous to that of the acetato compound above, employing Ag(O_3SCF_3) instead of Ag(O_2CMe). The bright yellow, moisture-sensitive *product*, [Rh(Me)(O_3SCF_3){$C_6H_3(CH_2NMe_2)_2$-2,6}], was obtained in 60% yield [Found: C, 37.5; H, 5.1; F, 11.8; N, 5.6%; m/z 458 (M^+, 5%), 309 ($M - O_3SCF_3$, 100%), 206 ($M - O_3SCF_3 - $ Rh, 50%). $C_{14}H_{22}F_3N_2O_3RhS$ requires C, 36.7; H, 4.9; F, 12.4; N, 6.1%; M, 458].

[Rh(Et)(O_3SCF_3){$C_6H_3(CH_2NMe_2)_2$-2,6}] was similarly synthesized from [Rh(Et)Cl{$C_6H_3(CH_2NMe_2)_2$-2,6}] and Ag(O_3SCF_3) (see below).

Table 1. Fractional atomic co-ordinates for $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I	0.239 17(7)	0.058 84(6)	0.384 38(7)	C(6)	0.104 8(9)	0.310 5(8)	0.128 5(9)
Rh	0.157 03(6)	0.155 48(6)	0.227 36(7)	C(7)	0.018 9(10)	0.089 8(8)	0.083 3(10)
N(1)	0.061 8(8)	0.062 5(7)	0.182 6(9)	C(8)	0.187 9(11)	0.339 3(8)	0.181 0(11)
N(2)	0.209 0(8)	0.276 4(7)	0.266 3(9)	C(9)	−0.005 1(11)	0.067 3(13)	0.266 9(13)
C(1)	0.087 2(7)	0.224 2(7)	0.134 1(8)	C(10)	0.092 1(13)	−0.0218 1(10)	0.169 1(14)
C(2)	0.018 4(8)	0.185 9(9)	0.079 3(10)	C(11)	0.150 5(15)	0.299 2(10)	0.356 1(11)
C(3)	−0.038 8(9)	0.237 2(10)	0.022 6(11)	C(12)	0.306 2(12)	0.282 2(12)	0.295 3(16)
C(4)	−0.023 9(9)	0.325 2(10)	0.019 0(11)	C(13)	0.246 4(10)	0.131 8(12)	0.114 8(12)
C(5)	0.046 7(11)	0.361 9(10)	0.071 9(11)				

Synthesis of $[Rh(Me)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.—To a stirred suspension of $[RhCl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (170 mg, 0.40 mmol) in pentane (12 cm^3) cooled to −30 °C was slowly added a solution of $AlMe_3$ in hexane (0.2 cm^3, 2.3 mol dm^{-3}). The reaction was stirred for 30 min and allowed to warm to room temperature during this time. Methanol (0.5 cm^3) was then added to decompose the organo aluminium compounds present. Volatiles were removed *in vacuo* and the residue extracted with benzene (15 cm^3). After filtering and concentrating the extract to *ca.* 5 cm^3, pentane (15 cm^3) was added whereupon yellow *crystals* were deposited. The supernatant solution was removed using a syringe. The crystals were washed once with pentane (15 cm^3) and then dried *in vacuo* to afford $[Rh(Me)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (100 mg, 73%) (Found: M^+, 344. $C_{13}H_{22}ClN_2Rh$ requires M, 344).

Synthesis of $[Rh(Et)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.—Yellow $[Rh(Et)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ was synthesized in a manner similar to that of the preceding methyl compound, using $AlEt_3$ instead of $AlMe_3$. Yield: 71% (Found: M^+, 358. $C_{14}H_{25}ClN_2Rh$ requires M, 359).

Reactions of $[RhCl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ *with* $ZnEt_2$, $LiBu^n$ *and* $Li(C_6H_4Me\text{-}p)$.—Reactions of $[RhCl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ with 1 mol equiv. of either $ZnEt_2$, $LiBu^n$, or $Li(C_6H_4Me\text{-}p)$ were carried out as described above for the reaction of $AlMe_3$. No reaction was observed in the case of $ZnEt_2$ and $Li(C_6H_4Me\text{-}p)$ in pentane, whereas formation of $C_6H_4(CH_2NMe_2)_2\text{-}m$ was found for $LiBu^n$ in benzene, pentane, and thf.

Synthesis of $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.—Solid $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (0.23 g, 0.53 mmol) was added to a stirred solution of $AgBF_4$ (0.2 g, 1 mmol) in thf (10 cm^3). An immediate precipitation of AgI occurred. The pale yellow solution was filtered and the filtrate added to a suspension of Li(acac) (0.38 g, 3.6 mmol) in thf (7 cm^3). The virtually colourless reaction mixture was stirred for 1 h and the thf was then removed *in vacuo*. The residue was extracted with benzene (2 × 5 cm^3) and the extracts filtered and evaporated to dryness. The crude yellow *product* was extracted with pentane (12 cm^3). Filtration and concentration of this extract followed by cooling to −30 °C afforded pale yellow $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (183 mg, 85%) (Found: M^+, 408. $C_{18}H_{29}N_2O_2Rh$ requires M, 408).

Reaction of $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ *with* $AlMe_3$.—To a stirred solution of $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (175 mg, 0.43 mmol) in pentane (5 cm^3) at −30 °C was slowly added a solution of $AlMe_3$ in hexane (0.2 cm^3, 2.3 mol dm^{-3}). Upon warming to room temperature the initially yellow reaction mixture gradually darkened. After 1 h the solvents were removed *in vacuo* yielding a brownish tar. A benzene extract of this residue contained $C_6H_4(CH_2NMe_2)_2\text{-}m$ as the only product with an aryl group.

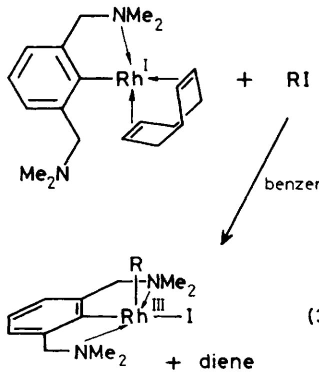
X-*Ray Analysis.—Crystal data for* $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$. $C_{13}H_{22}IN_2Rh$, $M = 436.14$, orthorhombic, $a = 14.899(3)$, $b = 15.744(3)$, $c = 13.191(2)$ Å, $U = 3\,094(2)$ Å^3, Zr-filtered Mo-K_α radiation $\lambda = 0.710\,69$ Å (graphite monochromatized), space group *Pbca*, $Z = 8$, $D_c = 1.87$ g cm^{-3}, $F(000) = 1\,696$. Crystal size: 0.13 × 0.15 × 0.25 mm, μ(Mo-K_α) = 30.5 cm^{-1}.

Data collection and processing. Nonius CAD4 diffractometer, 4 976 reflections measured ($1.1 < \theta < 30$, $+h,k,l$), 2 067 unique with $I > 2.5\sigma(I)$, correction for anomalous dispersion of Rh and I, empirical absorption correction (DIFABS),[46] reference reflection 0 2 1 (no decay).

Structure analysis and refinement. Heavy-atom technique (I, Rh). Anisotropic block-diagonal least-squares refinement with 154 refined parameters. Weighting scheme $w = 1/(160 + F_o + 0.002F_o^2)$. No hydrogen atoms located. Final R and R' values are 0.055, 0.073. The programs used were from XTAL (1983).[47] Final fractional atomic co-ordinates are listed in Table 1. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

Synthesis of $[Rh^{III}(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.—The compounds $[Rh^{III}(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (X = Cl, I, or O_3SCF_3, R = Me or Et; X = O_2CMe or acac, R = Me) were synthesized by two main routes: (*i*) oxidative addition of MeI or EtI to $[Rh^I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(cod)]$ [equation (3), R = Me or Et], or (*ii*) transmetallation of $[Rh^{III}Cl(acac)\text{-}$



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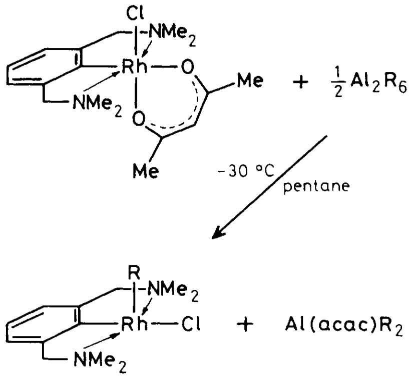

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$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ with $AlMe_3$ or $AlEt_3$ [equation (4)], or LiMe–LiI.

Their structures were determined by elemental analyses, ^1H and ^{13}C n.m.r., f.d. mass spectroscopy and a single-crystal structure determination of $[Rh^{III}(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.

Using method (*i*) [equation (3)], $[Rh^{III}(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ was obtained in high yield in benzene at room temperature. In contrast, the reaction of $[Rh^{I}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(cod)]$ with EtI was only induced by refluxing the reaction mixture; $[Rh(Et)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ was formed as a minor product together with $[\{RhI(cod)\}_2]$ and other, unidentified products.

The driving force for the synthesis of $[Rh(R)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (R = Me or Et) using method (*ii*) [equation (4)] is probably provided by the simultaneous formation of $Al(acac)R_2$. This method is therefore successful for aluminium reagents, but not for other well known alkylating and arylating organometallic reagents like $ZnEt_2$, $LiBu^n$, and $Li(C_6H_4Me\text{-}p)$. An exception is the reaction of $[Rh^{III}Cl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ with LiMe–LiI affording $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ in 85% yield.

The halide in $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (X = Cl or I) can be conveniently substituted by use of silver salts [method (*iii*)]; in this way compounds having X = O_2CMe, R = Me and X = O_3SCF_3, R = Me or Et were prepared. Successive addition of $AgBF_4$ and Li(acac) to $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ afforded $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$. This latter complex was reacted with $AlMe_3$, in an attempt to produce a tris(organo-ligand)rhodium(III) compound, *i.e.* $[Rh(Me)_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, but only formation of the free aryl ligand $C_6H_4(CH_2NMe_2)_2\text{-}m$ was observed.

The bright orange compounds $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ are soluble in common organic solvents and are all air stable in the solid state. However, $[Rh(R)(O_3SCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ is moisture sensitive and needs to be stored in an inert atmosphere. In solution all complexes decompose within several weeks at room temperature, even when stored under nitrogen; the iodide complexes decompose within days. The decomposition of some of the rhodium(III) compounds in $[^2H_{10}]p$-xylene, when followed by ^1H n.m.r., showed that the methyl complexes decomposed at *ca.* 85 °C and the ethyl ones at *ca.* 110 °C. This decomposition, leading to the formation of insoluble black substances, was accompanied by the formation of $C_6H_4(CH_2NMe_2)_2\text{-}m$ (and several other unidentified organic products), but not by the C–C coupling product $RC_6H_3(CH_2NMe_2)_2\text{-}2,6$. For the ethyl compounds, formation of ethene was observed during decomposition. The variety of products suggests that decomposition occurs *via* a homolytic splitting of the rhodium–alkyl bond and subsequent radical processes.

Table 2. Selected bond distances (Å) and angles (°) for $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$

Rh–I	2.846 5(11)	Rh–N(2)	2.118(8)
Rh–N(1)	2.122(8)	Rh–C(1)	1.940(8)
		Rh–C(13)	2.029(11)
I–Rh–N(1)	97.0(3)	N(1)–Rh–C(1)	81.4(5)
I–Rh–N(2)	98.4(3)	N(1)–Rh–C(13)	96.2(6)
I–Rh–C(1)	171.8(2)	N(2)–Rh–C(1)	81.3(5)
I–Rh–C(13)	98.8(5)	N(2)–Rh–C(13)	95.9(6)
N(1)–Rh–N(2)	158.7(3)	C(1)–Rh–C(13)	89.5(6)

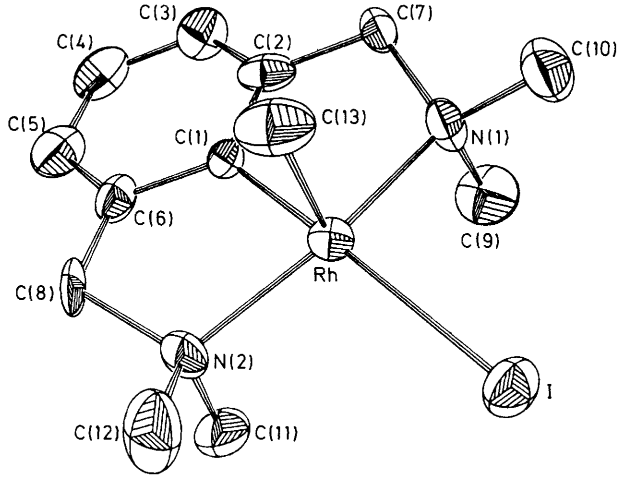

Figure 1. ORTEP drawing (50% probability) and adopted numbering scheme of $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$

Solid-state Structure of $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.—An ORTEP drawing of the *X*-ray molecular structure of $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ and its atomic numbering scheme is shown in Figure 1. Bond distances and angles are listed in Table 2. The crystal structure is built up from discrete five-co-ordinate monomers. The co-ordination around rhodium can be described as approximately square pyramidal, with atoms C(1), N(1), and N(2) of the chelating aryl ligand and the I atom defining the basal plane, and atom C(13) of the methyl group lying at the apex. The molecule has a non-crystallographic mirror plane running through the atoms Rh, I, C(1), C(4), and C(13). The co-ordination geometry shows only a 3% distortion (*D*) along the Berry pseudorotation co-ordinate, from a square pyramid towards a trigonal bipyramid.[48] The structural features around rhodium resemble those of complexes $[Rh(Me)I_2(PPh_3)_2]$ (D = 8%),[49] [Rh(Me)(oep)] [D = −10%; oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)],[50] $[Rh(Me)Cl\{PPh(CH_2CH_2CH_2PPh_2)_2\}]^+$,[3] $[Rh(H)Cl\{C_6H_3(CH_2PBu^t{}_2)_2\text{-}2,6\}]$,[18] and $[Ir(Me)I\{N(SiMe_2CH_2Pr^i{}_2)_2\}]$ (D = −2%).[8]

The rhodium atom in $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ lies 0.210(5) Å above the basal plane of the square pyramid. The puckering in the five-membered chelate rings is such that the N(1) and N(2) donor atoms lie on the same side of the aryl plane [0.44(3) Å] away from the apical C(13) atom. The N(1)–M–N(2) angle of 158.7(3)° resembles that of 159.5(4)° in square-pyramidal $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pt(\mu\text{-}p\text{-}MeC_6H_4NCHNPr^i)HgBrCl]$ (D = 25%),[27] but is not as acute as in $[NiI_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[29] and $[FeCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[35] where it is 152.0(2) and 142.98(6)°, respectively. The geometrical constraints of the chelating aryl ligand are

Table 3. ^{1}H N.m.r. data of the $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ compounds[a]

Compound	Aryl[b]	NCH_2[c]	NMe	R Group[d]
$[Rh(Me)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	6.71 (d), 6.96 (t)	3.34 (d), 2.68 (dd)	2.33, 2.33	1.52 (d)
$[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	6.67 (d), 6.96 (t)	3.30 (d), 2.67 (dd)	2.46, 2.33	1.66 (d)
$[Rh(Me)(O_3SCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[e,f]	6.88 (s)	3.94 (d), 3.51 (dd)	2.77, 2.63	1.43 (d)
$[Rh(Me)(O_2CMe)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[g]	6.61 (s)	3.16 (s, br)	2.23, 1.98	0.94 (d)
$[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[h]	6.90 (m)	3.41 (s, br)	2.05, 2.03	0.98 (d)
$[Rh(Et)Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	6.70 (d), 6.95 (t)	3.42 (d), 2.74 (dd)	2.43, 2.39	1.94 (dq), 1.32 (dt)
$[Rh(Et)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	6.65 (d), 6.93 (t)	3.36 (d), 2.65 (dd)	2.45, 2.39	1.99 (dq), 1.06 (dt)
$[Rh(Et)(O_3SCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$[e]	6.90 (s)	4.01 (d), 3.55 (dd)	2.78, 2.64	2.17 (dq), 0.95 (dt)

[a] Measured at 100 MHz in C_6D_6 unless stated otherwise; chemical shifts relative to external $SiMe_4$. [b] For resolved AB_2 pattern, ^2J(HH) = 7 Hz. [c] For resolved AB pattern, ^2J(HH) = 15 Hz; ^3J(RhH) = 2.5 Hz on low-field resonance. [d] ^2J(RhH) = 3 Hz; for R = Et, A_2B_3 pattern with ^3J(HH) = 7.5 Hz, ^3J(RhH) = 1 Hz. [e] Measured in CD_2Cl_2. [f] ^{19}F N.m.r. spectrum in C_6D_6, −77.7 p.p.m. [g] O_2CCH_3, 2.09 p.p.m. [h] Acac, 1.77 (Me), 2.11 (Me), and 5.31 p.p.m. (H).

Table 4. ^{13}C N.m.r. data of some $[Rh(Me)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ compounds*

	Aryl						
Compound	C(1)	C(2,6)	C(3,5)	C(4)	NCH_2	NMe	Me
$[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	Not observed	145.9	121.0	123.3	72.6	50.2 52.4	−6.6 (37)
$[Rh(Me)(O_3SCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	162.2 (36.5)	146.3	121.1	124.1	72.5	48.3 49.8	−7.3 (40)

* Measured at 62.89 MHz in CD_2Cl_2; chemical shifts relative to external $SiMe_4$; ^1J(RhC) given in parentheses.

responsible for the acute C(aryl)–Rh–N angles of 81.4(5) and 81.3(5)° respectively, and the Rh–C(aryl) bond of 1.940(8) Å. This bond is short in comparison with analogous bonds in unstrained aryl–rhodium(III) compounds [*ca.* 1.99 (±0.01) Å],[38] and is more comparable with the 1.913(3) Å in *trans*-$[RhCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(H_2O)]$.[38] The two Rh–N distances [2.122(8) and 2.118(8) Å] are similar to those found in *trans*-$[RhCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(H_2O)]$ [2.160(3) and 2.152(3) Å].[38] The Rh–I bond length of 2.846 5(11) Å is one of the longest encountered so far.[51] This is probably a combined result of the *trans* influence of the aryl group and steric repulsion of the two NMe_2 units. The Rh–C(methyl) bond length of 2.029(11) Å is similar to those of other apical methyls as in $[Rh(Me)I_2(PPh_3)_2]$ (2.08 Å)[49] and [Rh(Me)(oep)] [2.031(6) Å].[50]

N.M.R. Spectroscopy.—The ^{1}H n.m.r. data of $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ are shown in Table 3. The pattern for the aryl ligand indicates that the CH_2 protons and NMe_2 methyl groups are diastereotopic, which is in accord with different environments above and below the plane of the aryl ring. Of the two AB doublets, arising from the CH_2 groups, only the one at low field shows a measurable ^3J(RhH) coupling (*ca.* 2.5 Hz). This long-range coupling is probably associated with the proton (H_{eq}) of the C–H bond that is more coplanar with the Rh–N bond (see Newman projection in Figure 2). The resonances of the apical, aliphatic R groups are very characteristic. When R = Me, a sharp doublet with ^2J(RhH) = 3 Hz is seen. This value is in accord with generally observed couplings in the range 2—3 Hz in other rhodium–methyl compounds.[52] If R = Et, an A_2B_3 pattern is encountered. However, the resonances of the CH_2 quartet and Me triplet are further split due to coupling with the rhodium nucleus [^2J(RhH) = 3, ^3J(RhH) = 1 Hz].

The ^{1}H n.m.r. spectrum of $[Rh(Me)(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ shows two singlets for the two methyls of the acac group. This pattern is consistent with an acac group that is co-ordinated to rhodium in either a monodentate (five-co-ordinate Rh) or a bidentate manner (six-co-ordinate Rh, as in $[RhCl(acac)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$); considering that all related species have five-co-ordinate structures, the former seems more likely. The ^{19}F n.m.r. spectrum of $[Rh(Me)(O_3SCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ in C_6D_6 shows a singlet at −77.7 p.p.m., indicative of a direct Rh–O bond.[53,54]

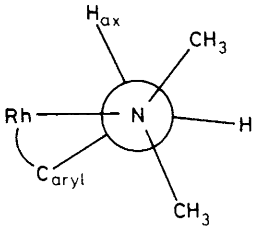

Figure 2. Newman projection along N–C(benzylic), based on data from the *X*-ray structure of $[Rh(Me)I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, showing axial and equatorial CH_2 protons

The ^{13}C-{^{1}H} n.m.r. data of two $[Rh(Me)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ compounds (X = I or O_3SCF_3) are shown in Table 4. The diastereotopicity of the NMe_2 methyl groups is illustrated by the presence of two signals for the NMe_2 carbons. The presence of a direct rhodium–aryl bond in the O_3SCF_3 complex is evidenced by a ^1J(RhC) coupling of 36.5 Hz on the aryl C atom at 162.2 p.p.m. These chemical shift and coupling data are similar to those found for other aryl–rhodium complexes.[37,38] The signal of the methyl carbon attached to the rhodium nucleus appears at −7.3 p.p.m., with ^1J(RhC) = 40 Hz which is indicative of a direct Rh–C bond.

The ^{103}Rh chemical shifts of $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (R = Me or Et; X = Cl or I) are listed in Table 5. These shifts are all to higher frequency of the arbitrary reference, Ξ = 3.16 MHz, and fall within the range normally observed for rhodium(III) compounds.[55–57] A striking aspect is that the resonance for the present five-co-ordinate rhodium(III)

Table 5. ^{103}Rh N.m.r. chemical shifts of some [Rh(R)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] compounds*

	X	
R	Cl	I
Me	+3 165	+3 179
Et	+3 163	+3 201

* Measured in C_6D_6 at 295 K, referenced to $\Xi(^{103}Rh) = 3.16$ MHz, adopting the sign convention that shifts to high frequency are positive.

compounds appear in a rather narrow range (3 163—3 201 p.p.m.), confirming the isostructural relationship between them. The chemical shifts are only marginally dependent on the R groups, reflecting the similar electronic properties of the Me and Et groups involved. Only a small increase in the ^{103}Rh chemical shift is observed on going from X = Cl to I (+14 for R = Me and +38 p.p.m. for R = Et). In octahedral complexes, similar substitutions of I for Cl result in chemical shift differences of several hundred p.p.m. which, in addition, are usually of opposite sign.[55–57]

Chemical shifts are influenced by dia- and para-magnetic contributions to the shielding constant (Ramsey equation): $\delta = \sigma_{dia} - \sigma_{para}$, the latter term being approximately inversely proportional to the average electronic excitation energy ΔE.[56] Apparently, in the present square-pyramidal rhodium(III) complexes both the dia- and para-magnetic contributions vary very little and it would seem that ΔE for these species is a constant. This deduction is corroborated by the unitary orange colour of all the complexes. It is possible, therefore, that ΔE in these d^6 ML_5-type complexes largely corresponds to the energy difference between the filled orbitals of the d_{xy},d_{xz},d_{yz} set and the lowest unoccupied molecular orbital (most likely the d_{z^2} orbital), with halide substitution primarily affecting orbitals lying along the x and y axes (*e.g.* $d_{x^2-y^2}$).

Discussion

Several mechanisms (nucleophilic attack, free radical pathways, *etc.*) have been proposed for the oxidative addition of alkyl halides to square-planar metal d^8 complexes.[58,59] The reaction of alkyl iodides with [Rh^I{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)] illustrates the high reactivity of *ortho*-chelated arylrhodium(I) complexes towards electrophiles.[37] The aspecific product formation with EtI, affording among other compounds [Rh(Et)I{$C_6H_3(CH_2NMe_2)_2$-2,6}] and [{RhI(cod)}$_2$], suggests a significant radical character for this addition. However, addition of MeI, leading to the exclusive formation of [Rh(Me)I{$C_6H_3(CH_2NMe_2)_2$-2,6}], is believed to be more likely the result of an initial S_N2-like electrophilic attack of the methyl on the unsaturated rhodium(I) centre, as with isoelectronic [PtX{$C_6H_3(CH_2NMe_2)_2$-2,6}].[34] At some stage in the following reaction sequence, cod is evolved and the terdentate *C,N,N′*-bonding of the aryl ligand (initially it was only bidentate *C,N*-bonded in [Rh{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)]) is realized, eventually affording the rhodium(III) product. In this scheme the presence of the 'hard' C and N atoms of the aryl ligand will assist the change in oxidation state of the rhodium centre from the 'soft' d^8 Rh^I to the 'hard' d^6 Rh^{III} configuration.

This oxidative addition reaction of [Rh^I{$C_6H_3(CH_2NMe_2)_2$-2,6}(cod)] with MeI stands in contrast with the reactions of [Pt^{II}{$C_6H_3(CH_2NMe_2)_2$-2,6}]$^+$ and [Pt^{II}X{$C_6H_3(CH_2NMe_2)_2$-2,6}] with MeI.[26,34] Although MeI does add to these platinum(II) complexes, forming [Pt^{IV}(Me)X{$C_6H_3(CH_2NMe_2)_2$-2,6}]$^+$, subsequent reductive elimination from this platinum(IV) intermediate occurs rapidly; see equations (1) and (2). However, the new [Rh^{III}(Me)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] compounds, which are isoelectronic to this intermediate and have *cis*-orientated organo groups, are inert towards reductive elimination of either $MeC_6H_3(CH_2NMe_2)_2$-2,6 or MeX. Since it has been shown that the chelate effect of the aryl ligand does not prevent reductive elimination of a C–C coupling product,[26] the stability of the present rhodium(III) complexes must be due to electronic factors. It is known that reductive elimination is enhanced by decreased electron density at the central metal,[60,61] and therefore this process is more likely in the cationic platinum than in the neutral rhodium complex, the latter having both a lower formal oxidation state (III *vs.* IV) and lacking a positive charge. However, there are related rhodium phosphine systems which do show reductive elimination. For example, the reaction of [Rh^{I}Me(PPh_3)$_3$] with aryl iodides (R′I), or of [Rh^I(R′)(PPh_3)$_3$] with MeI, yields R′Me, and [Rh^{I}I(PPh_3)$_3$], and attempts to isolate the presumed intermediate [Rh^{III}(Me)(R′)I(PPh_3)$_3$] failed.[62] Therefore, we conclude that reductive elimination of a C–C or C–X coupling product from [Rh(Me)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] is prevented by the enhanced electron density at the metal centre resulting from the donative co-ordination of the C and N atoms of the aryl ligand.

The recent syntheses of stable *cis* bis(alkyl)-rhodium and -iridium complexes [by means of oxidative addition of alkyl halides to alkyl-rhodium(I) or -iridium(I) complexes][63–65] suggest that their resistance to a C–C reductive coupling reaction is largely governed by kinetic factors. These complexes rather decompose by α- and β-elimination sequences, which have a lower barrier of activation. These results are consistent with calculations, which show that concerted C–C reductive elimination is hampered by the highly localized nature of the sp^n hybrid orbitals of the carbon atoms that prevents the attainment of an energetically favourable transition state.[66]

The thermal stability of [Rh(R)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] resembles that of the porphyrin complexes [Rh(R)(oep)].[50,67] In the latter complexes the α- and β-elimination pathways and reductive coupling are blocked by the strong planar co-ordination of the chelating porphyrin nitrogens. In [Rh(R)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] these decomposition pathways are also difficult to attain, since they require an open site *cis* to the R group, and this can only be achieved if the halide X moves *trans* to the apical R group, a process that is obviously hindered for both steric and kinetic reasons.

The [Rh(R)X{$C_6H_3(CH_2NMe_2)_2$-2,6}] compounds are unsaturated 16-electron systems and, as with several other five-co-ordinated d^6 complexes in which an alkyl group occupies the apical position,[3,8,49,50] there is no tendency for monodentate ligands to occupy the sixth co-ordination site. Their inability to attract a ligand *trans* to R, which would result in the formation of an saturated octahedral 18-electron complex, seems to stem from the strong *trans* influence of the alkyl group. Although it can, in principle, also be ascribed to the puckering of the chelate rings of the aryl ligand, which shield this sixth position by means of two axial methyl(amine) groups, even small molecules such as carbon monoxide, acetonitrile, and pyridine show no tendency to co-ordinate. An analogous complex, [Rh(Me)I{N($SiMe_2CH_2PR_2$)$_2$}] (R = Pr^i or Ph), forms only a weak adduct with carbon monoxide.[8]

To improve the reactivity of this type of five-co-ordinate rhodium(III) compounds one needs to gain access to a position *cis* to the apical R group. Therefore, [Rh(R)(O_3SCF_3){$C_6H_3(CH_2NMe_2)_2$-2,6}] (R = Me or Et) was synthesized, because from this species it should be possible to form ionic complexes by substitution of the O_3SCF_3 anion with neutral ligands. Indeed, in dichloromethane [Rh(R)(O_3SCF_3){$C_6H_3(CH_2NMe_2)_2$-2,6}] does react, in contrast to the other rhodium(III) complexes, with ligands (L) such as water, carbon monoxide, triphenylphosphine, and pyridine. However, instead of formation of an isolable $[Rh(R)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(L)][O_3SCF_3]$ species, a complete disruption of the complex co-ordination occurs. Despite the presumed formation of a cationic intermediate, which would favour reductive elimination of $RC_6H_3(CH_2NMe_2)_2$-2,6,[60,61] this decomposition in fact produces $C_6H_4(CH_2NMe_2)_2$-*m* by, as yet, unidentified pathways.

Conclusions

The 16-electron complexes $[Rh(R)X\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ represent a new class of stable unsaturated five-co-ordinate diorganorhodium(III) compounds in which an aryl and alkyl group are *cis* positioned. Compared to their cationic platinum analogues, their remarkable stability seems to result from an enhanced electron density on the metal centre, that diminishes the tendency for reductive elimination, while the rigid square-pyramidal co-ordination prevents α- and/or β-elimination pathways of the alkyl group.

Acknowledgements

Professor K. Vrieze is thanked for helpful discussions.

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Received 16*th June* 1988; *Paper* 8/02590H