Reactions of Rhodium(v) Hydrido–Silyl Complexes with Butyl-lithium and with Lithium Triethylhydridoborate

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Reaction of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiR_3)_2]$ (R_3 = Me_3, Et_3, or Me_2Ph) with $LiBu^n$ gave $[(\eta^5\text{-}C_5Me_5)RhH(SiR_3)_2]^-$; these species regenerated $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiR_3)_2]$ on reaction with methanol. By contrast, $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ reacted with $Li[BEt_3H]$ slowly to give $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]^-$, which, with methanol gave the trihydride, $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$. The anion, $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-$ also reacted with CO_2 to give the labile $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)(CO)]$, which was also made by reaction of $[(\eta^5\text{-}C_5Me_5)Rh(CO)_2]$ with $SiMe_3H$. Syntheses of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiR_3)_2]$ (R_3 = Me_3 or Me_2Ph) are described. The secondary isotope shift of $^1H/^2H$ on the ^{103}Rh chemical shift on going from $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$ to $[(\eta^5\text{-}C_5Me_5)Rh(H)_2D(SiEt_3)]$ has been determined as −9 p.p.m.

We have described the preparation and structures of the rhodium(v) dihydrido–bis(triethylsilyl) complex (**1**),[1] and of its iridium analogue.[2] Some reactions of complex (**1**) have also been reported; for example, it reacted readily with electrophiles in complex reactions such as that in equation (1). Reactions

$$4\,[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2] + 2\,H^+ + 4\,H_2O \longrightarrow \underset{(\mathbf{1})}{} [\{(\eta^5\text{-}C_5Me_5)Rh\}_4(H)_4]^{2+} + 4\,(Et_3Si)_2O + 8\,H_2 \quad (1)$$

with neutral ligands in which reductive elimination of $Et_3Si\text{–}H$ occurs have also been noted,[1–4] equation (2).

$$[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2] + L \longrightarrow \underset{(\mathbf{1})}{} [(\eta^5\text{-}C_5Me_5)Rh(H)(SiEt_3)L] + Et_3SiH \quad (2)$$

We now describe the reactions of (**1**), and of its homologues, $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiR_3)_2]$ [R_3 = Me_3 (**4**) or Me_2Ph (**7**)], with charged nucleophiles. Such reactions might have been expected to proceed very easily since the complexes are in a high formal (positive) oxidation state. However, our experience so far is that only the most powerful nucleophiles react at a reasonable rate. Thus, for example, sodium methoxide in either methanol or tetrahydrofuran gave no significant reaction with (**1**), even over prolonged periods at 70 °C.

Results and Discussion

Formation of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]^-$ *and of* $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$.—The triethylsilyl complex (**1**) reacted only sluggishly even with $Li[BEt_3H]$ in tetrahydrofuran (thf) (90 °C, 48 h, sealed n.m.r. tube). When the reaction was monitored (^1H n.m.r.) the characteristic hydride doublet of (**1**) at δ −14.0 was replaced by another doublet at δ −17.6, *J*(Rh–H) 41 Hz. A similar reaction to give the same material (**2**) occurred, but less conveniently, when (**1**) and $Li[BEt_3H]$ were irradiated in thf for 3 d.

The species (**2**) could not be isolated but the ^{103}Rh n.m.r. spectrum (*via* INEPT) showed an out-of-phase doublet with separation 83 Hz, at δ −1 321, indicating that the Rh was still attached to two hydrogens in that species. The identification of (**2**) as $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]^-$ was suggested by the isolation of an extremely air-sensitive oil (**3**), in 70% yield, when (**2**) was reacted *in situ* with methanol. The oil showed the presence of Rh–H in the i.r. spectrum [ν(Rh–H) 2 040 cm^{-1} in cyclohexane] and in the ^1H n.m.r. spectrum [doublet at δ −12.05, *J*(Rh–H) 30 Hz]. The ^1H n.m.r. spectrum also showed one $(C_5Me_5)Rh$ (δ 1.79) and one $SiEt_3$ [δ 0.71 (q), and 1.02 (t), *J* 7.5 Hz]; the integration also showed that three hydrides were present. The presence of one $(C_5Me_5)Rh$ and of one $SiEt_3$ was confirmed by the ^{13}C n.m.r. spectrum. The ^{103}Rh n.m.r. spectrum (*via* INEPT) showed an −1 : −1 : +1 : +1 quartet with separation 30 Hz, at δ −1 623, confirming that the rhodium was attached to three hydrogens; together these data showed unequivocally that complex (**3**) was indeed $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$. A di-, tri-, or other polynuclear species can also be ruled out from the n.m.r. spectra since wide experience has shown that when hydrides are present there, the rhodiums are always joined by hydride bridges.[5] The hydrides then appear as multiplets in the ^1H n.m.r. spectrum.

The structure of the dihydride–disilyl complex (**1**) can loosely be described as a square-based 'piano stool' (with the C_5Me_5 as the 'seat');[1] one would anticipate that (**3**) would be similar with the hydrides and the triethylsilyl group as the 'legs'. In that case one hydride should be *trans* to (and different from) the other two which are *cis* to the triethylsilyl group. The observation of sharp resonances (and of only one hydride signal) in the ^1H n.m.r. spectrum of (**3**) implies that the molecule must be dynamic at ambient temperature. Cooling the toluene solution to −80 °C only caused a slight broadening of these resonances indicating that the fluxional process was fast even at that temperature.

A number of different dynamic processes may be responsible for the observed averaging. The hydrides, being very small, may exchange *via* a type of twist mechanism, in which the $Rh(H)_3$ effectively rotates through *ca.* 120°, or by a pairwise exchange. An alternative intriguing possibility is that the exchange occurs *via* a species in which the hydrogen at least in part is present as the dihydrogen (H_2) ligand, equation (3).

$$[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)] \rightleftharpoons [(\eta^5\text{-}C_5Me_5)Rh(H_2)H(SiEt_3)] \quad (3)$$

Numerous complexes with dihydrogen as ligand are now known and various diagnostic tests are available to show its presence, the commonest being the observation of a hydrogen–deuterium coupling of *ca.* 30—35 Hz in species which contain the HD ligand.[6]

We therefore prepared a sample of (**3**) containing some $[(\eta^5\text{-}C_5Me_5)Rh(H)_2D(SiEt_3)]$ by quenching a solution of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]^-$ with CD_3OD. The ^1H n.m.r. spectrum of this mixture showed a broad asymmetric doublet at δ -12.06. When the C_5Me_5 protons were decoupled, the spectrum consisted of a doublet, due to $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$, centred at δ -12.054, and a doublet of triplets, centred at -12.065, with the same coupling to Rh (30.0 Hz) but with *J*(H–D) 1.2 Hz. This set of resonances is due to the isotopomer $[(\eta^5\text{-}C_5Me_5)Rh(H)_2D(SiEt_3)]$ (see also below).

If an $\eta^2\text{-}H_2$ dihydrogen species with a significant lifetime were present, then the expected *J*(H–D) should be substantial, somewhere between 20 and 30 Hz, even allowing for the presence of species $Rh(H_2)D$ in addition to Rh(HD)H. Our observation of a coupling at 1.2 Hz is very much in the range expected for H and D ligands *cis* to each other and this shows that the hydrogen in (**3**) is present as three hydride ligands, and that dihydrogen species can have at most only transitory existence in equilibrium with (**3**). It is quite possible, however, that a dihydrogen complex is the transition state in the equilibration. An iridium analogue of (**3**) has recently been obtained *via* equation (4).[7]

$$[(\eta^5\text{-}C_5Me_5)Ir_2(H)_3]^+ \xrightarrow{Li[BEt_3H]} [(\eta^5\text{-}C_5Me_5)Ir(H)_3]^- \xrightarrow{SiMe_3Cl} [(\eta^5\text{-}C_5Me_5)Ir(H)_3(SiMe_3)] \quad (4)$$

Formation of $[(\eta^5\text{-}C_5Me_5)RhH(SiR_3)_2]^-$.—The bis(trimethylsilyl) complex (**4**) was prepared from $[(\eta^5\text{-}C_5Me_5)_2Rh_2Cl_4]$ by a similar route to that used to make (**1**), and was also conveniently obtained by reaction of $SiMe_3H$ with $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}C_2H_4)_2]$.[8] Complex (**4**) reacted more easily with nucleophiles than did the triethylsilyl complex (**1**). This probably reflects the greater ease of access to the incoming nucleophile when the metal is screened by only six methyls [as in (**4**)] compared to six ethyls.

The reaction of (**4**) with $Li[BEt_3H]$ was complicated (see below), but that with butyl-lithium was straightforward and led to the formation of butane and a solution species which we identify as $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-$ (**5**). The reaction proceeded rapidly (15 min, 20 °C, thf) and when it was monitored by ^1H n.m.r. spectroscopy, the doublet due to (**4**) at $\delta -13.5$ was found to have been replaced by a new doublet at δ -17.2 [*J*(Rh–H) 36.5 Hz]. The ^{103}Rh n.m.r. spectrum (*via* INEPT) showed an $-1:+1$ doublet with a separation of 37 Hz indicating that the rhodium was bound to only one hydride. When this solution was exposed to any source of protons (moisture, methanol, *etc.*) reaction immediately occurred with the reformation of (**4**). We therefore interpret this reaction sequence to proceed as in equation (5).

$$\underset{(\mathbf{4})}{[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]} \xrightleftharpoons[H^+]{LiBu^n} \underset{(\mathbf{5})}{[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-} \quad (5)$$

A very similar reaction occurred when (**1**) was treated with n-butyl-lithium; in this case the reaction took *ca.* 90 min to go to completion (thf, 20 °C). The new species was identified as $[(\eta^5\text{-}C_5Me_5)RhH(SiEt_3)_2]^-$ (**6**); the presence of one hydride on the rhodium [*cf.* (**2**) above] was shown by the n.m.r. spectra [^1H, δ -17.3, *J* 35 Hz; ^{103}Rh (*via* INEPT), $-1:+1$ doublet, separation 35 Hz]. Anion (**6**) was again converted very easily back into (**1**) by reaction with proton sources.

The reactions of one further rhodium(v)–silyl complex, $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_2Ph)_2]$ (**7**) [made in the same way as (**1**) and (**4**)] with various nucleophiles were examined. This reacted the most easily of any of the complexes and in all cases only deprotonation occurred, to give (**8**) [^1H n.m.r., δ -15.1, d, *J*(Rh–H) 35 Hz; ^{103}Rh n.m.r. (*via* INEPT), δ $-1\,515$, $-1:+1$ doublet, separation 35 Hz]. The anionic species (**8**) regenerated (**7**) on reaction with proton sources, equation (6).

$$\underset{(\mathbf{7})}{[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_2Ph)_2]} \xrightleftharpoons[H^+]{LiBu \text{ or } Li[BEt_3H]} \underset{(\mathbf{8})}{[(\eta^5\text{-}C_5Me_5)RhH(SiMe_2Ph)_2]^-} \quad (6)$$

One possible reason why the dimethyl(phenyl)silyl complex reacted more readily than the others is that the presence of the two phenyls helps to stabilise the negative charge in the anion. It is, however, also possible that the phenyls assist the reaction with the nucleophile, perhaps by improving the association in a transition state.

All three of these rhodium(v) complexes also reacted with $Li[BH_4]$ in thf; complexes (**4**) and (**7**) gave the deprotonated anions (**5**) and (**8**), while the triethylsilyl complex (**1**) again lost one silyl to give (**2**).

Although the reaction of the bis(trimethylsilyl) complex (**4**) with $Li[BEt_3H]$ again proceeded more easily than that of (**1**) and required only 1 h (thf, 90 °C), analysis of the solution by n.m.r. spectroscopy showed the presence of three anionic hydrido species. One was identified as $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-$ by comparison of the parameters with those described above; another appeared to be $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)]^-$ [^1H n.m.r., δ -17.5, *J*(Rh–H) 40 Hz; ^{103}Rh n.m.r. (*via* INEPT), δ $-1\,577$, $-1:0:+1$ 'triplet' with separation 78 Hz, indicating that the Rh is coupled to two hydrides]. The third species was tentatively identified as $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_2Et)(SiMe_3)]^-$. On protolysis with methanol, a mixture of four hydrido species was obtained. One of these was (**4**): owing to the low amounts present, complete spectroscopic identification was not possible, but the species present may well have been $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiMe_3)]$ [^1H n.m.r., δ -11.8, *J* 38.5 Hz], $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)(SiMe_2Et)]$ {^1H n.m.r., δ -13.7 [d, *J*(Rh–H) 38.5 Hz], 1.09 and 0.87 [t and q, Et, *J*(H–H) 7.5 Hz], and 0.54 and 0.49 (2 × s, $SiMe_3$ and $SiMe_2$); ^{103}Rh n.m.r. (*via* INEPT), δ $-1\,600$, $-1:+1$ doublet, separation 76 Hz}, and $[(\eta^5\text{-}C_5Me_5)Rh(H_3)(SiMe_2Et)]$ [^1H n.m.r., δ -11.90, d, *J*(Rh–H) 30 Hz].

The variety of types of reaction which occur between these rhodium(v) complexes and charged nucleophiles is surprising; fuller understanding will require closer examination of the states of the various nucleophiles in different solvents. It is pertinent to note, however, that the replacement of ethyl on silyl in (**1**) by alkoxy, which we described recently,[9] may be related to the formation of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)(SiMe_2Et)]$ with $Na[BEt_3H]$ as the source of Et.

Reaction of $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-$ *with Carbon Dioxide*.—In each case when the anionic species (**2**), (**5**), (**6**), or (**8**) was generated, the easiest reaction was the protolysis. Attempts to cause other reactions to proceed were thwarted by the very high moisture sensitivity of these anions; in only one case was a different product obtained.

The anion (**5**) from the trimethylsilyl complex reacted quite easily with carbon dioxide gas. When the reaction was monitored the hydride signal of (**5**) at δ -17.2 in the ^1H n.m.r. spectrum was replaced by a doublet [*J*(Rh–H) 37 Hz] at δ -11.6. The species responsible for this signal could be isolated but it was quite labile. It was shown to be $[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)(CO)]$ (**9**) by n.m.r. spectroscopy {^{103}Rh (*via* INEPT), δ 1 453 $-1:+1$ doublet, separation 36 Hz, indicating one hydride; ^{13}C, δ 7.9 ($SiMe_3$), 10.6 and 101.1 (C_5Me_5), and 193.7

[d, J(Rh–C) 77 Hz, CO]}. The presence of the carbonyl was confirmed by the i.r. spectrum which showed a terminal metal carbonyl stretch [ν(CO) 1 995 cm^{-1}]. We presume that the reaction proceeds according to equation (7).

$$\underset{\textbf{(5)}}{[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)_2]^-} + CO_2 \longrightarrow \underset{\textbf{(9)}}{[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)(CO)]} + SiMe_3O^- \quad (7)$$

Complex (**9**) has also been made by reaction of $[(\eta^5\text{-}C_5Me_5)Rh(CO)_2]$ with $SiMe_3H$,[8] but it decomposes very easily to the stable dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(CO)_2]$, equation (8).

$$[(\eta^5\text{-}C_5Me_5)RhH(SiMe_3)(CO)] \longrightarrow [\{(\eta^5\text{-}C_5Me_5)Rh\}_2(CO)_2] + SiMe_3H \quad (8)$$

Secondary Isotope Shift of $^1H/^2H$ *on the* ^{103}Rh *Chemical Shift*.—We have measured the chemical shift difference in the ^{103}Rh n.m.r. spectrum (*via* INEPT) between $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$ and $[(\eta^5\text{-}C_5Me_5)Rh(H)_2D(SiEt_3)]$ (prepared above). The first resonated at δ −1 616, the latter at −1 625 [$^1J(^{103}Rh\text{-}^2H)$ 4.5 Hz], giving an isotope shift of −9 p.p.m. This large shift for a single deuterium substitution reflects the large range of chemical shifts found for ^{103}Rh, from δ 9 992 for $[Rh(H_2O)_6]^{3+}$ [10] to −1 931 for $[(\eta^5\text{-}C_5H_5)Rh(H)_2(SiEt_3)_2]$.[11]

There have been many reports of secondary isotope effects on the chemical shifts of lighter nuclei,[12] but fewer of secondary deuterium isotope shifts for heavier nuclei. However, shifts for ^{77}Se in H_2Se of −7.02 p.p.m.,[13] for ^{93}Nb of −6 p.p.m. in $[(\eta^5\text{-}C_5H_5)NbH(CO)_3]^-$,[14] and for ^{183}W of −10 p.p.m. in $[(\eta^5\text{-}C_5H_5)WH(CO)_3]$,[15] on replacement of H by D have been reported.

Experimental

All reactions were carried out under dry nitrogen or argon, as the anions were exceedingly air- and moisture-sensitive. N.m.r. spectra were measured on Bruker WH-400 and AM-250 spectrometers; i.r. spectra on a PE 1710 FT spectrometer. Hydrogen-1 and ^{29}Si n.m.r. spectra were referenced to $SiMe_4$; ^{103}Rh n.m.r. spectra (obtained *via* INEPT) were referenced to Ξ 3.16 MHz. Microanalyses were by the University of Sheffield Microanalytical Service.

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ (**4**).—(*i*) *From* $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2Cl_4]$. A mixture of $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2Cl_4]$ (1.0 g, 1.6 mmol), $SiMe_3H$ (4 cm^3, 34.4 mmol), NEt_3 (1 cm^3), and toluene (20 cm^3) in a Schlenk tube was stirred at 40 °C for 14 h. After removal of volatiles at reduced pressure the brown residue was extracted and chromatographed on Florisil in pentane to yield a colourless solution which, after removal of solvent, afforded colourless crystals of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ (0.7 g, 57%) (Found: C, 50.0; H, 9.0. Calc. for $C_{16}H_{33}RhSi_2$: C, 50.0; H, 8.7%). I.r. in cyclohexane: 2 027 cm^{-1} [ν(Rh–H)]. ^1H N.m.r. in C_6D_6, δ −13.54 [d, J(Rh–H), 38.6 Hz, 2 H, Rh–H], 1.72 (s, 15 H, C_5Me_5), and 0.55 (s, 18 H, $SiMe_3$); $^{13}C\text{-}\{^1H\}$ n.m.r., δ 10.5 (s, C_5*Me*$_5$), 10.9 (s, $SiMe_3$), and 101.2 [d, J(Rh–C) 4.1 Hz, *C*$_5Me_5$]; ^{103}Rh n.m.r., δ −1 573 [−1 : +1 doublet, separation 78, 2 H, J(Rh–H) 39 Hz].

(*ii*) *From* $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}C_2H_4)_2]$. Irradiation of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}C_2H_4)_2]$ (0.2 g, 0.68 mmol), $SiMe_3H$ (1 cm^3, 8.6 mmol), and cyclohexane (1 cm^3) for 18 h, followed by a similar work-up to that described above, yielded colourless crystals of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ (0.21 g, 80%).

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_2Ph)_2]$ (**7**).—A mixture of $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2Cl_4]$ (0.5 g, 0.8 mmol), $SiMe_2HPh$ (1 cm^3, 6.5 mmol), NEt_3 (0.5 cm^3), and toluene (10 cm^3) was stirred (40 °C, 14 h). Removal of volatiles *in vacuo*, followed by chromatography of the resultant residue on Florisil using pentane as eluant, yielded a colourless solution which after removal of solvent under reduced pressure afforded an oily product that was crystallised from MeCN at −20 °C to yield (**7**) (225 mg, 55%) (Found: C, 61.7; H, 7.5. Calc. for $C_{26}H_{39}RhSi_2$: C, 61.2; H, 7.8%). I.r. in cyclohexane: 2 015 cm^{-1} [ν(Rh–H)]. ^1H N.m.r. in C_6D_6, δ −12.81 [d, J(Rh–H) 38 Hz, 2 H, Rh–H], 1.34 (s, 15 H, C_5Me_5), 0.74 (s, 12 H, Si*Me*$_2$Ph), 7.73 [d, J(H–H) 7.5 Hz, 4 H, *o*-H(Ph)], and 7.19 (d), 7.30 (dd), and 7.73 (d) [*p*-, *m*-, and *o*-H(Ph) respectively, J(H–H) 7.5 Hz]; $^{13}C\text{-}\{^1H\}$ n.m.r., δ 9.6 (s, C_5*Me*$_5$), 10.0 (s, Si*Me*$_2$Ph), 101.1 [d, J(Rh–C) 3.1 Hz, *C*$_5Me_5$], 127.6, 127.9, 134.3, and 145.6 [*m*-, *p*-, *o*-, and *i*-C(Ph) respectively]; ^{103}Rh n.m.r., δ −1 619 [−1 : +1 doublet, separation 77 Hz, J(Rh–H) 38 Hz].

Preparation of $[Li(thf)_n][(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]$ (**2**).—A mixture of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ (60 mg, 0.1 mmol) and a solution of $Li[BEt_3H]$ in thf (0.5 cm^3, 1 mol dm^{-3}) was heated in a 5-mm n.m.r. tube. The hydride signal of the starting material [^1H n.m.r., δ −14.0, d, J(Rh–H) 37 Hz] disappeared (90 °C, 48 h) and was replaced by a new hydrido species [^1H n.m.r., δ −17.6, d, J(Rh–H) 41 Hz; ^{103}Rh n.m.r. of the reaction mixture, δ −1 321, −1 : +1 doublet, separation 83 Hz, J(Rh–H) 42 Hz]. This species could not be isolated, but these data together with the reaction with methanol (below) suggest strongly the formulation $[Li(thf)_n][(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]$.

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$ (**3**).—Methanol (1 cm^3) was added to a solution of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)]^-$, freshly prepared by reacting a mixture of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ (120 mg, 0.3 mmol) and $Li[BEt_3H]$ in thf (1 cm^3, 1 mol dm^{-3}). The hydride signal (δ −17.6) immediately disappeared and a new one emerged at δ −12.0 (d). After removing the volatiles *in vacuo*, the resulting residue was extracted with pentane and chromatographed on alumina using pentane as eluant. Removal of the solvent *in vacuo* from the resultant solution afforded a very air-sensitive oily product which was characterised as $[(\eta^5\text{-}C_5Me_5)Rh(H)_3(SiEt_3)]$ (yield *ca.* 60%) [No microanalysis was possible owing to instantaneous decomposition on exposure to air.] I.r. in cyclohexane: 2 040 cm^{-1} [ν(Rh–H)]. ^1H N.m.r. ($C_6D_5CD_3$, 20 °C), δ −12.05 [d, J(Rh–H) 30.0 Hz, 3 H, Rh–H], 1.79 (s, 15 H, C_5Me_5), 1.02 [t, J(H–H) 7.5 Hz, 9 H, $SiCH_2C$*H*$_3$], and 0.71 [q, J(H–H) 7.5 Hz, 6 H, SiC*H*$_2CH_3$] (some broadening of the peaks was observed on cooling to −80 °C but this might be due to viscosity problems); $^{13}C\text{-}\{^1H\}$ n.m.r. ($C_6D_5CD_3$, 20 °C), δ 9.5 (s, C_5*Me*$_5$), 10.9 (s, $SiCH_2$*C*H_3), 11.9 (s, Si*C*H_2CH_3), and 100.2 [d, *C*$_5Me_5$, J(Rh–C) 3.4 Hz]; $^{29}Si\text{-}\{^1H\}$ n.m.r. ($C_6D_5CD_3$, room temperature), 32.6 [d, J(Rh–Si) 15.9 Hz]; ^{103}Rh n.m.r. (room temperature), δ −1 623 [−1 : −1 : +1 : +1 quartet, J(Rh–H) 30.0 Hz].

Reactions of Complexes (**4**), (**1**), *and* (**7**) *with* n*-Butyl-lithium*.—A solution of $LiBu^n$ (0.15 cm^3, 2.5 mol dm^{-3}) was added to a solution of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ (75 mg, 0.194 mmol) in thf (0.4 cm^3) at room temperature in a 5-mm n.m.r. tube. After 15 min the hydride signal due to $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiMe_3)_2]$ at δ −13.5 [d, J(Rh–H) 38.6 Hz] had been replaced by a new hydride signal at δ −17.2 [d, J(Rh–H) 36.5 Hz]. ^{103}Rh N.m.r. of this solution [$(CD_3)_2CO$ as external reference], δ −1 434 [−1 : +1 doublet, J(Rh–H) 37 Hz]. On addition of methanol to this solution the characteristic ^1H n.m.r. spectrum of complex (**4**) reappeared. The data indicate that formation of (**5**) has occurred.

The analogous species $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiEt_3)_2]^-$ (**6**) was prepared by deprotonation with $LiBu^n$ of $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$; in this case the reaction was slower (90 min). The solution showed hydride signals in the ^1H n.m.r. at δ −17.3 [*J*(Rh–H) 35 Hz] and in the ^{103}Rh n.m.r. at δ −1 533 [−1 : +1 doublet, *J*(Rh–H) 35 Hz].

The species $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_2Ph)_2]^-$ (**8**) was also prepared by reaction of complex (**7**) with $LiBu^n$ as above. ^1H N.m.r., δ −15.1 [d, *J*(Rh–H) 35 Hz, Rh–H]; ^{103}Rh n.m.r. of the solution [$(CD_3)_2CO$ as external lock], −1 515 (−1 : +1 doublet, separation 35 Hz).

Reaction of $Li[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_3)_2]$ *with* CO_2.—A smooth stream of carbon dioxide was bubbled (1 min) through a solution of $Li[(\eta\text{-}C_5Me_5)Rh(H)(SiMe_3)_2]$, freshly prepared by deprotonation of complex (**4**) (150 mg) with $LiBu^n$ as described above. The ^1H n.m.r. spectrum showed that the monoanionic hydride $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_3)_2]^-$ had disappeared and a new hydride had appeared at δ −11.6 (d). Removal of volatiles by blowing a nitrogen stream over the reaction mixture was followed by chromatography of the residue over alumina using pentane as eluant to give a colourless solution. The solvent was again removed by blowing a nitrogen stream over the solution yielding an oily residue which was characterised as $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_3)(CO)]$ (yield *ca.* 60%; very unstable compound) (Found: C, 44.6; H, 6.9. Calc. for $C_{14}H_{25}ORhSi$: C, 49.9; H, 7.4%). I.r. (cyclohexane): 1 995 [ν(CO)], 2 025 cm^{-1} [ν(Rh–H)]. ^1H N.m.r. (in C_6D_6 at 25 °C), δ −11.6 [d, *J*(Rh–H) 36.5 Hz, 1H, Rh–H], 1.75 (s, 15 H, C_5Me_5), and 0.55 (s, 9 H, $SiMe_3$); $^{13}C\text{-}\{^1H\}$ n.m.r., δ 7.9 (s, Si*Me*$_3$), 10.6 (s, C$_5$*Me*$_5$), 101.1 (s, *C*$_5$Me$_5$), and 193.7 [d, *J*(Rh–C) 77 Hz, CO]; ^{103}Rh n.m.r., δ −1 453 [−1 : +1 doublet, *J*(Rh–H) 36 Hz]. The product slowly lost $SiMe_3H$ and the formation of $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(CO)_2]$ was detected by i.r. [ν(CO) 1 746 cm^{-1} in cyclohexane] and its characteristic blue colour.

Acknowledgements

We thank the S.E.R.C. for support, the D.R.U.I. of Murcia for an award (to J. R.), Johnson Matthey for the loan of precious-metal salts, and Dr. P. O. Bentz for some preliminary experiments. We also acknowledge very helpful exchanges of information with Dr. R. N. Perutz.

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Received 22nd October 1986; *Paper* 6/2060