Synthesis, X-ray, and Low-Temperature Neutron Diffraction Study of a Rhodium(V) Complex: Dihydridobis(triethylsilyl)pentamethylcyclopentadienylrhodium

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Abstract: Reaction of $[(C_5Me_5Rh)_2Cl_4]$ (**1**) with triethylsilane leads to the novel rhodium(V) complex $[\eta^5\text{-}C_5Me_5Rh(H)_2(SiEt_3)_2]$ (**2**) characterized by NMR spectra (^1H, ^{13}C, ^{29}Si, and ^{103}Rh), X-ray diffraction, and neutron diffraction at 20 K. The complex shows a "four-legged piano stool" geometry with the pentamethylcyclopentadienyl η^5-bonded to the rhodium [average Rh–C, 2.283 (9) Å] on top and the two triethylsilyl ligands trans in the basal plane [Rh–Si, 2.379 (2) Å]. The neutron diffraction analysis located the two hydrides, which are trans to each other and cis to the triethylsilyls in the basal plane. The mean Rh–H distance is 1.581 (3) Å, and the H–Rh–H angle is 94.8 (2)°. Complex **2** is rather stable, but it reacts under forcing conditions with neutral ligands (triphenylphosphine, CO, or maleic anhydride) to give $[C_5Me_5Rh(PPh_3)H(SiEt_3)]$, $[C_5Me_5Rh(CO)_2]$, or $[C_5Me_5Rh(\text{maleic anhydride})_2]$. It reacts more easily with electrophiles such as HBF_4 to give $[(C_5Me_5Rh)_4H_4]^{2+}$, with HCl to give **1**, with $AgBF_4$ in MeCN to give $[C_5Me_5Rh(MeCN)_3]^{2+}$, and with I_2 to give $[(C_5Me_5Rh)_2I_4]$. The predominant mode of reaction involves reductive elimination of $Et_3Si–H$, which can be strongly promoted by an electrophile.

We have been investigating the mechanism of the unusual hydrosilylation with dehydrogenation reaction (A), which is

$$RCH_2CH_2{=}CH_2 + Et_3SiH \rightarrow RCH_2CH{=}CHSiEt_3 + RCH{=}CHCH_2SiEt_3 + R(CH_2)_3SiEt_3 + R(CH_2)_3H \quad (A)$$

catalyzed by $[(C_5Me_5Rh)_2Cl_4]$ (**1**).[2] When this reaction was carried out using larger amounts of **1**, we noted the formation of a white crystalline organometallic complex. This proved to contain rhodium–silicon bonds and to be the very novel and unexpected rhodium(V) complex $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (**2**). A preliminary communication on part of this work has appeared.[3]

The higher oxidation state compounds of rhodium have hitherto been limited to RhF_6,[4] $[RhF_5]_4$, and $[RhF_6]^-$ [5] and some rather ill-defined oxy species.[6] The fluoride complexes in particular are extremely reactive and are very strong oxidants. Iridium forms a more substantial series of high oxidation state complexes,[7] and these now include the bis(phosphine)iridium(V) hydrides[8] as well as the (pentamethylcyclopentadienyl)iridium(V) tetramethyl that was recently reported from this laboratory.[9] We have also very recently described a series of hydrido(triethylsilyl)iridium(V) complexes including the analogue of **2**.[10]

Although high oxidation state organometallic complexes are now well-known for many of the earlier transition metals,[11] there have been few reports of such species among the platinum metals.[12] Indeed for rhodium the organometallic chemistry has been limited

Table I. Selected Interatomic Distances (Å)[a] and Bond Angles (deg)[a]

Rh–Si	2.379 (2)	C(7)–C(8)	1.436 (1)
Rh–H(1)	1.578 (3)	C(8)–C(9)	1.433 (1)
Rh–H(2)	1.583 (3)	C(9)–C(9)′	1.437 (2)
		C–C$_{av}$	1.435 (1)[b]
Rh–C(7)	2.282 (2)		
Rh–C(8)	2.300 (1)	C(7)–C(10)	1.502 (2)
Rh–C(9)	2.268 (2)	C(8)–C(11)	1.500 (1)
Rh–C$_{av}$	2.283 (9)[b]	C(9)–C(12)	1.499 (1)
		C–C$_{av}$	1.500 (1)[b]
Rh–C$_5$(ring)	1.930 (2)		
		C–H(methylene)$_{av}$	1.098 (2)[b]
Si–C(1)	1.903 (2)		
Si–C(3)	1.899 (2)		
Si–C(5)	1.900 (2)	C–H(methyl)$_{av}$	1.089 (2)[b]
Si–C$_{av}$	1.901 (2)[b]		
C(1)–C(2)	1.539 (2)		
C(3)–C(4)	1.534 (1)		
C(5)–C(6)	1.534 (1)		
C–C$_{av}$	1.536 (2)[b]		
H(1)–Rh–H(2)	94.84 (18)	C(8)–C(7)–C(8)′	108.12 (10)
Si–Rh–Si′	107.90 (8)	C(7)–C(8)–C(9)	107.85 (7)
		C(8)–C(9)–C(9)′	108.05 (4)
Rh–Si–C(1)	118.51 (7)		
Rh–Si–C(3)	111.20 (7)	C(8)–C(7)–C(10)	125.72 (5)
Rh–Si–C(5)	111.84 (7)	C(7)–C(8)–C(11)	125.88 (7)
		C(9)–C(8)–C(11)	125.49 (7)
Si–C(1)–C(2)	113.69 (7)	C(8)–C(9)–C(12)	127.26 (7)
Si–C(3)–C(4)	114.64 (7)	C(9′)–C(9)–C(12)	123.79 (4)
Si–C(5)–C(6)	115.34 (7)		

[a] Esd's in parentheses. Atoms related by the mirror plane are primed. [b] Standard deviations of mean values are given as the larger of the individual esd's or $\sigma(x_{av}) = [\sum_{i=1}^{n}(x_i - x_{av})^2/(n(n-1))]^{1/2}$, where x_{av} is the mean value and x_i are individual values.

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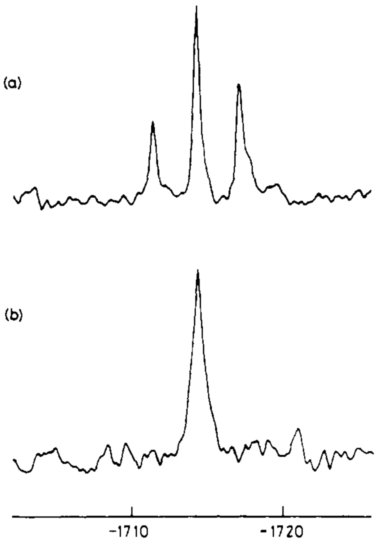

Figure 1. ^{103}Rh NMR spectrum of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (**2**): (a) no decoupling; (b) with irradiation at the hydride frequency.

to complexes of oxidation state no higher than +3.[13] As a consequence, for example, the many reactions homogeneously catalyzed by rhodium are all interpreted in terms of the participation of only two oxidation states, +1 and +3. The complex **2** and the recently discovered large family of dinuclear rhodium(IV) complexes[14] may thus be seen to open up a new area of high oxidation state organometallic chemistry with potential consequences for our view of the chemistry of the whole platinum metals area.

Results and Discussion

Preparation and Structure. The complex **2** was conveniently prepared (50–94% yield) by stirring the complex **1**, triethylsilane, and triethylamine in 1,2-dichloroethane (20 °C/2 h). It crystallized in large colorless plates, which were freely soluble in hydrocarbon solvents, and was reasonably stable to air.

The ^{1}H NMR spectrum of the complex showed the presence of η^5-C_5Me_5, ethyl, and hydride resonances the integrals of which, together with the elemental analysis and solution molecular weight, suggested the formula $[C_5Me_5Rh(H)_2(SiEt_3)_2]$. The presence of two hydride ligands was elegantly confirmed by the ^{103}Rh NMR spectrum; this showed (Figure 1) a triplet at δ −1714 (J = 36.6 Hz), which collapsed to a singlet on irradiation at the hydride frequency.

Final proof of the structure came from an X-ray crystallographic structure determination at room temperature and from a neutron diffraction study at 20 K (Figures 2 and 3 and Table I). These showed the C_5Me_5 ring to be accurately pentagonal [average C–C, 1.435 (1) Å][15] and η^5-bonded to the metal [average Rh–C, 2.283 (9) Å]. The ring is bisected by a mirror plane containing the hydrides [average Rh–H, 1.581 (3) Å] in which the two triethylsilyl ligands are reflected [Rh–Si, 2.379 (2) Å]. The Rh–H distance is the shortest reported thus far based on neutron data[16,17] for a 4d or 5d transition metal. It is intriguing to speculate that this may reflect the small size of rhodium in a complex in which it is formally in the +5 oxidation state, but confirmation of this hypothesis must await neutron diffraction studies of further group 8 hydrides.[16] It is perhaps noteworthy that the C_5Me_5 ring in complex **2** is not especially tightly bound; indeed the perpendicular distance to the plane of the ring [1.930 (2) Å] is substantially longer than for the majority of C_5Me_5–Rh^{III} or C_5Me_5–Rh^{I} complexes.[18] We suggest that this is to minimize nonbonded intramolecular interactions between the ring methyl hydrogens and the triethylsilyl hydrogens; the shortest such contact here is 2.115 (3) Å. The methyl groups in **2** are also displaced from the plane of the ring away from the metal, so that the perpendicular distance from rhodium to the Me_5 ring is 2.131 (2) Å.

The angle H–Rh–H of 94.84 (18)° leads to an intramolecular H···H distance of 2.328 (4) Å and shows there to be little, if any, direct interaction. Similarly the average Si···H distance of 2.27 (6) Å indicates no significant direct bonding either. This may be contrasted with the situation in $[Pt_2H_2(\mu\text{-}SiMe_2)_2((cyclohexyl)_3P)_2]$ where the hydride is considered to bridge Pt and Si (Pt–H, 1.78; Pt–Si, 2.420 (2); and Si–H, 1.72 Å).[19]

There are no unusual intermolecular contacts in the structure of **2**, the shortest such H···H distance being 2.11 Å. A view of the crystal packing is shown in Figure 3.

The complex may therefore be defined as possessing a total of five formally uninegative ligands about the metal and to have the metal formally in the +5 state. However, this does not necessarily imply a high charge on the metal, since a characteristic of the C_5Me_5 ring seems to be its great ability to act as an electron reservoir which supplies electron density to the metal when it is needed. For example, in recent photoelectron spectroscopic studies it has been shown that in the series $[C_5Me_5Ir(CO)_2]$, $[C_5Me_5IrMe_2(Me_2SO)]$, $[C_5Me_5IrMe_4]$ the first ionization energy was roughly constant despite a formal change in oxidation state of the iridium from +1 through +3 to +5; indeed the average d orbital ionization energy was actually *more* for the Ir(I) than for either the Ir(III) or the Ir(V) complex.[20] We anticipate the same to hold true for complex **2**, and therefore it is perhaps not surprising that in the chemistry shown by this complex there are no signs of the reactivity normally expected from highly polar bonds or strongly oxidizing metal centers.

As expected for a complex of rhodium(V), d^4, **2** is diamagnetic.

Mode of Formation of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (2). In the absence of base the reaction of **1** and triethylsilane initially gave a deep purple solution, which then turned brown. The purple solution was shown to contain the mono-μ-hydride $[(C_5Me_5Rh)_2HCl_3]$,[21] which was isolated. From the brown solution was obtained the colorless complex **2** and a less soluble brown solid, which contained some **1**. Hydrogen was given off during the reaction, approximately 1.5 mol per mol of rhodium. The main silicon compound obtained was $(Et_3Si)_2O$, identified by GC-MS and by comparison with an authentic sample. It was

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(15) Values of bond distances and angles quoted are from the neutron study.

(16) Very recent neutron studies of $[(PEt_3)_2Pt(\mu_2\text{-}H)_2IrH_2(PEt_3)_2][BPh_4]$ (ref 17b) and $[Pt_2H_3(dppe)_2][BPh_4]$ (ref 17c) have yielded terminal Ir–H and Pt–H distances of 1.589 (3) and 1.610 (2) Å, respectively.

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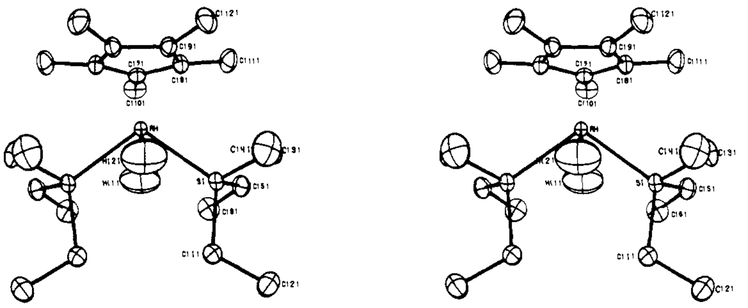

Figure 2. Stereoview of the $C_5Me_5RhH_2(SiEt_3)_2$ molecule with thermal ellipsoids drawn to enclose 97% probability density.[43]

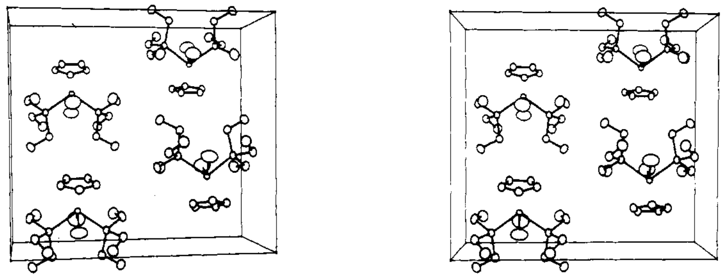

Figure 3. Stereoview of the packing in a unit cell, viewed down the crystallographic *c* axis with thermal ellipsoids as in Figure 1.

presumably formed from Et_3SiCl by hydrolysis during workup and analysis.

The overall reaction approximates to eq B, and the reason for

$$[(C_5Me_5Rh)_2Cl_4] + 8Et_3SiH = 2[C_5Me_5Rh(H)_2(SiEt_3)_2] + 4Et_3SiCl + 2H_2 \quad (B)$$

$$Et_3SiH + HCl = Et_3SiCl + H_2 \quad (C)$$

$$2Et_3SiCl + H_2O = (Et_3Si)_2O + 2HCl \quad (D)$$

the higher than expected amount of hydrogen is a fast reaction (C), catalyzed by **1** and followed by (D) caused by traces of water.

In the presence of base (triethylamine) the reaction was accelerated and the color changes were initially to blue and then to red. ^1H NMR spectroscopy again showed the intermediacy of $[(C_5Me_5Rh)_2HCl_3]$. In addition to **2** another hydride complex[22] was observed at the end of the reaction, present in the ratio ca. 2.3:1, which could not, however, be isolated in pure form.

The mono-μ-hydrido complex probably arises from the reaction E. Recent studies on the reaction of $[(C_5Me_5Ir)_2Cl_4]$ with Et_3SiH

$$[(C_5Me_5Rh)_2Cl_4] + Et_3SiH = [(C_5Me_5Rh)_2HCl_3] + Et_3SiCl \quad (E)$$

have shown that both the blue $[(C_5Me_5Ir)_2H_2Cl_2]$ and $[C_5Me_5Ir(H)_2(Cl)(SiEt_3)]$ are intermediates there[10] and that the latter can arise from the former by a reaction with Et_3SiH which is formally an oxidative addition, Ir(III) to Ir(V). We suggest that the rhodium reaction proceeds similarly (eq F–H) but that

$$[(C_5Me_5Rh)_2HCl_3] + Et_3SiH = [(C_5Me_5Rh)_2H_2Cl_2] + Et_3SiCl \quad (F)$$

$$[(C_5Me_5Rh)_2H_2Cl_2] + 2Et_3SiH = 2[C_5Me_5RhH_2Cl(SiEt_3)] \quad (G)$$

$$[C_5Me_5RhH_2Cl(SiEt_3)] + 2Et_3SiH = [C_5Me_2Rh(H)_2(SiEt_3)_2] + Et_3SiCl + H_2 \quad (H)$$

the corresponding intermediates are more labile than their iridium counterparts and are present in too low concentration for detection here. In fact, previous attempts to make $[(C_5Me_5Rh)_2H_2Cl_2]$ have not been successful, and this complex remains unknown.

The significance of our observation of the bridged hydrides is not straightforward. We have shown before that rhodium and iridium μ-hydrides have rather low reactivities, and our investigations of such complexes as hydrogenation catalysts has favored the intermediacy of mononuclear complexes with terminal hydrides as the reactive species.[23] Thus an alternative explanation for the formation of **2** from **1** involves mononuclear complexes as intermediates and the dinuclear μ-hydrides arising from reversible side reactions.

The oxidative addition of Si–H to low-valent metal centers is very well established,[24,25] and even double additions are quite common.[26] However, in every case of double addition so far described, a reductive elimination, usually of H_2, has also occurred, e.g., eq I and J.[26a] It is a notable property of the pentamethylcyclopentadienyl ligand that it can stabilize complexes with two silyl hydrides.

$$[Pt(diphos)_2] + H\text{–}SiCl_3 = [Pt(diphos)(H)(SiCl_3)] \quad (I)$$

$$[Pt(diphos)(H)(SiCl_3)] + H\text{–}SiCl_3 = [Pt(diphos)(SiCl_3)_2] + H_2 \quad (J)$$

Reactions of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$. The most remarkable feature of **2** is its stability. It is little affected by air or moisture and does not react with neutral ligands, L, except on heating under rather forcing conditions. Thus, for example, there was no reaction with trimethyl phosphite or *tert*-butyl isocyanide over 24 h at 60 °C or with carbon monoxide at 1 atm and ambient temperature. However, heating **2** with CO at 90 °C and 10 atm of pressure for 24 h gave a high yield of $[C_5Me_5Rh(CO)_2]$[27] and triethylsilane (eq K) by a double reductive elimination, corresponding to Rh(V) (d^4) → Rh(I) (d^8).

$$[C_5Me_5Rh(H)_2(SiEt_3)_2] + 2CO = [C_5Me_5Rh(CO)_2] + 2Et_3SiH \quad (K)$$

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[22] ^1H NMR resonances at δ 2.1 (s, C_5Me_5), −12.0 (d, J = 29.3 Hz, 3 H?). Et_3Si resonances could not be distinguished from those of other materials.

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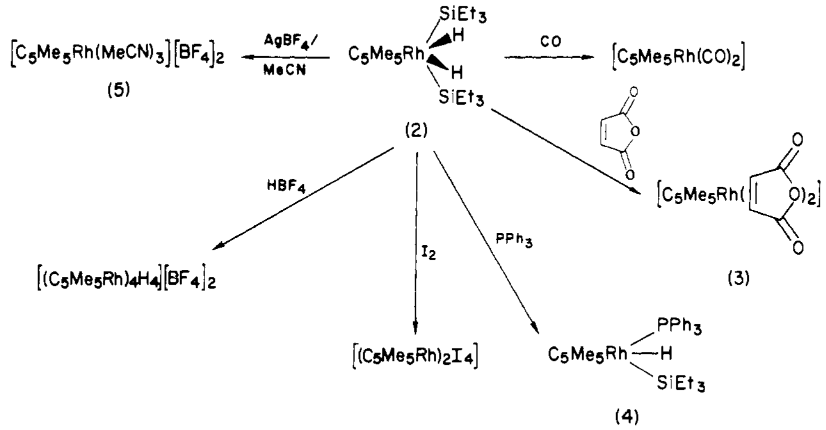
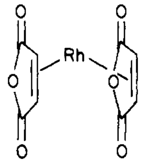
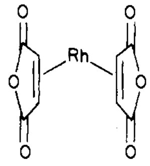
Scheme I



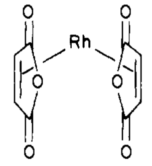
Complex **2** also reacted slowly with maleic anhydride (benzene/48 h/80 °C) to give a yellow solid, identified as the rhodium(I) bis(maleic anhydride) complex **3**. Both the ^{1}H and the ^{13}C NMR spectra showed an asymmetry involving the coordinated maleic anhydride (two =CH, two =CH, and two >C=O resonances). We suggest this arises from the two maleic anhydrides having different orientations, as shown schematically in **3a**, which leads to a difference in environment. This may occur for steric reasons to minimize nonbonded contacts, which are presumably greater in the other forms, **3b** or **3c**.



3a



3b



3c

Reaction with triphenylphosphine caused reductive elimination of only one triethylsilane and the formation of the rhodium(III) complex **4** (Scheme I). Triethylphosphine and trimethyl phosphite reacted analogously.

$$[C_5Me_5Rh(H)_2(SiEt_3)_2] + Ph_3P = \underset{\mathbf{4}}{[C_5Me_5Rh(H)(SiEt_3)(Ph_3P)]} + Et_3SiH$$

Complex **2** did, however, react much more easily with electrophiles. For example, with $AgBF_4$ in benzene–acetonitrile the reaction L occurred instantaneously at 20 °C. The complex **5**[28]

$$[C_5Me_5Rh(H)_2(SiEt_3)_2] + AgBF_4 = \underset{\mathbf{5}}{[C_5Me_5Rh(MeCN)_3][BF_4]_2} + H_2 + 2Et_3SiF + Ag + BF_3 \quad (L)$$

was identified by NMR spectroscopy and the Et_3SiF by mass spectrometry. A separate experiment showed that triethylsilane itself reacted directly with $AgBF_4$ to give triethylfluorosilane and silver according to eq M.

$$Et_3SiH + AgBF_4 = Et_3SiF + Ag + BF_3 + {}^1/_2H_2 \quad (M)$$

The complex **2** reacted with HBF_4 to give H_2 (ca. 1.5 equiv per rhodium) and a green solution, which was shown to contain the known tetranuclear tetrahydride dication $[(C_5Me_5Rh)_4H_4][BF_4]_2$ by ^{1}H NMR spectroscopy.[29] The overall reaction corresponded to eq N.

$$4[C_5Me_5Rh(H)_2(SiEt_3)_2] + 2H^+ + 4H_2O = [(C_5Me_5Rh)_4(H)_4]^{2+} + 7H_2 + 4(Et_3Si)_2O \quad (N)$$

Complex **2** also reacted readily with HCl to give first the mono-μ-hydride, and then the starting complex **1** (eq O). This

$$[C_5Me_5Rh(H)_2(SiEt_3)_2] \xrightarrow{HCl} [(C_5Me_5Rh)_2HCl_3] \xrightarrow{HCl} [(C_5Me_5Rh)_2Cl_4] \quad (O)$$

is a direct reversal of the reactions leading to its formation.

Although no reaction occurred with iodine in the cold, on refluxing in benzene the $[(C_5Me_5Rh)_2I_4]$ complex was slowly formed, and $(Et_3Si)_2O$ was detected by GC.

Conclusions

The structural data show $[C_5Me_5Rh(SiEt_3)_2(H)_2]$ unambiguously to be a Rh(V) complex. This is the first well-characterized organometallic compound of rhodium in such a high formal oxidation state. The stability of the complex therefore comes as a surprise but suggests that it will be possible to prepare many other similar complexes. It also implies that it is unrealistic to limit the organometallic and catalytic chemistry of mononuclear rhodium to the +1 and +3 oxidation states, as has largely been the case so far. The possibility that reactions (both catalytic and stoichiometric) may proceed through Rh(V) intermediates must now be seriously considered.

The most prevalent mode of reaction of complex **2** involves the reductive elimination of Et_3SiH and the formation of a Rh(III) or a Rh(I) product. It is even quite useful to view Et_3SiH as "equivalent to a neutral ligand" but one that enables the metal to increase its coordination number. This concept also allows a rationalization of the otherwise surprising ability of reactions to be initiated by electrophiles. The details of these reactions have not been investigated so far; they may involve direct electrophilic attack at silicon, or possibly even at hydride, implying a substantial electron density there. Alternatively electrophiles may act by direct attack at, or electron transfer from, the metal, again implying that this center is relatively electron rich. Such reactions have direct parallels in a variety of carbon–carbon coupling reactions that proceed via an oxidatively induced reductive elimination.[30]

Experimental Section

Reactions were carried out under a protective atmosphere of nitrogen. Microanalyses and molecular weight measurements are by the University of Sheffield Microanalytical Service; high-resolution and multinuclear NMR spectra were run on the S.E.R.C. High Field WH400 spectrometer at Sheffield University.

Dihydridobis(triethylsilyl)pentamethylcyclopentadienylrhodium(V) (2). $[(C_5Me_5Rh)_2Cl_4]$, complex **1** (1.0 g, 1.6 mmol), triethylsilane (4 cm^3), and triethylamine (1 cm^3) were stirred in 1,2-dichloroethane (10 cm^3) (20 °C/2 h). The solution turned blue and then brown and deposited

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[31] If the purified complex **2** still contained small amounts of liquid siloxanes [chiefly $(Et_3Si)_2O$], these could be removed by washing with cold methanol.

a solid, which was filtered off and shown to be triethylammonium chloride. The solvent and other volatile materials were removed on a rotary evaporator. The brown residue was extracted with hexane to give a colorless solution which was purified by chromatography on Florisil using hexane as eluant.[31] On crystallization from hexane large colorless plates of complex **2** (0.7 g, 50%) were obtained (mp 95 °C dec). Anal. Calcd for $C_{22}H_{47}RhSi_2$: C, 56.1; H, 10.1%; M, 470. Found: C, 55.8; H, 10.0; M, 465 (osmometric in toluene). Spectroscopy: (i) UV (cyclohexane) λ_{max} 250 nm ($\epsilon = 2.5 \times 10^3$); (ii) IR ν (Rh–H) 2019, (cyclohexane) 2012, 2040 (Nujol) cm^{-1}; (iii) ^{1}H NMR (400 MHz, in C_6D_6) δ −13.85 [d, RhH, J(Rh–H) = 36.9, J(Si–H) = 7.9 Hz], 0.89 [q, SiCH_2CH$_3$, J(H–H) = 7.8 Hz], 1.09 [t, SiCH$_2$$CH_3$, J(H–H) = 7.8 Hz], 1.70 [q, C_5Me_5, J(Rh–H) ≈ J(hydride H) = 0.6 Hz]; (iv) $^{13}C\{^1H\}$ NMR δ 9.50 (s, SiCH$_2$$CH_3$), 10.96 (s, Si$CH_2CH_3$), 11.17 (s, C$_5$$Me_5$), 101.44 [d, C_5Me$_5$, J(Rh–C) = 3.5 Hz]; (v) $^{29}Si\{^1H\}$ NMR δ 38.33 [d, J(Rh–Si) = 15.9 Hz]; (vi) ^{103}Rh NMR δ −1714 (with respect to 3.16 MHz = 0 ppm) t, decoupled to s on irradiation at the hydride frequency (Figure 1).

An alternative, higher yield,synthesis involves stirring complex **1** (0.5 g) and triethylsilane (3 cm^3) in dry toluene (15 cm^3) for 5 h at 60 °C and then 3 days at 20 °C. A similar workup to that described above gave crystals of **2** (0.72 g, 94%).

GC analysis (molecular sieve 5A column) of the gases given off when a reaction was carried out in a sealed vessel showed the presence of hydrogen, approximately 1.5 mol being produced per mol of Rh. GC analysis (OV-1 column, temperature programmed 100–290 °C) of the liquid phase showed the presence of $(Et_3Si)_2O$ and $Et_3SiOSiEt_2OSiEt_3$ (established by mass spectrometry) as well as small amounts of other siloxanes and solvents.

Reaction of Complex 2 with Carbon Monoxide. A solution of complex **2** (200 mg) in benzene (4 cm^3) in a glass-lined small autoclave was reacted with CO (10 atm, 90 °C, 24 h). On removal of the solvent and workup, $[C_5Me_5Rh(CO)_2]$ (0.115 g, 92%) was isolated and characterized by comparison with an authentic sample (IR, NMR, and mass spectra). GC-MS analysis of the recovered solvent showed the presence of triethylsilane.

Bis(maleic anhydride)pentamethylcyclopentadienylrhodium(I) (3). A solution of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (0.2 g, 0.425 mmol) and maleic anhydride (0.17 g, 1.7 mmol) in benzene (50 cm^3) was refluxed (48 h). The resultant brown solution contained a yellow precipitate, which was filtered off and shown to be complex **3** (0.092 g, 50%). Anal. Calcd for $C_{18}H_{19}O_6Rh$: C, 49.8; H, 4.4%; M, 434. Found: C, 50.2; H, 4.6; N, 456. Spectroscopy: IR (KBr disc) ν(CO) 1750, 1815, 1827 cm^{-1}; ^{1}H NMR (220 MHz, CDCl$_3$) δ 1.66 (s, 15 H, C_5Me_5), 3.11 [d, 2 H, J(Rh–H) = 2.2 Hz], 3.43 [d, 2 H, J(Rh–H) = 2.2 Hz]; $^{13}C\{^1H\}$ NMR (25 MHz, CDCl$_3$) δ 7.8 (s, C$_5$$Me_5$), 50.6 [d, J(Rh–C) = 13.7 Hz, =CH], 52.5 [d, J(Rh–C) = 13.7 Hz, =CH], 104.7 [d, J(Rh–C) = 4.6 Hz, C_5Me$_5$], 168.5, 169.5 (2 s, 2 >C=O).

Reaction of Complex 2 with Triphenylphosphine. The reaction of complex **2** (0.130 g, 0.27 mmol) and triphenylphosphine (75 mg, 0.28 mmol) dissolved in benzene (0.5 cm^3) in a sealed 5-mm NMR tube was followed by ^{1}H NMR spectroscopy at 85–90 °C. After 15 h the spectra showed that a new species, identified by NMR spectroscopy as **4**, was formed to the extent of ca. 25%; after 48 h the spectra showed the presence of only a small residual amount of **2**. The formation of free triethylsilane was shown by the appearance of the characteristic septet of the Si–H at δ 4.0. After removal of the benzene and other volatiles in vacuo, the ^{1}H NMR spectrum in C_6D_6 showed the following resonances ascribed to **4**: δ −13.8 [1 H, t, Rh–H, J(P–H) = J(Rh–H) = 30 Hz], 0.6–1.4 (15 H, m, SiEt$_3$), 1.8 [15 H, d, C_5Me_5, J(P–H) = 3 Hz], 7.0–8.2 (15 H, m, Ph$_3$P); $^{31}P\{^1H\}$ NMR δ 59.3 [d, J(Rh–P) = 181 Hz]. Very similar reactions giving strictly analogous products at very similar rates were observed when **2** was reacted with triethylphosphine or trimethyl phosphite.

Reaction of Complex 2 with HBF$_4$. Complex **2** (10 mg) dissolved in 1,2-dichloroethane (1 cm^3) was treated with fluoroboric acid (0.1 cm^3) (5 h/20 °C). GC analysis showed the formation of hydrogen gas, ca. 1.5 equiv per Rh. The solvent was removed from the resultant green solution, and the residue washed with diethyl ether. The ^{1}H NMR spectrum of the dark green solid showed the characteristic bands of $[(C_5Me_5Rh)_4H_4][BF_4]_2$ at δ 1.95(s) and −15.4 (q).[29]

Reaction of Complex 2 with AgBF$_4$. Complex **2** (10 mg, 0.021 mmol) dissolved in a mixture of benzene and acetonitrile (1:1 v/v; 1 cm^3) was treated with AgBF$_4$ (18 mg, 0.084 mmol). An immediate reaction occurred with the formation of hydrogen gas, detected by GC (ca. 0.01 mmol). The solution was shown to contain Et$_3$SiF (by GC-MS) and the complex **5** (by ^{1}H NMR[28]).

X-ray Structure Determination of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (2). A single crystal was selected from a batch grown as described above.

Crystal data: $C_{22}H_{47}RhSi_2$, M_r = 470.7, orthorhombic, a = 8.66 (3) Å, b = 16.75 (6) Å, c = 17.74 (6) Å, U = 2574 (16) Å^3 at room temperature (obtained from a least-squares fit to the setting angles of 62 manually centered reflexions). Z = 4, space group *Pbcm* (No. 57), D_c = 1.22 g cm^{-3}, $F(000)$ = 1.008. Mo Kα radiation (graphite monochromator) λ = 0.71069 Å. Single-crystal X-ray data in the range 6.5 < θ < 50° were collected on a Stoe STADI-2 diffractometer with the crystal mounted along the b axis using the ω-scan mode. Intensities of 1429 independent reflections were measured with $I > 3\sigma(I)$ and background difference $\Delta < 4\sigma(B)$. Corrections were made for Lorentz and polarization effects but not for extinction or absorption. The structure was solved using Patterson and Fourier methods. The molecule lies across a mirror plane and block diagonal matrix least-squares refinement has reduced R to 0.057, thereby confirming the choice of the centric space group.

Table II. Experimental Details and Refinement Parameters for $[C_5Me_5Rh(H)_2(SiEt_3)_2]$

Neutron Data at 20 K	
cryst wt	8.76 mg
cryst vol	7.18 mm^3
cryst boundary faces	{110}, {001}
cald transmissn range (μ = 3.588 cm^{-1})	0.313–0.870
no. reflcns measd	4775[a]
no. independent reflcns (n)	4212[b]
agreement factor for averaging $R_c = \sum_{i=1}^{n'} \lvert \langle F_o^2 \rangle - F_{oi}^2 \rvert / \sum n' \langle F_o^2 \rangle$	0.027
no. variable params (m)	338
final indices of fit	
$R(F^2) = \sum \lvert F_o^2 - (k^2F_o^2) \rvert / \sum \lvert F_o^2 \rvert$	0.061
$R_w(F^2) = [\sum w(F_o^2 - (k^2F_c^2))^2 / \sum wF_o^4]^{1/2}$	0.068[c]
$S = [\sum w(F_o^2 - (k^2F_o^2))^2/(n - m)]^{1/2}$	1.347

Extinction Parameters (×10^8)[d]

Y_{11} 0.032 (7)	Y_{22} 0.660 (60)	Y_{33} 6.367 (832)	Y_{12} 0.113 (20)

Eigenvalues (Arc-Seconds) and Direction Cosines (Crystal System)

η^1	8.28	0.00	0.00	1.00
η^2	2.71	0.17	0.99	0.00
η^3	0.37	0.99	−0.17	0.00

[a] Single octant was sampled out to (sin θ/λ) = 0.61 Å^{-1} and two octants between (sin θ/λ) = 0.61 and 0.69 Å^{-1}. [b] Repeated measurements of the same reflection were averaged. [c] Weights chosen as $w = (\sigma^2(F_o^2))^{-1} = (\sigma_{count}^2(F_o^2) + (0.015F_o^2)^2)^{-1}$. [d] It was necessary to constrain $Y_{13} = Y_{23} = 0$ to achieve convergence.

Low-Temperature Neutron Diffraction Structure of 2. The crystal chosen for neutron diffraction was a diamond-shaped plate with a volume of 7.18 mm^3.

Crystal Data: a = 8.671 (2) Å, b = 16.049 (4) Å, c = 17.598 (5) Å, U = 2449(1) Å^3 (T = 20.0 (5) K). The specimen was mounted on an aluminum pin oriented along the crystallographic (010) direction. The sample was sealed under a helium atmosphere in an aluminum container and placed in a closed-cycle helium refrigerator[32] mounted on a four-circle diffractometer[33,34] at the Brookhaven High Flux Beam Reactor. A germanium(220) single-crystal monochromator was used to yield a neutron beam of wavelength 1.161 13 (20) Å based on KBr (a = 6.6000 Å at T = 298 K).[35] The temperature of the sample was maintained at 20.0 (5) K[36] during the experiment, and unit cell dimensions at this temperature were determined by a least-squares fit of the observed sin^2 θ values of 32 reflections (50° < 2θ < 63°).

Three-dimensional intensity data were obtained over one octant of reciprocal space with 2θ ≤ 107° [(sin θ/λ ≤ 0.69 Å^{-1}) by using θ/2θ step scans. A second octant was sampled for 90° ≤ 2θ ≤ 107°. The scan range was varied according to $\Delta 2\theta = (1.83 + 1.72 \tan \theta)°$ for the high-angle data (60° ≤ 2θ ≤ 107°) and $\Delta 2\theta$ = 2.8° for low-angle data. The step size was adjusted to give between 65 and 98 steps per scan, and

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Table III. Atomic Parameters for $[C_5Me_5Rh(H)_2(SiEt_3)_2]^a$

atom	x	y	z	U_{iso}
Rh	17358 (14)	18276 (7)	25000	47 (2)
Si	20723 (14)	9744 (7)	35930 (7)	54 (2)
C(1)	28576 (10)	-1234 (5)	34601 (5)	84 (1)
C(2)	32302 (10)	-5712 (5)	42114 (5)	104 (1)
C(3)	34445 (9)	14760 (5)	42986 (5)	87 (1)
C(4)	51268 (10)	15212 (6)	40330 (5)	126 (2)
C(5)	1894 (9)	8112 (5)	41245 (5)	84 (1)
C(6)	-10772 (10)	3591 (6)	36772 (5)	113 (1)
C(7)	-2321 (13)	27718 (7)	25000	70 (2)
C(8)	6951 (9)	29290 (5)	31606 (5)	67 (1)
C(9)	22161 (9)	31423 (5)	29083 (4)	66 (1)
C(10)	-19299 (14)	25857 (8)	25000	102 (2)
C(11)	1143 (10)	30041 (5)	39608 (4)	100 (1)
C(12)	35216 (10)	34669 (5)	33821 (5)	95 (1)
H(1)	8124 (36)	9800 (18)	25000	259 (7)
H(2)	33819 (33)	14006 (19)	25000	261 (7)
H(101)	-26035 (36)	31634 (21)	25000	363 (10)
H(102)	-22711 (25)	22310 (18)	20047 (15)	358 (6)
H(111)	-1133 (34)	36566 (13)	40957 (13)	338 (6)
H(112)	9362 (27)	27816 (17)	43795 (12)	313 (6)
H(113)	-9589 (25)	26662 (16)	40495 (13)	318 (6)
H(121)	34219 (29)	32862 (17)	39688 (12)	347 (6)
H(122)	46303 (23)	32483 (17)	31767 (15)	335 (6)
H(123)	35562 (28)	41453 (13)	33610 (16)	332 (6)
H(11)	38940 (25)	-1015 (14)	31020 (12)	264 (5)
H(12)	20120 (26)	-4876 (13)	31336 (12)	257 (5)
H(21)	42005 (28)	-2841 (15)	45024 (14)	324 (6)
H(22)	22639 (27)	-5672 (15)	46078 (13)	306 (5)
H(23)	35313 (29)	-12244 (14)	41205 (14)	307 (5)
H(31)	33697 (25)	11094 (14)	48257 (11)	255 (5)
H(32)	30263 (24)	20987 (12)	44520 (13)	252 (5)
H(41)	52267 (26)	18537 (17)	34965 (13)	335 (6)
H(42)	58728 (26)	18323 (18)	44451 (15)	369 (6)
H(43)	56059 (26)	9009 (15)	39375 (17)	359 (6)
H(51)	-2506 (25)	14006 (13)	43439 (13)	258 (5)
H(52)	4920 (24)	4472 (15)	46334 (11)	257 (5)
H(61)	-15539 (28)	7582 (16)	32335 (15)	335 (6)
H(62)	-20312 (25)	1670 (16)	40429 (14)	316 (6)
H(63)	-6454 (27)	-1990 (15)	33897 (16)	327 (6)

[a] Positional parameters ×10^5 and equivalent isotropic thermal parameters ×10^4.

counts were accumulated for approximately 1.7 s at each step, the exact time interval being determined by monitoring the incident beam intensity. The intensities of two monitor reflections were measured every 200 reflections and showed no significant variation over the course of data collection.

Integrated intensities were obtained with the first and last tenth of each scan taken as background. Lorentz factors, and absorption corrections ($\mu = 3.558$ cm^{-1}) calculated by means of numerical integration over a Gaussian grid of points,[37] were applied to yield squared structure factors, F_o^2, for 4212 reflections. Further details are given in Table II.

Initial coordinates for the non-hydrogen atoms were taken from the X-ray results, and after a few cycles of differential-synthesis refinement,[38] difference scattering-density maps revealed the positions of all hydrogen atoms. Least-squares refinements were carried out by a full-matrix procedure,[39] minimizing $\Sigma w(F_o^2 - (k^2F_c^2))^2$, with weights taken as $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = \sigma_{count}^2 + (0.015F_o^2)^2$. The final model included positional and anisotropic thermal parameters for all 39 atoms, a scale factor k, and four parameters describing an anisotropic type I extinction correction[40] with mosaic spread as defined by Nelmes and Thornley,[41] for a total of 338 variable parameters. The extinction was quite severe, the most significant correction being 0.52 dividing F_o^2 for the 1 10 0 reflection.

Neutron scattering lengths were taken to be $b_{Rh} = 0.593 \times 10^{-12}$, $b_{Si} = 0.4149 \times 10^{-12}$, $b_C = 0.6648 \times 10^{-12}$, and $b_H = -0.3741 \times 10^{-12}$ cm.[42] The refinement was terminated when the maximum shift/esd for positional and thermal parameters was less than 0.03. A difference synthesis computed at this stage was essentially featureless. Final indices of fit are included in Table II, while positional and equivalent isotropic thermal parameters for all atoms are given in Table III. Selected interatomic distances and bond angles are given in Table I.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters, observed and calculated structure factors, and complete bond distance and angle data (11 pages). Ordering information is given on any current masthead page.

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