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# THE SYNTHESIS AND STRUCTURE DETERMINATION OF A NOVEL $\eta^6$-ARENERHODIUM(III) COMPLEX, $[(Me_2SiC_6H_5)_4Rh_2H_2]$, AND THE SYNTHESIS OF $[(Me_2SiC_6H_5)_4Ir_2H_2]$ *

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## Summary

Reaction of $Me_2PhSiH$ (DMPS) with $[(indenyl)Rh(C_2H_4)_2]$, $[\{CODRhCl\}_2]$, or $[\{CODRh(OMe)\}_2]$ in the presence of benzoyl peroxide, gave $[(Me_2SiC_6H_5)_4Rh_2H_2]$, (**1a**); reaction of $[\{CODIr(OMe)\}_2]$ in the presence of benzoyl peroxide, gave $[(Me_2SiC_6H_5)_4Ir_2H_2]$ (**1b**) similarly. The X-ray structure of **1a** showed the molecule to be a centrosymmetric dinuclear complex, each rhodium being $\eta^6$-bonded to a phenyldimethylsilyl (Rh–C(phenyl) av. 2.33 Å) which was in turn $\sigma$-bonded to the other rhodium through the silicon (Rh–Si 2.294(6) Å). In addition each rhodium bore another $\sigma$-bonded $PhMe_2Si$ (Rh–Si 2.328(6) Å) and a hydride ligand. The rhodiums were 4.48 Å apart and not bonded. Complexes **1a** and **1b** were rather insoluble and inert..

## Introduction

Some years ago we reported on the dehydrogenative hydrosilylation of olefins (eq. 1). This reaction, together with the normal hydrosilylation (eq. 2), is well

$$2RCH{=}CH_2 + HSiR'_3 \rightarrow RCH{=}CHSiR'_3 + RCH_2CH_3 \qquad (1)$$

$$RCH{=}CH_2 + HSiR'_3 \rightarrow RCH_2CH_2SiR'_3 \qquad (2)$$

catalysed by a number of rhodium complexes, especially but not exclusively those with pentamethylcyclopentadienyl on the metal [1,2] and the mechanism has been explored [1]. Some iridium complexes also catalyse this reaction [3].

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* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to chemistry.

In our investigation of the mechanism we have examined the reactions of a variety of silanes and olefins with rhodium an diridium complexes. We found that reactions involving dimethylphenylsilane ($Me_2PhSiH$, DMPS) and rhodium or iridium complexes gave an unexpected result. That work forms the subject of this paper.

## Results and discussion

### *Synthesis and X-ray structure determination of* $[(Me_2SiC_6H_5)_4Rh_2H_2]$ *(**1a**)*

The rhodium complex $[(Me_2SiC_6H_5)_4Rh_2H_2]$ (**1a**) was initially synthesised by reaction of $[(\eta^5\text{-indenyl})Rh(C_2H_4)_2]$ [4] with DMPS. This reaction was undertaken in an attempt to prepare $[(\eta^5\text{-indenyl})Rh(H)_2(SiPhMe_2)_2]$ analogous to $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ (**2**) and its iridium counterpart [5,6].

When the indenylethene complex was irradiated with DMPS in benzene colourless crystals of a solid slowly precipitated. Owing to its extremely low solubility it was very difficult to carry out spectroscopic determinations. However, the IR spectrum showed a band, assigned to $\nu$(Rh–H) at 2102 $cm^{-1}$ and a weak signal could be seen in the $^1H$ NMR spectrum at $\delta$ −13.7 ppm (d, $J$(Rh–H) 42 Hz). Both of these are consistent with the presence of a terminal hydride. Neither the IR nor the NMR spectra showed any bands characteristic of the presence of an indenyl ligand.

One of the crystals was used for an X-ray determination which revealed the structure shown in Fig. 1; key bond lengths and angles are in Table 1. The indenyl

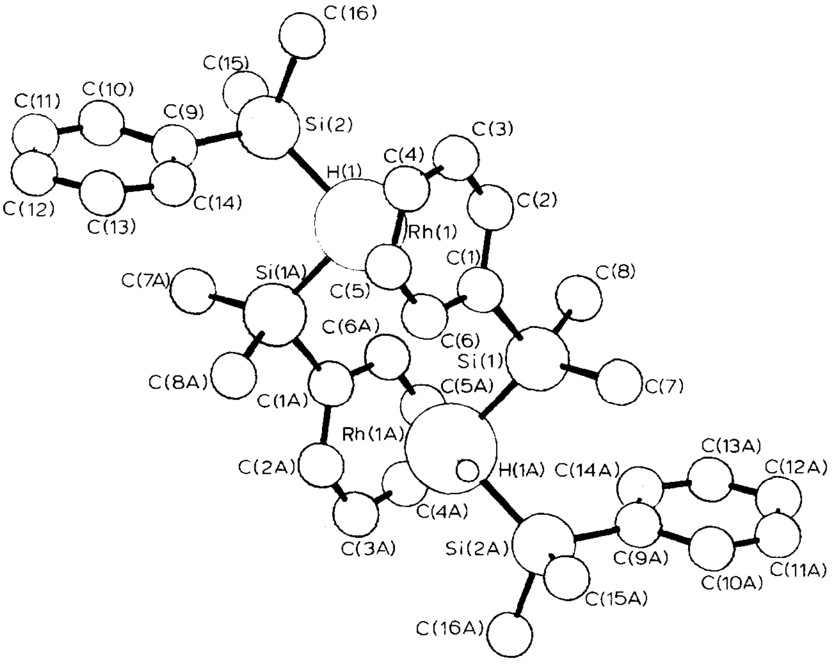

Fig. 1. View of the molecular structure of $[(Me_2SiC_6H_5)_4Rh_4H_4]$, hydrogens omitted except on rhodium.

TABLE 1

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $[(Me_2PhSi)_4Rh_2H_2]$

| | | | |
|---|---|---|---|
| Rh(1)–Rh(1A) | 4.480(2) | Rh(1)–Si(1A) | 2.294(6) |
| Rh(1)–Si(2) | 2.328(6) | | |
| Rh(1)–C(1) | 2.38(2) | Rh(1)–C(2) | 2.29(2) |
| Rh(1)–C(3) | 2.32(2) | Rh(1)–C(4) | 2.33(3) |
| Rh(1)–C(5) | 2.34(2) | Rh(1)–C(6) | 2.31(2) |
| | av. Rh(1)–C(phenyl) 2.33 Å | | |
| Si(1)–C(1) | 1.89(2) | Si(1)–C(7) | 1.85(2) |
| Si(1)–C(8) | 1.86(2) | Si(2)–C(9) | 1.85(2) |
| Si(2)–C(15) | 1.86(2) | Si(2)–C(16) | 1.88(2) |
| Si(2)–Rh(1)–Si(1A) | 90.9(2) | C(1)–Si(1)–Rh(1A) | 107.4(7) |
| C(7)–Si(1)–Rh(1A) | 123.5(7) | C(8)–Si(1)–Rh(1A) | 112.2(7) |
| C(1)–Si(1)–C(7) | 100.1(9) | C(1)–Si(1)–C(8) | 105.8(9) |
| C(7)–Si(1)–C(8) | 105.9(9) | C(15)–Si(2)–Rh(1) | 117.8(7) |
| C(16)–Si(2)–Rh(1) | 110.6(7) | C(9)–Si(2)–Rh(1) | 114.9(7) |
| C(15)–Si(2)–C(16) | 102.1(9) | C(15)–Si(2)–C(9) | 105.7(9) |
| C(16)–Si(2)–C(9) | 104.1(9) | | |

ligand and the ethenes have all gone and the data show that the molecule contains two rhodiums and is centrosymmetric about a point midway between them. The rhodiums are 4.48 Å apart, too far for there to be any significant interaction [7].

Each rhodium is $\eta^6$-bonded to one phenyl of a $PhSiMe_2$ ligand which has a Si–Rh $\sigma$-bond to the other rhodium which is, in turn, $\eta^6$-bonded to the phenyl bearing $SiMe_2$ bonded to the first rhodium. In addition each rhodium has a $\sigma$-bond to the silicon of another $SiPhMe_2$ ligand which is not involved in $\pi$-bonding. The rhodium is bonded equivalently to the six carbons of the one phenyl (within the accuracy of the determination), the average Rh–C(phenyl) distance being 2.33 Å. Although this is longer than the corresponding distance from the $C_5Me_5$ ring carbons to the metal in the rhodium(V) complex, $[C_5Me_5Rh(H)_2(SiEt_3)_2]$, (**2**), 2.283(9) Å [5], the difference is not significant.

The Rh–Si bonds at 2.294(6) (to the Si carrying the $\eta^6$-bonded phenyl), and 2.328(6) Å to the other phenyl are significantly shorter than those in **2**, 2.379(2) Å. These data suggest that complex **1a** is rather tightly bound..

The angle Si(2)–Rh(1)–Si(1A) in **1a** is small (90.9°). By comparison, the Si–Rh–Si angle in **2** is 107.9°; the difference probably reflects the different sizes of the substituents about the two silyls in the two molecules as well as the fact that in **1a** the metal also ligands to an $\eta^6$-arene and a hydride. In fact the angles X-Rh–Si(1′) and X-Rh–Si(2) (where Rh–X is the vector from the metal to the centre of the $\eta^6$-ring) are 129 and 132°, respectively. A hydrogen atom was located at about the correct distance (1.6 Å) from each rhodium atom.

For comparison with arenerhodium comlexes [7] which have had their structures determined by X-ray methods, the rhodium tetraphenylborate complexes, $[\{(MeO)_3P\}_2Rh(\eta^6\text{-}C_6H_5BPh_3)]$ (**3a**) [8], $[(Ph_2PCH_2CH_2PPh_2)Rh(\eta^6\text{-}C_6H_5BPh_3)]$ (**3b**) [9], and particularly the dinuclear dicationic complex $[\{Rh(\eta^6\text{-}C_6H_5PhPCH_2CH_2PPh_2)\}_2]^{2+}$, (**4**), are especially relevant.

In complex **4** one rhodium is $\eta^6$-bonded to the phenyl of a diphos ligand which also chelates the other rhodium [10]. The Rh–Rh distance (4.27 Å) is actually shorter than that in **1a**, but the Rh–C(phenyl) distance is the same. Complexes **3a** and **3b** are mononuclear and the structure determinations were sufficiently precise to show deformations from planarity in the $\eta^6$-phenyl ring; in each case the average Rh–C distances (2.34 Å in **3a** and 2.336 Å in **3b**) were very close to those found for **1a**.

Another complex structurally relevant to **1a** is $[(\eta^6\text{-}C_6H_5SiMe_3)Cr(CO)_3]$ [11].

Once the structure of complex **1a** had been determined, more rational syntheses could be applied. Thus, reaction of the much simpler to prepare $[\{CODRhCl\}_2]$ (COD = 1,5-cyclooctadiene) with DMPS in toluene in air at 20 ° C gave crystals of complex **1a** directly in good yield. Reaction of the two components in dichloromethane under nitrogen gave no product.

### *Synthesis of $[(Me_2SiC_6H_5)_4Ir_2H_2]$ (1b)*

A related route, reaction of $[\{CODM(OMe)\}_2]$ with DMPS in dichloromethane was used to prepare both **1a** and its iridium analogue, $[(Me_2SiC_6H_5)_4Ir_2H_2]$ (**1b**). No reaction occurred when the reactants were mixed under nitrogen, but a low yield of **1b** was obtained when the reaction was carried out in air. It was found that these reactions were considerably promoted by addition of benzoyl peroxide. This suggests that radicals may well play a vital role.

Attempts to exchange the $\eta^6$-arene for another (hexamethylbenzene, or benzene) were not successful. Thus **1b** was also the product when $[\{CODIr(OMe)\}_2]$ was treated with DMPS in the presence of benzene or hexamethylbenzene.

Both **1a** and **1b** were very inert; thus the iridium complex **1b** was recovered unchanged after treatment with CO (1 atm, 25 ° C) or $PPh_3$ (benzene, 80 ° C, 4 days). The complex reacted with electrophiles (e.g., perchloric acid), but with decomposition. When $[\{CODIr(OMe)\}_2]$ was treated with DMPS and *o*-phenanthroline in the presence of benzoyl peroxide a blue solid, formulated as $[\{Ir(Me_2PhSi)(o\text{-phen})\}_n]$, was obtained. This showed no $\nu$(Ir–H) in the IR but was otherwise too insoluble for spectroscopic characterisation.

## Experimental

### *Syntheses of $[(Me_2SiC_6H_5)_4Rh_2H_2]$ (1a)*

(i) A solution of $[(\eta^6\text{-indenyl})Rh(C_2H_4)_2]$ [4] (50 mg, 0.18 mmol) and DMPS ((0.2 $cm^3$) in benzene (0.5 $cm^3$) was irradiated under nitrogen in a sealed tube (Hanovia medium pressure lamp; 14 h, 20 ° C). Colourless crystals of **1a** slowly formed at the bottom of the tube. These were filtered off, washed with pentane and dried. Yield, 58 mg, 85%. One of them proved suitable for the X-ray determination. Analysis: Found: C, 51.8; H, 6.3. $C_{32}H_{46}Rh_2Si_4$ calcd.: C, 51.3; H, 6.2%. Ir $\nu$(Rh–H) 2101 $cm^{-1}$ (KBr disc). $^1H$ NMR spectrum ($CDCl_3$) $\delta$ −13.8 (d, *J*(Rh–H) 42 Hz), 0.3, 0.4 (Me), 7.0–7.7 (aromatic); sample very poorly soluble and slowly decomposes in solution.

(ii) A solution of $[\{CODRhCl\}_2]$ (0.15 g, 0.27 mmol) and DMPS (1 $cm^3$) in toluene (4 $cm^3$) was allowed to stand in air (ca. 2 h, 20 ° C). Colourless crystals of **1a** (165 mg, 83%) were obtained.

### *Synthesis of $[(Me_2SiC_6H_5)_4Ir_2H_2]$ (1b)*

The complex $[\{CODIr(OMe)\}_2]$ (0.4 g, 0.6 mmol) was added to a solution of DMPS (1 $cm^3$) and benzoyl peroxide (5 mg, 0.02 mmol) in dichloromethane (20 cm$^3$). The solution turned red, hydrogen was evolved, and white solid complex **1b** slowly precipitated. This was filtered off (after 6 h at 25 °C); yield, after washing and drying, 0.4 g, 72%. Analysis: Found: C, 41.5; H, 4.8. $C_{32}H_{46}Ir_2Si$ calcd.: C, 41.5; H, 5.0%. IR $\nu$(Ir–H): 2225 cm$^{-1}$ (Nujol mull). The complex was too insoluble for NMR spectroscopy.

### *X-Ray structure analysis of* $[(Me_2SiC_6H_5)_4Rh_2H_2]$ *(1a)*

*Crystal data.* $C_{32}H_{46}Rh_2Si_4$, $M$ 748.87, monoclinic, $a$ 11.755(15), $b$ 10.708(8), $c$ 12.675(13) Å, $\beta$ 91.12(9)°, $U$ 1595 Å$^3$, $Z = 2$, $D_c$ 1.56 g cm$^{-3}$, $F(000) = 767.91$, space group $P2_1/n$ from systematic absences. Mo-$K_\alpha$ radiation (graphite monochromator), $\lambda$ 0.71069 Å, $\mu$ 11.87 cm$^{-1}$.

Unit cell parameters were obtained from a least-squares fit of the setting angles of 25 well-centred reflections. X-Ray reflection data in the range $3.5 < 2\theta < 42°$ were collected on a Nicolet R3M four-circle diffractometer from a prismatic crystal measuring approximately 0.1 × 0.15 × 0.4 mm. 899 Independent reflections with $I > 4\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects.

The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-diagonal matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.0006F_i^2]$ to a final $R$ value of 0.0643 ($R_w = 0.0570$). All the non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters.

Most of the hydrogen atoms were located from a low angle difference Fourier map. The carbon-bonded hydrogens were constrained to ride on their adjacent heavy atom with calculated bond lengths and angles; all the hydrogen (isotropic) vibration parameters were fixed at 1.2 times the $U_{eq}$ values for their respective

TABLE 2

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å$^2 \times 10^3$)

| Atom | x | y | z | U [a] |
|---|---|---|---|---|
| Rh(1) | 4276(1) | 6810(2) | 5565(1) | 36(1) |
| Si(1) | 6920(5) | 4649(5) | 5184(4) | 39(2) |
| Si(2) | 2945(5) | 8381(5) | 5246(4) | 39(2) |
| C(1) | 6015(18) | 5760(16) | 5968(15) | 37(8) |
| C(2) | 6163(16) | 7088(18) | 5976(15) | 52(8) |
| C(3) | 5587(20) | 7884(19) | 6610(17) | 50(9) |
| C(4) | 4801(22) | 7391(26) | 7280(20) | 62(11) |
| C(5) | 4528(20) | 6124(22) | 7303(17) | 50(9) |
| C(6) | 5121(16) | 5328(21) | 6649(14) | 38(8) |
| C(7) | 8033(18) | 4266(20) | 6186(15) | 62(9) |
| C(8) | 7631(17) | 5627(21) | 4175(15) | 60(9) |
| C(9) | 1504(15) | 8053(21) | 5736(15) | 45(8) |
| C(10) | 475(14) | 8444(17) | 5257(14) | 33(7) |
| C(11) | −536(14) | 8220(19) | 5642(18) | 49(8) |
| C(12) | −641(19) | 7627(21) | 6609(17) | 54(9) |
| C(13) | 313(18) | 7312(19) | 7154(17) | 53(9) |
| C(14) | 1384(18) | 7470(19) | 6730(17) | 51(9) |
| C(15) | 2735(17) | 8927(18) | 3865(12) | 47(8) |
| C(16) | 3380(18) | 9861(17) | 5946(15) | 51(8) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

neighbours. The rhodium-bonded hydrogen was initially held fixed at the position found from its Fourier map, but its $U$ was refined. The parameter shifts (except for those involving H(1)) obtained on the final cycle of refinement were in all cases less than 0.1 of the corresponding e.s.d.'s. A final difference Fourier synthesis showed no peak higher than 0.7 e $Å^{-3}$ and none which could be interpreted as an atom. The final analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL suite of crystallographic programs was used throughout [12]. Selected bond lengths and angles are given in Table 1 and atomic coordinates in Table 2.

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## References

1 A. Millan, E. Towns, and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1981) 673; A. Millan, M.-J. Fernandez, P.O. Bentz, and P.M. Maitlis, J. Mol. Catal., 26 (1984) 89.
2 A.J. Cornish, M.F. Lappert, G.L. Filatov, and T.A. Nile, J. Organomet. Chem., 177 (1977) 153; H.M. Dickers, R.N. Haszeldine, L.S. Malkin, A.P. Mather and R.V. Parish, J. Chem. Soc., Dalton Trans., (1980) 308; A. Onopchenko, E.T. Sabourin, and D.L. Beach, J. Org. Chem., 49 (1984) 3389. See also G. Kuncova and V. Chvalovsky, Coll. Czech. Chem. Commun., 40 (1980) 2240; Y. Seki, E. Takeshita, K. Kawamoto, S. Murai, and N. Sonoda, Angew. Chem. Int. Ed. Engl., 19 (1980) 928; see also C.L. Randolph and M.S. Wrighton, J. Am. Chem. Soc., 108 (1986) 3366.
3 L.A. Oro, M.J. Fernandez, N.A. Esteruelas, and M.S. Jimenez, J. Mol. Catal., 37 (1986) 151; M.J. Fernandez, M.A. Esteruelas, M.S. Jimenez, and L.A. Oro, Organometallics, 5 (1986) 1519.
4 P. Caddy, M. Green, E. O'Brien, L.E. Smart, and P. Woodward, J. Chem. Soc., Dalton Trans., (1980) 962; H.E. Hosseini and J.F. Nixon, J. Less Common Metals, 61 (1978) 107.
5 M.J. Fernandez, P.M. Bailey, P.O. Bentz, J.S. Ricci, T.F. Koetzle, and P.M. Maitlis, J. Am. Chem. Soc., 106 (1984) 5458; M.-J. Fernandez and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1982) 310.
6 M.-J. Fernandez and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1984) 2063; M.-J. Fernandez and P.M. Maitlis, Organometallics, 2 (1983) 164; J.S. Ricci, T.F. Koetzle, M.-J. Fernandez, P.M. Maitlis, and J.C. Green, J. Organomet. Chem., 299 (1986) 383.
7 P.M. Maitlis, Chem. Soc. Revs., 10 (1981) 1; R.P. Hughes, in G. Wilkinson, F.G.A. Stone and E. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, vol. 5, p. 488 and ref. therein.
8 M.J. Nolte, G. Gafner, and L.M. Haines, J. Chem. Soc., Chem. Commun., (1969) 1406; M.J. Nolte and G. Gafner, Acta Crystallogr., Sect. B, 30 (1974) 738.
9 P. Albano, M. Aresta, and M. Manassero, Inorg. Chem. 19 (1980) 1069.
10 J. Halpern, D.P. Riley, A.S.C. Chan, and J.J. Pluth, J. Am. Chem. Soc., 99 (1977) 8055; J. Halpern, A.S.C. Chan, D.P. Riley, and J.J. Pluth, Adv. Chem. Ser., 173 (1979) 16.
11 D. van der Helm, Cryst. Struct. Commun., 8 (1979) 899.
12 G.M. Sheldrick, SHELXTL System of Computing Programs, University of Cambridge, 1976.