Dihydrido(pentamethylcyclopentadienyl)bis(triethylsilyl)iridium(V) and Related Triphenylsilyl-rhodium(V) and -iridium(V) Complexes

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Reaction of $[\{(C_5Me_5)Ir\}_2Cl_4]$, (1b), with triethylsilane gave $[(C_5Me_5)Ir(H)_2Cl(SiEt_3)]$,(4b), which, under more drastic conditions, reacted further to give $[(C_5Me_5)Ir(H)_2(SiEt_3)_2]$, (5b). Complex (4b) was also formed by reaction of $SiEt_3H$ with the di-μ-hydrido-complex $[\{(C_5Me_5)Ir\}_2(H)_2Cl_2]$; this is an example of the highly unusual oxidative addition Ir^{III} to Ir^{V} (d^6 to d^4). Reaction of (1b) with triphenylsilane gave $[(C_5Me_5)Ir(H)_2Cl(SiPh_3)]$, analogous to (4b). By contrast, $[\{(C_5Me_5)Rh\}_2Cl_4]$ reacted with triphenylsilane to give $[(C_5Me_5)Rh(H)_2(SiPh_3)_2]$ and $[(C_5Me_5)Rh(H)_2(SiPh_3)(SiPh_2Cl)]$. These reactions are compared and mechanistic schemes for the formation of the various products are proposed, based upon sequences of oxidative addition and reductive elimination reactions.

We recently reported [1] the synthesis of dihydrido(pentamethylcyclopentadienyl)bis(triethylsilyl)rhodium, $[(C_5Me_5)Rh(H)_2(SiEt_3)_2]$, (5a), by reaction of $[\{(C_5Me_5)Rh\}_2Cl_4]$, (1a), with triethylsilane. The structure of the complex has now been fully defined with the help of an *X*-ray and a low-temperature neutron diffraction study. These showed the expected geometry, with the two triethylsilyl groups and the hydrides *trans* in the base of a square pyramid which was itself capped by the C_5Me_5 ligand.[2] As we have published in a preliminary communication, $[\{(C_5Me_5)Ir\}_2Cl_4]$, (1b), reacted similarly to the rhodium analogue to give, eventually, $[(C_5Me_5)Ir(H)_2(SiEt_3)_2]$, (5b).[3] There are some interesting and instructive differences between the reactions of (1a) and of (1b) with triethylsilane and also with triphenylsilane, details of which we present here. Pentamethylcyclopentadienyl-rhodium and -iridium complexes [4] and transition metal silyl complexes [5] have been reviewed.

Results and Discussion

In the case of the reaction of the rhodium complex (1a) with triethylsilane, we were able to detect the intermediacy of the dinuclear mono-μ-hydrido-complex (2a), but of no silicon–rhodium-containing compounds other than the end-product (5a). The reaction with the iridium complex (1b) proceeds similarly, and indeed we have evidence concerning a further dinuclear intermediate (see below). In this case, however, the first iridium–silicon containing-complex that can be detected and isolated is the chloro-dihydridomonosilyl complex (4) (Scheme 1). The Rh analogue of (4) was not detected in the reaction of (1a) with triethylsilane.

The complex (4) was formed readily and in good yield when (1b) and triethylsilane were reacted at room temperature in dichloromethane. The complex was not air-sensitive but was readily degraded by moisture. It was identified by microanalysis and particularly by the 400-MHz ^1H n.m.r. spectrum, the integrals of which showed the presence of two hydrides but of only one triethylsilyl ligand per C_5Me_5. We presume that for steric reasons the bulky chloro and triethylsilyl ligands will prefer to be *trans*, and that therefore the hydrides will also be *trans*, as in (5a). The single ν(Ir–H) band at 2 135 cm^{-1} in the i.r. spectrum agrees with this geometry.

Complex (4) was also formed directly by reaction of triethylsilane with the di-μ-hydride (3); the reaction was monitored by n.m.r. spectroscopy and, in dichloromethane, it proceeded essentially quantitatively and gave no other products. The di-μ-hydride (3) has a characteristic very dark blue colour and although we have not been able to quantify our visual impression further, the appearance of dark green colours in, for example the reaction leading to (5b) (see Experimental section), is consistent with the intermediacy of (3) also in the through reaction.

If we accept that the formal oxidation state of the iridium is +3 in (3) and +5 in (4), the reaction shown below corresponds to the oxidative addition d^6–d^4 at each iridium centre.

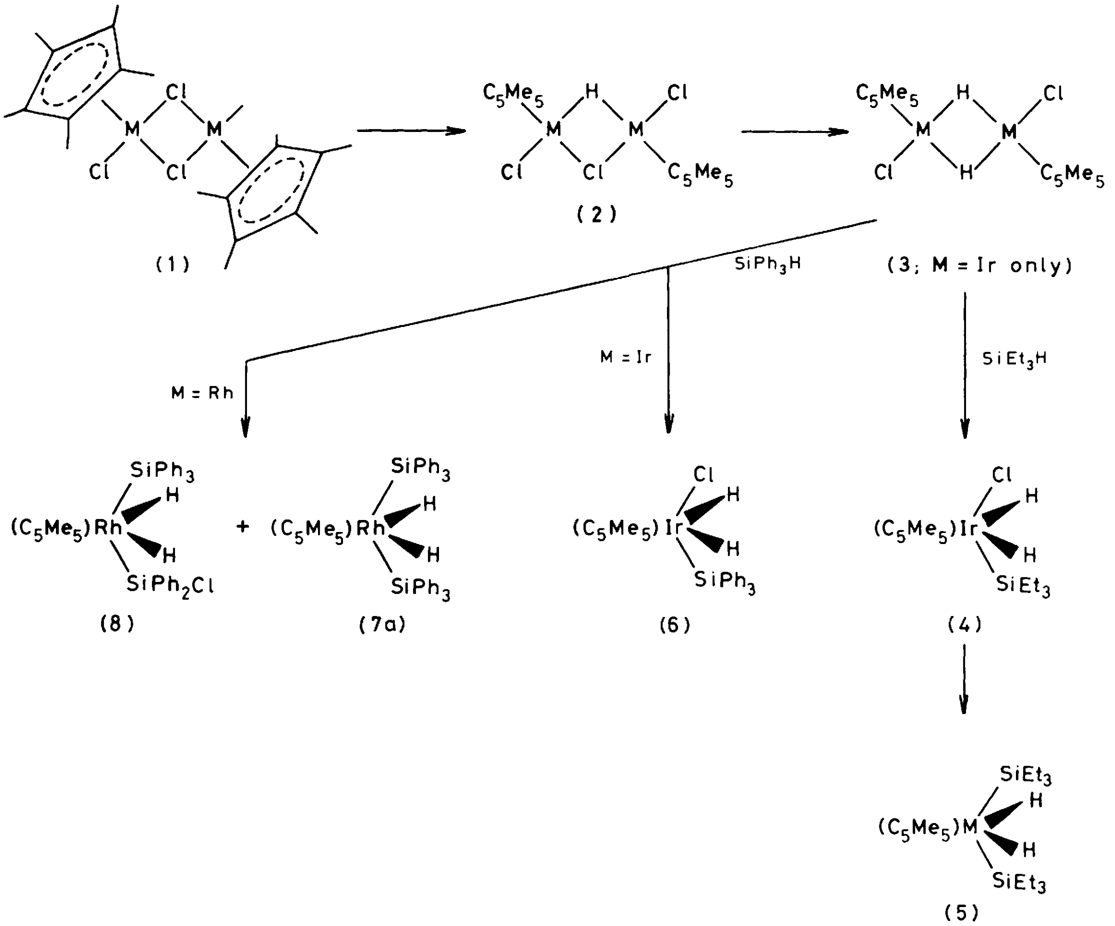
$$\underset{(3)}{[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_2Cl_2]} + 2SiEt_3H \longrightarrow \underset{(4)}{2[(C_5Me_5)Ir(H)_2Cl(SiEt_3)]}$$

While there are precedents elsewhere for a d^6–d^4 oxidative addition, for example Os^{II}—Os^{IV},[6] Ru^{II}–Ru^{IV},[7] and W^0–W^{II},[8] this is a most unusual reaction for iridium, in particular with Si–H as addend since even Ir^{I} sometimes only adds Si–H with reluctance.[9] It should however be emphasised that the assignment of such a high oxidation state to the metal in (4) and its analogues is very much a formalism. As is the case for (5a), the complexes show few if any of the properties normally associated with the +5 state (*e.g.*, strongly oxidising behaviour, polar bonds, *etc.*).[2]

When the chloro-dihydrido-monosilyl complex (4) [or (1b) or (3)] was reacted with triethylsilane under more forcing conditions (base and or higher temperature), the dihydrido-bis(triethylsilyl) complex (5b) was formed. The isolated yield was rather low (30—40%), but this reflects the difficulty of purifying the compound more than an inherent difficulty in the reaction. Another triethylsilyl iridium hydride complex was the significant by-product here and from the relative intensities of the pentamethylcyclopentadienyl, the ethyl, and the hydride ligands, we tentatively suggest that this may be the monohydride, $[(C_5Me_5)IrH(Cl)(SiEt_3)_2]$.

Like the rhodium complex (5a), the iridium analogue (5b) was a very stable and rather inert complex which, when pure, crystallised from hexane in large colourless crystals. The structure proposed for (5b) arises from its n.m.r. spectra, especially the integrals of the proton spectra, which indicate clearly the presence of two hydrides and two triethylsilyl ligands per C_5Me_5 group. By analogy to (5a) the structure shown is proposed. Preliminary data from *X*-ray and neutron diffraction determinations indicate that the two complexes are isostructural.[10]

The most successful of a number of experiments designed to extend these reactions to other silanes has been the reaction of (1b) with triphenylsilane which, in acetonitrile, gave a good



Scheme 1. (a, M = Rh; b, M = Ir)

yield of (6), the triphenylsilyl analogue of (4). Attempts to push this reaction further, to obtain $[(C_5Me_5)Ir(H)_2(SiPh_3)_2]$, (7b), were not successful even though (6) was a very reactive compound (for example, it was decomposed in dichloromethane solution to give benzene).

By contrast, the reaction of the rhodium complex (1a) with triphenylsilane gave two complexes, usually in a mixture which was very difficult to separate. From samples which were 70% or better pure, it was possible to show that the one, obtained in higher yield in hydrocarbon solvents, was indeed the bis(triphenylsilyl) dihydride, (7a). This was again largely derived from the 400-MHz ^1H n.m.r. spectrum which showed a high-field doublet at δ -11.50 with $J(Rh-H)$ 34 Hz, and which integrated in agreement with the formula shown.

From the microanalysis it was clear that this complex was contaminated with a small amount of a chloride-containing complex, (8). This was formed in better yield when the reaction between (1a) and triphenylsilane was carried out in 1,2-dichloroethane solution and was rather easier to purify. From the microanalysis, the solution molecular weight, and a careful analysis of the 400-MHz ^1H and the 100-MHz ^{13}C n.m.r. spectra, which showed the presence of two different types of phenyls in the approximate ratio of 3 : 2, the complex is formulated as shown, with two hydrides, one triphenylsilyl, and one chlorodiphenylsilyl ligand.

We do not know how (8) is formed but, in view of the formation of benzene when complex (6) was reacted with chlorinated solvents, it is possible that it arises from (7a) by a similar reaction. Although a direct analogue of such a reaction is not known, two related ones have been reported,[5,11,12] as shown below. These reactions indicate that substitution at the

$$[(H_3Ge)Mn(CO)_5] + CCl_4 \longrightarrow [(Cl_3Ge)Mn(CO)_5] + CHCl_3$$

$$[(Ph_3Si)Mn(CO)_5] + Cl_2 \longrightarrow [(Cl_xPh_{3-x}Si)Mn(CO)_5]$$

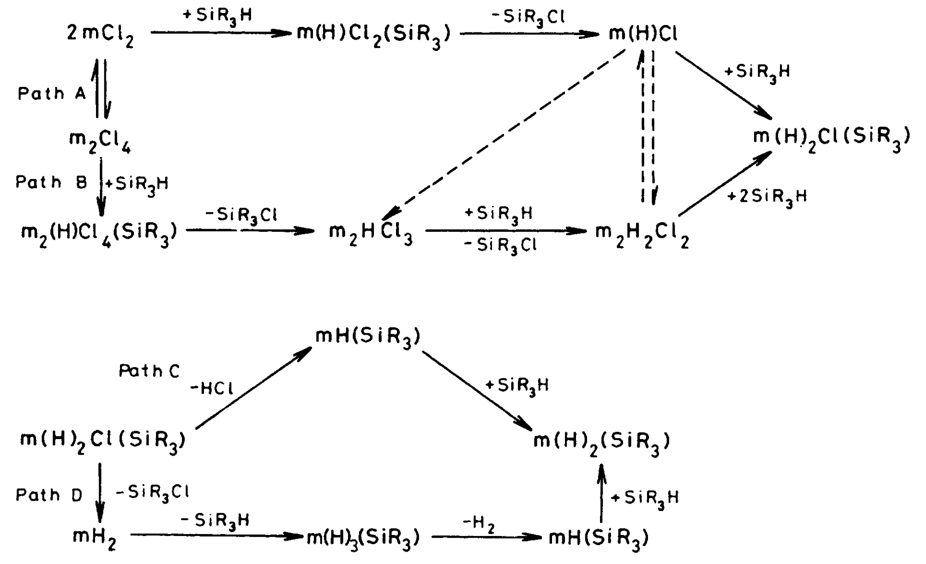
Group 4 centre without cleavage of the element-metal bond is quite possible if the latter is inert enough.

Conclusions

We may therefore summarise, (*i*) that the rhodium and the iridium complexes (1a) and (1b) react with R_3Si-H along similar paths, (*ii*) that the rhodium intermediates are more labile, react more easily, and hence are more difficult to detect than their iridium analogues, and (*iii*) that triphenylsilane reacts less readily than triethylsilane to give the dihydrido-disilyl complexes.

The overall reaction sequences that we suggest for the formation of the various hydrido-silyl complexes are shown in Scheme 2. The reactions are seen as oxidative additions of Si–H followed, initially, by reductive eliminations of Si–Cl, until the stage of (3) or its equivalent is reached.

A further oxidative addition of Si–H to this then gives (4). The path from here to (5) probably involves reductive elimination of HCl followed by oxidative addition of a further Si–H (path C). (Alternatively, this intermediate may reductively eliminate Si–Cl, and then add more Si–H, eliminate H_2, and readd a further Si–H to give the dihydrido-disilyl



Scheme 2. m = $(C_5Me_5)Rh$ or $(C_5Me_5)Ir$

complex, path D.) It is quite plausible that the reductive elimination of HCl (or Si–Cl) is more difficult for iridium than for rhodium (reflecting the greater stabilities of higher oxidation states in the 5*d* compared with the 4*d* series). This would explain the relatively ready formation of (4) and (6) on the one hand and (5a) and (7a) on the other.

Two distinct paths to (3) (or its equivalent) are possible starting from (1). In path A the reactions proceed *via* highly reactive mononuclear intermediates formed by breaking chloride bridges in (1) and then replacing a chloride by hydride. The observed dinuclear μ-hydride intermediates must then arise from reversible side-reactions. Alternatively, as in path B, the first two oxidative addition–reductive elimination sequences may proceed at dinuclear centres giving the observed μ-hydrides directly.

We have previously noted, in investigations using such complexes as hydrogenation catalysts, that the more μ-hydrides that were present the poorer was the activity of the complex. Thus, for example, the tri-μ-hydrido-di-iridium complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-}H)_3]^+$ has zero activity and that of (3) is also low.[13] Such di- and tri-μ-hydrido-complexes have not been obtained or detected for the rhodium complexes. The relative stability and lack of reactivity of these μ-hydrides may account for their appearance in these reactions too and may also account for the lower reactivity of the iridium compared to the rhodium systems.

Experimental

All reactions were run under a protective blanket of nitrogen even though neither the reactants nor the products were appreciably air-sensitive. Microanalyses were carried out by the University of Sheffield Microanalytical Service; ^{1}H and ^{13}C n.m.r. spectra were run on a Bruker WH-400 spectrometer at 400 and 100 MHz respectively.

Chlorodihydrido(pentamethylcyclopentadienyl)triethylsilyl-iridium, (4).—A solution of complex (1b) (0.50 g, 0.62 mmol) and triethylsilane (2 cm^3, 12.6 mmol) in dichloromethane (5 cm^3) was stirred (5 min at 20 °C). The solution turned yellow and gas (hydrogen) was given off (subsequent experiments showed that the hydrogen was formed by interaction with wet solvent and that when the solvent was quite dry this was not observed). The dichloromethane solvent was then removed *in vacuo*, and the resultant oil cooled (−78 °C) to give a yellow solid which was washed with cold hexane to leave crystals of (4) (0.42 g, 70%). The solid was rather moisture-sensitive (Found: C, 38.2; H, 6.7; Cl, 8.1. $C_{16}H_{32}ClIrSi$ requires C, 40.0; H, 6.7; Cl, 7.4%). I.r.: ν(Ir–H) 2 135 and ν(Ir–Cl) 305 cm^{-1}. ^{1}H N.m.r. (CD_2Cl_2): δ −12.60 (s, 2 H, IrH_2), 0.80 [q, *J*(H–H) 7.5 Hz, 6 H, $SiCH_2$–], 0.94 [t, *J*(H–H) 7.5 Hz, 9 H, $SiCH_2CH_3$], and 1.91 (s, 15 H, C_5Me_5).

The same complex (4) was also formed, essentially quantitatively as monitored by ^{1}H n.m.r. spectroscopy, when an excess of triethylsilane was reacted with the dinuclear di-μ-hydrido-complex (3)[14] in dichloromethane (30 min at 25 °C); this reaction also occurred (but at 80 °C, and in the presence of triethylamine) in benzene as solvent. However, under these conditions further reaction to give the bis-triethylsilyl complex (5b) also took place (see below).

Dihydrido(pentamethylcyclopentadienyl)bis(triethylsilyl)-iridium, (5b).—A solution of complex (1b) (0.50 g, 0.62 mmol), triethylsilane (2 cm^3, 12.6 mmol), and triethylamine (2 cm^3) in benzene (10 cm^3) was refluxed (15 min). The solution turned first green and then yellow. It was then allowed to cool, triethylammonium chloride was filtered off, and the solvent and other volatiles were removed *in vacuo*. An oil containing the desired products but contaminated with various organosilicon compounds remained; the organosilicon compounds were removed by washing with cold methanol to leave a white solid, which was further purified by chromatography in hexane on Florisil to give colourless crystals of (5b) (250 mg, 30%). The complex was also formed (40% yield) when the dinuclear di-μ-hydride (3) was refluxed (1 h) in benzene with triethylsilane and triethylamine and worked-up in the same manner as indicated above [Found: C, 47.1; H, 8.5%; *M* (osmometric in toluene), 551. $C_{22}H_{47}IrSi_2$ requires C, 47.2; H, 8.4%; *M*, 559]. I.r. (cyclohexane): ν(Ir–H) 2 160br cm^{-1}. U.v. (cyclohexane): $\lambda_{max.}$ 222 (ε 3.2 × 10^4) and 248(sh) nm (1.5 × 10^4 dm^3 mol^{-1} cm^{-1}). ^{1}H N.m.r. ($CDCl_3$): δ −17.40 (s, 2 H, IrH_2), 0.67 [q, *J*(H–H) 8 Hz, 12 H, $SiCH_2$–], 0.82 [t, *J*(H–H) 8 Hz, 18 H, $SiCH_2CH_3$], and 1.97 (s, 15 H, C_5Me_5). ^{13}C N.m.r. ($CDCl_3$): δ 8.81 ($SiCH_2CH_3$), 9.81 (s, $SiCH_2$–), 10.48 (s, C_5Me_5), and 97.65 (s, C_5Me_5).

Chlorodihydrido(pentamethylcyclopentadienyl)triphenylsilyliridium, (6).—Triphenylsilane (1.5 g, 5.7 mmol) and complex (1b) (0.5 g, 0.62 mmol) were stirred (30 min at 20 °C) in acetonitrile (25 cm^3). The solution turned yellow and a yellow precipitate formed; this was filtered off, washed and dried to give essentially pure complex (6) (0.5 g, 64%) (Found: C, 53.3; H, 5.2; Cl, 5.3. $C_{28}H_{32}ClIrSi$ requires C, 53.9; H, 5.1; Cl, 5.7%). I.r.: ν(Ir–H) 2 100 and 2 140 * and ν(Ir–Cl) 305 cm^{-1}. ^{1}H N.m.r. (CD_2Cl_2): δ −11.65 (s, 2 H, IrH_2), 1.62 (s, 15 H, C_5Me_5), 7.2—7.4 (m, 9 H, Si–Ph, H_m and H_p), 7.6 [dd, 6 H, H_o, $J(H_o–H_m)$ 7, $J(H_o–H_p)$ 1.5 Hz]. The complex slowly decomposed on standing in dichloromethane to give benzene as shown by g.c.m.s. analysis.

Reactions of Complex (1a) *with Triphenylsilane to give* (7a) *and* (8).—A solution of complex (1a) (0.3 g, 0.48 mmol) and triphenylsilane (1.5 g, 5.7 mmol) in 1,2-dichloroethane (50 cm^3) was refluxed (1 h) to give a brown solution. This was then concentrated (to *ca.* 5 cm^3) *in vacuo* and chromatographed on Florisil in hexane to remove organosilicon compounds, and in dichloromethane to elute the complexes. Removal of dichloromethane from this fraction left a white solid, which was washed with methanol and acetonitrile and then rechromatographed on Florisil in benzene. This gave a white solid (240 mg) which n.m.r. spectroscopy showed to contain more than 90% of a single material, identified as (8) [Found: C, 66.9; H, 5.8; Cl, 5.3%; *M* (osmometric in toluene), 707. $C_{40}H_{42}ClRhSi_2$ requires C, 67.0; H, 5.9; Cl, 4.9%; *M*, 717]. I.r.: ν(Rh–H) 2 000 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ −11.17 [d, J(Rh–H) 35 Hz, 2 H, RhH_2], 1.45 (s, 15 H, C_5Me_5), 7.05 [m, 4 H, $SiPh_2Cl$, H_m, $J(H_m–H_p)$ 7.5 Hz], 7.06 (m, 2 H, $SiPh_2Cl$, H_p), 7.12 (m, 9 H, $SiPh_3$, H_m and H_p), 7.37 [m, 4 H, $SiPh_2Cl$, H_o, $J(H_o–H_m)$ 7.7, $J(H_o–H_p)$ 1.5 Hz], and 7.49 [m, 6 H, $SiPh_3$, H_o, $J(H_o–H_m)$ 6.5, $J(H_o–H_p)$ 2.8 Hz]. ^{13}C N.m.r. ($CDCl_3$): δ 9.52 (C_5Me_5), 103.78 [d, J(Rh–C) 3.4 Hz, C_5Me_5]; 127.10, 127.93, 136.34, and 139.80 ($SiPh_3$, C_m, C_p, C_o, and C_i respectively); 127.15, 128.53, 134.36, and 140.84 ($SiPh_2Cl$, C_m, C_p, C_o, and C_i respectively).

A solution of complex (1a) (0.3 g, 0.48 mmol) and triphenylsilane (1.5 g, 5.7 mmol) dissolved in benzene (50 cm^3) was refluxed (16 h). The resultant brown solution was worked-up in the same manner as described above to give a white solid (60 mg) which was shown by n.m.r. spectroscopy to contain at least 70% of a single material, identified as (7a) (Found: C, 70.3; H, 5.7; Cl, 1.5. $C_{46}H_{47}RhSi_2$ requires C, 72.8; H, 6.2; Cl, 0%). I.r.: ν(Rh–H) 2 060 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ −11.50 [d, J(Rh–H) 34 Hz, 2 H, RhH_2], 1.25 (s, 15 H, C_5Me_5), 7.05 (m, 12 H, H_m), 7.1 (t, 6 H, H_p), 7.55 (dd, 12 H, H_o); $J(H_o–H_m)$ 6.5, $J(H_o–H_p)$ 2.7, $J(H_m–H_p)$ 3.5 Hz.

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* KBr disc; the band is split owing to solid-state effects.