Low temperature *in situ* UV irradiation of $[(\eta^5-C_5H_5)Co(C_2H_4)_2]$ in the NMR probe: formation of Co(III) silyl hydride complexes

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Low temperature *in situ* UV irradiation of $[(\eta^5-C_5H_5)Co-(C_2H_4)_2]$ in the presence of silanes enables the characterisation of unstable fluxional Co(III) silyl hydride complexes $[(\eta^5-C_5H_5)Co(SiR_3)(H)(C_2H_4)]$ (SiR₃ = SiEt₃, SiMe₃ or SiHEt₂) by NMR spectroscopy; the reaction of $[Co(\eta^5-C_5H_5)(C_2H_4)_2]$ with HSiR₃ proceeds thermally to reach an equilibrium when SiR₃ = Si(OMe)₃ or SiClMePh.

The study of half sandwich complexes of cobalt, rhodium, and iridium with ethene ligands has shown that there are substantial differences in their chemical behaviour. $[(\eta^5-C_5H_5)Co(C_2H_4)_2]$ is very labile towards thermal loss of ethene,¹⁻⁵ whereas the rhodium and iridium analogues are much more thermally inert.⁶ It is a rarity to find analogous reactions with all three metals.⁷ The rhodium complex and its analogues lose ethene readily under photochemical conditions,⁸⁻¹³ but the half sandwich iridium ethene complexes are prone to photochemical isomerization to vinyl hydride complexes in addition to photodissociation of ethene.¹⁴⁻¹⁷

Several studies have been carried out on the reactivity of $[(\eta^5-C_5H_5)Rh(C_2H_4)_2]$ and $[(\eta^5-C_5Me_5)Rh(C_2H_4)_2]$ towards silanes and species of the type $[(\eta^5-C_5H_5)Rh(SiR_3)(H)(C_2H_4)]$ have been characterised following irradiation of $[(\eta^5-C_5H_5)Rh(C_2H_4)_2]$.^{8,18-24} Much less is known about the reactivity of their cobalt analogues. Heaton *et al.* isolated the Co(III) disilyl $[(\eta^5-C_5H_5)Co\{1,2 (SiMe_2)_2C_6H_4$ (C₂H₄)] by reaction of $[(\eta^5-C_5H_5)Co(C_2H_4)_2]$ with C₆H₄(1,2-SiMe₂H)₂.²⁵ More recently, Brookhart et al. reported the formation of the Co(V) complex $[(\eta^5-C_5Me_5)Co(SiHPh_2)_2(H)_2]$ by reacting $[(\eta^5-C_5Me_5)Co(C_2H_4)_2]$ with diphenylsilane.²⁶ It was suggested that it was formed via the Co(III) silvlhydride species $[(\eta^5 -$ C₅Me₅)Co(SiHPh₂)(H)(C₂H₄)], but no direct evidence was presented for this intermediate. The only half sandwich Co(III) silyl hydrides characterised so far, are $[(\eta^5-C_5H_5)Co(SiR_3)(H)(CO)]$ (R = Cl, Et) formed by photochemical reaction of $[(\eta^5-C_5H_5)Co(CO)_2]$ with $HSiR_3$.^{27,28,29} In thermal reactions, $[CpCo(C_2H_4)_2]$ acts as a very effective source of $[(\eta^5-C_5H_5)Co]$,¹⁻³ but such thermal reactions rarely give $(\eta^5-C_5H_5)Co(C_2H_4)$ products³⁰ and $[(\eta^5-C_5H_5)Co(C_2H_4)]$ C_5H_5 $C_0(C_2H_4)_2$ is therefore normally unsuitable as a precursor for detection of very labile species of this type. Presuming that the corresponding Co(III) silvl hydride products would be very labile, we have investigated the photochemistry of $[(\eta^5-C_5H_5)Co(C_2H_4)_2]$ at low temperatures using laser photolysis inside the NMR probe head to generate $[(\eta^5-C_5H_5)Co(C_2H_4)]$.³¹ We show that photolysis of $[CpCo(C_2H_4)_2]$ in the presence of silanes does indeed yield several silvl hydride complexes that react very readily with ethene. Reaction with a chiral silane generates two diastereomeric

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complexes that interconvert on the NMR timescale as shown by ¹H NMR spectroscopy at 400 MHz.

An NMR tube, charged with $[(\eta^5-C_5H_5)Co(C_2H_4)_2]^{32}$ 1, in deuterated toluene and excess HSiEt₃, was irradiated (He-Cd laser, 325 nm) inside the NMR probe at 203 K. In the ¹H NMR spectrum, a hydride resonance started to appear at δ -20.25, which grew in intensity during prolonged photolysis. After 3 h photolysis, a photostationary state was reached at approximately 30% conversion. A new Cp resonance at δ 4.28 and other proton resonances could also be detected as well as ¹³C and ²⁹Si resonances. NMR characterisation with COSY, NOESY and HMQC methods showed that these resonances belonged to the Co(III) complex, $[(\eta^5 C_5H_5$)Co(SiEt₃)(H)(C_2H_4)], 2.[†] Four distinct proton resonances could be distinguished for the ethene protons, indicating that the ethene ligand does not rotate rapidly at 203 K, in accordance with the failure to detect any exchange peaks connecting the four resonances in the corresponding EXSY spectrum. There was no sign of any other hydride resonances in the ¹H spectrum suggesting that double oxidative addition does not take place under these conditions. This contrasts with $[(\eta^5-C_5H_5)Rh(SiEt_3)(H)(C_2H_4)]$ which readily reacts further to form $[(\eta^5-C_5H_5)Rh(SiEt_3)_2(H)_2]$ under such conditions.^{20,21} The value of ${}^{2}J_{SiH}$ for the hydride resonance of 2 was determined in a gradient-filtered ¹H-²⁹Si correlation as 30 ± 3 Hz and is therefore substantially larger than that in the corresponding Rh(III) analogue where it was estimated as 12.2 Hz. When complex 2 was slowly warmed up, its resonances started to disappear from the associated NMR spectra above 223 K. At the same time, the free ethene in the sample, produced during photolysis, was observed to react with complex 2 to regenerate complex 1 (eqn (1)). A small amount of decomposition also takes place. When the sample was cooled back down and photolysed again, complex 2 was formed once more.



In order to establish the effect of the silicon substituents on the reaction, complex 1 was photolysed in the presence of HSiMe₃, H₂SiEt₂ and HSiPh₃. During photolysis in the presence of HSiMe₃ at 203 K a hydride resonance at δ –20.04 appeared after several minutes, which grew in intensity during prolonged photolysis. The corresponding value of ²J_{SiH} was 35 ± 3 Hz. A limiting conversion of approximately 30% was again reached and the product was identified as [(η^5 -C₅H₅)Co(SiMe₃)(H)(C₂H₄)], 3 (Fig. 1).†Complex 3 proved to be stable until 253 K, a slightly higher temperature than **2**. When the corresponding reaction was carried out under an ethene atmosphere, the formation of **3** was quenched entirely,



Fig. 1 $2D^{+}H^{-1}H$ COSY NMR spectrum recorded at 203 K in toluene-d₈ of complexes 1 and 3 with cross peaks due to the four inequivalent ethene resonances of 3 indicated.

suggesting a similar equilibrium to that shown in eqn (1). The reaction between **1** and diethylsilane proceeded in a similar manner to form $[(\eta^5-C_5H_5)Co(SiHEt_2)(H)(C_2H_4)]$, **4**.[†] In the associated NMR spectra of **4**, NOE's could be measured from the Cp resonance to the resonances of the ethyl groups indicating that the two ethyl groups of the silane point towards the C_5H_5 ring. An NOE connection could also be seen from the SiH proton resonance to H_c of the ethene ligand, where the labelling is consistent with that used in eqn (1).



When 1 was left to react with triphenylsilane at 295 K, some thermal reaction occurred resulting in detection of a hydride resonance at δ –18.95 and the resonance of free ethene (δ 5.3). With a ratio of 1: Ph₃SiH of 2.6, thermal conversion to the product was less than 2% and the yield only increased to 8% during photolysis at 203 K. Nevertheless, the product could be identified as $[(\eta^5-C_5H_5)Co(SiPh_3)(H)(C_2H_4)]$, 5 (the integrals of other hydride resonances were ca. fifty times smaller than that of 5).[†] The small amount of conversion, even after photolysis, suggests that the rate of oxidative addition is very slow compared to the back reaction with ethene. The rapid back reaction can probably be attributed to the bulk of the silane in agreement with the observations made by Duczmal and co-workers who found that for RhCl(cod)PPh₃ the rate of oxidative addition of silanes is reduced as the steric bulk of the silane increases.33,34 The percentage conversion reverts to less than 1% if the sample is kept at 253 K after photolysis, suggesting that the thermodynamic equilibrium position lies in favour of complex 1.

The reaction of 1 and trimethoxysilane (1 : $HSi(OMe)_3 \approx 2$) also proceeded thermally at room temperature and reached approximately 10% conversion to $[(\eta^5-C_5H_5)Co{Si(OMe)_3}(H)(C_2H_4)]$, **6.**† Neither photolysis at room temperature, nor at 203 K, increased the yield. When all the volatiles were removed, the sample redissolved in toluene and further trimethoxysilane added, the percentage conversion could be increased to 15%. On repetition of this process, the conversion progressed further to 21%. Clearly, only a very small amount of ethene is necessary to affect the position of equilibrium dramatically. The removal of the ethene shifts the equilibrium towards complex **6**, according to eqn (2). The value of ${}^{2}J_{\text{SiH}}$ in **6** was 50 ± 3 Hz and clearly lies outside the range associated with classical oxidative addition products.^{35–37} We suggest that these Co species show substantial Co(1), η^{2} -SiH character, decreasing in the order Si(OMe)₃ > SiMe₃ > SiEt₃> SiHEt₂

$$CpCo(C_{2}H_{4})_{2} + HSi(OMe)_{3} \xrightarrow{\frac{295K}{C_{2}H_{4}}} (2)$$

$$1$$

$$CpCo{Si(OMe)_{3}}(H)(C_{2}H_{4}) + C_{2}H_{4}$$

$$6$$

When a sample containing a mixture of complexes **1** and **6**, ethene and trimethoxysilane, was heated for 10 min at 313 K, the ¹H NMR spectrum, recorded at 295 K, showed three new resonances at δ 0.62, 1.05 and 3.43 consistent with the hydrosilation product C₂H₅Si(OMe)₃.³⁸ The volatiles were transferred into another NMR tube, and the ²⁹Si resonance of the product was detected at δ –41.8 in agreement with the literature.³⁹ In previous studies [(η^5 -C₅H₅)Rh(SiEt₃)(H)(C₂H₄)] has been shown to be involved in the hydrosilation process of C₂H₄ and HSiEt₃, forming both SiEt₄ and CH₂=CHSiEt₃.²¹ It is suggested that [(η^5 -C₅H₅)Co{Si(OMe)₃}(H)(C₂H₄)] is the catalyst in the hydrosilation of C₂H₄ and HSi(OMe)₃. There was no evidence for the formation of CH₂=CHSi(OMe)₃.

In previous studies, we have shown that the equivalence of the two enantiomers of $[(\eta^5-C_5H_5)Rh(SiR_3)(H)(alkene)]$ in the NMR spectra can be lifted by use of a mono-substituted alkene. The resulting diastereomers undergo exchange via $Rh(\eta^2$ -silane) intermediates.⁴⁰ A similar result was achieved by photolysis of $[(\eta^5-C_5H_5)Rh(C_2H_4)_2]$ in the presence of a chiral silane.⁴¹ Upon addition of racemic HSiClMePh to complex 1 (1 : HSiClMePh \approx 5), two isomers of $[(\eta^5-C_5H_5)Co(SiClMePh)(H)(C_2H_4)]$, 7a and **7b**, are formed thermally at room temperature in almost equal quantities.[†] The conversion of 44% is not altered by photolysis, suggesting an equilibrium between 1 and 7 similar to that between 1 and 6. The hydride resonances sharpen and separate on cooling reaching an optimum at 223 K, but on further cooling, they broaden again. On heating, the resonances coalesce at 303 K (Fig. 2), but further heating causes decomposition. The changes in the spectrum between 223 and 303 K are consistent with exchange between the two isomers, 7a and 7b. The broadening of the resonances at lower temperatures probably arises from restricted rotation of the silane ligand. Confirmation of free rotation of the silvl ligand at higher temperatures comes from NOE measurements which show connections between the hydride resonance and the methyl and phenyl resonances in both isomers. The value of ${}^{2}J_{\text{SiH}}$ was estimated to be 35 \pm 3 Hz in both 7a and 7b.

Rates of exchange at the coalescence temperature were determined using the method developed by Shanan-Atidi and Bar-Eli for unequal populations ($k_{AB} = 382$, $k_{BA} = 422$ s⁻¹).⁴² Activation barriers at 303 K could then be estimated from



Fig. 2 Variable temperature ¹H NMR spectra of 7a and 7a in toluene-d₈ in the hydride region.

transition state theory; $\Delta G^{\ddagger}_{303} = 59.3 \text{ kJ mol}^{-1}$ for **7a** to **7b** and $\Delta G^{\ddagger}_{303} = 59.0 \text{ kJ mol}^{-1}$ for **7b** to **7a**. These barriers are similar to those determined previously for isomer interconversion in [(η^{5} -C₃H₃)Rh(SiR₃)(H)(C₂H₃CO₂'Bu)] where the value of ΔG^{\ddagger} at 303 K is calculated to be 56.6 kJ mol⁻¹.⁴⁰ These experiments are consistent with exchange between **7a** and **7b** *via* [(η^{5} -C₃H₃)Co(η^{2} -HSiClMePh)(C₂H₄)] either as a transition state or an intermediate. However, this mechanism is not the only one that could explain the limited mechanistic data. We did not use line-shape analysis because exchange is not the only factor contributing to the variation of line shape with temperature in these cobalt complexes.

In conclusion, we have used NMR spectroscopy to study the formation of Co(III) silvl hydride complexes $[(\eta^5-C_5H_5) Co(SiR_3)(H)(C_2H_4)$] by reaction of hydrosilanes with $[(\eta^5 C_5H_5$)Co(C_2H_4)₂] 1. The stability of these complexes is dependent on the silane involved. When SiR₃ is SiEt₃, SiMe₃ or SiHEt₂, the product can only be formed photochemically at low temperatures. These species react very readily with the ethene released in the initial reaction to regenerate 1. When SiR₃ is SiPh₃, the product is formed thermally but the yield can be improved photochemically at low temperature. When SiR₃ is Si(OMe)₃ or SiClMePh, the reaction proceeds thermally at room temperature to yield 6 and 7, respectively. Although 6 and 7 are observable at room temperature, neither of them is stable for long periods, making it difficult to isolate them as pure materials. The conversion can be improved by removal of liberated ethene, as there is a clear equilibrium between the products and $[(\eta^5-C_5H_5)Co(C_2H_4)_2]$. Complex 7 exists as two isomeric hydride species which interconvert with a free energy of activation of ca. 59 kJ mol⁻¹. In situ laser photolysis has proved to be a valuable tool for the study of labile Co(III) silyl hydrides. Contrary to our initial expectations some of the Co(III) silvl hydrides are observable at room temperature.

Notes and references

[†] NMR data complexes 2–7 in toluene-d₈ at 203 K (¹H 400.13 MHz, ¹³C 100.62 Hz, ²⁹Si 79.49 MHz). ¹³C and ²⁹Si NMR spectra were collected as 2D HMQC spectra with delays set both for short range and long range coupling in the case of ¹³C spectra.

 $\begin{bmatrix} (\eta^5 - C_5 \tilde{H}_5)Co(SiEt_3)(H)(C_2 \tilde{H}_4) \end{bmatrix}, \ \mathbf{2} \quad {}^{1}H: -20.25 \quad (s), \quad 0.68 \quad (q, \quad 7 \quad Hz, \\ Si(CH_2 CH_3)_3), \quad 1.10 \quad (m, \quad C_2 H_4), \quad 1.12 \quad (t, \quad 7 \quad Hz, \quad Si(CH_2 CH_3)_3), \quad 1.61 \quad (m, \\ C_2 H_4), \quad 2.02 \quad (m, \quad C_2 H_4), \quad 2.74 \quad (m, \quad C_2 H_4), \quad 4.28 \quad (s, \quad Cp), \quad {}^{13}C\{{}^{1}H\}: \quad 9.8 \\ (Si(CH_2 CH_3)_3), \quad 10.3 \quad (Si(CH_2 CH_3)_3), \quad 28.7 \quad (C_2 H_4), \quad 30.5 \quad (C_2 H_4), \quad 84.2 \quad (Cp), \\ {}^{29}Si: \quad 38.9, \quad {}^{2}J_{SiH} = 30 \quad Hz.$

 $\begin{array}{l} [(\eta^{5}\text{-}C_{5}\text{H}_{3})\text{Co}(\text{SiHEt}_{2})(\text{H})(\text{C}_{2}\text{H}_{4})], \ \textbf{4}^{-1}\text{H}: -20.10 \ (\text{s}), \ 0.58 \ (\text{q}, \ 7 \ \text{Hz}, \\ \text{Si}CH_{2}\text{C}\text{H}_{3}), \ 1.08 \ (\text{q}, \ 7 \ \text{Hz}, \ \text{Si}CH'_{2}\text{C}\text{H}'_{3}), \ 1.09 \ (\text{m}, \ \text{C}_{2}\text{H}_{4}), \ 1.20 \ (\text{t}, \ 7 \ \text{Hz}, \\ \text{Si}\text{CH}_{2}CH_{3}), \ 1.32 \ (\text{t}, \ 7 \ \text{Hz}, \ \text{Si}\text{C}\text{H}'_{2}C\text{H}'_{3}), \ 1.77 \ (\text{m}, \ \text{C}_{2}\text{H}_{4}), \ 1.20 \ (\text{t}, \ 7 \ \text{Hz}, \\ \text{Si}\text{C}\text{H}_{2}CH_{3}), \ 1.32 \ (\text{t}, \ 7 \ \text{Hz}, \ \text{Si}\text{C}\text{H}'_{2}C\text{H}'_{3}), \ 1.77 \ (\text{m}, \ \text{C}_{2}\text{H}_{4}), \ 2.12 \ (\text{m}, \ \text{C}_{2}\text{H}_{4}), \\ 2.77 \ (\text{m}, \ \text{C}_{2}\text{H}_{4}), \ 3.72 \ (\text{s}, \ \text{Si}\text{H}), \ 4.21 \ (\text{s}, \ \text{Cp}), \ ^{13}\text{C}\{^{1}\text{H}\}: \ 7.0 \ (\text{Si}\text{C}\text{H}'_{2}\text{C}\text{H}'_{3}), \\ 7.1 \ (\text{Si}CH_{2}\text{C}\text{H}_{3}), \ 11.0 \ (\text{Si}\text{C}\text{H}_{2}CH_{3}), \ 11.6 \ (\text{Si}\text{C}\text{H}'_{2}C\text{H}'_{3}), \ 29.1 \ (\text{C}_{2}\text{H}_{4}), \ 32.4 \ (\text{C}_{3}\text{H}_{4}), \ 84.4 \ (\text{Cp}), \ ^{29}\text{Si}: \ 28.7, \ ^{2}J_{\text{SiH}} = 25 \ \text{Hz}. \end{array}$

[$(\eta^5-C_5H_5)Co(SiPh_3)(H)(C_2H_4)$], **5**¹H: -18.95 (s), 1.23 (m, C₂H₄), 1.65 (m, C₂H₄), 2.11 (m, C₂H₄), 2.79 (m, C₂H₄), 4.18 (s, Cp), 7.73 (m, Ph_n), 7.73 (m, Ph_p), 7.97 (m, Ph_o), ¹³C{¹H}: 31.9 (C₂H₄), 33.5 (C₂H₄), 86.1 (Cp), ²⁹Si: 27.9.

 $\begin{array}{l} [(\eta^{5}\text{-}C_{5}H_{5})\text{Co}\{\text{Si}(\text{OMe})_{3}\}(\text{H})(\text{C}_{2}\text{H}_{4})], \ \textbf{6}^{-1}\text{H}: -20.14 \ (s), \ 1.86 \ (m, \ \text{C}_{2}\text{H}_{4}), \\ 1.88 \ (m, \ \text{C}_{2}\text{H}_{4}), \ 2.09 \ (m, \ \text{C}_{2}\text{H}_{4}), \ 2.79 \ (m, \ \text{C}_{2}\text{H}_{4}), \ 3.57 \ (s, \ \text{Si}(\text{OCH}_{3})_{3}), \ 4.45 \ (s, \ \text{Cp}), \ ^{13}\text{C}\{^{1}\text{H}\}: \ 30.7 \ (\text{C}_{2}\text{H}_{4}), \ 30.9 \ (\text{C}_{2}\text{H}_{4}), \ 50.1 \ (\text{Si}(\text{OCH}_{3})_{3}), \ 86.1 \ (\text{Cp}), \ ^{29}\text{Si}: -1.1, \ ^{2}J_{\text{SiH}} = 50 \ \text{Hz}. \end{array}$

[(η⁵-C₅H₃)Co(SiClMePh)(H)(C₂H₄)], **7a** (at 253 K): ¹H: -18.95 (s), 0.69 (s, CH₃), 1.32 (m, C₂H₄), 1.65 (m, C₂H₄), 2.22 (m, C₂H₄), 2.79 (m, C₂H₄), 4.30 (s, Cp), 7.19 (m, Ph_m), 7.52 (m, Ph_p), 7.68 (m, Ph_o), ¹³C{¹H}: 9.2 (CH₃), 32.0 (C₂H₄), 34.9 (C₂H₄), 86.3 (Cp), 128.0 (Ph_m), 128.4 (Ph_p), 132.4 (Ph_o), 143.7 (Ph_i), ²⁹Si: 57.8, ²J_{SiH} = 35 Hz.

 $[(\eta^{5}-C_{5}H_{5})Co(SiClMePh)(H)(C_{2}H_{4})],$ **7b** $(at 253 K): {}^{1}H: -19.26 (s), 0.77 (s, CH_{3}), 1.44 (m, C_{2}H_{4}), 1.54 (m, C_{2}H_{4}), 2.26 (m, C_{2}H_{4}), 2.74 (m, C_{2}H_{4}), 4.21 (s, Cp), 7.13 (m, Ph_{m}), 7.43 (m, Ph_{p}), 7.65 (m, Ph_{o}), {}^{13}C {}^{1}H]: 12.4 (CH_{3}), 32.9 (C_{2}H_{4}), 36.0 (C_{2}H_{4}), 85.8 (Cp), 128.1 (Ph_{m}), 128.8 (Ph_{p}), 132.7 (Ph_{o}), 142.2 (Ph_{i}), {}^{29}Si: 59.7, {}^{2}J_{SiH} = 35 Hz.$

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