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RING- VERSUS METAL-HYDRIDE DEPROTONATION IN *cis*-(η^5-C_5H_5)$(CO)_2$Re($SiPh_3$)H: A ROUTE TO *cis*- AND *trans*-(η^5-C_5H_4($SiPh_3$))$(CO)_2ReH_2$

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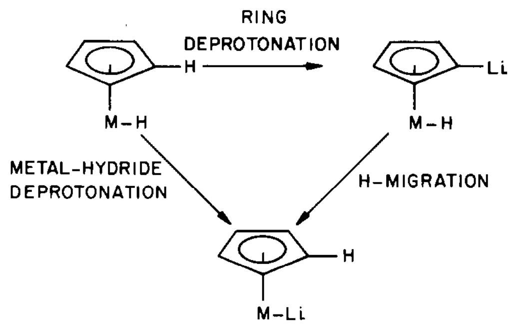
Summary

Deprotonation of *cis*-(η^5-C_5H_5)$(CO)_2$Re($SiPh_3$)H by neopentyllithium at −78°C in THF gives an anionic species, which is shown by spectroscopic and chemical methods to be [(η^5-C_5H_4($SiPh_3$))$(CO)_2$ReH]Li. Its formation is explained by initial deprotonation of the cyclopentadienyl ligand, followed by an intramolecular silyl-group migration. Protonation of the anion at room temperature gives *trans*-(η^5-C_5H_5($SiPh_3$))$(CO)_2ReH_2$; at −78°C the major product is *cis*-(η^5-C_5H_4($SiPh_3$))-$(CO)_2ReH_2$. The latter isomerizes to the *trans* dihydride complex at room temperature ($t_{1/2}$ 12 h).

Introduction

Deprotonation of transition-metal hydride complexes is a valuable method of generating anionic metal complexes which can serve as starting points for new organometallic chemistry. In many cases these metal hydrides bear cyclopentadienyl ligands; these are known to have rather acidic C–H bonds [1], yet ring deprotonation appears not to be a side reaction in the deprotonation of these complexes [2]. The recently reported [3] deprotonation of (η^5-C_5H_5)(NO)(PPh_3)ReH is, in fact, the first example of a transition-metal hydride complex stabilized by a cyclopentadienyl ligand which can selectively be deprotonated either at the ring or at the metal, depending on the reaction conditions. As the authors of that study pointed out, the deprotonation of the cyclopentadienyl ring may in many cases have been overlooked, due to a fast metal-to-ring proton transfer following the ring-deprotonation reaction. Clearly, the latter process cannot be distinguished from the direct metal-hydride deprotonation, unless labelling experiments are performed (Scheme 1).

We report below on the deprotonation of *cis*-(η^5-C_5H_5)$(CO)_2$Re($SiPh_3$)H, which has two possible sites of deprotonation, and in addition possesses two different



SCHEME 1

ligands (viz. H and $SiPh_3$) with the potential to participate in a metal-to-ring group transfer reaction in the event of deprotonation of the cyclopentadienyl ligand.

Results and discussion

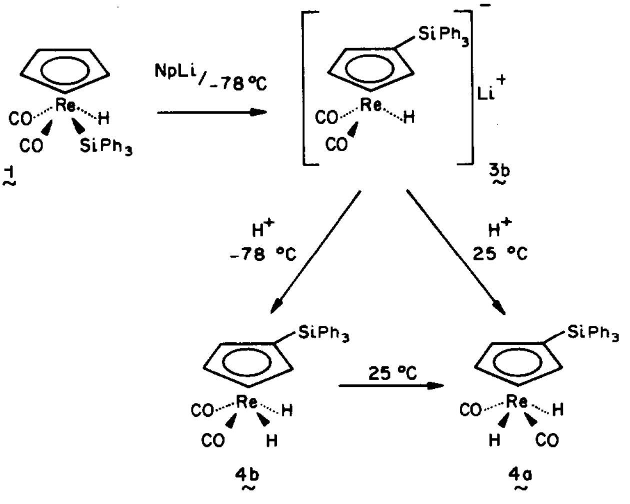
Deprotonation of $(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$

It has been reported [4] that *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$ (**1**) is deprotonated by ethanolic KOH at the metal to yield $[(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)]K$ (**2a**). When **1** is treated with neopentyllithium in THF at room temperature, however, not only $[(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)]Li$ (**2b**) is formed, but also a new hydride complex **3b**, as indicated by the appearance of a resonance at δ −12.43 ppm in the ^1H NMR spectrum. When the deprotonation is performed at −78°C **3b** is the only product formed. The ^1H NMR spectrum displays, in addition to the hydride resonance, an *AA'BB'* pattern for the cyclopentadienyl ligand, suggesting that the new product comes from deprotonation of the $\eta^5\text{-}C_5H_5$ ligand. Surprisingly, protonation of **3b** at room temperature does not regenerate **1** (or the corresponding *trans* isomer); instead, *trans*-$(\eta^5\text{-}C_5H_4(SiPh_3))(CO)_2ReH_2$ (**4a**) is obtained. (Product **4a** was fully identified by spectroscopic methods and microanalysis (cf. Tables 1 and 2 and

TABLE 1

^1H NMR SPECTROSCOPIC DATA FOR COMPLEXES **2b**, **3b** AND **4a**, **b** (25°C, THF-d_8, δ in ppm rel. to TMS; $SiPh_3$ resonances omitted)

Complex		
$[(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)]Li$	**(2b)**	4.82 (5H, s, C_5H_5)
$[(\eta^5\text{-}C_5H_4(SiPh_3)(CO)_2ReH]Li$	**(3b)**	5.08 (2H, *AA'*BB', C_5H_4Si); 5.19 (2H, AA'*BB'*,C_5H_4Si); −12.43 (1H, s, ReH)
trans-$(\eta^5\text{-}C_5H_4(SiPh_3))(CO)_2ReH_2$	**(4a)**	5.36 (2H, *AA'*BB', C_5H_4Si); 5.63 (2H, AA'*BB'*, C_5H_4Si); −9.71 (2H, s, ReH)
cis-$(\eta^5\text{-}C_5H_4(SiPh_3))(CO)_2ReH_2$	**(4b)**	5.52 (2H, *AA'*BB', C_5H_4Si); 5.76 (2H, AA'*BB*, C_5H_4Si); −9.01 (2H, s, ReH)



SCHEME 2

Experimental).) We therefore conclude that in product **3b** the silyl group has already migrated to the cyclopentadienyl ring, and hence the product should be formulated as [(η^5-$C_5H_4(SiPh_3)$)$(CO)_2$ReH]Li (cf. Scheme 2).

The potassium salt **3a** was prepared by deprotonation of **4** with potassium t-butoxide in THF. The spectroscopic data for this complex (^{1}H NMR (THF-d_8): δ -12.48 ppm (Re–H); IR (THF): 1856s; 1775s cm^{-1}) are in close agreement with those reported [5] for [(η^5-C_5H_5)$(CO)_2$ReH]K (^{1}H NMR (CD_3CN): δ -12.38 ppm (Re–H); IR (THF): 1859s; 1775s; 1760sh cm^{-1}), which further supports the structural assignment of **3b**.

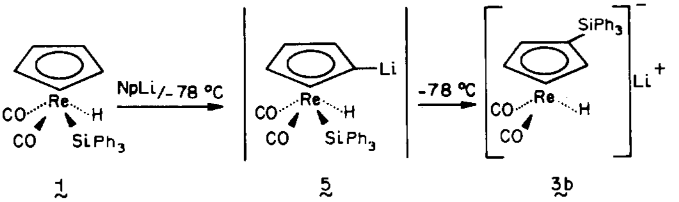
The formation of [(η^5-$C_5H_4(SiPh_3)$)$(CO)_2$ReH]Li suggests that two different modes of deprotonation of *cis*-(η^5-C_5H_5)$(CO)_2$Re($SiPh_3$)H are available: metal deprotonation gives the "thermodynamic" product **2b**, whereas removal of a proton from the cyclopentadienyl ligand results in the formation of the "kinetic" product (η^5-C_5H_4Li)$(CO)_2$Re($SiPh_3$)H (**5**) (cf. Scheme 3). The latter cannot be observed due to a metal-to-ring silyl group migration which is fast even at -78°C, and which forms the anionic complex [(η^5-$C_5H_4(SiPh_3)$)$(CO)_2$ReH]Li.

The silyl group migration is an intramolecular process, since formation of the bis-silylated product (η^5-$C_5H_4(SiPh_3)$)$(CO)_2$Re($SiPh_3$)H, which would result from

TABLE 2

IR SPECTROSCOPIC DATA FOR COMPLEXES **2b**, **3a**, AND **4a**, **b** (25°C, in THF, ν(CO) in cm^{-1})

Complex		
[(η^5-C_5H_5)$(CO)_2$Re($SiPh_3$)]Li	(**2b**)	1875s; 1759s
[(η^5-$C_5H_4(SiPh_3)$)$(CO)_2$ReH]K	(**3a**)	1856s; 1775s
trans-(η^5-$C_5H_4(SiPh_3)$)$(CO)_2ReH_2$	(**4a**)	2014s; 1940ss
cis-(η^5-$C_5H_4(SiPh_3)$)$(CO)_2ReH_2$	(**4b**)	1966s; 1923s



SCHEME 3

intermolecular migration is not observed. Such rapid silyl group migration has previously been postulated to explain the formation of [(η^5-$C_5H_4(SiMe_3)$)Fe(CO)$_2$]Li in the deprotonation of (η^5-C_5H_5)Fe(CO)$_2$(SiMe$_3$) [6]. In contrast, it has recently been reported [3] that when (η^5-C_5H_5)(NO)(PPh$_3$)ReH is deprotonated at the ligand, the intermediate (η^5-C_5H_4Li)(NO)(PPh$_3$)ReH only slowly rearranges to the thermodynamic product [(η^5-C_5H_5)(NO)(PPh$_3$)Re]Li, and it is tempting to conclude that the silyl group is a much better migrating group in this type of rearrangement than a proton. Quantitative information on the migratory aptitude can be obtained from the ring deprotonation of *cis*-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)H, since in this system a silyl group and a proton can undergo a competitive migration to the (deprotonated) cyclopentadienyl ligand within the same molecule.

Clearly at −78°C silyl group migration predominates, but we cannot a priori rule out the possibility that the formation of **2b** at room temperature proceeds via hydrogen migration in **5** rather than via direct metal deprotonation. To check this possibility we have studied the interaction of neopentyllitium with *cis*-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)D. At room temperature **2b** and **3b** were the only products formed, and no deuterium was incorporated in the former, indicating that **2b** is mainly formed via direct metal deprotonation. Furthermore, this experiment precludes intermolecular hydrogen transfer (e.g. deprotonation of **1** by **5**) as an important route to **2b**. Interestingly, the ratio in which **2b** and **3b** are formed changes from 3/2 for *cis*-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)*H* to 1/3 for *cis*-(η^5-C_5H_5)(CO)$_2$-Re(SiPh$_3$)*D*. This implies that there is an isotope effect $k_H/k_D = 6$ in the metal deprotonation reaction, assuming a negligible secondary isotope effect on the cyclopentadienyl-ring deprotonation. Control of the site of deprotonation may thus be achieved by simple isotopic substitution.

Finally, it should be noted that the selectivity of the deprotonation reaction is greatly dependent on the geometry of the complex, as is demonstrated by the deprotonation of *trans*-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)H (**6**), which only occurs at the metal, even under "kinetic" conditions, and which leads to the exclusive formation of **2b**. Apparently, the Re–H bond in **6** is weakened by the *trans*-silyl substituent compared to the Re–H bond in **1**, resulting in a strongly increased rate of deprotonation at the metal in the former isomer.

Protonation of [(η^5-$C_5H_4(SiPh_3)$)(CO)$_2$ReH]Li

Protonation of [(η^5-$C_5H_4(SiPh_3)$)(CO)$_2$ReH]Li at room temperature results in the formation of *trans*-(η^5-$C_5H_4(SiPh_3)$)(CO)$_2$ReH$_2$ (**4a**). Assignment of the configuration around the metal is based on the relative intensities of the C≡O absorptions in the IR spectrum [7] (cf. Table 2). Various routes to (η^5-C_5H_5)(CO)$_2$ReH$_2$ have been reported recently [7–10] and in all cases the product has the *trans*-configuration around the metal. When $[(\eta^5\text{-}C_5H_5(SiPh_3))(CO)_2ReH]Li$ is protonated at -78°C, monitoring of the ^1H NMR, reveals the appearance of two metal-hydride resonances in a 1/10 ratio. The minor signal is ascribed to the *trans*-dihydride **4a** (δ -9.71 ppm), and the other, which also accounts for two hydrogens (δ -9.01 ppm), is assigned to the isomeric product *cis*-$(\eta^5\text{-}C_5H_5(SiPh_3))(CO)_2ReH_2$ (**4b**). The IR spectrum of the latter product shows C≡O absorptions (1996 and 1923 cm^{-1}) of almost equal intensity, as expected for the *cis*-configuration [7].

At room temperature **4b** slowly isomerizes to the thermodynamically more stable product **4a** ($t_{1/2}$ 12 h). Attempts to isolate the pure *cis*-dihydride have so far been unsuccessful.

Concluding remarks

We have shown that under suitable conditions *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$ can be deprotonated at the cyclopentadienyl ligand. Furthermore we have shown that the anion thus formed rearranges via intramolecular metal-to-ring group transfer and we have been able to compare the migratory aptitudes of the silyl and the hydride group in this rearrangement. The $Cp(CO)_2Re$ fragment may prove very useful in studying this type of anionic rearrangement by incorporating different migrating groups.

Finally, we have described a new route to $Cp(CO)_2ReH_2$ complexes and we have prepared ths *cis*-dihydride for the first time. The latter is thermodynamically less stable than the corresponding *trans*-dihydride, and thus could not be isolated pure.

Experimental

Materials. *trans*-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$ [4], *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)D$ [4] and neopentyllithium [11] were prepared by literature procedures.

Reactions. All the reactions were carried out under argon in rigorously dried solvents.

Preparation of cis-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$ (1)

The literature procedure [4] was slightly modified. A solution of 2.3 g (6.9 mmol) $(\eta^5\text{-}C_5H_5)(CO)_3Re$ in 800 ml of THF in a quartz vessel was irradiated with a 125 W-high-pressure mercury lamp while being purged with nitrogen. The reaction was monitored by IR and when no further change in the constitution of the reaction mixture was found the irradiation was terminated. A two-fold excess of triphenylsilane was added and the mixture was refluxed for 2 h. The solvent was removed in vacuum and the tarry residue was extracted with four 100-ml portions of n-hexane, to remove unconverted starting material and silane. The residue was flash-chromatographed through 100 g of silica with 200 ml of 70/30 n-hexane/dichloromethane to give *cis*-$(\eta^5\text{-}C_5H_5)(CO)_2Re(SiPh_3)H$. Yield: 1.5 g (38%).

*Preparation of trans-$(\eta^5\text{-}C_5H_4(SiPh_3))(CO)_2ReH$ (**4a**)*

A solution of **1** in THF was cooled to -78°C and treated with one equivalent of neopentyllithium (0.27 *M* solution in benzene). The mixture was stirred for 15 min and then warmed to room temperature and treated with one equivalent of trifluoromethanesulphonic acid or trifluoroacetic acid. The solvent was removed in vacuum the residue was taken up in 70/30 hexane/dichloromethane, and the solution was filtered. After removal of the solvents the dihydride was obtained as a white solid. The product was recrystallized from hexane. M.p. 127–128°C. Yield: 89% after recrystallization. Anal. Found: C, 52.80; H, 3.80; Si, 4.93. * $C_{25}H_{21}O_2ReSi$ calcd.: C, 52.89; H, 3.73; Si, 4.95%.

*Deprotonation of **1** with neopentyllithium*

A solution of 4 mg of **1** in 0.3 ml THF-d_8 was treated with one equivalent of neopentyllithium (0.27 *M* solution in benzene-d_6) at the appropriate temperature. The reaction was monitored by ^{1}H NMR. Resonances due to **2b** were identified by comparison with an authentic sample.

*Deprotonation of **1** with lithium t-butoxide*

A reference sample of **2b** was prepared by treatment of **1** with lithium t-butoxide in THF-d_8 [4].

*Deprotonation of **6** with neopentyllithium*

Deprotonation of **6** with neopentyllithium was performed by a procedure analogous to that described for **1**.

Deprotonation of cis-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)D with neopentyllithium

A solution of 4 mg *cis*-(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)D in 0.3 ml THF-d_8 was treated with one equivalent of neopentyllithium (0.27 *M* solution in benzene-d_6) at room temperature. Resonances ascribed to [(η^5-C_5H_4(SiPh$_3$))(CO)$_2$ReD]Li and [(η^5-C_5H_5)(CO)$_2$Re(SiPh$_3$)]Li were observed in the ^{1}H NMR spectrum. To check for deuterium incorporation in the latter complex the reaction was quenched with trifluoromethanesulphonic acid and the resonances due to *trans*-(η^5-C_5H_5)(CO)$_2$-Re(SiPh$_3$)H were carefully integrated. Within experimental error no incorporation of deuterium was detected.

*Protonation of **3b***

Samples of **3b** prepared in the above described manner were treated with an equivalent of trifluoromethanesulphonic acid or trifluoroacetic acid at the appropriate temperature and the products were examined by ^{1}H NMR spectroscopy.

*Thermal conversion of **4b** to **4a***

A sample of **3b** prepared as described above was quenched with trifluoroacetic acid at −78°C. The mixture was quickly brought to 25°C and examined by ^{1}H NMR spectroscopy every 2 h. Conversion of **4b** to **4a** was observed over a period of 25 h.

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* Since the starting material and product are isomers, the purity was further checked by ^{1}H NMR, which showed no residual resonances due to **1**.

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