Dehydrogenation. Dihydridotetrakis(triphenylphosphine)dichlorodirhodium Formation from Ethylenyl Moieties and Tris(triphenylphosphine)chlororhodium

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A new source of hydrogen for preparation of rhodium(III) dihydrides is reported. Hydrides of Group VIII transition metals are of current intererest [1].

The structure of the subject dihydrides **4** (which were formed *in situ* from diatomic hydrogen and a solution of tetrakis(triarylphosphine)dichlorodirhodium(I), **2**) is based [2] on characteristic spectroscopic values (^1H and $^{31}P\{^1H\}$ NMR, ultraviolet-visible of **1a**, **2a**, and **4a**), a molecular weight determination of **2a**, and quantitation of the uptake of diatomic hydrogen by **2a**. The dihydrido compound **4a** was found to be favored upon equilibration with **2a** and diatomic hydrogen at 25 °C in a closed system; and, in the absence of added triarylphosphine **3a**, warming from ~25 to 45 °C enhanced conversions of **1a** to **2a** and **3a** (in solution) [2]. An analogous sequence is reported herein (**1b** $\xrightarrow{-3b}$ **2b** → **4b**, in eqn. (1)), with a significant difference (from literature reports) being the source of hydrogen for **4**.

$$2RhCl(PAr_3)_3 \rightleftharpoons [RhCl(PAr_3)_2]_2 + 2\,PAr_3$$

1 **2** **3**

$$-[H] \uparrow\downarrow +[H]$$

$$H_2[RhCl(PAr_3)_2]_2 \qquad (1)$$

4

a, Ar = p-tolyl
b, Ar = Ph

Two components, **1b** and elementally-pure $CH_3(OCH_2CH_2)_{10}O(CH_2CH_2)_8H$ (**5**)* [3] (0.14 M: 0.06 M in anhydrous $CDCl_3$), sealed under nitrogen (and in the absence of added diatomic hydrogen), lead after 10 min at 23 °C to **2b** [2, 4] accompanied by **3b**, following warming of their quenched solution from −55 to −30 °C. Upon heating to 0 °C, the characteristic ^1H and $^{31}P\{^1H\}$ NMR bands of **4b** [2, 4] appear. At 30 °C, the resonances for **4b** become more intense than those for **2b**. The literature (*cf.* the preceding paragraph) is fully consistent with these observations that (a) **1b** yields **2b** and **3b** upon heating and (b) **4b** predominates over **2b** in a reducing medium.

The hydrogen source for the step **2b** → **4b** is apparent from ^1H and $^{13}C\{^1H\}$ NMR spectra (Table I) of this closed, dynamic reaction system. When the proton resonance of **4b** appears, another broad band at δ 5.29–5.24 is present. (A second, less intense, broadened band at 5.16–5.11 ppm also exists at −15 °C and, again, at −55 °C after a reaction period of 17 h). These broad resonances are well-identified [6] with rhodium bound alkenes. (Appropriate $^{13}C\{^1H\}$ resonances for rhodium complexed, alkyl-substituted alkenes also are noted (Table I) following the reaction of **1b** and **5**). After a 17 h interval, based on the relative intensity of δ 5.29–5.24, the calculated conversion of **5** to monoenes is 40–70%, which agrees with the observed consumption of ~50% of the initial amount of **1b**. These results support the conclusion that $-CH_2CH_2-$ units are a new source

*Compound **5** is a solubilizing agent for **1b** and its products (**2b**, **3b**, and **4b**).

TABLE I. Selected NMR Values.

Species	Nucleus	δ_{found}[a]	δ_{lit}[a]	Ref.
$L_nRh-\overset{CH-}{\underset{CH-}{\|}}$	^1H	5.29–5.24(br); 5.16–5.11(br)	5.3–2.9(br)	5, 6
$L_nRh-\overset{CH\begin{pmatrix}H\\CH_2-\end{pmatrix}}{\underset{CH\begin{pmatrix}H\\CH_2-\end{pmatrix}}{\|}}$	$^{13}C\{^1H\}$	62.07–61.72(br); 55.39–54.75(br); 17.66–17.55(:$CHCH_2$)	61.67–61.65, 17.82	7

[a]In ppm, with $CDCl_3$ as solvent and $(CH_3)_4Si$ as internal standard.

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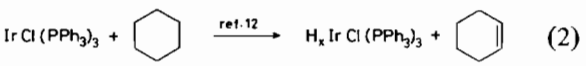
of hydrogen for dihydridorhodium compound formation. (A dialkylated $-OCH_2CH_2O-$ group reportedly donates hydrogen to simple alkenes in the presence of **1b** with formation of the corresponding $-OCH=CHO-$ moiety; however, reaction temperatures of ≥ 100 °C were required and the role of the rhodium was not elucidated [8, 9]).

Polyether **5** complexes through its oxygen atoms with rhodium(I) compounds and enhances electron density at the rhodium [3]. In this way [3], oxidative addition of **5** to rhodium(I) is promoted. The product mixture contains hydridoalkylrhodium(III) compounds (^{1}H NMR: -14.4 to -14.8 (broad) ppm, which as expected [10] are observed only at <0 to -15 °C), rhodium-bound alkenes [11], and **4b**. Hydrogen-capture by rhodium(I) is most closely precedented in a report with iridium(I) (eqn. (2)) [12].



(2)

In closed dynamic systems, simple alkenes and their rhodium complexes coexist with the known [2] hydrogenation reagent 4, $RhCl(PAr_3)_3$ (**1**), and their corresponding $-CH_2CH_2-$ groups [2, 13, 14]. Under new, mild conditions reverse hydrogenation of $-CH_2CH_2-$ moieties occurs to yield alkenes and 4.

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