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Preliminary communication

The direct deprotonation of the η^5-pyrrolyl ligand in $(\eta^5\text{-}C_4H_4N)(Ph_3P)_2ReH_2$

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Abstract

Treatment of $(\eta^5\text{-}C_4H_4N)(Ph_3P)_2ReH_2$ (C_4H_4N = pyrrolyl) with n-BuLi at −78 °C leads to regioselective (α-position) ring deprotonation. Reaction of the deprotonated product with RI (R = Me, n-Bu) gives $(\eta^5\text{-}2\text{-}RC_4H_3N)(Ph_3P)_2ReH_2$ in high yield.

The deprotonation of η^5-cyclopentadienyl (Cp) ligands has abundant precedents and has frequently been utilized in the preparation of functionalized Cp complexes [1]. However, difficulties may arise when the starting complex contains some δ-bonded ligands (hydrides, silyls, germyls, etc.), which can migrate to the initially deprotonated ring to afford more stable, metal-centered anions [2]. In such cases kinetic control (low temperature) is required to obtain ring deprotonated products.

Here I describe an extension of this methodology for the η^5-pyrrolyl ($\eta^5\text{-}C_4H_4N$) ligand, which is isoelectronic with Cp. Although deprotonation of this ligand has been observed in the reaction of azaferrocene, $(\eta^5\text{-}C_4H_4N)(\eta^5\text{-}Cp)Fe$, with n-BuLi [3], the competitive deprotonation of the Cp ring markedly limits its synthetic potential.

In contrast, I have found that (η^5-pyrrolyl)rhenium dihydrido complex **1**, when treated with n-BuLi at −78 °C affords exclusively ring deprotonated product **2** (Scheme 1). No significant migration of the hydrido ligand to the deprotonated ring (i.e. **2** → **3**) was observed at this temperature. Reaction of **2** with electrophiles (RI; R = Me, n-Bu) gave the corresponding 2-substituted pyrrolyl complexes **4** in high yield.

In a typical experiment 0.2 mmol of **1**, dissolved in THF at −78 °C was treated with 0.25 mmol of n-BuLi in hexane. The solution rapidly changed color from yellow to deep red. Control by deuteriolysis showed that formation of **2** was complete after 1 h. Methyl iodide (0.3 mmol) was then added at −78 °C, and the red coloration of the reaction mixture turned yellow within ~ 10 min. The solvent was removed in vacuo, the residue dissolved in dichloromethane and chromato-

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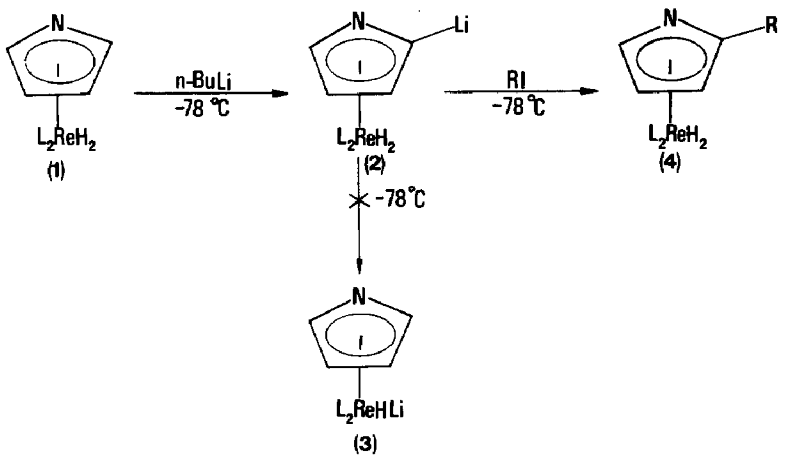

Scheme 1. L = PPh_3, R = Me (**a**), R = n-Bu (**b**).

graphed on alumina(I). A single, yellow band was eluted with dichloromethane to give **4a** in 92% yield. Analogously, reaction with n-butyl iodide gave **4b**, in 84% yield. These complexes were found, by use of TLC, IR and ^1H NMR spectroscopy, to be identical with authentic samples prepared by a published procedure [4].

I have previously reported that complexes of the type **4** can be readily converted into the corresponding NH- and N-substituted pyrroles [5,6]. The deprotonated complex **2** can thus be used as an equivalent (synthon) of the 2-pyrrolyl anion. It is noteworthy that the iodo derivatives of **4**, (η^5-pyrrolyl)$(Ph_3P)_2$ReHI, have proven to be useful, "umpoled" synthons of 2-pyrrolyl cation [4,6]. Moreover, the "umpolung" is very facile on treatment with I_2/K_2CO_3. All these facts clearly demonstrate the considerable synthetic potential offered by coordination of the pyrrole system to a transition metal.

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