Journal of Organometallic Chemistry, 317 (1986) C28–C30
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

TRANSITION METAL PROMOTED REACTIONS

XVI *. ACTIVATION OF C–S BONDS IN COMPLEXED THIOLATO LIGANDS. REDUCTION OF THE C–S BOND IN $Cp_2Ni_2(\mu\text{-}SR)_2$

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(Received July 24th, 1985)

Summary

The carbon–sulfur bond in $Cp_2Ni_2(\mu\text{-}SR)_2$ is reductively cleaved by treatment with lithium aluminium hydride to give the corresponding carbon–hydrogen bond. Preliminary examination of the reaction mechanism is described.

Raney nickel has been widely used for the reduction of various organosulfur compounds for over several decades [2]. The mechanism for this important reaction, however, is not very clear. Some kind of interaction between the sulfur moiety and metal followed by "hydrogen transfer" from the metal surface has been suggested [3]. Organosulfur compounds can form different types of complex with transition metals [4]. It is noted that the carbon–sulfur bond of thiolato or related ligands in certain hydrido-osmium clusters can be cleaved by thermolysis [5] or photolysis [6]. The chelated thiolato ligands in niobium complexes behaved similarly [7]. Transi-

TABLE 1

REACTION OF I WITH $LiAlH_4$

Substrate	Product	Yield (%) [a]
Ia	Benzene	50
Ib	Toluene	55
Ic	Decane	80
Id	Naphthalene	80
Ie	*o*-Xylene	58

[a] Isolated yield.

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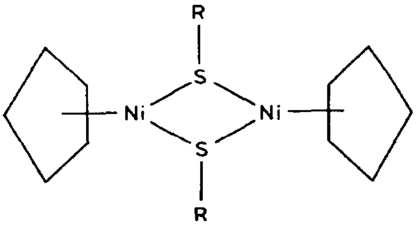
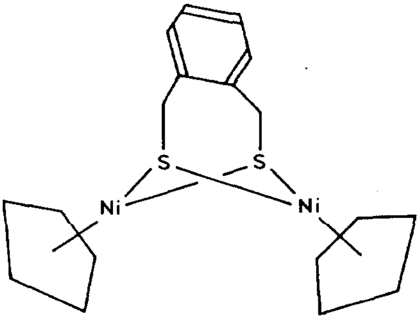
* For part XV see ref. 1.

0022-328X/86/$03.50

tion metal hydrides are known to reduce carbon–sulfur bonds of various organosulfur compounds [8–11]. We felt that the carbon–sulfur bond in certain thiolato complexes may also be activated and hence susceptible to reduction. Stable bridged nickel-organosulfur complexes such as I [12] may serve as a useful model to test this hypothesis. We now wish to describe the reaction of I with $LiAlH_4$.



(Ia: R = Ph;
Ib: R = $PhCH_2$;
Ic: R = 1-Decyl;
Id: R = 2-Naphthyl)



(Ie)

In a typical procedure, treatment of I with one to two equivalents $LiAlH_4$ in ether at ambient temperature for 2 h afforded the corresponding hydrocarbon in moderate to good yield. The results are summarized in Table 1.

As can be seen from Table 1, various carbon–sulfur bonds can be reduced under the reaction conditions. There is no apparent difference in reactivity among these substrates, although the nature of the carbon–sulfur bond in I is quite distinct. Treatment of Ib with $LiAlD_4$ gave toluene-d_1 in 55% yield. These results rule out possible radical-like mechanisms.

Preliminary examination on the mechanism of the reaction has been carried out by using ^1H NMR to follow the reaction. The lithium aluminum hydride was instantaneously consumed upon treatment with one equivalent of Ib in THF-d_8 and a new broad singlet at $\delta - 5.7$ ppm was observed *. This latter signal disapeared when lithium aluminum deuteride was employed. Presumably, some kind of metal hydride was formed. The signal due to the cyclopentadienyl moiety shifted from δ 4.50 ppm in Ib to δ 5.85 ppm and this latter peak remained unchanged throughout the reduction process. In addition, the absorption of the benzylic proton of this reaction mixture moved to higher field at δ 3.05 ppm **. This signal and the one at δ −5.7 ppm gradually disappeared and a new singlet at δ 2.31 ppm attributed to the absorption of the methyl protons of the product toluene appeared. The yield of toluene in this NMR experiment is essentially quantitative.

The infrared spectrum for a mixture of Ib and one equivalent of lithium aluminum hydride in THF exhibited only one absorption at 1697 cm^{-1} in the region between 1600–2600 cm^{-1} ***. Since lithium aluminum hydride has been

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* The absorption of protons in $LiAlH_4$ in THF-d_8 appears as broad sextet J(Al–H) 167 Hz) centered at δ 2.83 ppm

** The benzylic protons in Ib absorb at 3.30 ppm while those in free benzyl mercaptan at δ 370 ppm.

*** The infrared absorption of $LiAlH_4$ in THF appears at 1693 and 1644(sh) cm^{-1} (cf. A.E. Shirk and D.F. Shriver J. Am. Chem. Soc., 95 (1973) 5904). The shoulder at 1644 cm^{-1} disappeared in the reaction mixture.

found to react with the substrate instantaneously as discerned above, the absorption at 1697 cm^{-1} is assigned to some kind of metal hydride species. It is important to note that, as the reaction prolonged, the absorbance at this frequency gradually decreased. Such observation is consistent with our NMR results.

Attempts to isolate the metallic or sulfur product(s) were unsuccessful. Although the NMR spectrum of the reaction mixture and product in THF-d_8 solution appears to be quite simple as described above, decomposition may occur in the absence of solvent.

In summary, we have depicted the first example of the reduction of thiolato ligands in organonickel complexes by $LiAlH_4$. Our model suggests that the carbon–sulfur bond is indeed activated by complexation with nickel and subsequent hydride transfer affords the corresponding reduced hydrocarbon. The reaction may serve as a model for understanding the mechanism of Raney nickel desulfurization.

Acknowledgement. This research was made possible by the generous financial support of the Croucher Foundation. We thank Mr. Arthur Birch and Ms. O.Y. Lam of Dow Chemical (HK) Ltd. for the arrangement and measurement of Fourier transform IR data.

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