Inorganica Chimica Acta, 54 (1981) L241–L242
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Reactions of Coordinated Dinitrogen.
11 [1]. Enantioselective Carbon–Nitrogen Bond Formation

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Received July 23, 1981

Inorganic and organic chemists are actively looking for efficient methods of enantioselectively synthesizing compounds as a way of avoiding the need for resolution of enantiomers (and diastereomers) [2]. As part of our program for the synthesis of organonitrogen compounds from coordinated dinitrogen (eqn. 1; R = alkyl; X = Br, I; dppe = $Ph_2PCH_2CH_2PPh_2$)

$$\textit{trans}\text{-}Mo(N_2)_2(dppe)_2 + RX \longrightarrow MoX(NNR)(dppe)_2 + N_2 \qquad (1)$$

[3, 4] we undertook to prepare optically active bis(dinitrogen) complexes of molybdenum and react them with racemic organic halides as a route to enantioselective carbon-nitrogen bond formation. We prepared the pure diastereomer *trans*-$Mo(N_2)_2$[(S,S)-Chiraphos]$_2$**, *1*, where (S,S)-Chiraphos = (–)-(2S, 3S)-bis(diphenylphosphino)butane, $Ph_2PCH^*(CH_3)$-$CH^*(CH_3)PPh_2$ [5] (eqn. 2)

$$MoCl_3(THF)_3 + 2(S,S)\text{-Chiraphos} \xrightarrow[N_2]{Na/Hg;\,THF} \mathit{1}\ (52\%) \qquad (2)$$

and reacted it with racemic 2-bromooctane (RX) in benzene solution (eqn. 3).

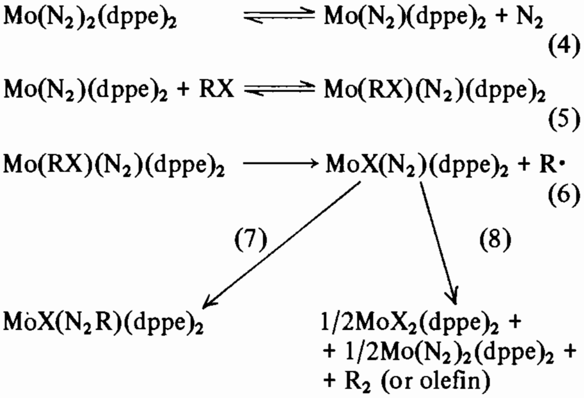
$$\mathit{1} + 2RX \longrightarrow \underset{\mathit{2}}{MoBr(NNR)[(S,S)\text{-Chiraphos}]_2} + N_2 + RX \qquad (3)$$

Solvent and unreacted 2-bromooctane were removed from the product mixture and the optical rotation measured. This reading indicated an excess of (S)-2-bromooctane in the recovered 2-bromooctane. The 2-octyldiazenido complex *2* was isolated in yields up to 78% and a small amount of $MoBr_2$[(S,S)-Chiraphos]$_2$ was also isolated.

Since complex *2* is diastereomeric, the α-methyl group (NNCH(CH_3)-) will display different chemical shifts in the ^1H NMR spectrum. We therefore recorded the ^1H NMR spectrum of *2* at 100, 200 and 396 MHz*. All three spectra showed the two resonances due to the α-methyl group of the two diastereomers, $MoBr(NNC_8H_{17}$-(S))[(S,S)-Chiraphos]$_2$, *2a* and $MoBr(NNC_8H_{17}$-(R))[(S,S)-Chiraphos]$_2$, *2b*. In addition all three spectra indicated that one diastereomer was in excess. In the 396 MHz ^1H NMR spectrum each methyl group appeared as a doublet, δ 0.23 and 0.32 ppm with $J_{H-H}(CHCH_3) = 6.0$ Hz.

In order to account for these interesting results it is necessary to look at the mechanism of the alkylation of $Mo(N_2)_2(dppe)_2$. This is shown in Scheme I [7].

Scheme I^a [7]



$$Mo(N_2)_2(dppe)_2 \rightleftharpoons Mo(N_2)(dppe)_2 + N_2 \qquad (4)$$

$$Mo(N_2)(dppe)_2 + RX \rightleftharpoons Mo(RX)(N_2)(dppe)_2 \qquad (5)$$

$$Mo(RX)(N_2)(dppe)_2 \longrightarrow MoX(N_2)(dppe)_2 + R\cdot \qquad (6)$$

$$MoX(N_2)(dppe)_2 \xrightarrow{(7)} MoX(N_2R)(dppe)_2$$

$$MoX(N_2)(dppe)_2 \xrightarrow{(8)} 1/2MoX_2(dppe)_2 + 1/2Mo(N_2)_2(dppe)_2 + R_2 \text{ (or olefin)}$$

The rate determining step is loss of N_2 (eqn. 4). The five coordinate mono(dinitrogen) intermediate reacts with bromo- or iodoalkanes to form a complex in which homolysis of the carbon–halogen bond occurs. The final molybdenum-containing products arise from radical coupling (eqn. 7) to give the alkyldiazenido complex and from disproportionation of $MoX(N_2)(dppe)_2$ (eqn. 8).

Our results with *2* and racemic 2-bromooctane fit nicely into this Scheme. Recovery of unreacted 2-bromooctane (eqn. 2) in which there is an excess of the (S)-enantiomer means that $\Delta G^{\ddagger}$ for the reaction of *1*(-N_2) with the (R)-enantiomer is less than that for the (S)-enantiomer. We are therefore seeing kinetic resolution at this stage of the reaction. The formation of the octyldiazenido complex (eqn. 7) involves reaction between the 2-octyl radical and the molybdenum(I) complex (eqn. 9). That this is a slow reaction has been shown

$$2\text{-}C_8H_{17}\cdot + MoBr(N_2)[(S,S)\text{-Chiraphos})]_2 \longrightarrow \mathit{2a} + \mathit{2b} \qquad (9)$$

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**$[\alpha]^{25}_{589} = +671°(C_6H_6)$; ν_{NN} 1962 cm^{-1} (CsI).

*See Acknowledgements.

by studies of the reaction of 6-bromo-1-hexene with $Mo(N_2)_2(dppe)_2$ [3, 6]. In this latter reaction, the product is exclusively the cyclopentylmethyldiazenido complex. The 6-hexenyl radical which is known to cyclize with a rate constant of *ca.* 10^4 s^{-1}, cyclizes before alkylation occurs. Therefore, the 2-octyl radical will have completely equilibrated before alkylation occurs (eqn. 9). We are therefore again seeing kinetic resolution. The excess of one diastereomer over the other (we cannot say which predominates from our data) arises because $\Delta G^{\ddagger}$ is different for the interaction of each of the two faces of prochiral trigonal carbon radical with chiral *1* (asymmetric synthesis [7]).

Acknowledgements

We thank the National Science Foundation and University of Nebraska Research Council for their generous support of this work. The 396 MHz ^1H NMR spectra were obtained in the Fourier transform mode on an instrument designed and constructed by Professor F.A.L. Anet of the Department of Chemistry, University of California, Los Angeles. We thank Dr. D. C. Busby for recording the 200 and 396 MHz spectra.

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