Journal of Organometallic Chemistry, 173 (1979) C9—C12
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Preliminary communication

REDUCTION OF COORDINATED CARBON MONOXIDE, FORMYL, AND HYDROXYMETHYL LIGANDS: MODELS FOR FISCHER–TROPSCH AND RELATED REACTIONS

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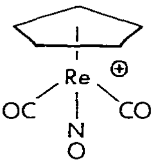
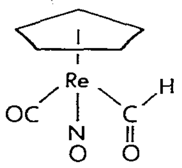
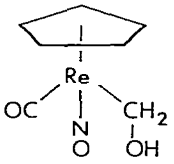
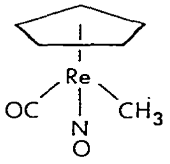
(Received March 27th, 1979)

In 1972 we reported the reduction of $[(\eta\text{-}C_5H_5)Re(CO)_2NO]^+[BF_4]^-$ (I) with $NaBH_4$ in tetrahydrofuran (THF) to form the methyl derivative $(\eta\text{-}C_5H_5)$-$ReCO(NO)CH_3$ (IV) [1]. This reaction, as well as prior observations by Treichel and Shubkin on Mo and W carbonyl cations [2], provided an early indication of the way in which coordination could activate carbon monoxide towards reduction. The current high level of interest in Fischer–Tropsch related processes, including the characterization of a number of anionic and neutral transition metal formyl complexes [3, 4], prompted us to examine the sodium borohydride reduction of I in detail.


I (BF_4^- salt)


II


III


IV

We now describe the preparation of the formyl complex II (reported by Casey et al. [5] during the course of our work and later by Gladysz et al. [6]), the hydroxymethyl derivative III, and a demonstration of all possible reduction steps in high yield among compounds I, II, III, and IV using a $NaBH_4$/THF/H_2O system. This is the first instance in which models for all presumed Fischer—Tropsch stages [7] (viz., M—CO, MCHO, MCH_2OH, and M—CH_3) have been isolated and their sequential reduction demonstrated. The following reactions summarise our findings*.

We believe that reaction 3 and the details below constitute the first synthesis

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*THF/H_2O is approximately 1:1 in which all compounds are soluble. NMR was used as follows to determine yields. A solution of the products in a known volume of CH_2Cl_2 was obtained either by solvent extraction (reactions 2, 3, 5, 7) or by removal of THF in vacuum and dissolution of the residue (reactions 1, 4, 6). An aliquot of the CH_2Cl_2 solution was evaporated at —30°C, THF-d_8 was added, and product estimated by integreation versus added benzene.

$$[CpRe(CO)_2NO]^+ + 1NaBH_4 \xrightarrow[25^\circ C,\ 60\ min]{THF} CpReCO(NO)CH_3\ (95\%) \qquad (1)$$

$$[CpRe(CO)_2NO]^+ + 1NaBH_4 \xrightarrow[0^\circ C,\ 15\ min]{THF/H_2O} CpReCO(NO)CHO\ (93\%) \qquad (2)$$

$$[CpRe(CO)_2NO]^+ + 2NaBH_4 \xrightarrow[0^\circ C,\ 30\ min]{THF/H_2O} CpReCO(NO)CH_2OH\ (97\%)(3)$$

$$CpReCO(NO)CHO + 1NaBH_4 \xrightarrow[25^\circ C,\ 60\ min]{THF} CpReCO(NO)CH_3\ (92\%) \qquad (4)$$

$$CpReCO(NO)CHO + 1NaBH_4 \xrightarrow[0^\circ C,\ 15\ min]{THF/H_2O} CpReCO(NO)CH_2OH\ (94\%)\ (5)$$

$$CpReCO(NO)CH_2OH + 1NaBH_4 \xrightarrow[25^\circ C,\ 5\ h]{THF} CpReCO(NO)CH_3\ (97\%) \qquad (6)$$

$$CpReCO(NO)CH_2OH + 1NaBH_4 \xrightarrow[25^\circ C,\ 5\ h]{THF/H_2O} CpReCO(NO)CH_3\ (88\%) \qquad (7)$$

and characterization of a hydroxymethyl transition metal complex,* notwithstanding an earlier claim [8]**. Two substituted hydroxymethyl complexes have been reported, (η-C_5H_5)$(OC)_2FeC(CF_3)_2OH$ [9] and the very unstable $(OC)_5MnCH(C_6H_5)OH$, for which evidence has been obtained as a reaction intermediate [10]. Moreover, the reduction of coordinated formyl to hydroxymethyl (reaction 5) has not previously been achieved; thus reaction of II with $Li[HBEt_3]$ resulted in hydride attack on the carbonyl ligand to form a bis(formyl) anion [5, 6]. The reduction of hydroxymethyl III to methyl IV (equations 6 and 7) provides a striking example of activation of a coordinated ligand, since normal alcohols are not reduced by $NaBH_4$.

The widely different reaction modes of sodium borohydride in anhydrous THF and in THF/H_2O require comment, and in our view have important synthetic applications. In the absence of water (reaction 1), cation I is reduced to the methyl complex IV by one mole of $NaBH_4$, showing that $NaBH_4$ can donate up to three hydrides under these conditions. In THF/H_2O (reaction 2) reduction of the cation proceeds only to the formyl (II). Similarly, one mole of $NaBH_4$ reduced formyl to methyl in THF (reaction 4) but only to hydroxymethyl in THF/H_2O (reaction 5). Clearly sodium borohydride transfers only one hydride in THF/H_2O, owing no doubt to the rapid hydrolysis of the initially formed BH_3 adduct, as indicated by gas evolution.

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*After the submission of this Communication, we learned that III had been prepared by an alternative route [11].

**We find, as did Casey et al. [5], that under the reported [8] conditions (benzene/water, 1.3 moles $NaBH_4$) the main product is II. In addition we observe traces of III and IV by NMR.

Suggestions [1, 2, 5] that formyl or hydroxymethyl derivatives are intermediates in the three-step sodium borohydride reduction of $[M{-}CO]^+$ to $M{-}CH_3$ under anhydrous conditions are imprecise in an important respect. Such intermediates are most probably present as borane adducts or esters, differing from the "free" formyl or hydroxymethyl compounds wich are obtained upon hydrolysis. Thus we observe that the rate of reaction of pure $CpReCO(NO)CH_2OH$ (III) in THF (reaction 6) is qualitatively much slower than the overall reduction of cation (I) to the methyl derivative (IV) (reaction 1); hence the hydroxymethyl complex III as such cannot be an intermediate in the overall reduction of eq. 1.

The hydroxymethyl complex III is recovered from reaction 3 by dichloromethane extraction and n-hexane precipitation. Recrystallization from $CH_2Cl_2/n\text{-}C_6H_{14}$ affords III in 70% yield as orange, air-stable crystals*, m.p. 95–96°C (sealed capillary under N_2), which are insoluble in hexane, moderately water soluble, and very soluble in THF, CH_2Cl_2, and C_6H_6. These properties are not in accord with those of the previous claim of III [8]**. The mass spectrum at 16 eV showed only peaks due to $[CpReCO(NO)CH_2OH]^+$, $[CpRe(NO)CH_2OH]^+$, $[CpRe(CO)CH_2OH]^+$, and $[CpReCH_2OH]^+$. The infrared spectrum (THF) shows ν(OH) at 3460 (s,br), ν(CO) at 1956 (s), and ν(NO) at 1700 (s) cm^{-1}. The proton NMR was definitive, showing in dimethylsulfoxide-d_6 a sharp singlet (5H) at δ 5.88 ppm and the expected ABX pattern for the $-CH_2OH$ group ($\delta(H_A)$ 5.14, $\delta(H_B)$ 5.55, $\delta(H_X)$ 3.94 ppm; $^3J_{AX}$ 6.1, $^3J_{BX}$ 5.5, $^2J_{AB}$ 9.3 Hz).

Casey's very recent preparation of II as slightly impure, thermally unstable orange oil utilized the reduction of I (PF_6^- salt) in THF with $K[HB(O\text{-}i\text{-}Pr)_3]$ or $Li[HBEt_3]$, followed by hydrolysis [5]. We find that II is conveniently prepared from I with equimolar $NaBH_4$ in water. After initial hexane extractions to remove traces of IV, II is extracted into additional portions of hexane which are combined and cooled to −30°C affording an orange, microcrystalline solid, thermally stable to about −10°C and not very air sensitive below that temperature. IR(hexane): 2001 (s), ν(CO); 1737 (s), ν(NO); 1635 (m) cm^{-1} ν(CHO). Proton NMR (methylcyclohexane-d_{14}) δ 5.51 (5H), 16.2 (1H) ppm. These values are in reasonable agreement with those reported in other solvents [5, 6].

Acknowledgment

We thank the National Science and Engineering Research Council of Canada for support and for a scholarship to JRS.

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**See also second footnote on previous page.

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