Journal of Organometallic Chemistry, 215 (1981) C53—C56
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOTOCHEMICAL REACTION OF $(\eta^5\text{-}C_5H_5)_2NbH_3$ WITH $Mn_2(CO)_{10}$: STRUCTURE OF $[((\eta^5\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$

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(Received February 19th, 1981)

Summary

The photochemical reaction of $(\eta^5\text{-}C_5H_5)_2NbH_3$ with $Mn_2(CO)_{10}$ leads to an ionic product, $[((\eta^5\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$, whose crystal structure suggests a localized, asymmetric bonding description, $Cp_2(CO)NbH \rightarrow Nb(CO)Cp_2^+$, with Nb—Nb = 3.7739(8) Å. The NMR signal for the bridging hydrogen sharpens at lower temperatures.

We have previously reported upon thermal reactions of Cp_2NbH_3 (Cp = $\eta^5\text{-}C_5H_5$) with a variety of metal carbonyls [1—5]. With $Mn_2(CO)_{10}$, $Cp_2NbH(CO)$ was the only product obtained, presumably arising via hydridic attack on CO, leading to a bimetallic compound which (in this case) is unstable to the reaction conditions [5]. Herrmann has reported that stable bimetallic compounds of this type can often be more readily obtained photochemically: for example, photolysis of Cp_2NbH_3 with $Cr(CO)_6$ gives $Cp_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$ [6], whereas the thermal reaction again gives only $Cp_2NbH(CO)$ [4,5]. We anticipated that photolysis of Cp_2NbH_3 with $Mn_2(CO)_{10}$ might give $Cp_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4$, the isoelectronic analog of $Cp_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ which we have previously made and structurally characterized [3]; however, quite different products are formed instead.

Near-UV irradiation of a toluene solution of the two reagents at –15°C leads to a new compound (by NMR) which is too unstable to isolate: on standing in the dark at –20°C the solution darkens, evolves gas bubbles, and gradually deposits a red precipitate (I) as plates or as an oil. Addition of hexane to the supernatant solution and further cooling gives small crystals of a reddish-brown product (II). These have distinctly different properties: I is insoluble in non-polar solvents but dissolves in acetone or CH_2Cl_2; exhibits CO stretches in the IR (Nujol mull) at 2045w, 2010s, 1975m, 1935s, 1900m,

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1890m, 1870(sh) and 1850m cm^{-1}; and NMR signals (acetone-d_6) at δ 5.56 and –23.44 ppm. II is readily soluble in benzene, has CO stretches (Nujol mull) at 2075m, 2000s, 1970(br), 1935s, 1920(sh) and 1900m cm^{-1} and NMR peaks (benzene-d_6) at δ 4.60 and –20.89 ppm. I and II were also obtained from the thermal reaction (25°C) of Cp_2NbH_3 with either $HMn(CO)_5$ or $CH_3Mn(CO)_5$ [7].

The solubility properties of I suggest an ionic compound, and the appearance of IR bands characteristic of the $Mn(CO)_5^-$ ion [8] support this. A crystal of I of dimensions 0.6 × 0.3 × 0.1 mm was selected for crystallographic study. The crystal is orthorhombic, with cell dimensions a = 13.583(3), b = 15.565(3), c = 12.622(2) Å: space group $P2_12_12_1$; Z = 4. Diffraction data were collected on a Syntex P$\bar{1}$ diffractometer, using Mo-K_α radiation; $3.5° < 2\theta < 60°$; 3514 independent reflections used. The Nb atoms were located from the Patterson function, and Mn, C and O atoms from a series of difference Fourier maps; Cp ring hydrogens were assigned fixed positions. After correcting for absorption, a bridging hydrogen atom was located by using only low-angle data [9]. All non-hydrogen atoms were refined anisotropically; the final agreement factors are R = 0.040 and R_w = 0.045.

The structure of I is shown in Fig. 1. Although crystallographic location of the metal-bonded, bridging hydrogen is not completely conclusive*, its presence is unequivocal from the NMR: not only is a high-field signal observed, but a cationic species without an H would be paramagnetic. The cation, $[(Cp_2(CO)Nb)_2(\mu\text{-}H)]^+$, may be considered from either of two points of view: (i) as a symmetric dimer, containing two equivalent, 17-electron, $(Cp_2Nb(CO))$ fragments, joined by a protonated metal—metal bond; or (ii) as an asymmetric

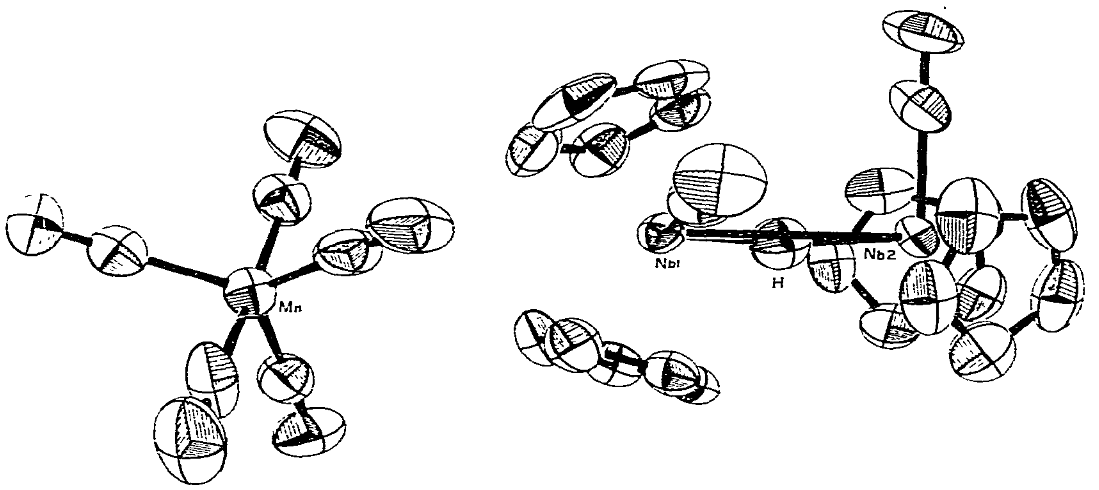

Fig. 1. Structure of compound I.

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* Although the H position refined properly, its intensity was not significantly greater than noise levels; also, it has a non-bonded distance from one of the Cp carbons that is considerably shorter (2.38 (6) Å) than expected.

member of the series of compounds $Cp_2(CO)Nb(\mu\text{-}H)ML_n$, wherein the 18-electron grouping $Cp_2NbH(CO)$ acts as a two-electron donor to a 16-electron fragment ML_n. Previously reported examples of this class have ML_n = $Fe(CO)_4$ [2]; $CpMn(CO)_2$ [6]; $Cr(CO)_5$ [6]; $CpV(CO)_3$ [6] and $CpNb(CO)_3$ [10]; here ML_n would be $[Cp_2Nb(CO)]^+$, which has previously been generated as an unstable, trappable intermediate [11].

Certain details of the structure suggest, though not conclusively, that the second description may be more accurate. In all previous structures of this type, the atoms Nb, H, CO and M are all coplanar. In I, the two ($Cp_2Nb(CO)$) units are staggered by 71.3(3)° with respect to one another (a similar staggering, ca. 90°, was recently found for isoelectronic $[(Cp_2HW)_2(\mu\text{-}H)]^+$ [12]); instead of being symmetrically placed with respect to the two Nb—Nb—CO planes, though, the bridging H lies strictly in one plane (that defined by the two Nb atoms and the CO on Nb(1), and well out of the other (0.36(2) Å). The Nb—H and Nb—C(O) distances also differ (Nb(1)—H = 1.90(6); Nb(2)—H = 1.96(6); Nb(1)—C(O) = 2.056(7); Nb(2)—C(O) = 2.026(6) Å), although only the latter difference is statistically significant. These points appear consistent with the asymmetric model, with Nb(1) acting as the 18-electron donor center. In either case, the long Nb—Nb distance, 3.7739(8) Å, is consistent with the implicit formulation of the interaction as a two-electron three-center bond [2,13].

The asymmetry does not persist in solution, at least by NMR criteria: the sharp singlet observed for the Cp protons remains so down to the point where viscosity broadening sets in (about −80°C) (This means that rotation about the Nb—Nb axis must also be fast, since the staggered conformation makes the two Cp's on each metal nonequivalent).One might thus argue that the molecular asymmetry in the solid state should be ascribed to crystal packing, rather than to inherent bonding preferences. (A useful analogy may be made to the trihalide ions, X_3^-, which could similarly be viewed as symmetric or asymmetric (i.e., X^- acting as a donor to X_2), and which can exhibit either type of structure depending upon the counterion [14]). Of note is the fact that the signal for the bridging hydride sharpens considerably as the temperature is lowered, from a half-width of 30—35 Hz at ambient temperature to 10 Hz below −20°C. This must be due to thermal decoupling [15], where the increased viscosity at lower temperatures increases the relaxation rate of the quadrupolar ^{93}Nb nuclei and thus effectively removes the broadening caused by ^1H—^{93}Nb coupling.

The $Mn(CO)_5^-$ anion has structural parameters quite similar to those previously reported [16], although there is slightly more distortion from ideal trigonal bipyramidal geometry than in the previous structures. For example, the C_{axial}—Mn—C_{axial} angle is 172.4(3)° in I and 179° in the two prior structures.

Compound II has not yet been characterized; although it appears to be a non-ionic complex, analytical results are not compatible with the looked-for $Cp_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4$, and the NMR shows the presence of a metal hydride. Further work on this species and on the mechanism leading to these products is in progress [17].

Acknowledgments

This work was supported by National Science Foundation grants CHE 77-01585 and CHE 80-06518. We thank Mr. Don Schifferl for assistance with NMR studies and the University of Notre Dame Computer Center for providing computing time. We are also grateful to Dr. W.A. Herrmann for communicating results prior to publication, and to Dr. T.P. Fehlner for helpful discussions.

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17 *Note added in proof.* In the tantalum analog, a compound which spectroscopically resembles II has been crystallographically characterized as $Cp_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$, isoelectronic (and structurally quite similar) to known $HRe_3(CO)_{14}$ and $HMnRe_2(CO)_{14}$.