Journal of Organometallic Chemistry, 323 (1987) C25–C28
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

SYNTHESIS AND STRUCTURE OF [1–5-η-6-*exo*-Re(CO)$_5$C$_7$H$_8$]Mn(CO)$_3$. THE FIRST EXAMPLE OF METAL CARBONYL ANION ADDITION TO A COORDINATED CYCLIC π-HYDROCARBON

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(Received November 1st, 1986)

Summary

The metal carbonyl anion Re(CO)$_5^-$ adds to the cycloheptatriene ligand in [(η-C$_7$H$_8$)Mn(CO)$_3$]BF$_4$ to give the title cycloheptadienyl complex, whose X-ray-determined structure shows the Re(CO)$_5$ moiety to be in an *exo* position. Although previous attempts to add metal carbonyl anions to cyclic π-hydrocarbons were unsuccessful, the present report clearly demonstrates that such reactions are possible.

A variety of nucleophiles are known [1] to add to coordinated π-hydrocarbon ligands; however, analogous reactions of transition metal carbonyl anion nucleophiles have received little attention. Additions to ethylene were achieved in the reactions of CpM(CO)$_3$(η^2-C$_2$H$_4$)$^+$ (M = Mo, W) with CpM(CO)$_3^-$ (M = Mo, W) and Re(CO)$_5^-$ [2], CpW(CO)$_2$(PPh$_3$)(η^2-C$_2$H$_4$)$^+$ with CpW(CO)$_2$(PPh$_3$)$^-$ [2], and M′(CO)$_5$(η^2-C$_2$H$_4$)$^+$ with M′(CO)$_5^-$ (M′ = Mn, Re) [3]. Attempts to add metal carbonyl anions to π-tropylium and π-benzene complexes have been unsuccessful [3], resulting in reductive coupling of (η^7-C$_7$H$_7$)M(CO)$_3^+$ through the tropylium ligand (M = Cr, Mo, W) or in complex salt formation with (η^7-C$_7$H$_7$)Mn(η^5-C$_5$H$_4$Me)$^+$, (η^6-C$_6$H$_6$)Mn(CO)$_3^+$, and (η^6-C$_6$H$_6$)Mn(CO)$_2$(PBu$_3$)$^+$. Extending our interest [4] in nucleophilic additions to π-hydrocarbon complexes, we now report the reaction (eq. 1) of Re(CO)$_5^-$ with (η^6-cycloheptatriene)Mn(CO)$_3^+$ to form [1-5-η-6-*exo*-Re(CO)$_5$C$_7$H$_8$]Mn(CO)$_3$ (**1**), the first example of a complex resulting from nucleophilic addition of a metal carbonyl anion to a coordinated cyclic π-hydrocarbon.

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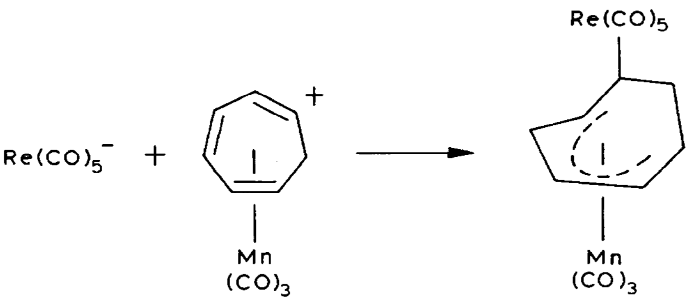

(1)

(1)

Addition of a slight excess of $NaRe(CO)_5$ in THF solution to a stirred suspension of $[(\eta^6\text{-}C_7H_8)Mn(CO)_3](BF_4)$ [5] (102 mg, 0.321 mmole) in THF at 0 °C for 5 min under N_2, resulted in a clear orange solution whose IR spectrum in the ν(CO) region showed **1** as the major product. Evaporation of the solvent gave an orange residue which was chromatographed on silica gel; a broad yellow product band was eluted with hexane. The yellow solution was concentrated, and successive crystallizations from hexane at −20 °C yielded pale yellow crystals (24.1 mg, 13.5%) of $[1\text{-}5\text{-}\eta\text{-}6\text{-}exo\text{-}Re(CO)_5C_7H_8]Mn(CO)_3$, **1**. An additional 23.0 mg (12.8%) of the product was isolated by evaporation of the mother liquor as a slightly impure powder. The relatively low yield appears to be due to losses during purification; no attempt was made to optimize the yield. The product was characterized by elemental analysis and its IR, ^{1}H NMR and mass spectra [6]; all data were consistent with the formulation of the compound as $[\eta\text{-}C_7H_8 \cdot Re(CO)_5]Mn(CO)_3$. A single crystal X-ray diffraction study [7] of **1** has confirmed the identity of the product and also clearly established the *exo*-orientation of the $Re(CO)_5$ fragment at C(6) (Fig. 1). The Re–C(6) bond distance is 2.335(9) Å, which is slightly longer than rhenium–methylene carbon bond lengths in $(\eta\text{-}C_5H_5)Re(CO)_2H(CH_2Ph)$ (2.29(1) Å) [8], $(CO)_5ReCH_2CH_2Re(CO)_5$ (2.304(8) Å) [3], and (−)-(*R*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ph)$ (2.203(8) Å) [9], but is in the range of Re–C(η^1-C_5H_5) bond lengths in $(\eta^1\text{-}C_5H_5)Re(Me)(CO)(NO)(PMe_3)_2$ (2.32(1) Å) [10] and $(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$ (2.360(10) Å) [11].

The Mn is bonded to the η-cycloheptadienyl ligand through the five unsaturated carbons with Mn–C distances of 2.218(10) (C(1)), 2.090(11) (C(2)), 2.145(13) (C(3)), 2.132(11) (C(4)), and 2.285(9) Å (C(5)). Carbon–carbon distances in the ring are 1.425(20) (C(1)–C(2)), 1.413(20) (C(2)–C(3)), 1.437(20) (C(3)–C(4)), 1.372(14) (C(4)–C(5)), 1.474(12) (C(5)–C(6)), 1.549(12) (C(6)–C(7)), and 1.530(14) Å (C(1)–C(7)). The C(5)–C(6) distance of 1.474(12) Å is somewhat shorter than C(1)–C(7) (1.530(14) Å), a typical C(sp^2)–C(sp^3) bond distance. The C(5)–C(6) length is, however, similar to those found for C–C bonds adjacent to the Re–C bonds in η^1-C_5H_5 compounds, $(\eta^1\text{-}C_5H_5)Re(Me)(CO)(NO)(PMe_3)_2$ (1.48 and 1.44 Å) [10] and $(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$ (1.475 and 1.448 Å) [11]. The C–C–C angles at each of the ring carbon atoms are 120.6(11) (C(1)), 123.5(10) (C(2)), 120.2(11) (C(3)), 128.7(10) (C(4)), 132.5(8) (C(5)), 116.7(7) (C(6)), and 112.7(8)° (C(7)).

The C(5)–C(6)–C(7)–C(1) linkage is twisted as depicted in Fig. 2. The planes defined by C(5), C(6), C(1) and C(5), C(7), C(1) are bent 37° and 54°, respectively,

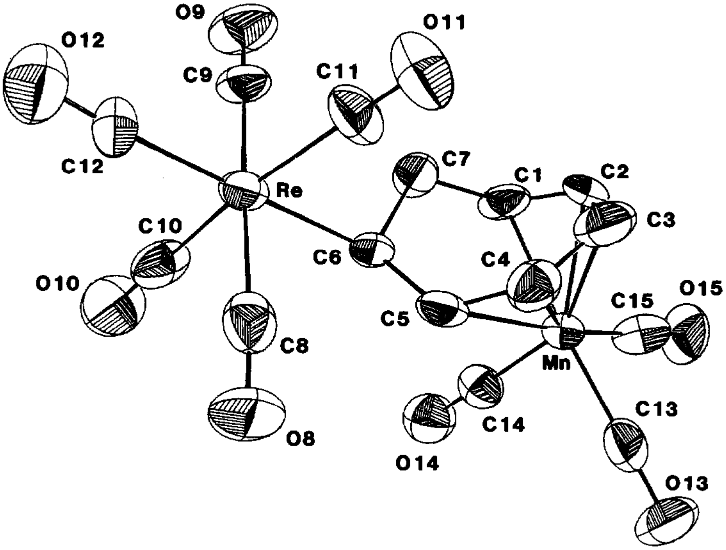

Fig. 1. ORTEP drawing of [1–5-η-6-*exo*-Re(CO)$_5$C$_7$H$_8$]Mn(CO)$_3$, **1**; hydrogen atoms omitted.

away from the plane of the pentadienyl carbons, resulting in a twist angle of 17° for the saturated carbon bridge. This distortion is not observed for the related PPh$_3$ adduct, [(η^5-6-*exo*-PPh$_3$C$_7$H$_8$)Mn(CO)$_3$](BF$_4$) [12], which has an essentially planar set of carbon atoms corresponding to C(5), C(6), C(7), and C(1) in **1**.

The Mn–C distances to the CO carbons, 1.837(10) (C(13)), 1.792(10) (C(14)), and 1.796(12) Å (C(15)), are within the normal range [13]. The Re–C carbonyl distances range from 1.97 to 2.01 Å (average of 1.99 Å), again similar to distances observed in other rhenium carbonyl compounds [3,14].

Since **1** involves Mn bonded to five cycloheptadienyl carbon atoms and Re to only one, it was of interest to explore the possibility that **1** could be converted to a

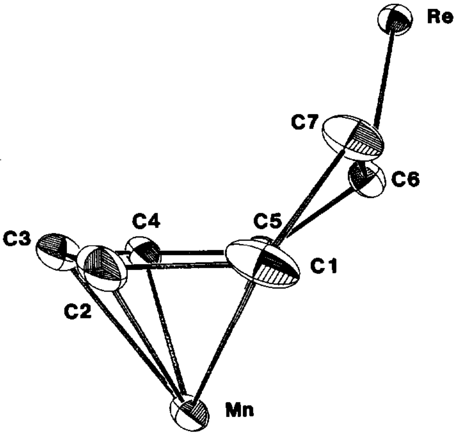

Fig. 2. ORTEP drawing of **1** illustrating the ligand geometry. Hydrogen atoms and carbonyls have been omitted for clarity.

complex in which both Mn and Re were bonded to 3 carbon atoms (η^3) while shifting a CO ligand from Re to Mn. In attempts to induce these changes, a hexane solution of **1** was heated at 45 °C for 1 h while CO was bubbled through the reaction flask. However, no reaction was observed, even after heating at 60 °C for an additional 30 min. Photolysis of **1** in hexane in the presence of CO for 3 h resulted only in decomposition of the starting material.

In summary, the occurrence of reaction 1 demonstrates that despite earlier unsuccessful attempts, metal carbonyl anion additions to cyclic π-hydrocarbons are possible, and other reactions of this type may be anticipated in the future.

Supplementary material (selected bond distances and angles, atomic coordinates, temperature factors, and structure factors for **1**) are available from the authors.

Acknowledgment. Support by the National Science Foundation (Grant CHE-8401844 to R.J.A.) of this research is gratefully acknowledged. The X-ray diffraction investigation was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, under contract W-7405-Eng-82. We thank Lance L. Miller for assistance with the X-ray studies.

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6 IR (hexanes) ν(CO) 2126(w), 2019(vs), 1993(s), 1949(ms), 1936(ms) cm^{-1}; ^1H NMR($CDCl_3$): δ 1.45 (m, H(7)*exo*), 2.07 (dt, H(7)*endo*), 3.36 (td, H(6)), 3.99 (m, H(1)), 4.44 (dd, H(4)), 5.31 (dd, H(5)), 5.50 (dd, H(2)), 5.69 (brt, H(3)); Coupling Constants: J_{1-2} 8.1 Hz, J_{2-3} 5.6 Hz, J_{3-4} 6.3 Hz, J_{4-5} 9.9 Hz, J_{5-6} 3.6 Hz, $J_{6-7exo} \cong 9.8$ Hz, $J_{6-7endo} \cong 8.6$ Hz, J_{1-7exo} 3 Hz, $J_{1-7endo} \cong 8.6$ Hz, $J_{7endo-7exo}$ 13 Hz, $J_{1-3} \cong 2$ Hz. Assignments were made on the basis of observed coupling in the spectrum run in $CDCl_3$ solvent and a 2-D proton-proton coupling experiment carried out on a C_6D_6 solution of **1**. Anal. Found: C, 32.15; H, 1.69. $C_{15}H_8O_8MnRe$ calc: C, 32.32; H, 1.45%. MS (16 eV), m/e (intensity): 473.7(0.72)$M^+ - 3CO$, 445.8(0.27)$M^+ - 4CO$, 417.8(0.89)$M^+ - 5CO$, 231.0(100.0)$M^+ - Re - 5CO$.

7 Crystallographic data for **1**: mol wt. 557.36; triclinic; space group $P\bar{1}$; a 11.098(6), b 12.177(3), c 6.823(3) Å, α 106.35(3), β 106.45(5), γ 87.27(5)°, V 848.1 $Å^3$, $Z = 2$, ρ_{calc} 2.182 g cm^{-3}, μ 79.8 cm^{-1}. Diffraction data were collected using an automated diffractometer (Mo-K_α radiation, ω scan) and corrected for absorption (3308 measured reflections with $2\theta \leqslant 50°$, 2745 observed reflections with $I \geqslant 1.5\ \sigma I$ were used for structural solution and refinement). The structure was solved by analysis of a sharpened Patterson map to locate the metal atoms. Successive electron density maps were used to locate the lighter atoms. The structure was refined by a combination of block and full matrix refinement techniques with all non-hydrogen atoms anisotropic. The hydrogen atoms were fixed at calculated positions. $R = 0.049$ and $R_w = 0.065$ ($w = \sigma F^{-2}$).

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