Electrochemistry and Oxidatively Induced CO Insertion of $(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5)$

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Electron transfer has been shown to initiate many organometallic reactions including isomerization, ligand substitution, cleavage of metal—metal bonds, and migratory insertion of CO [1, 2]. The reactions can be stoichiometric or catalytic with respect to net electron transfer. One particularly interesting reaction which proceeds through electron transfer catalysis is the oxidatively induced migratory insertion of CO in $CpFe(CO)(PPh_3)CH_3$ ($Cp = \eta^5\text{-}C_5H_5$) [3]. Since the reaction is catalytic with respect to electrons, reaction with only a few mole percent of a chemical oxidant can result in complete conversion to the acyl complex. Non-catalytic oxidatively induced CO insertion has also been observed for this and related iron complexes [4–6] as well as for tungsten and molybdenum complexes of the type $CpM(CO)_3R$ [7, 8].

During the course of an investigation of the electrochemistry of cyclopentadienyl molybdenum complexes, we became aware of the existence of cycloheptatrienyl molybdenum complexes which are isoelectronic with the above iron complexes. We decided to investigate the electrochemistry of such complexes to determine whether they too would undergo electron transfer catalyzed oxidatively induced CO insertion. Very few examples of alkyl and aryl complexes of the type $(\eta^7\text{-}C_7H_7)Mo(CO)_2R$ have been reported. The simplest members of the series, with R = methyl and phenyl, have been synthesized and shown to undergo direct insertion of chalcogen dioxides and zinc [9]. However, the methyl complex decomposes within one day at −78 °C and the phenyl complex is stable for only a few minutes at room temperature. The alkynyl complex $(\eta^7\text{-}C_7H_7)Mo(CO)_2CCPh$ has been prepared and is much more stable [10]. The corresponding diphos complex $(\eta^7\text{-}C_7H_7)Mo(dppe)CCPh$ displayed a reversible one-electron oxidation in dichloromethane, but the electrochemistry of the dicarbonyl was not reported.

To our knowledge, the only other reported $(\eta^7\text{-}C_7H_7)Mo(CO)_2R$ complex is the pentafluorophenyl complex $(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5)$ [11]. This com-

plex is synthesized by reaction of pentafluorophenylmagnesium bromide with $(\eta^7\text{-}C_7H_7)Mo(CO)_2I$ and is quite stable. The structure of this unique complex has been examined in detail [11, 12] but neither its electrochemistry nor its redox reactivity has been investigated.

Experimental

The complex $(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5)$ was prepared according to the literature procedure [11]. Dichloromethane (Fisher, optima grade) used for electrochemical studies was distilled from calcium hydride and stored under nitrogen. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) obtained from Southwestern Analytical Chemicals (electrometric grade) and was used as received. All other chemicals were reagent grade or better.

Electrochemical experiments were conducted with either a Bioanalytical Systems BAS 100A electrochemical analyzer or a BAS CV 27 voltammograph. The working electrode for cyclic voltammetry was a 0.5 mm diameter platinum disk polished with 0.3 micron alumina polishing powder (Buehler). The working electrode for controlled potential electrolysis was a 25 × 25 mm platinum foil. The reference electrode was either an aqueous saturated KCl Ag/AgCl reference electrode or a silver wire quasi-reference electrode. Potentials are expressed relative to the formal potential of the ferrocenium/ferrocene (Fc^+/Fc) couple, which we measure as +0.60 V *versus* Ag/AgCl.

Organic product analyses were performed with a Hewlett Packard Model 5840A gas chromatograph equipped with an OV-210 column and a thermal conductivity detector. Methyl pentafluorobenzoate and pentafluorobenzene were identified and quantitated by comparison of retention times and peak areas with authentic samples obtained from Aldrich Chemical Co.

Results and Discussion

As a part of our study of oxidatively induced CO insertion we have examined the electrochemical and chemical oxidations of $(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5)$ (1). Cyclic voltammetry of 1 in nitrogen-purged dichloromethane revealed a reversible one-electron oxidation with a formal potential of +0.49 V *versus* Fc^+/Fc. Plots of peak current *versus* square root of scan rate were linear, and cathodic and anodic peak currents were equal over a range of scan rates from 20 to 500 mV/s. Peak separations were in

the range of 60–80 mV, the same as is observed under our conditions for the reversible one-electron oxidation of ferrocene. Similar behavior has been observed with the isoelectronic iron complexes [3–6]. However, unlike the iron complexes, saturating the solution with CO had no effect on the cyclic voltammograms. Electron-transfer catalyzed insertion of CO would have resulted in a sharp decrease in the peak currents and possibly the appearance of a new couple at a higher potential for the acyl complex.
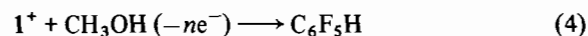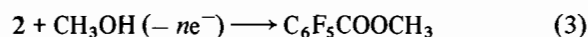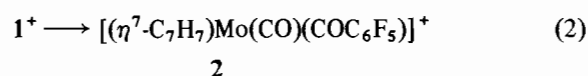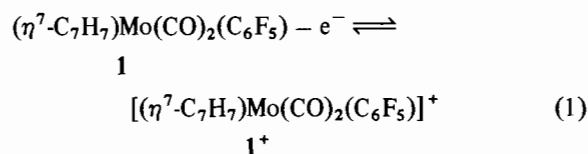
With the apparent stability of the 17-electron cation on the cyclic voltammetric time scale and the absence of electron-transfer catalyzed CO insertion, we decided to try to generate and isolate the cation. However, controlled potential electrolysis at room temperature at a potential approximately 200 mV positive of the formal potential of the reversible oxidation did not lead to a stable product. During the electrolysis the solution color changed from green to purple, but the oxidation consumed more than 1 Faraday of charge, the current never decreased to a background level, and the solution color changed back to green shortly after the electrolysis was stopped. Cyclic voltammetry of the product solution showed a significant decrease in peak currents, indicating that decomposition had occurred during the electrolysis. In an attempt to stabilize the oxidation product, the electrolysis was repeated at −10 °C. The current decreased to less than 10% of the initial value after passage of 1 Faraday of charge and the purple color of the product faded much more slowly, but cyclic voltammetry still indicated almost 50% decomposition. The 17-electron cation apparently is stable on the relatively short cyclic voltammetric time scale, but decomposes on the longer controlled potential electrolysis time scale.

Since we were unable to generate a stable cation from **1**, we next attempted to conduct the oxidation in the presence of ligands which might give rise to a stable product. Cyclic voltammetric experiments in the presence of nitric oxide and nucleophiles such as pyridine and trimethyl phosphite revealed that they caused the oxidation to become irreversible, presumably through chemical reaction with the cation. However, controlled potential electrolyses in the presence of CO, NO and trimethyl phosphite did not generate any identifiable products.

In a final attempt to observe oxidatively induced CO insertion, we conducted chemical oxidations of **1** in methanol at room temperature with 10 equivalents of ceric ammonium nitrate. Gas chromatographic analysis at 180 °C revealed rapid formation of 0.48 equivalents of methyl pentafluorobenzoate (average of five experiments). Further analysis of two of the oxidized solutions using

temperature programming from 70 to 200 °C found approximately 0.6–0.7 equivalents of pentafluorobenzene. Authentic methyl pentafluorobenzoate and the oxidation product identified as the ester had the same retention time under both isothermal and temperature-programmed conditions. Similar yields of methyl pentafluorobenzoate were also obtained with $NOBF_4$ as oxidant. Blank experiments demonstrated that the pentafluorobenzene does not arise from chemical oxidation of methyl pentafluorobenzoate by excess ceric ammonium nitrate.

Thus we have shown that $(\eta^7\text{-}C_7H_7)Mo(CO)_2\text{-}(C_6F_5)$ does undergo oxidatively induced CO insertion upon chemical oxidation in methanol. The reaction probably involves reversible electron transfer (eqn. (1)) followed by competing chemical reactions. Insertion of CO (eqn. (2)), followed by reaction with methanol and possibly further oxidation (eqn. (3)), yields methyl pentafluorobenzoate. Reaction with methanol before CO insertion (eqn. (4)), also possibly involving further oxidation, produces pentafluorobenzene.

$$(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5) - e^- \rightleftharpoons$$
$$\mathbf{1}$$
$$[(\eta^7\text{-}C_7H_7)Mo(CO)_2(C_6F_5)]^+ \qquad (1)$$
$$\mathbf{1^+}$$

$$\mathbf{1^+} \longrightarrow [(\eta^7\text{-}C_7H_7)Mo(CO)(COC_6F_5)]^+ \qquad (2)$$
$$\mathbf{2}$$

$$\mathbf{2} + CH_3OH \, (- ne^-) \longrightarrow C_6F_5COOCH_3 \qquad (3)$$

$$\mathbf{1^+} + CH_3OH \, (- ne^-) \longrightarrow C_6F_5H \qquad (4)$$

Under the conditions of our experiments the rates of reactions (2) and (4) are apparently similar so that about equal yields of ester and arene result. The IR spectrum of the product solution displayed no carbonyl bands which could be attributed to an organometallic molybdenum product, so the molybdenum is presumably oxidized to an inorganic species.

Having shown that cycloheptatrienyl complexes will undergo oxidatively induced CO insertion, we plan to study other examples. The phosphine-substituted iodo complex $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$ has been reported [13], but the corresponding pentafluorophenyl complex has not. We are pursuing this synthesis. Phosphine substitution will decrease the formal potential of the oxidation and should stabilize the 17-electron cation [4]. We also intend to search for other stable cycloheptatrienyl complexes which might undergo oxidatively induced CO insertion.

Acknowledgements

References

1 N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem., 23* (1984) 1.
2 W. E. Geiger and N. G. Connelly, *Adv. Organomet. Chem., 24* (1985) 87.
3 R. H. Magnuson, R. Meirowitz, S. J. Zulu and W. P. Giering, *Organometallics, 2* (1983) 460.
4 R. H. Magnuson, S. Zulu, W. M. Tsai and W. P. Giering, *J. Am. Chem. Soc., 102* (1980) 6887.
5 R. H. Magnuson, R. Meirowitz, S. Zulu and W. P. Giering, *J. Am. Chem. Soc., 104* (1982) 5790.
6 M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc., 109* (1987) 5127.
7 S. N. Anderson, C. W. Fong and M. D. Johnson, *J. Chem. Soc., Chem. Commun.,* (1973) 163.
8 J. Z. Chrzastowski and M. D. Johnson, *J. Chem. Soc., Dalton Trans.,* (1976) 2456.
9 W. H. Dell and M. L. Ziegler, *Z. Naturforsch., Teil B, 37* (1982) 1.
10 J. S. Adams, C. Bitcon, J. R. Brown, D. Collison, M. Cunningham and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.,* (1987) 3049.
11 M. D. Rausch, A. K. lgnatowicz, M. R. Churchill and T. A. O'Brien, *J. Am. Chem. Soc., 90* (1968) 3242.
12 M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A,* (1969) 1110.
13 T. W. Beall and L. W. Houk, *Inorg. Chem., 11* (1972) 915.