Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 23 (2004) 1371–1374

POLYHEDRON

www.elsevier.com/locate/poly

Oxidatively induced one-electron reductive elimination of pentafluorophenyl from $[Mo(C_6F_5)(CO)_5]^-$

Jungsook Kim, Stephen L. Gipson *

Department of Chemistry, Baylor University, Waco, TX 76798, USA

Received 11 December 2003; accepted 15 February 2004
Available online 12 April 2004

Abstract

The anionic molybdenum(0) complex $[Mo(C_6F_5)(CO)_5]^-$ displays a one-electron oxidation by cyclic voltammetry that is only partially chemically reversible. The partial chemical reversibility is caused by a slow chemical reaction following oxidation. This reaction has been shown to be cleavage of the Mo–C_6F_5 bond in a one-electron reductive elimination process. Chemical oxidation by ferrocenium in the presence of nucleophiles yields known $Mo(CO)_5L$ (L = Py, PPh_3) complexes, while oxidation with tropylium traps the C_6F_5 radical as $C_7H_7C_6F_5$. NMR and mass spectrometry were used to identify the oxidation products. Simulated cyclic voltammograms have been used to estimate the rate constant for cleavage of the Mo–C_6F_5 bond in the presence of pyridine as approximately 700 $M^{-1}\,s^{-1}$.

Keywords: Molybdenum complexes; Carbonyl complexes; Pentafluorophenyl; Oxidation; Bond cleavage; Reductive elimination

1. Introduction

For some years now we have been studying the redox-induced chemistry of pentafluorophenylmolybdenum carbonyl complexes. We have shown that the cycloheptatrienyl derivative $Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)$ undergoes an inefficient oxidatively induced CO insertion [1], while upon reduction it dimerizes by coupling of the cycloheptatrienyl rings to give the ditropyl complex $[\{Mo(C_6F_5)(CO)_2\}_2(\eta^6{:}\eta'^6\text{-}C_{14}H_{14})]^{2-}$ [2]. Displacement of the ditropyl ligand from the dimeric dianion by $P(OMe)_3$ yields *cis*-*mer*-$[Mo(C_6F_5)(CO)_2\{P(OMe)_3\}_3]^-$ [3], which undergoes other substitution reactions and an oxidatively induced isomerization [4]. In an effort to find a more convenient entry into related Mo(0) chemistry, we developed a synthesis of the $[Mo(C_6F_5)(CO)_5]^-$ anion [5]. We have now concluded an investigation of the oxidative chemistry of this complex, in which it was demonstrated that oxidation is followed by relatively slow one-electron, homolytic reductive elimination via cleavage of the Mo–C_6F_5 bond to yield the 16-electron $Mo(CO)_5$ fragment and a pentafluorophenyl radical.

While the possibility of one-electron reductive elimination from transition metal organometallic compounds has long been discussed, the literature contains relatively few reported examples. The chemical oxidation of R_4Pb (R = Me, Et), $Me_2Pt(PPh_3)_2$ and $Et_2Pt(PMe_2Ph)_2$ by $IrCl_6^{2-}$ is believed to be followed by metal–carbon bond cleavage to yield alkyl radicals which subsequently react with additional $IrCl_6^{2-}$ to yield RCl as the organic product of one-electron reductive elimination [6,7]. Similarly, chemical or electrochemical oxidation of tetramethylaurate [8] and dimethylcobalt macrocyclic chelates [9] produces methyl radicals. One-electron oxidation of several group 4 dicyclopentadienyl complexes Cp_2MR_2 (M = Ti, Zr; R = Me, Ph, Bz) produces organic radicals which subsequently dimerize [10–12]. Chemical or electrochemical oxidation of Cp*Ir(DMSO)Me_2 in DMSO as solvent yields CH_4 through Ir–CH_3 bond cleavage followed by hydrogen abstraction from adventitious water, while oxidation of the rhodium analog yields instead the two-

---

[*] Corresponding author. Tel.: +254-710-3311; fax: +254-710-2403.
E-mail address: stephen_gipson@baylor.edu (S.L. Gipson).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.02.022

electron reductive elimination product ethane [13]. Oxidation of Cp^*RuL_2R (L = PMe_3, PMe_2Ph, R = Me; L = PMe_3, R = CH_2CMe_3) and $CpRu(PPh_3)_2Me$ yield RH via Ru–C bond cleavage followed by H-atom abstraction from one of the other ligands [14]. In a similar study of the oxidations of $CpRu(CO)(PR_3)Me$ (R = Cy, Ph), it was concluded that coordination of solvent to the $17e^-$ cation precedes Ru–Me bond cleavage [15]. The only reported example of one-electron reductive elimination from group 6 compounds is that of Cp_2MX_2 (M = Mo, W; X = halide, thiolate) [16]. We report here the first oxidatively induced metal–carbon bond cleavage (one-electron reductive elimination) in a molybdenum complex, $[Mo(C_6F_5)(CO)_5]^-$, which also has the distinction of not having any hydrogen-containing ligands.

2. Experimental

2.1. Reagents

All reactions were carried out under argon using Schlenk techniques or in a nitrogen-atmosphere glovebox. All solvents were distilled from appropriate drying agents and stored under nitrogen. The compounds $PPN[Mo(C_6F_5)(CO)_5]$ [5] (PPN = bis(triphenylphosphoranylidene)ammonium) and Cp_2FeBF_4 [17] were prepared by published methods. All other reagents were obtained commercially and were used as received.

2.2. Instrumentation

IR spectra were obtained using a Mattson Instruments Genesis II FTIR and a cell with CaF_2 windows separated by a 0.1 mm spacer. ^1H, ^{31}P, and ^{19}F NMR spectra were obtained on a Bruker DPX 300 MHz NMR spectrometer. NMR chemical shifts were referenced to residual protons in the solvent (for ^1H), 85% H_3PO_4 external standard (for ^{31}P), or $CFCl_3$ external standard (for ^{19}F). Mass spectra were obtained on a VG/Fisons Prospec 3000 double focusing spectrometer using EI ionization. Peaks in the mass spectrum were referenced to perfluorokerosene.

Cyclic voltammetry was performed using a Bioanalytical Systems BAS 100B/W electrochemical analyzer. Solutions contained approximately 0.1 M $[Bu_4N]PF_6$ supporting electrolyte. Electrodes consisted of a 0.5 mm Pt disk working electrode, Pt wire auxiliary electrode, and Ag/AgCl reference electrode. Potentials were referenced to the formal potential of the decamethylferrocenium–decamethylferrocene couple ($Cp^*_2Fe^+/Cp^*_2Fe$), which we measure as approximately −0.1 V vs. Ag/AgCl. Simulations of the cyclic voltammetry were run using Bioanalytical Systems DigiSim 3.0 software.

3. Results and discussion

3.1. Cyclic voltammetry of $PPN[Mo(C_6F_5)(CO)_5]$

The cyclic voltammetry of $PPN[Mo(C_6F_5)(CO)_5]$ in CH_2Cl_2 displays a partially chemically reversible one-electron oxidation at +0.66 V vs. $Cp^*_2Fe^+/Cp^*_2Fe$. The ratio of the cathodic to the anodic peak currents for this couple ranges from near zero at scan rates below 20 mV/s to near unity at scan rates above 5 V/s. This change in chemical reversibility suggests that the presumed product of the oxidation, the neutral 17-electron complex $Mo(C_6F_5)(CO)_5$, undergoes a relatively slow chemical reaction. In THF and MeCN solvents the chemical reversibility is even lower, with the peak current ratio for a given scan rate decreasing in the order $CH_2Cl_2 >$ THF > MeCN. Given that this is the same order as the coordinating ability of the solvents, these results suggest that the decomposition of the 17-electron species involves nucleophilic attack by solvent.

The participation of nucleophiles in the chemical reaction following oxidation of $[Mo(C_6F_5)(CO)_5]^-$ is further supported by the observation that the addition of ligands such as pyridine and triphenylphosphine to CH_2Cl_2 solutions of $PPN[Mo(C_6F_5)(CO)_5]$ causes a decrease in chemical reversibility of the oxidation. At a scan rate of 0.2 V/s, the peak current ratio for a 1.0 mM solution of $PPN[Mo(C_6F_5)(CO)_5]$ in CH_2Cl_2 decreases from 0.72 in the absence of pyridine to essentially zero with 5.0 mM added pyridine. All of these observations are consistent with an EC mechanism for the oxidation of $[Mo(C_6F_5)(CO)_5]^-$.

3.2. Chemical oxidation of $PPN[Mo(C_6F_5)(CO)_5]$ by ferrocenium and tropylium

In order to identify the products of the reaction of $Mo(C_6F_5)(CO)_5$ with nucleophiles, $PPN[Mo(C_6F_5)(CO)_5]$ was treated with the mild oxidants Cp_2FeBF_4 and $C_7H_7BF_4$. The oxidations with ferrocenium (1 equiv.) were conducted in the presence of pyridine or triphenylphosphine (2 equiv.) in $CDCl_3$ as solvent. NMR spectroscopy of the resulting solutions identified the products as $Mo(CO)_5L$ (by ^1H and ^{31}P, L = Py or PPh_3), C_6F_5H (by ^1H and ^{19}F), and Cp_2Fe (by ^1H). Thus, the 16-electron $Mo(CO)_5$ fragment produced by the Mo–C_6F_5 bond cleavage was trapped as a stable 18-electron complex by the added ligand, while the C_6F_5 radical most likely abstracted a hydrogen atom from adventitious water to yield the pentafluorobenzene.

The reaction of $PPN[Mo(C_6F_5)(CO)_5]$ with $C_7H_7BF_4$ could not be performed in the presence of nucleophiles since the tropylium reacted more rapidly with the nucleophiles than with the Mo complex. Nevertheless, a slow reaction between $PPN[Mo(C_6F_5)(CO)_5]$ and $C_7H_7BF_4$ did occur in the absence of added nucleophile in $CDCl_3$ and the NMR spectra of the product solution were consistent with $C_7H_7C_6F_5$ being the pentafluorophenyl-containing product. Isolation of this species by preparative TLC followed by mass spectral analysis gave a parent ion at *m/z* 258.11 ($C_7H_7C_6F_5$) and fragments at 167.03 (C_6F_5) and 91.08 (C_7H_7). Thus the oxidation of $[Mo(C_6F_5)(CO)_5]^-$ by $C_7H_7BF_4$ is believed to involve the following sequence of reactions:

$$[Mo(C_6F_5)(CO)_5]^- + C_7H_7^+ \rightarrow Mo(C_6F_5)(CO)_5 + C_7H_7^{\bullet}$$

$$Mo(C_6F_5)(CO)_5 + S \rightarrow Mo(CO)_5S + C_6F_5^{\bullet}$$

$$C_7H_7^{\bullet} + C_6F_5^{\bullet} \rightarrow C_7H_7C_6F_5$$

where S in the above reactions could be solvent, the BF_4^- anion, or adventitious water.

3.3. Simulation of cyclic voltammetry

In order to understand more about the mechanism of the apparent one-electron reductive elimination of C_6F_5 from $Mo(C_6F_5)(CO)_5$, we have simulated the cyclic voltammetry of $PPN[Mo(C_6F_5)(CO)_5]$ in CH_2Cl_2 in the presence of pyridine using the reactions in Scheme 1.

At reasonably fast scan rates in the absence of pyridine, the electron transfer reaction appears chemically and electrochemically reversible and can be simulated using a slightly slow electron transfer with a rate constant of 0.06 cm/s and a transfer coefficient of 0.5. Fig. 1 shows the effect of pyridine concentration on the apparent chemical reversibility of experimental and simulated cyclic voltammograms of 1.0 mM PPN[Mo(C_6F_5)(CO)$_5$] at a scan rate of 0.2 V/s. In the absence of pyridine, simulations gave an optimum fit using a first-order rate constant for reaction (1) of 0.22 s^{-1}. This reaction almost certainly involves some nucleophile, but since this species can be neither conclusively identified nor quantitated, the reaction was modeled as a first-order process.

With all other parameters held constant at values given in Table 1, simulations were then run to obtain the second-order rate constant, k_2, for the reaction of pyridine with $Mo(C_6F_5)(CO)_5$, reaction (2). Optimum fits were obtained with k_2 values ranging from 646 to 1041 $M^{-1}\,s^{-1}$. Fig. 2 illustrates the effect of scan rate on the apparent chemical reversibility of experimental and simulated cyclic voltammograms of 1.0 mM $PPN[Mo(C_6F_5)(CO)_5]$ in the presence of 5.0 mM pyridine. Using the same values for other parameters as in Fig. 1, optimization of k_2 gave values ranging from 482 to 823 $M^{-1}\,s^{-1}$. Generally excellent agreement between experimental and simulated results was thus achieved using the parameters shown in Table 1 and an average value for k_2 of approximately 700 $M^{-1}\,s^{-1}$. This corresponds to a relatively slow reaction, much slower than the elimination of methyl radical from dimethylcobalt(IV) macrocycles [9], though significantly faster than the reaction of $CpRu(CO)(PR_3)CH_3$ with CH_3CN [15].

$$[Mo(C_6F_5)(CO)_5]^- \rightleftharpoons Mo(C_6F_5)(CO)_5 + e^- \qquad (E)$$

$$Mo(C_6F_5)(CO)_5 \longrightarrow Mo(CO)_5S + C_6F_5 \qquad (1)$$

$$Mo(C_6F_5)(CO)_5 + Py \longrightarrow Mo(CO)_5Py + C_6F_5 \qquad (2)$$

Scheme 1.

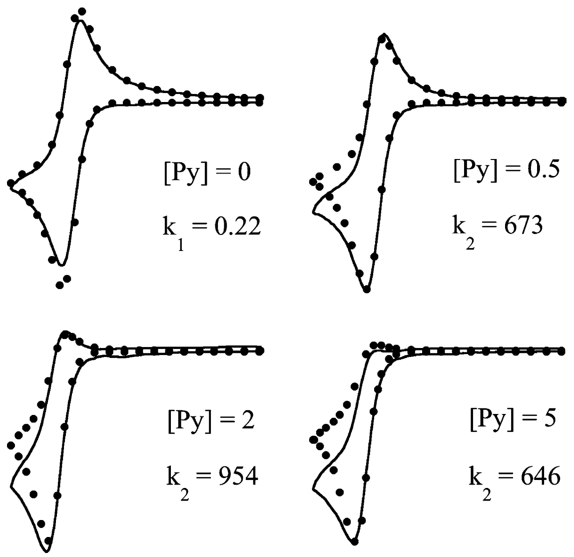

Fig. 1. Experimental (solid lines) and simulated (circles) cyclic voltammograms of 1.0 mM $PPN[Mo(C_6F_5)(CO)_5]$ + pyridine in CH_2Cl_2/ 0.1 M $[Bu_4N]PF_6$ at a 0.5 mm diameter Pt disk electrode at 0.2 V/s. Concentrations of pyridine labeled in mM. Optimized rate constant for k_1 labeled in s^{-1} and for k_2 in $M^{-1}\,s^{-1}$.

The mechanism of the oxidatively induced one-electron reductive elimination is proposed to involve nucleophilic attack (association) of the incoming ligand at the Mo, followed by extrusion of the C_6F_5 radical. Essentially identical results could be obtained by modeling the reaction with pyridine as either a rate-limiting pre-equilibrium between $Mo(C_6F_5)(CO)_5$ and pyridine followed rapid extrusion of C_6F_5 or a rapid pre-equilibrium followed by a rate-determining homolysis of the Mo–C_6F_5 bond. Therefore, the combination of nucleo-

Table 1
Parameters used in simulation of cyclic voltammetry of $PPN[Mo(C_6F_5)(CO)_5]$ in CH_2Cl_2 in the presence of pyridine

α	0.5	Electrode area	0.0023 cm^2
k_E	0.06 $cm\,s^{-1}$	Double layer capacitance	0.0013 μF
k_1	0.22 s^{-1}	Uncompensated resistance	2000 Ω
K_{eq1}	2.2×10^6		
K_{eq2}	2.7×10^8		

α, transfer coefficient; k_E, standard heterogeneous rate constant for electron transfer; k_1, first-order rate constant for reaction in absence of nucleophile; K_{eq}, equilibrium constants for reactions (1) and (2) (see Scheme 1).

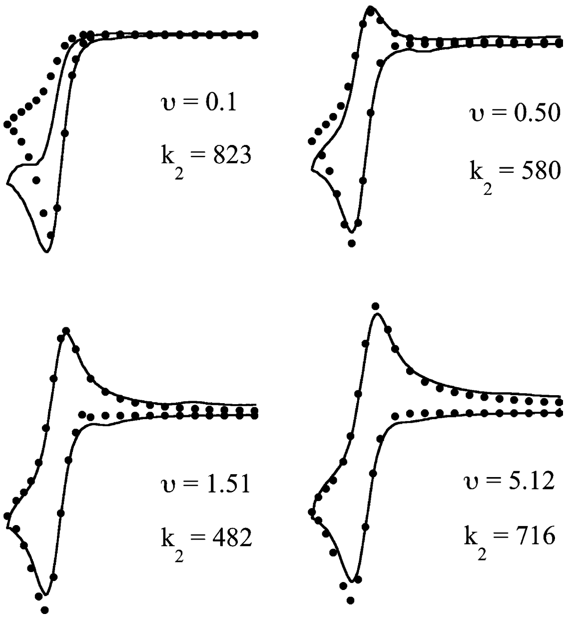

Fig. 2. Experimental (solid lines) and simulated (circles) cyclic voltammograms of 1.0 mM PPN[Mo(C_6F_5)(CO)$_5$] + 5.0 mM pyridine in CH_2Cl_2/0.1 M [Bu_4N]PF_6 at a 0.5 mm diameter Pt disk electrode. Scan rates labeled in V/s. Optimized rate constants labeled in M^{-1} s^{-1}.

philic attack and bond homolysis were modeled as the single second-order reaction shown in Scheme 1. Consistent with qualitative observations of the cyclic voltammetry, the reductive elimination in the presence of added nucleophile is significantly more rapid than in pure solvent. This observation lends support to the proposed associative nature of the overall reaction.

4. Conclusions

On the basis of experimentally observed cyclic voltammetry, simulations of this cyclic voltammetry, and products observed from chemical oxidation, a mechanism for the oxidatively induced one-electron reductive elimination of C_6F_5 from PPN[Mo(C_6F_5)(CO)$_5$] has been proposed. An initial one-electron oxidation produces the 17-electron species Mo(C_6F_5)(CO)$_5$. In agreement with previously published results for other systems [15], further reaction of this species is believed to involve prior association of the incoming ligand. The resulting 19-electron species then undergoes cleavage of the metal–carbon bond, effecting a one-electron reductive elimination reaction. The products of the reaction have all been identified by a combination of IR, NMR, and mass spectrometries.

Acknowledgements

We thank the Robert A. Welch Foundation (Grant No. AA-1083) and Baylor University, in part, for support of this research.

References

[1] S.L. Gipson, K. Kneten, Inorg. Chim. Acta 157 (1989) 143.
[2] M. Su, S.L. Gipson, D.F. Mullica, E.L. Sappenfield, D.H. Leschnitzer, J. Chem. Soc., Dalton Trans. (1993) 3323.
[3] S.L. Gipson, D.F. Mullica, E.L. Sappenfield, M.L. Hander, D.H. Leschnitzer, J. Chem. Soc., Dalton Trans. (1992) 521.
[4] D.F. Mullica, S.L. Gipson, M. Su, E.L. Sappenfield, Polyhedron 14 (1995) 2215.
[5] W.J. Doucette, J. Kim, J.A. Kautz, S.L. Gipson, Inorg. Chim. Acta 304 (2000) 237.
[6] H.C. Gardner, J.K. Kochi, J. Am. Chem. Soc. 97 (1975) 1855.
[7] J.Y. Chen, J.K. Kochi, J. Am. Chem. Soc. 99 (1977) 1450.
[8] D. Zhu, S.V. Lindeman, J.K. Kochi, Organometallics 18 (1999) 2241.
[9] W.H. Tamblyn, R.J. Klingler, W.S. Hwang, J.K. Kochi, J. Am. Chem. Soc. 103 (1981) 3161.
[10] S.L. Borkowsky, N.C. Baenziger, R.F. Jordan, Organometallics 12 (1993) 486.
[11] M.J. Burk, W. Tumas, M.D. Ward, D.R. Wheeler, J. Am. Chem. Soc. 112 (1990) 6133.
[12] R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.F. Echols, R. Willett, J. Am. Chem. Soc. 109 (1987) 4111.
[13] E. Fooladi, T. Graham, M.L. Turner, B. Dalhus, P.M. Maitlis, M. Tilset, J. Chem. Soc., Dalton Trans. (2002) 975.
[14] P. Diversi, M. Fontani, M. Fuligni, F. Laschi, S. Matteoni, C. Pinzino, P. Zanello, J. Organomet. Chem. 626 (2001) 145.
[15] T. Aase, M. Tilset, V.D. Parker, J. Am. Chem. Soc. 112 (1990) 4974.
[16] J.C. Kotz, W. Vining, W. Coco, R. Rosen, Organometallics 2 (1983) 68.
[17] D.N. Hendrickson, Y.S. Sohn, H.B. Gray, Inorg. Chem. 10 (1971) 1559.