Journal of Organometallic Chemistry, 272 (1984) C49—C53
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NOVEL ELECTROGENERATION OF REACTIVE FORMYLMETAL COMPLEXES FROM METAL CARBONYLS

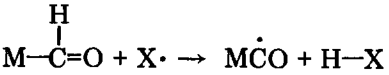
B.A. NARAYANAN and J.K. KOCHI*
Departments of Chemistry, Indiana University, Bloomington, Indiana 47405 (U.S.A.) and University of Houston, University Park, Houston, Texas 77004 (U.S.A.)

(Received March 29th, 1984)

Summary

Metal carbonyl radicals derived from various types of chromium, iron and manganese carbonyls by electroreduction are shown to undergo hydrogen atom transfer from trialkyltin hydrides to afford the corresponding formylmetal species.

Current interest in formylmetal complexes derives from their potential role as key intermediates in the industrially important catalytic reduction of carbon monoxide [1]. Although a variety of formylmetal species (MCHO) has been generated in different ways, only the method involving hydride transfer to metal carbonyls (MCO) from various types of borohydrides and related reducing agents has shown some semblance of generality [2]. As part of our interest in the electrochemistry of metal carbonyls, we recently found a series of facile homolytic reactions of 17- and 19-electron metal carbonyl radicals [3]. In particular, we noted the unusually rapid rate of hydrogen atom transfer, i.e.:



$$\mathrm{M{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{{=}O} + \mathrm{X}\cdot \rightarrow \mathrm{M}\dot{\mathrm{C}}\mathrm{O} + \mathrm{H{-}X} \qquad (1)$$

where X represents various organic and organometallic radicals [4]. The microscopic reverse of eq. 1 would represent a novel pathway for the generation of formylmetal species from a metal carbonyl. Accordingly we have investigated in this study the fate of electrochemically generated metal carbonyl radicals in the presence of one of the most efficient hydrogen atom donors available, viz. trialkyltin hydride [5].

---

*Address correspondence to the University of Houston.

0022-328X/84/$03.00

Previous studies have established the electroreduction of chromium carbonyl to produce the 17-electron radical anion $Cr(CO)_5^{\bar{\cdot}}$ which dimerized to $Cr_2(CO)_{10}^{2-}$ in high yields [6].

$$Cr(CO)_6 \xrightarrow{+e} Cr(CO)_6^{\bar{\cdot}} \xrightarrow{-CO} \tfrac{1}{2}\, Cr_2(CO)_{10}^{2-} \qquad (2)$$

When the same electroreduction is carried out in the presence of tri-n-butyltin hydride, the 19-electron precursor is intercepted by the hydrogen donor to afford the known formylchromium carbonyl [7] $Cr(CO)_5CHO^-$ in ~20% yields (Table 1). Similarly the use of tributyltin deuteride leads to the deuteriated formyl species $(OC)_5CrCDO^-$, which establishes direct hydrogen atom transfer by a process such as:

$$Cr(CO)_6^{\bar{\cdot}} + Bu_3SnH \rightarrow Cr(CO)_5CHO^-, \text{ etc.} \qquad (3)$$

We believe that the homolytic trapping of $Cr(CO)_6^{\bar{\cdot}}$ in eq. 3 is complete, being faster than the loss of CO and dimerization in eq. 2, since none of the dimeric $Cr_2(CO)_{10}^{2-}$ is formed. Furthermore ^1H and ^2H NMR analyses of the reaction mixture indicate that the formyl species is reduced further to the hydroxymethyl moiety [8] (vide infra), which accounts for its detection in less than quantitative yields in Table 1.

The electroreduction of iron pentacarbonyl is a one-electron process like that of chromium carbonyl and affords the dimeric $Fe_2(CO)_8^{2-}$ by a sequence of reactions akin to eq. 2 [10]. Analogously, we find the 19-electron intermediate $Fe(CO)_5^{\bar{\cdot}}$ to be intercepted by tri-n-butyltin hydride to afford the well-known formyliron carbonyl [11] $Fe(CO)_4CHO^-$ in 15–30% yield (Table 1) (eq. 4). Under these conditions, none of the dimeric $Fe_2(CO)_8^{2-}$ is formed.

TABLE 1

ELECTROREDUCTION OF METAL CARBONYLS IN THE PRESENCE OF TRI-n-BUTYLTIN HYDRIDE [a]

Metal carbonyl	Bu_3SnH [b] (equiv.)	Q (C) [c]	Products
$Cr(CO)_6$	0	1.15	$Cr_2(CO)_{10}^{2-}$ [d]
$Cr(CO)_6$	5	1.07	$Cr(CO)_5CHO^-$ [e]
$Fe(CO)_5$	0	1.12	$Fe_2(CO)_8^{2-}$ [f]
$Fe(CO)_5$	5	1.08	$Fe(CO)_4CHO^-$ [g]
$Mn(CO)_4(PPh_3)_2^+ PF_6^-$	0	1.40	$Mn(CO)_4PPh_3^-$ [h]
$Mn(CO)_4(PPh_3)_2^+ PF_6$	5	1.10	$CH_3Mn(L)_x$ [j]

[a] Electroreductions were carried out under galvanostatic conditions (10^4 μA) using 5×10^{-2} M metal carbonyl in tetrahydrofuran containing 0.2 M tetra-n-butylammonium perchlorate. [b] Molar equiv. added relative to metal carbonyl. [c] Total charge passed per equiv. of metal carbonyl. [d] Identified by its characteristic [6] IR bands at 1905 and 1870 cm^{-1}. [e] Identified by its ^1H NMR resonance at δ 15.2 ppm and IR band at 1595 cm^{-1} (CHO) [7]. Yield of 17% based on ^1H NMR analysis relative to p-dimethoxybenzene internal standard. [f] Identified by its characteristic [10] IR bands at 1920 and 1850 cm^{-1}. [g] Identified by its ^1H NMR resonance at δ 14.9 ppm and IR band at 1602 cm^{-1} (CHO) [11]. Formed in 33% based on ^1H NMR analysis relative to p-dimethoxybenzene internal standard. [h] Identified by its characteristic [15] IR bands at 1940, 1850 and 1810 cm^{-1}. Minor amounts of $HMn(CO)_3(PPh_3)_2$ (^1H NMR: δ −6.87 ppm (d, J 33 Hz) also formed. [j] Uncharacterized crystalline methylmanganese complex showing an unresolved band at δ 0.13 (CH_3) similar to that (δ −0.30 ppm) of authentic $CH_3Mn(CO)_4$-PPh_3. Minor amounts of $HMn(CO)_3(PPh_3)_2$ also formed.

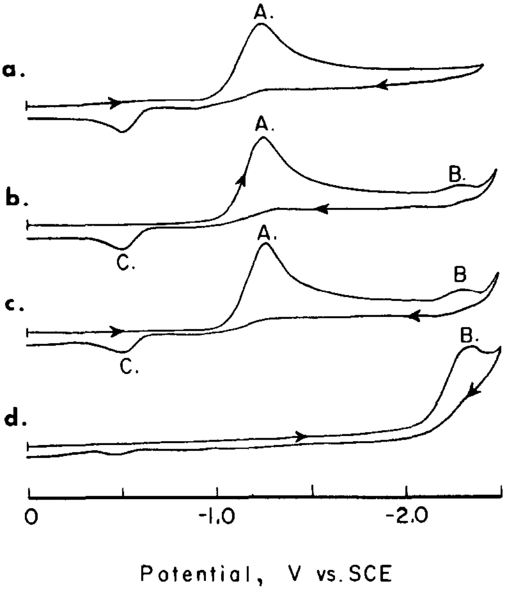


Fig. 1. Initial negative scan cyclic voltammogram of 5×10^{-3} *M* $Mn(CO)_4(PPh_3)_2{}^+ PF_6{}^-$ in tetrahydrofuran containing 0.1 *M* tetra-n-butylammonium perchlorate at a scan rate of 500 mV s^{-1}. (a) no Bu_3SnH, (b) 2.0×10^{-2} *M* Bu_3SnH, (c) 8×10^{-2} *M* Bu_3SnH. The cyclic voltammogram of 5×10^{-3} *M* $Mn(CO)_3(PPh_3)_2CHO$ under the same conditions is shown in (d).

$$Fe(CO)_5 \xrightarrow{+e} Fe(CO)_5{}^{\overline{\cdot}} \xrightarrow{Bu_3SnH} Fe(CO)_4CHO^- \text{ . etc.} \qquad (4)$$

The chromium and iron carbonyls have served in this study as prototypes for homolytic hydrogen transfer to generate formylmetal species, as in eq. 3 and 4. As such, hydrogen atom transfer must occur from the 19-electron metal carbonyl radical $Cr(CO)_6{}^{\overline{\cdot}}$ and $Fe(CO)_5{}^{\overline{\cdot}}$ at rates which are easily competitive with other facile processes, such as the rapid loss of CO and dimerization [12,13]. Indeed the rapidity of hydrogen atom transfer can be independently demonstrated by transient electrochemical techniques. Thus Fig. 1 (upper) shows the initial negative scan cyclic voltammogram of the cationic manganese carbonyl $Mn(CO)_4(PPh_3)_2{}^+$ with an irreversible one-electron cathodic wave A in an accessible potential region (i.e. E_p —1.27 V vs. SCE, v 500 mV s^{-1}). The addition of tri-n-butyltin hydride results in the appearance of a new cathodic wave *B* (E_p —2.37 V) which grows in importance as the amount of Bu_3SnH is increased. The new cathodic wave can be readily assigned to the neutral formylmanganese complex $Mn(CO)_3(PPh_3)_2CHO$ by comparison with that (Fig. 1 bottom) of an authentic sample prepared by hydridic reduction [14]. The appearance of the formyl species during the time scale ($\sim 10^{-2}$ s) of the cyclic voltammetric scan thus supports the rapid rate of hydrogen atom transfer in eq. 5.

$$Mn(CO)_4(PPh_3)_2{}^+ \xrightarrow{+e} Mn(CO)_4(PPh_3)_2{}^{\cdot} \xrightarrow{Bu_3SnH} Mn(CO)_3(PPh_3)_2CHO \quad (5)$$

In the absence of Bu_3SnH, the 19-electron radical $Mn(CO)_4(PPh_3)_2\cdot$ undergoes rapid fragmentation to the 17-electron species, followed by reduction to $Mn(CO)_4PPh_3^-$ [15], i.e.:

$$Mn(CO)_4(PPh_3)_2\cdot \xrightarrow[\text{(fast)}]{-PPh_3} Mn(CO)_4PPh_3\cdot \xrightarrow{+e} Mn(CO)_4PPh_3^- \qquad (6)$$

The latter is the principal product of the bulk electrolysis of $Mn(CO)_4(PPh_3)_2^+$ at a controlled potential slightly more negative than the CV wave *A* (i.e., —1.3 V). It appears in Fig. 1 as the CV wave *C*, the peak current of which is shown to diminish with increasing amounts of the stannane scavenger.

Preliminary evidence suggests that homolytic hydrogen transfer may also be involved in the further reduction of formylmetal species to the corresponding hydroxymethyl and to the methyl moieties. For example, the electroreduction of $Mn(CO)_4(PPh_3)_2^+$ at —1.3 V in the presence of Bu_3SnH produces a yellow crystalline methylmanganese compound (isolated in > 80% yields) which is similar to $CH_3Mn(CO)_4PPh_3$ prepared independently [16]. We hope that the complete characterization of this product, together with analogous species found in the electroreduction of $Cr(CO)_6$ and $Fe(CO)_5$ (vide supra) as well as other metal carbonyl complexes, will provide additional insight into the dual roles of formylmetal and hydridometal complexes as intermediates in the reduction of carbon monoxide.

Acknowledgment. We thank the National Science Foundation for financial support.

References

1 For example see: (a) G.H. Olivé and S. Olivé, Angew. Chem., Int. Ed. Engl., 15 (1976) 136; (b) E.L. Muetterties and J. Stein, Chem. Rev., 79 (1979) 479; (c) C. Masters, Adv. Organomet. Chem., 17 (1979) 61; (d) D.R. Fahey, J. Am. Chem. Soc., 103 (1981) 136; (e) C.P. Casey, S.M. Neumann, M.A. Andrews and D.R. McAlister, Pure Appl. Chem., 52 (1980) 625; (f) R.C. Brady III, and R. Pettit, J. Am. Chem. Soc., 103 (1981) 1287.

2 For a review see: J.A. Gradysz, Adv. Organometal. Chem., 20 (1982) 1.

3 (a) J.W. Hershberger, R.J. Klingler and J.K. Kochi, J. Am. Chem. Soc., 104 (1982) 3034; 105 (1983) 61; (b) J.W. Hershberger, C. Amatore and J.K. Kochi, J. Organomet. Chem., 250 (1983) 345; (c) B.A. Narayanan, C. Amatore, and J.K. Kochi, J. Chem. Soc. Chem. Commun., (1983) 397.

4 (a) B.A. Narayanan, C. Amatore, C.P. Casey, and J.K. Kochi, J. Am. Chem. Soc., 105 (1983) 6351; (b) B.A. Narayanan, C. Amatore, and J.K. Kochi, Organometallics 3 (1984) 802.

5 See e.g. J. Lusztyk, E. Lusztyk, B. Maillard, L. Lunazzi, and K.U. Ingold, J. Am. Chem. Soc., 105 (1983) 4475.

6 (a) R.E. Dessy, F.E. Stary, R.B. King, and M. Waldrop, J. Am. Chem. Soc., 88 (1966) 471; (b) C.J. Pickett and D. Pletcher, J. Chem. Soc. Dalton, (1975) 879; (1976) 749; (c) A. Seurat, P. Lemoine, and M. Gross, Electrochim. Acta, 23 (1978) 1219.

7 C.P. Casey, and S.M. Neumann, J. Am. Chem. Soc., 98 (1976) 5395.

8 For example, in the ^2H NMR spectrum of the reaction mixture from the reduction of $Cr(CO)_6$ in the presence of Bu_3SnD, a strong resonance at δ 3.7 ppm for the $HOCD_2$ group [9] was observed in addition to resonances at δ 8.8 (aldehydic), 15.2 (formyl) and —7.0 ppm (hydride) with relative intensities (by NMR integration) of 2.2/0.5/1.0/1.0, respectively.

9 See C.P. Casey et al. in ref. 1e.

10 See ref. 6 and (a) A.M. Bond, P.A. Dawson, B.M. Peake, B.H. Robinson, and J. Simpson, Inorg. Chem., 16 (1977) 2199; (b) D. Mikolova, J. Klima, and A.A. Vlcek, Inorg. Chim. Acta, 27 (1978) L67; (c) S.W. Blanch, A.M. Bond, and R. Colton, Inorg. Chem., 20 (1981) 755; (d) N. El Murr and A. Chaloyard, Inorg. Chem., 21 (1982) 2206; (d) For iron carbonyl radicals formed from the reduction of $Fe(CO)_5$, see P.J. Krusic, J. San Filippo, Jr., B. Hutchinson, R.L. Hance, and L.M. Daniels, J. Am. Chem. Soc., 103 (1981) 2129; J.K. Burdett, J. Chem. Soc. Chem. Commun., (1973) 763.

11 J.P. Collman and S.R. Winter, J. Am. Chem. Soc., 95 (1973) 4089.

12 For evidence relating to the substitution lability of metal carbonyl radicals, see ref. 4 and H.W. Walker, G.B. Rattinger, R.L. Belford and T.L. Brown, Organometallics, 2 (1983) 775.

13 Although we favor the trapping of the 19-electron metal carbonyl radicals as in eq. 3 and 4, we are unable to prove it solely on the basis of the product studies reported herein. Thus the less than quantitative yields of the formyl complexes and the identity of the tin-derived product do leave open the question of alternative pathways for their formation.

14 W. Tam, G.Y. Lin, and J.A. Gladysz, Organometallics, 1 (1982) 525.

15 W. Hieber, G. Faulhaver, and F. Theubert, Z. Naturforsch. B, 15 (1960) 326; Z. Anorg. Allg. Chem., 314 (1962) 125.

16 C.S. Kraihanzel, and P.K. Maples, Inorg. Chem., 7 (1968) 1806.