ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 614–615 (2000) 318–321

Journal of Organometallic Chemistry

Note

Polycarbon linked metal cluster compounds

Daphne M. Norton, D.F. Shriver *

Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA

Received 17 May 2000

Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

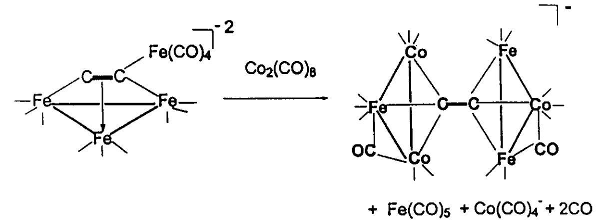
Abstract

The reactions between metal cluster anions and metal cluster cations containing carbide ligands were explored. In one case, a salt formed which consisted of a cluster cation along with a cluster anion. By contrast, the interaction of $[Rh_2Cl_2(CO)_4]$ with $[Fe_3(CO)_9C_2Fe(CO)_4]^{2-}$ produced a new monocarbide metal cluster, $[Fe_3Rh_3(CO)_5C]^-$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metal cluster compounds

1. Introduction

In previous work we described the generation of $[PPN]_2[Fe_3(Co)_3(CO)_{18}C_2]$, by the interaction of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, with $Co_2(CO)_8$ (Eq. (1)) [1]:



(1)

The present work explores the interaction of metal cluster electrophiles with metal cluster nucleophiles for the synthesis of new metal cluster carbides.

2. Experimental

All manipulations were performed under an inert atmosphere of prepurified N_2 [2]. Solvents were distilled from drying agents, CH_2Cl_2 from P_2O_5, THF and Et_2O from sodium–benzophenone, and *i*-PrOH from Mg/I_2, and they were stored under N_2. Acetyl chloride was purified by vacuum distillation from PCl_5. Published syntheses were used to prepare $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ [3], $[PPN]_2[Fe_3(CO)_9CCFeCp(CO)_2]$ [4], $[PPN][Fe_3(CO)_9Re(CO)_5]$ [5], and $[Mn(CO)_3(CH_3CN)_3][PF_6]$ [6].

Solution IR spectra were recorded on a Bomem MB FTIR at 2 cm^{-1} resolution, and samples were contained in cells having a 0.01 mm pathlength and CaF_2 windows. NMR spectra were recorded on a Varian XLA-400 (^1H, 399.942 MHZ; ^{13}C, 100.577 MHZ) spectrometer. FAB mass spectra were obtained on a VG70/250SE spectrometer (with Cs^+ ion bombardment of samples in a *m*-nitro benzyl alcohol matrix). The TOPOS [7] program was used to compare theoretical and experimental mass spectra.

2.1. Formation of $[PPN][Mn(CO)_3(CH_3CN)_3][Fe_3(CO)_9CCFe(CO)_4]$

Under an inert atmosphere $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, (71 mg, 0.06 mmol) and $[Mn(CO)_3(CH_3CN)_3][PF_6]$, (22 mg, 0.05 mmol) in 15 ml of CH_2Cl_2 were allowed to stir for 2 days. The solvent was

---

* Corresponding author. Tel.: + 1-847-491-5655; fax: + 1-847-491-7713.

E-mail address: shriver@chem.nwu.edu (D.F. Shriver).

PII: S0022-328X(00)00593-3

then evaporated leaving a dark brown powder, which was extracted with 20 ml of diethyl ether. The remaining insoluble light brown solid was collected under an inert atmosphere. The IR spectrum of this product in CH_2Cl_2 contains absorption frequencies that are representative of the metal cluster anions of both starting materials. Similarly, the FAB mass spectrum of the product contains a parent peak at 873 amu, with successive loss of three CH_3CN molecules and eight carbonyl groups, which is consistent with the formation of a metathesis product: $[(Mn(CO)_3(CH_3CN)_3]^+$ $[Fe_3(CO)_9CCFe(CO)_4)]^-$, rather than a mixed-metal dicarbide cluster.

2.2. Synthesis of $[PPN][Fe_3Rh_3(CO)_{15}C]$

Under a nitrogen atmosphere, 25 mg (0.06 mmol) of $Rh_2Cl_2(CO)_4$ was allowed to react with a solution of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, (35 mg, 0.03 mmol in 10 ml of CH_2Cl_2), resulting in the formation of a very dark product. Solvent was removed under vacuum to form a black oil which was dissolved in 15 ml of diethyl ether, and concentrated under vacuum to form black microcrystals, identified as $[PPN][Fe_3Rh_3(CO)_{15}C]$ based on IR and mass spectral data. The FAB mass spectrum of this compound displays a parent peak at 909 amu with successive loss of seven carbonyl ligands.

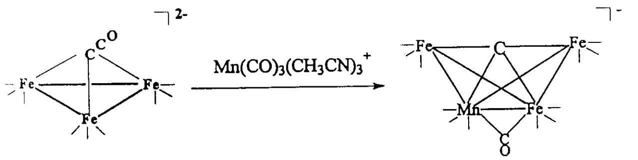
2.3. Electrochemistry

Electrochemical measurements were performed using a BAS-10B electrochemical analyzer, on samples contained in a two-compartment cell under N_2. Cyclic voltammograms were determined on acetonitrile solutions containing the electrolyte, $[Bu_4N][PF_6]$, 0.27 M. A Pt disk working electrode was employed with a Pt flag counter electrode and a silver wire reference electrode. The potential was calibrated by the ferrocene (Fc^+/Fc) couple. Half wave potentials were assigned at the average of the anodic and cathodic peak potentials for reversible couples.

3. Results and discussion

3.1. Synthesis of $[PPN][Mn(CO)_3(CH_3CN)_3]$-$[Fe_3(CO)_9CCFe(CO)_4]$

In previous research we have shown that the condensation of $[PPN]_2[Fe_3(CO)_9CCO]$ with labile electrophilic metal carbonyls results in the formation of mixed-metal carbide cluster compounds [8], but in the present work, the reaction of $[PPN]_2[Fe_3(CO)_9(CCO]$, with $[Mn(CO)_3(CH_3CN)_3][PF_6]$ was found to cleave the central C–C bond of the ketenylidene ligand (CCO) and incorporate the $Mn(CO)_3$ fragment into the framework of a butterfly shaped cluster carbide, Eq. (2):



(2)

The interaction of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, with $[Mn(CO)_3(CH_3CN)_3][PF_6]$ results in simple cation exchange as indicated by IR data and the FAB mass spectra which exhibit a parent peak at 873 amu, corresponding to the ion pair $[Mn(CO)_3(CH_3CN)_3]^+$ $[Fe_3(CO)_9CCFe(CO)_4]^{1-}$. Similarly, no reaction occurs when $[Mn(CO)_3(CH_3CN)_3][PF_6]$ is added to a THF solution of $[PPN][Fe_3(CO)_9CCRe(CO)_5]$. These results conform to the relative nucleophilicities of $[FeCp(CO)_2]^{1-}$ and $[Re(CO)_5]^{1-}$, which are 2.8×10^6 and 1.0×10^3 M^{-1} S^{-1}, respectively [9].

The reaction of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ with $Co_2(CO)_8$ may reflect the affinity of $Co_2(CO)_8$ for polyenes [10]. By contrast, the interaction of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, with $Rh_2Cl_2(CO)_4$ results in C–C bond cleavage and the formation of $[PPN]_2[Fe_3Rh_3(CO)_{15}]$, which was previously synthesized by the reaction of $Rh_2Cl_2(CO)_4$ with $[PPN]_2[Fe_3(CO)_9CCO]$ [8].

3.2. Displacement of a pendant ML_n ligand

Although $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$, undergoes simple ion exchange with $[Mn(CO)_3(CH_3)_3][PF_6]$ to produce the organometallic salt $[Mn(CO)_3(CH_3)_3]$-$[Fe_3(CO)_9CCFe(CO)_4]^{1-}$, photolysis or forcing thermal conditions will cleave $FeCp(CO)_2$ from $[PPN]_2$-$[Fe_3(CO)_9CCFeCp(CO)_2]$ or $Re(CO)_5$ from $[PPN]$-$[Fe_3(CO)_9CCRe(CO)_5]$, resulting in the formation of an interesting new six metal polycarbon cluster, $[Fe_6(CO)_{18}C_4]^{2-}$. The loss of the pendant ligand from $[PPN][Fe_3(CO)_9CCML_n]$ may result in the formation of an acetylide group bound to a tri-iron framework, $Fe_3(CO)_9CC^-$, which undergoes dimerization to yield the larger six-metal four-carbon cluster.

The reaction of $[PPN]_2[Fe_3(CO)_9CCFeCp(CO)_2]$, with $[Mn(CO)_3(CH_3CN)_3][PF_6]$, produces three products: $[PPN]_2[Fe_6(CO)_{18}C_4]$, $[FeCp(CO)_2)]_2$ and an unidentified compound with IR stretching frequencies at 2035(w), 1989(vs), 1980(vs), 1966(s), and 1937(w). The unidentified diethyl ether soluble product compound may undergo reduction to generate $[PPN]_2[Fe_6(CO)_{18}C_4]$, which will be described in a forthcoming paper. Clearly, the pathway to the six metal cluster linked by a tetracarbide is complex.

3.3. Electrochemistry of [PPN][$Fe_3(CO)_9CCRe(CO)_5$]

The cyclic voltammogram of [PPN][$Fe_3(CO)_9CCRe(CO)_5$] reveals that the cluster undergoes two irreversible oxidation reactions at $E_p = 1.23$ V and $E_p = 1.42$ V versus Ag wire in acetonitrile, as seen in Fig. 1. The compounds [$Mn(CO)_3(CH_3)_3$]$Re_2(CO)_{10}$ [9], and [PPN][$Fe_3(CO)_9CCRe(CO)_5$] oxidize more readily than $Re_2(CO)_{10}$; for example, no reduction waves were found for $(OC)_5ReCeCRe(CO)_5$ potentials as low as −2.1 V (Table 1) [11]. Similarly, $[PPN]_2[Fe_3(CO)_9CCRe(CO)_5]$ was not reduced in this range. The first oxidation for a representative aliphatic acetylene, *t*-butylacetylene, occurs beyond +2.0 V (versus Ag) in CH_3CN [11].

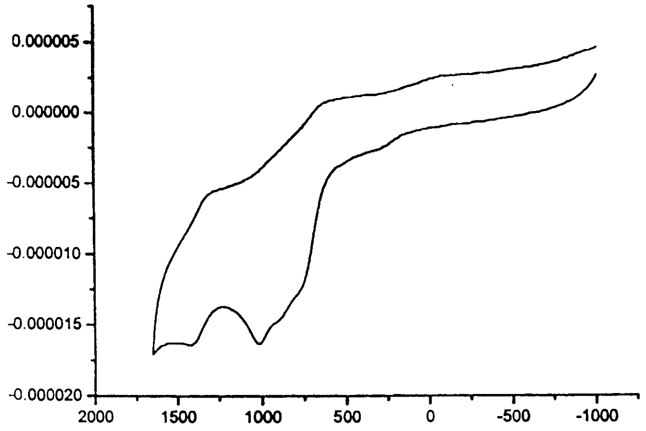


Fig. 1. Cyclic voltammogram of $[Fe_3(CO)_9CCRe(CO)_5]^{1-}$ versus Ag wire.

Table 1
Oxidation potentials for compounds containing $-Re(CO)_5$ units [a]

Compound	E_p anodic	E_p cathodic	Reference
$Re_2(CO)_{10}$		1.40	[11]
$(OC)_5ReCCRe(CO)_5$	1.02	1.55	[11]
$[Fe_3(CO)_9CCRe(CO)_5]^{1-}$	1.23	1.42	[b]

[a] Electrochemistry was performed in acetonitrile solutions and referenced to Ag wire.
[b] This work.

Table 2
Oxidation potentials for clusters containing CC units [a]

Compound	E_p anodic		E_p cathodic
$[Fe_3(CO)_9CCRe(CO)_5]^{1-}$	1.23	1.42	
$[Fe_3(CO)_9CCOC(O)CH_3]^{1-}$	0.73	1.12	
$[Fe_3(CO)_9CCFeCp(CO)_2]^{1-}$	0.72 [b,c]	0.88	0.63

[a] Electrochemistry was performed in acetonitrile solutions and referenced to Ag wire.
[b] Part of a reversible wave.
[c] Cyclic voltammetry performed at low temperature, −20°C.

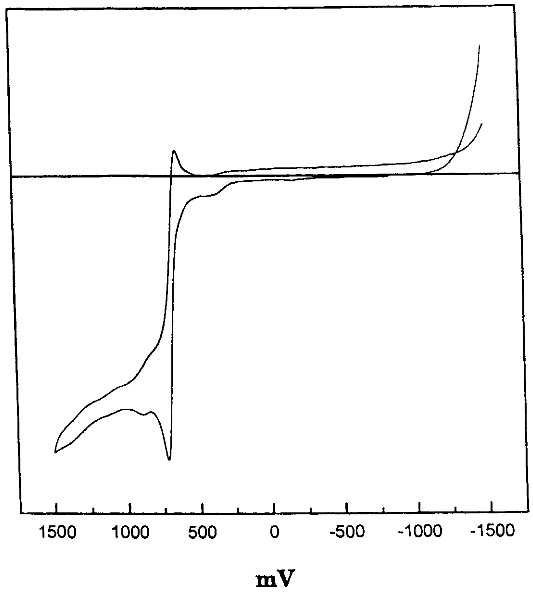


Fig. 2. Cyclic voltammogram of $[Fe_3(CO)_9CCFeCp(CO)_2]^{1-}$ versus Ag wire.

3.4. Electrochemistry of $[PPN]_2[Fe_3(CO)_9CCFeCp(CO)_2]$

Simpson and Robinson have demonstrated that the electrochemistry of organometallic cluster compounds can be most effectively probed at low temperatures [3]. The relative oxidation potentials determined for the series of metallated acetylides at room temperature are presented in Table 2. At low temperatures, reversible waves were observed for [PPN][$Fe_3(CO)_9CCFeCp(CO)_2$].

As shown in Fig. 2, the cyclic voltammogram of a solution of $[PPN]_2[Fe_3(CO)_9CCFeCp(CO)_2]$ in CH_3CN displays a reversible wave and this compound oxidizes more readily than $[PPN]_2[Fe_3(CO)_9CCRe(CO)_5]$, which is consistent with reactivity patterns for the heavier metal acetylides. Low temperatures are necessary to obtain a reversible wave.

4. Summary

The reactivity of $[Fe_3(CO)_9CCRe(CO)_5]^{1-}$, $[Fe_3(CO)_9CCFeCp(CO)_2]^{1-}$, and $[Fe_3(CO)_9CCFe(CO)_4]^{2-}$ is related to the nature of the pendant ligand bound to the CC unit. For the series of metal acetylides studied here, those containing $FeCp(CO)_2$ are the most susceptible to attack by electrophiles. The $FeCp(CO)_2$ moiety can also be excised from $[PPN]_2[Fe_3(CO)_9CCFeCp(CO)_2]$ by either pyrolysis or photolysis.

The acetylide compounds display a variety of reactions with [$Mn(CO)_3(CH_3CN)_3$][PF_6]. For example, [PPN][$Fe_3(CO)_9CCFeCp(CO)_2$] loses the pendant,

$FeCp(CO)_2$, ligand, $[PPN]_2[Fe_3(CO)_9CCRe(CO)_5]$ does not react with $[Mn(CO)_3(CH_3CN)_3][PF_6]$, and $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ undergoes cation exchange with $[Mn(CO)_3(CH_3CN)_3][PF_6]$ to form $[Mn(CO)_3(CH_3CN)_3][Fe_3(CO)_9CCFe(CO)_4]^{1-}$.

References

[1] M.P. Jensen, D.A. Phillips, M. Sabat, D.F. Shriver, Organometallics 11 (1992) 1859.

[2] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 2nd Edn., 1986.

[3] (a) B.M. Peake, B.H. Robinson, J. Simpson, D. Watson, Inorg. Chem. 16 (1977) 405. (b) A.M. Bond, B.M. Peake, B.H. Robinson, J. Simpson, Inorg. Chem. 16 (1977) 410. (c) S.B. Colbran, B.H. Robinson, J. Simpson, Organometallics 3 (1984) 1344. (d) G.H. Worth, B.H. Robinson, J. Simpson, J. Organomet. Chem. 387 (1990) 337. (e) G.H. Worth, B.H. Robinson, J. Simpson, Organometallics 11 (1992) 3863. (f) J. Borgdorff, N.W. Duffy, B.H. Robinson, J. Simpson, Inorg. Chim. Acta 224 (1994) 73.

[4] M.P. Jensen, D.F. Shriver, J. Cluster Sci. 1 (1990) 75.

[5] D.M. Norton, R.W. Eveland, J.C. Hutchison, C. Stern, D.F. Shriver, Organometallics, in press.

[6] D. Drew, D.J. Darensbourg, M.Y. Darensbourg, Inorg. Chem. 14 (1975) 1579.

[7] D. Johnston, Thesis results, Northwestern University, 1994.

[8] (a) J.A. Hriljac, P.N. Swepston, D.F. Shriver, Organometallics 4 (1985) 158. (b) J.A. Hriljac, E.M. Holt, D.F. Shriver, Inorg. Chem. 26 (1987) 2943.

[9] C.-K. Lai, W.G. Feighery, Y. Zhen, J.D. Atwood, Inorg. Chem. 28 (1989) 3929.

[10] Examples include: P. Magnus, D.P. Becker, J. Chem. Soc. Chem. Commun. (1985) 640.

[11] (a) T. Weidmann, V. Weinrich, B. Wagner, C. Robl, W. Beck, Chem. Ber. 124 (1991) 1363. (b) W. Beck, B. Niemer, J. Breimair, J. Heidrich, J. Organomet. Chem. 372 (1989) 79. (c) J. Heidrich, M. Steimann, M. Appel, W. Beck, J.R. Phillips, W.C. Trogler, Organometallics 9 (1990) 1296. (d) M. Appel, J. Heidrich, W. Beck, Chem. Ber. 120 (1987) 1087.