3916 *Organometallics* **1996,** *15,* 3916−3919

# *Articles*

## Reaction of $[PPN][Fe_3(CO)CCOC(O)CH_3]$ with the Metal Nucleophile $[Re(CO)_5]^-$ To Generate a Mixed-Metal Acetylide, $[PPN][Fe_3(CO)_9CCRe(CO)_5]$

Daphne M. Norton, Randal W. Eveland, John C. Hutchison, Charlotte Stern, and Duward F. Shriver*

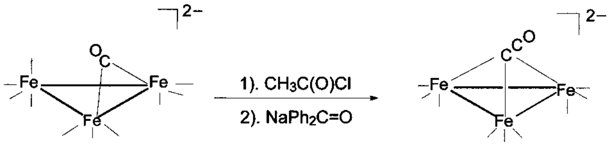
*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

*Received February 27, 1996*[⊗]

The cluster $[PPN][Fe_3(CO)_9CCOC(O)CH_3]$, **2**, reacts with $[PPN][Re(CO)_5]$ to generate a metalated acetylide species, $[PPN][Fe_3(CO)_9CCRe(CO)_5]$, **3**, which was characterized by infrared and $^{13}C$ NMR spectroscopy. A byproduct of this reaction, $[PPN]_2[Fe_3(CO)_9CCO]$, appears to result from the attack of $[Re(CO)_5]^-$ on the acyl carbon in compound **2**, and a strategy was devised to suppress this side reaction. The structure of **3** was determined by single-crystal X-ray diffraction. The central C−C bond distance is 1.28(1) Å.

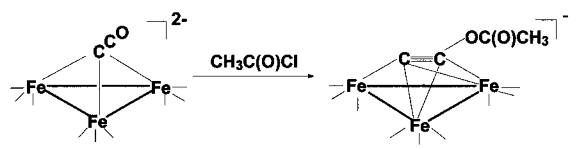
### Introduction

The synthetically versatile ketenylidene ligand, CCO, can be generated by electrophilic attack of acetyl chloride on a bridging CO ligand in an anionic cluster compound, followed by the reductive cleavage of the CO bond of the acylated bridging carbonyl, eq 1.[1]



1

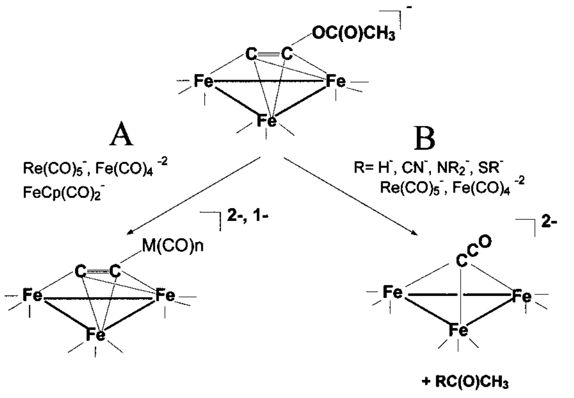
When the resulting metal cluster ketenylidene compound $[PPN]_2[Fe_3(CO)_9CCO]$, **1**, is treated with acetyl chloride, the acyl group is found to attack the ketenylidene oxygen, eq 2.[2]



1 2

The product of reaction **2**, $[PPN][Fe_3(CO)_9CCOC(O)CH_3]$, provides an entry to a wide variety of $C_2$-containing organometallic complexes.[3] As illustrated in Scheme 1, these reactions proceed by the attack of an organometallic nucleophile on the $C_\beta$ of the $C_\alpha C_\beta OC(O)CH_3$ ligand with displacement of the acetate ion, $OC(O)CH_3^-$.[4] An alternative reaction is attack of the nucleophile on the acyl carbon to regenerate the ketenylidene, **1**, as shown in Scheme 1B. Typically, strong and bulky organometallic nucleophiles follow path 1A, whereas strong and compact main-group nucleophiles such as $CN^-$, $SR^-$, and $NR_2^-$ follow path 1B.[5] In the present research we found that the metal nucleophile $Re(CO)_5^-$, produces both types of products, so a strategy was devised to steer the reaction toward the desired $C_2$ organometallic product.

**Scheme 1**



### Experimental Section

**General Procedures.** All manipulations were performed under an atmosphere of prepurified $N_2$ with the use of Schlenk techniques or in a Vacuum Atmospheres drybox. Solvents were prepurified by distillation from drying agents ($CH_2Cl_2$ from $P_2O_5$; THF and $Et_2O$ from sodium/benzophenone; *i*-PrOH from $Mg/I_2$) and were stored under $N_2$ until needed. Published syntheses were used to prepare $[PPN]_2[Fe_3(CO)_9CCO]$,[1] $[PPN][Fe_3(CO)_9CCOC(O)CH_3]$,[2] and $[PPN][Re(CO)_5]$.[6]

Solution IR spectra were recorded on a Bomem MB series benchtop FTIR at 2 $cm^{-1}$ resolution with the use of 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. $^1H$ and $^{13}C$ chemical shifts are reported positive if downfield from TMS and were internally referenced

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(2) Hriljac, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6010.

(3) Jensen, M. P.; Shriver, D. F. *J. Cluster Sci.* **1990**, *1*, 75.

(4) Jensen, M. P. Thesis results, Northwestern University.

(5) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(6) Zhen, Y.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 1506.

S0276-7333(96)00135-5 CCC: $12.00

to solvent. FAB mass spectra were recorded on a VG70/250SE spectrometer (with $Cs^+$ ion bombardment of samples in a *m*-nitrobenzyl alcohol matrix) by Dr. D. L. Hung of Northwestern University Analytical Service Laboratory. Elemental analyses were performed by Elbach Analytical Laboratories (Gummersbach, Germany).

**Synthesis of $[PPN][Fe_3(CO)_9CCRe(CO)_5]$.** A 90 mg (0.086 mmol) sample of $[PPN][Fe_3(CO)_9CCOC(O)CH_3]$, **2**, and 106 mg (0.105 mmol) of $[PPN][Re(CO)_5]$ were dissolved in 10 mL of THF, and the solution was stirred for 96 h. The consumption of **2** in this reaction mixture was followed by the intensity decrease of infrared bands at 1990 and 1983 $cm^{-1}$. Simultaneously, another CO absorption band at 1963 $cm^{-1}$ increased in intensity and developed a shoulder that later grew in as a strong band at 1971 $cm^{-1}$, which is characteristic of one of the products, $[PPN][Fe_3(CO)_9CCRe(CO)_5]$, **3**. The emergence of another carbonyl stretch at 1925 $cm^{-1}$ signaled the concomitant formation of the initial starting material, $[PPN]_2[Fe_3(CO)_9CCO]$, **1**, which was subsequently precipitated by the addition of diethyl ether to the reaction mixture, collected by filtration, and identified by $^{13}C$ NMR. The filtrate from this reaction mixture was evaporated to dryness, the resulting red oil was dissolved in 10 mL $CH_2Cl_2$, and 2-propanol was added dropwise until a cloudy solution resulted. Upon the application of a slight vacuum, red microcrystals of **3** formed and were collected by filtration. IR data for **3** in $CH_2Cl_2$: 2141 (vw), 2032 (vs), 1971 (s), 1965 (s), 1945 (m), 1917 (w) $cm^{-1}$. The FAB-MS had a parent peak at 772 amu ($[PPN][Fe_3(CO)_9CCRe(CO)_5] + H^+$) and fragments corresponding to the successive loss of 8 carbonyls. An analysis of the experimental data in comparison to the expected isotope distribution for $[PPN][Fe_3(CO)_9CCRe(CO)_5]$ gave a *R*-factor of 0.1 over a five mass number range around $m/e = 772$. $^{13}C$ NMR ($CD_2Cl_2$): 207.5 ($C_\alpha$), 66.7 ($C_\beta$), 220 ppm (broad, CO); $J_{CC} = 18.5$ Hz. Yield: 0.027 g of **1** (20%) and 0.010 g of **3** (8.8%). Anal. Calc (found) for $Fe_3ReP_2NO_{14}C_{52}H_{30}$: Fe, 12.82 (12.55); C, 47.67 (47.57); H, 2.31 (2.33).

**Synthesis of $[PPN][Fe_3(CO)_9CCRe(CO)_5]$ Free of Byproduct 1.** A 93 mg (0.089 mmol) sample of **2** and 102 mg (0.102 mmol) of $[PPN][Re(CO)_5]$ were dissolved in 20 mL of THF and stirred for 24 h. The infrared spectrum of the reaction mixture indicated partial consumption of **2** and simultaneous formation of **1** as a byproduct. Next, about 15 $\mu$L of acetyl chloride was added dropwise by gas tight microsyringe. Within minutes, [PPN]Cl precipitated from solution. The infrared spectrum of the filtrate showed the presence of CO stretching frequencies representative of $[PPN][Fe_3(CO)_9CCOCOCH_3]$, **2**, and the absence of a CO stretch at 1925 $cm^{-1}$ for **1**. In this process the initially formed byproduct **1** is converted back to the starting material, **2**, for further reaction. After the reaction mixture was stirred for ~48 h, the solvent was evaporated, the resulting solid was redissolved in 10 mL of $CH_2Cl_2$, and 2-propanol (15 mL) was added while stirring. Red microcrystals formed upon slow evaporation of the solvents, and these were characterized as **3** by infrared spectroscopy and FAB mass spectrometry. Yield: 0.029 g (25%).

**X-ray Crystal Structure of $[PPN][Fe_3(CO)_9CCRe(CO)_5]$.** A red, equidimensional crystal of $[PPN][Fe_3(CO)_9CCRe(CO)_5]$ was grown by slow diffusion of 2-propanol into a solution of **3** in $CH_2Cl_2$. The crystal was mounted with the use of oil (Paratone-N, Exxon) on a glass fiber and transferred to the cold $N_2$ stream (−120 °C) on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 uniquely centered reflections. Parameters of the monoclinic crystal and details of the data collection are listed in Table 1.

The structure was solved by direct methods (SHELXS-86) and with full-matrix least-squares refinement.[7] Calculations were performed with the TEXSAN 4.0 crystallographic software package on the Micro Vax 3600 computer.[8] Hydrogen atoms were introduced in idealized positions but not refined. The largest peak remaining in the final difference map was 0.58 e/Å$^3$. All non-hydrogen atoms were refined with anisotropic thermal parameters.

**Table 1. X-ray Crystal Structure Data for $[PPN][Fe_3(CO)_9CCRe(CO)_5]$**

| | |
|---|---|
| formula | $Fe_3C_{52}O_{14}ReNP_2H_{30}$ |
| $M_r$ | 1308.50 |
| cryst size, mm | 0.30 × 0.30 × 0.10 |
| cryst system | monoclinic |
| space group | $P2_1/n$ (No. 14) |
| *a*, Å | 22.181(7) |
| *b*, Å | 9.956(3) |
| *c*, Å | 23.088(7) |
| $\beta$, deg | 96.88(3) |
| *V*, Å$^3$ | 5062 |
| Z | 4 |
| *d*(calc), g cm$^{-3}$ | 1.717 |
| $\mu$(Mo Kα), cm$^{-1}$ | 33.86 |
| radiation ($\lambda$, Å) | Mo Kα (0.710 69) |
| scan type | $\omega-\theta$ |
| $2\theta$ max, deg | 48.0 |
| unique data | 8460 |
| obsd data, $I > 3\sigma(I)$ | 4842 |
| no. of variables | 658 |
| reflcn/param ratio | 7.36 |
| $R(F)^a$ | 0.036 |
| $R_w(F)^b$ | 0.035 |
| GOF | 1.13 |

$^a$ $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b$ $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

**Table 2. Selected Bond Distances (Å) with Standard Deviations for $[PPN][Fe_3(CO)_9CCRe(CO)_5]$**

| | | | |
|---|---|---|---|
| Fe1−Fe2 | 2.496(2) | Fe2−C6 | 2.208(8) |
| Fe1−Fe3 | 2.607(2) | Fe2−C7 | 2.022(8) |
| Fe2−Fe3 | 2.612(2) | Fe1−C11 | 1.78(1) |
| Fe1−C6 | 2.180(8) | Fe1−C12 | 1.764(9) |
| Fe1−C7 | 2.031(8) | Fe1−C13 | 1.76(1) |
| C1−Fe1 | 2.031(8) | Fe2−C21 | 1.749(9) |
| C1−Fe2 | 2.022(8) | Fe2−C22 | 1.77(1) |
| C1−Fe3 | 1.842(8) | Fe2−C23 | 1.79(1) |
| C1−C2 | 1.28(1) | Fe3−C31 | 1.79(1) |
| C2−Fe1 | 2.180(8) | Fe3−C32 | 1.76(1) |
| C2−Fe2 | 2.208(8) | Fe3−C33 | 1.77(1) |
| C2−Re | 2.161(8) | Fe3−C7 | 1.842(8) |
| C6−C7 | 1.28(1) | C11−O11 | 1.14(1) |
| Re−C3 | 2.00(1) | C12−O12 | 1.16(1) |
| Re−C4 | 1.954(9) | C13−O13 | 1.14(1) |
| Re−C5 | 2.015(9) | C21−O21 | 1.16(1) |
| Re−C6 | 1.989(9) | C22−O22 | 1.14(1) |
| Re−C7 | 2.00(1) | C23−O23 | 1.14(1) |
| C3−O3 | 1.129(9) | C31−O31 | 1.14(1) |
| C4−O4 | 1.149(9) | C32−O32 | 1.15(1) |
| C5−O5 | 1.119(9) | C33−O33 | 1.14(1) |
| C6−O6 | 1.131(9) | C7−O7 | 1.13(1) |

## Results and Discussion

Although bimetallic systems are known which are linked by dicarbide units, clusters containing a $C_2$ fragment are less common.[9] The synthetic pathways to clusters containing a dicarbide unit fall into three categories. The first involves cluster building upon an ethynediyldimetal compound, LMCCML. A recent example by Selegue and co-workers is the reaction of $Cp(CO)RuCCRuCp(CO)$ with $Fe_2(CO)_8$ to form $Fe_2Ru_2(CO)_8(Cp)_2C_2$.[10] In this case the $C_2$ unit is intact and

---

(7) Sheldrick, G. M. *SHELXS86: A Program for Crystal Structure Determination;* University of Goettingen: Goettingen, Germany, 1986.

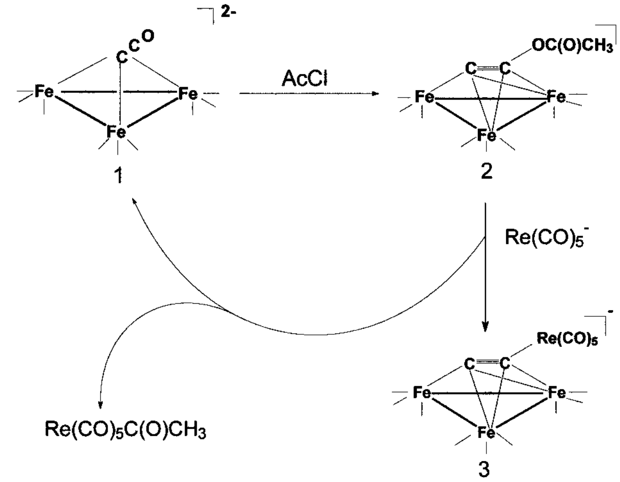
(8) Swepston, P. W. *TEXSAN, Version 4.0, the TEXRAY Structure Analysis Program Package*; Molecular Structure Corp.: College Station, TX, 1987.

**Table 3. Selected Bond Angles (deg) with Standard Deviations for [PPN][$Fe_3(CO)_9CCRe(CO)_5$]**

| | | | |
|---|---|---|---|
| C1−Re−C2 | 90.1(3) | C6−Fe1−C7 | 35.3(3) |
| C1−Re−C3 | 86.9(3) | C6−Fe1−C11 | 98.7(3) |
| C1−Re−C4 | 92.1(3) | C6−Fe1−C12 | 156.4(4) |
| C1−Re−C5 | 176.6(3) | C6−Fe1−C13 | 90.3(4) |
| C1−Re−C6 | 95.2(3) | C7−Fe1−C11 | 97.9(3) |
| C2−Re−C3 | 94.1(3) | C7−Fe1−C12 | 128.7(4) |
| C2−Re−C4 | 94.9(3) | C7−Fe1−C13 | 124.8(4) |
| C2−Re−C5 | 87.3(3) | C11−Fe1−C12 | 101.6(4) |
| C2−Re−C6 | 174.7(3) | C11−Fe1−C13 | 100.1(4) |
| C3−Re−C4 | 171.0(3) | C12−Fe1−C13 | 97.7(4) |
| C3−Re−C5 | 91.1(3) | Fe1−Fe2−Fe3 | 61.35(5) |
| C3−Re−C6 | 87.1(3) | Fe1−Fe2−C6 | 54.8(2) |
| C4−Re−C5 | 90.3(4) | Fe1−Fe2−C7 | 52.1(2) |
| C4−Re−C6 | 84.1(3) | Fe1−Fe2−C21 | 94.4(3) |
| C5−Re−C6 | 87.5(3) | Fe1−Fe2−C22 | 102.5(3) |
| Fe2−Fe1−Fe3 | 61.52(5) | Fe1−Fe2−C23 | 155.5(3) |
| Fe2−Fe1−C6 | 55.9(2) | Fe3−Fe2−C6 | 78.9(2) |
| Fe2−Fe1−C7 | 51.8(2) | Fe3−Fe2−C7 | 44.6(2) |
| Fe2−Fe1−C11 | 149.6(3) | Fe3−Fe2−C21 | 83.1(3) |
| Fe2−Fe1−C12 | 101.0(3) | Fe3−Fe2−C22 | 163.8(3) |
| Fe2−Fe1−C13 | 96.7(3) | Fe3−Fe2−C23 | 98.7(3) |
| Fe3−Fe1−C6 | 79.5(2) | C6−Fe2−C7 | 35.0(3) |
| Fe3−Fe1−C7 | 44.7(2) | C6−Fe2−C21 | 149.0(3) |
| Fe3−Fe1−C11 | 100.6(3) | C6−Fe2−C22 | 93.0(4) |
| Fe3−Fe1−C12 | 85.1(3) | C6−Fe2−C23 | 110.2(4) |
| Fe3−Fe1−C13 | 158.0(3) | C7−Fe2−C21 | 125.5(4) |
| C7−Fe2−C22 | 127.9(4) | Fe1−C13−O13 | 179.3(8) |
| C7−Fe2−C23 | 103.9(4) | Fe1−C11−O11 | 177.0(7) |
| C21−Fe2−C22 | 97.6(4) | Fe1−C12−O12 | 175.7(9) |
| C21−Fe2−C23 | 97.3(4) | Fe2−C21−O21 | 175.7(8) |
| C22−Fe2−C23 | 97.2(4) | Fe2−C22−O22 | 177.8(8) |
| Fe1−Fe3−Fe2 | 57.13(5) | Fe2−C23−O23 | 174.0(9) |
| Fe1−Fe3−C7 | 50.8(2) | Fe3−C31−O31 | 178.0(8) |
| Fe1−Fe3−C31 | 106.6(3) | Re−C1−O1 | 175.1(7) |
| Fe1−Fe3−C32 | 93.4(3) | Re−C2−O2 | 178.3(8) |
| Fe1−Fe3−C33 | 149.1(4) | Re−C3−O3 | 175.9(7) |
| Fe2−Fe3−C7 | 50.5(2) | Re−C4−O4 | 174.0(7) |
| Fe2−Fe3−C31 | 103.6(3) | Re−C5−O5 | 178.3(8) |
| Fe2−Fe3−C32 | 148.9(3) | Re−C6−Fe1 | 135.5(4) |
| Fe2−Fe3−C33 | 98.9(3) | Re−C6−Fe2 | 135.9(4) |
| C7−Fe3−C31 | 150.9(4) | Re−C6−C7 | 150.0(7) |
| C7−Fe3−C32 | 104.7(4) | Fe1−C6−Fe2 | 69.3(2) |
| C7−Fe3−C33 | 99.6(4) | Fe1−C6−C7 | 66.0(5) |
| C31−Fe3−C32 | 93.7(4) | Fe2−C6−C7 | 64.6(5) |
| C31−Fe3−C33 | 97.3(5) | Fe1−C7−Fe2 | 76.0(3) |
| C32−Fe3−C33 | 104.3(5) | Fe1−C7−Fe3 | 84.5(3) |
| Fe1−C7−C6 | 78.7(5) | Fe3−C32−O32 | 177.7(9) |
| Fe2−C7−Fe3 | 84.9(3) | Fe3−C33−O33 | 179.0(1) |
| Fe2−C7−C6 | 80.5(5) | Fe3−C7−C6 | 159.9(7) |

already bound to two metals. A second route to $C_2$-containing clusters is the formation of a carbon−carbon bond between two pre-existing monocarbide clusters. For example, Braga and co-workers observed that pyrolysis of Na[$Co_6C(CO)_{15}$] generates [$Co_{13}C_2(CO)_{24}$]$^{4-}$ and [$Co_{11}C_2(CO)_{22}$]$^{3-}$.[11] The outcome of these pyrolytic reactions is not very predictable, and product yields are generally low. In a third route to dicarbide clusters a more complex $C_2$-containing ligand attached to a cluster is converted into a simple $C_2$ ligand. In the present research, the CCOC(O)$CH_3$ ligand served as the precursor for the $C_2$ ligand. In an earlier example of this reaction type, Bruce and co-workers[12] utilized $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with $Fe_2(CO)_8$ produce $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$. In their reaction, the cleavage of the C−P bond in the $C_2PPh_2$ ligand resulted in the formation of the dicarbide ligand.

**Scheme 2**



The reaction of **2**, [PPN][$Fe_3(CO)_9C(O)CH_3$], with the strong nucleophile Na[FeCp$(CO)_2$] is complete within 1 h,[3] but in the present case the reaction with [PPN][Re$(CO)_5$] required 6 days to go to completion. This disparity is consistent with the relative nucleophilicities of [PPN][FeCp$(CO)_2$] and [PPN][Re$(CO)_5$]. Rate constants for reaction of these metal carbonyl anions with $CH_3I$ are $2.8 \times 10^6$ and $1.0 \times 10^3$ $M^{-1}$ $s^{-1}$, respectively.[13]

The attack of the $C_\alpha$ carbon of $C_\alpha C_\beta O$ in **2** by Na[FeCp$(CO)_2$] may occur because of lack of access to the crowded acyl carbon by the relatively bulky [FeCp$(CO)_2$]$^-$ nucleophile. In keeping with this interpretation, other bulky ligands, $PPh_3$ and $PPh_2Me$, displace the acetate group to yield [$Fe_3(CO)_9CCPR_3$].[4] IR spectra show that the milder nucleophile [Mn$(CO)_5$]$^-$ (rate constant of 7.4 $M^{-1}$ $s^{-1}$ for reaction with $CH_3I$)[13] reacts very slowly with **2** to yield the ketenylidene product $[PPN]_2Fe_3(CO)_9CCO$ in a reaction which did not go to completion in 13 days at room temperature. These comparisons suggest that relatively bulky nucleophiles attack the $C_\alpha$ position of the $C_\alpha C_\beta O$ group to produce an acetylide product. Very weak nucleophiles, such as [PPN][Co$(CO)_4$], do not react with **2**.

To circumvent the formation of $[PPN]_2$[$Fe_3(CO)_9CCO$] as a major byproduct, acetyl chloride was added to the reaction mixture of [PPN][$Fe_3(CO)_9CCOC(O)CH_3$] and [PPN][Re$(CO)_5$] with the objective of regenerating [$Fe_3(CO)_9CCOC(O)CH_3$]$^-$ from the byproduct $[PPN]_2$[$Fe_3(CO)_9CCO$], **1**, as shown in Scheme 2. The presence of [PPN][$Fe_3(CO)_9CCOC(O)CH_3$] and consumption of [$PPN_2$[$Fe_3(CO)_9CCO$] was monitored by $\nu_{CO}$ in the infrared spectrum. Indeed, the concentration of the acetylide cluster [PPN][$Fe_3(CO)_9CCRe(CO)_5$] was observed to increase and the concentration of **1** became negligible as the reaction proceeded.

---

(9) Examples of early work in the preparation of clusters containing a dicarbide unit include: (a) Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381. (b) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Inorg. Chem.* **1984**, *23*, 2073. (c) Arrigoni, A.; Ceriotti, A.; Della Pergola, R.; Longoni, G.; Manassero, M.; Masciocchi, N.; Sansoni, M. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 322. (d) Arrigoni, A.; Ceriotti, A.; Della Pergola, R.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1985**, *296*, 243. (e) Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc. A* **1971**, 1457. (f) Albano, V. G.; Chini, P.; Martinego, S.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1978**, 459. (g) Bor, G.; Marko, L.; Marko, B. *Chem. Ber.* **1962**, *95*, 333. (h) Allegra, G.; Peronaci, E. M.; Ercoli, R. *Chem. Commun.* **1966**, 549.

(10) Koutsantonis, G. A.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1992**, *11*, 2704.

(11) Albano, V. G,; Braga, D.; Chini, P.; Ciani, G.; Martinego, S. *J. Chem. Soc., Dalton Trans.* **1982**, 645−9.

(12) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3336−3338.

(13) Lai, C.-K.; Feighery, W. G.; Zhen, Y.; Atwood, J. D. *Inorg. Chem.* **1989**, *28*, 3929−3930.

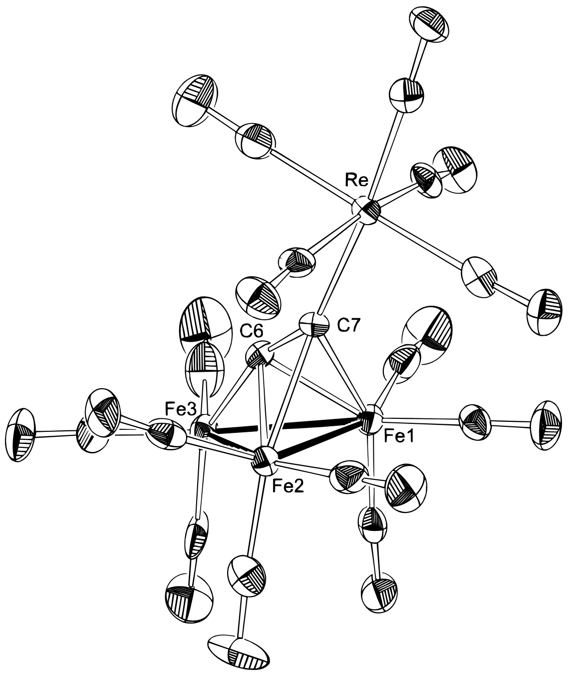


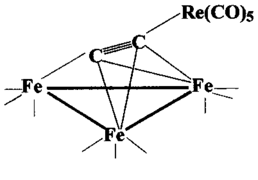
**Figure 1.** ORTEP drawing of [PPN][$Fe_3(CO)_9CCRe(CO)_5$], **3**. Ellipsoids are drawn at the 50% probability level.

Structurally, **3** is similar to previously reported dicarbide clusters. Frapper and Halet[14] have reported a theoretical analysis of organometallic clusters containing a supported $C_2$ ligand to clarify the bonding and reactivity of this ligand. Several coordination modes have been observed for the $C_2$ moiety including end-on bonding, face bridging, and encapsulation within a cluster. In addition to the previous example by Selegue *et al.*, Beck and co-workers[15] demonstrated the formation of dicarbide clusters by the reaction of an ethynediyldimetal compound, $L_nMC{\equiv}CML_n$, with a cluster building reagent. Thus the cluster, $Co_2Re_2(CO)_{14}C_2$, **4**, was generated by the reaction of $(CO)_5ReC{\equiv}CRe(CO)_5$ with $Co_2(CO)_8$. As shown in Table 4, the resulting cluster, $Co_2Re_2(C_2)(CO)_{14}$, has a strikingly similar framework to **3**. Both structures include a supported or side-on-bonded $C_2$ fragment. In Beck's complex, one rhenium atom and two cobalt atoms form a metal triangle. The acetylide linkage and pendant $Re(CO)_5$ unit contain a bond length and a Re−C−C angle comparable to those seen for **3**. The Re−C6 bond lengths are identical, with only a slight deviation in the bond angles Re−C6−C7 (150° for **3** versus 158° for **4**). As shown in Table 4, compound **3** is structurally similar to the previously reported [PPN][$Fe_3(CO)_9CCFeCp(CO)_2$]. Both acetylide units have the same C≡C bond length, 1.28 Å, and coordinate with the triangular framework in an $\eta^3$:$\eta^2$ fashion. There are many examples of cluster building around an acetylide fragment. For example, Akita[16] and co-workers prepared $Cp^*Fe[Co(CO)_2]_2(CO)_2C{\equiv}CFp^*$ from $Co_2(CO)_8$ and $Fp^*C{\equiv}CFp^*$.

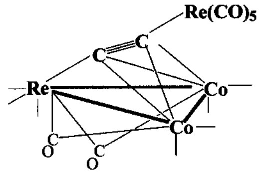
**Table 4. Bond Lengths (Å) and Angles (deg) in Clusters Containing Acetylides**

| | C−C | C−C−R | ref |
|---|---|---|---|
| [PPN][$Fe_3(CO)_9CCOC(O)CH_3$] | 1.314(8) | 143.4(5) | 2 |
| [PPN][$Fe_3(CO)_9CCFeCp(CO)_2$] | 1.288(5) | 147.3(3) | 3 |
| [PPN][$Fe_3(CO)_9CCRe(CO)_5$] | 1.28(1) | 150.0(7) | a |
| $Co_2Re(CO)_{10}CCRe(CO)_5$ | 1.282(17) | 152.4(12) | 15 |
| $CpRuFe_2(CO)_7CCRuCp(CO)_2$ | 1.35(1) | 147.6(7) | 10 |
| $Cp^*(CO)_2FeCo_2(CO)_6CCFeCp^*(CO)_2$ | 1.34(3) | 153(2) | 16d |

[a] This work.



**3**



**4**

**Acknowledgment.** We gratefully acknowledge the initial support by the National Science Foundation Grant No. CHE-9417250 and more recent support by the Department of Energy Grant No. DE-FG02-ER13640. Dr. D. L. Hung of the Northwestern University Analytical Services Lab provided the mass spectral analysis. D.M.N. also thanks Thy P. Do for completing reactivity studies on [PPN][$Fe_3(CO)_9CCRe(CO)_5$] and Dr. Gail B. Karet for interesting scientific discussions.

**Supporting Information Available:** Listings of positional parameters of all atoms, complete bond distances and angles, and thermal parameters for **3** (11 pages). Ordering information is given on any current masthead page.

OM9601357

---

[14] Frapper, G.; Halet, J. F. *Organometallics* **1995**, *14*, 5044−53.

[15] Weidmann, T.; Weinrich, V.; Wagner, B.; Robl, C.; Beck, W. *Chem. Ber.* **1991**, *124*, 1363−1368.

[16] (a) Akita, M.; Terada, M.; Oyama, S.; Sugimoto, S.; Moro-Oka, Y. *Organometallics* **1990**, *9*, 816−825. (b) Akita, M.; Terada, M.; Oyama, S.; Sugimoto, S.; Moro-Oka, Y. *Organometallics* **1991**, *10*, 1561−1568. (c) Akita, M.; Sugimoto, S.; Tanaka, M.; Moro-Oka, Y. *J. Am. Chem. Soc.* **1992**, *114*, 7581−7582. (d) Akita, M.; Terada, M.; Moro-Oka, Y. *Organometallics* **1992**, *11*, 1825−1830.