

## CpMoCo<sub>2</sub>(CO)<sub>8</sub>CCO<sup>+</sup>: SYNTHESIS AND CHARACTERIZATION OF A MIXED METAL ACYLIUM CATION

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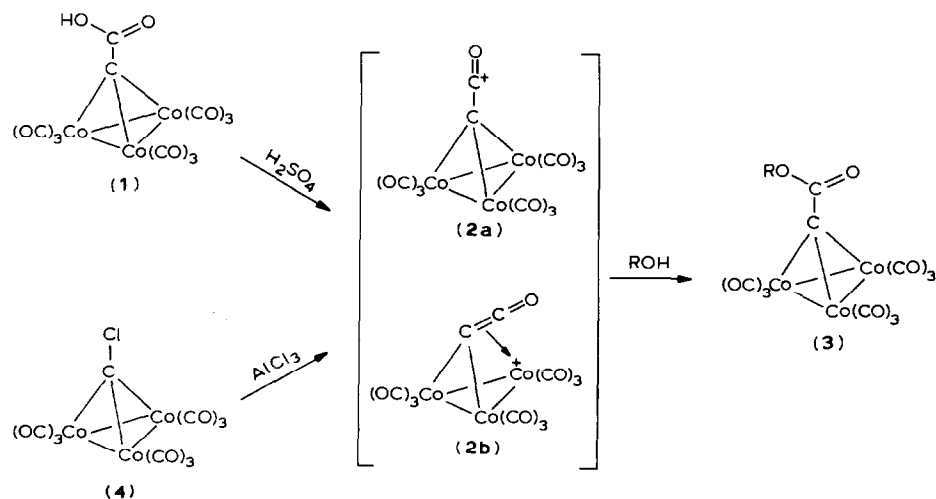
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### Summary

CpMoCo<sub>2</sub>(CO)<sub>8</sub>CCO<sub>2</sub>CHMe<sub>2</sub> in propionic anhydride reacts with HPF<sub>6</sub> to yield the mixed metal acylium cation CpMoCo<sub>2</sub>(CO)<sub>8</sub>CCO<sup>+</sup> which reacts with a variety of nucleophiles, e.g., ROH, R<sub>2</sub>NH, yielding cluster-bound esters and amides, respectively. The cation also reacts with PhNMe<sub>2</sub> in a Friedel–Crafts process. In the presence of water, Co<sub>3</sub>(CO)<sub>9</sub>CCO<sup>+</sup> can also decompose to yield the neutral dimer [(Co<sub>3</sub>(CO)<sub>9</sub>C]<sub>2</sub>.

### Introduction

One of the most fascinating and widely studied reactions is the heterogeneous, transition metal catalyzed Fischer–Tropsch process [1]. With a view to developing a



SCHEME 1. Generation and characterization of the known Co<sub>3</sub>(CO)<sub>9</sub>CCO<sup>+</sup> molecule.

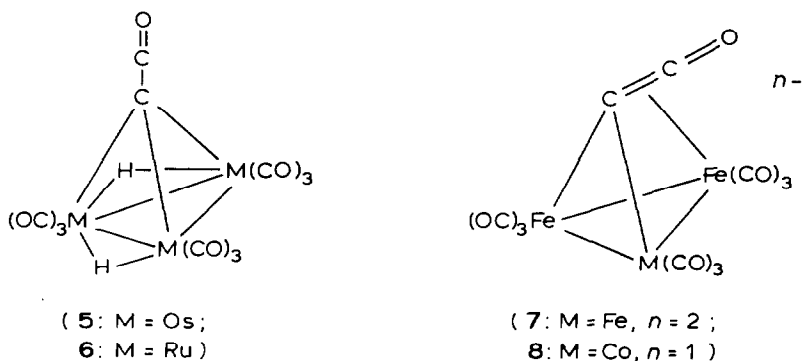


Fig. 1. Structures of known metal cluster ketenylidenes.

homogeneous process, many systems have been examined as models for the key intermediates [2-4]. Perhaps the most interesting model clusters have been those containing a carbonyl bonded to a carbon atom which is itself part of the metal cluster skeleton.

The first synthesis of a cluster of this type was described in 1972 when it was reported that treatment of the cluster  $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{H}$  (**1**) with concentrated sulfuric acid and subsequently with various alcohols led to the formation of the respective esters [5]. The cation **2** was isolated as a salt via treatment of a propionic anhydride solution of acid **1** or ester **3** with  $\text{HPF}_6$  [5]. A later study from the same laboratory demonstrated that the acylium cation could be generated by treatment of  $\text{Co}_3(\text{CO})_9\text{CCl}$  (**4**) with three equivalents of  $\text{AlCl}_3$  [6]. Similar results were reported for  $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CX}$  (X = Cl, Br) and  $\text{H}_3\text{Os}_3(\text{CO})_9\text{CBr}$  when they were likewise treated with  $\text{AlCl}_3$  [7].

Thermal rearrangement of  $\text{HOs}_3(\text{CO})_{10}\text{CH}$  led to the first neutral ketenylidene cluster, viz.  $\text{H}_2\text{Os}_3(\text{CO})_9\text{CCO}$  (**5**) [8]; the ruthenium analogue **6** was similarly prepared [9]. The first example of an anionic ketenylidene cluster,  $\text{Fe}_3(\text{CO})_9\text{CCO}^{2-}$  (**7**) was obtained by acylation of a bridging carbonyl in  $\text{Fe}_3(\text{CO})_{11}^{2-}$  followed by reductive cleavage [10]. We are aware of only one report of a mixed cluster containing a ketenylidene linkage, viz.,  $\text{Fe}_2\text{Co}(\text{CO})_9\text{CCO}^-$  (**8**) [11]; no neutral or cationic mixed species appear to have been reported. X-ray crystallographic data have revealed that in **5**, [12] the  $\text{C}=\text{C}=\text{O}$  moiety lies along the  $C_3$  axis while in **7** and **8** [10,11], the ketenylidene linkage is tilted through  $33^\circ$  and  $24^\circ$ , respectively (see Fig. 1). Despite numerous attempts to obtain suitable crystals, the structure of the cation **2** is still a matter of conjecture and the  $C_{3v}$ , **2a**, and  $C_s$ , **2b**, geometries are viable.

We now report the synthesis of the mixed metal cation  $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{Co}_2(\text{CO})_6\text{CCO}^+$  (**9**) and some preliminary indications of its reactivity vis-à-vis the exhaustively investigated tri-cobalt complex [13].

## Results and discussion

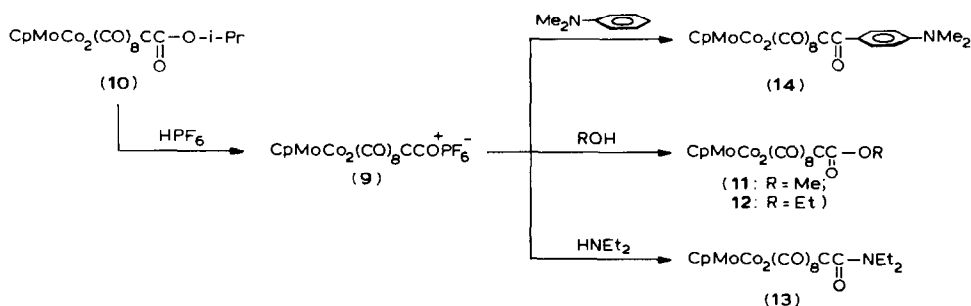
The ready availability [14-17] of mixed metal clusters of the  $\text{M}_3\text{CR}$  type prompted us to attempt to synthesize mixed trimetallic systems bearing a ketenylidene moiety. The prototypical molecule in this category was Seyferth's

$\text{Co}_3(\text{CO})_9\text{CCO}^+$  cation, **2**, the chemistry of which has been extensively studied [18]. The cluster system selected for the initial study was  $\text{CpMoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ , (**10**) since our previous work [17] on this complex indicated it to be the best behaved of the new mixed clusters. The synthesis of the mixed metal acylium cation **9** followed that developed by Seyferth for the tri-cobalt complex **2**. Dissolution of **10** in propionic anhydride produced a dark green coloration which, upon addition of  $\text{HPF}_6$ , turned brown and deposited a brown-black microcrystalline solid. Addition of ether resulted in complete precipitation of  $[\text{CpMoCo}_2(\text{CO})_8\text{CCO}^+][\text{PF}_6^-]$  (**9**), which, like its tri-cobalt analogue **2**, was insoluble in and unaffected by ethers and saturated hydrocarbons. In contrast to **2**, which dissolves only in nitromethane, **9** is sparingly soluble in methylene chloride and reacts with acetonitrile. **9** exhibits increased solubility when three equivalents of  $\text{AlCl}_3$  are added to a slurry of the  $\text{PF}_6^-$  salt in  $\text{CH}_2\text{Cl}_2$ ; this parallels the behaviour of **2**.

To confirm the identity of the mixed metal acylium salt, a slurry of **9** was allowed to react with several nucleophiles. Treatment with methanol or ethanol resulted in the immediate formation of a dark green homogeneous solution and the products of the reaction were the expected methyl and ethyl esters, **11** and **12**, respectively. Reaction of the  $\text{MoCo}_2$  cation, **9**, with diethylamine once again occurred spontaneously. However, the resulting amide, **13**, was rather unstable and attempts to purify the product by column chromatography under a nitrogen atmosphere have not yet proven successful. Nevertheless, immediate removal of solvent upon completion of the reaction yielded a solid which could be stored under an inert atmosphere and characterized spectroscopically. As with the tri-cobalt system **2**, reaction of the mixed acylium salt **9** with *N,N*-dimethylaniline led to the Friedel–Crafts product, **14**, in which the electrophile has attacked *para* to the bulky and electron-releasing dimethylamino group. This site of attack is in complete accord with conventional Friedel–Crafts chemistry.

In comparing the cations **2** and **9** we note that, while a  $\text{Co}(\text{CO})_3$  vertex has been replaced by an isolobal  $\text{CpMo}(\text{CO})_2$  fragment, the cyclopentadienyl moiety not only maintains the steric crowding around the apical carbon but also enhances the solubility of the salt. Preliminary data on other clusters support the assertion that acylium cation formation is favored by the presence of bulky ligands.

An interesting result was obtained from an attempt to prepare a sample of  $[\text{Co}_3(\text{CO})_9\text{CCO}^+][\text{PF}_6^-]$  for NMR studies. A small scale reaction of  $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{CHMe}_2$  and  $\text{HPF}_6$  resulted in no immediate precipitation of the



SCHEME 2. Synthetic scheme relating molecules **9** through **14**.

acylium salt. In the hope of precipitating the salt from solution, anhydrous ether was added and resulted in the formation of black crystals. As the structure of the cation has been the subject of some conjecture [19], the product was examined by X-ray crystallography. In fact, we were surprised to find that the crystals were not of the cation but rather of the neutral dimer  $[\text{Co}_3(\text{CO})_9\text{C}]_2$  the structure of which had been previously determined by Penfold and co-workers [20]. The bond length and angle data agreed completely with those previously published.

This dimer has previously been synthesized in low yield by refluxing  $\text{Co}_3(\text{CO})_9\text{CBr}$  in toluene [21] or by the thermolysis of  $\text{Co}_3(\text{CO})_9\text{CCl}$  in the presence of triphenylarsine [22]. The reaction conditions in these latter two syntheses are relatively vigorous and would seem to suggest a free radical mechanism. In contrast, a synthetic process carried out at room temperature which utilizes  $\text{HPF}_6$  in propionic anhydride is hardly conducive to radical formation! A possible rationale could involve formation of the anhydride  $(\text{Co}_3(\text{CO})_9\text{CCO})_2\text{O}$  via reaction of **2** with  $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{H}$ ; subsequent loss of CO [23] and  $\text{CO}_2$  would then lead to the dimer. Further experiments are in progress in an attempt to clarify the mechanism of this reaction. It is noteworthy that dimeric products were previously observed during attempted alkylations of  $[\text{Co}_3(\text{CO})_9\text{CCO}^+][\text{PF}_6^-]$  with alkylolithiums or with Grignard reagents and in these cases dimer formation was attributed to complex electron transfer processes [18].

We have evidence for the existence of other mixed metal acylium cations including those derived from  $\text{CpNiCo}_2(\text{CO})_6\text{CCO}_2\text{CHMe}_2$ ,  $\text{Cp}_3\text{Co}_2\text{Ni}(\text{CO})\text{CCO}_2\text{CHMe}_2$  and  $(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ . The detailed chemistry of these acylium cations will be presented in future publications. At present, attempts are being made to obtain crystals of one or more of these cations suitable for X-ray diffraction studies so as to determine the orientation of the  $\text{C}=\text{C}=\text{O}$  moiety with respect to the metal triangle.

To conclude, we report that  $\text{CpMoCo}_2(\text{CO})_8\text{CCO}_2\text{R}$  reacts with  $\text{HPF}_6$  to yield the cation  $\text{CpMoCo}_2(\text{CO})_8\text{CCO}^+$  which can be trapped using a variety of nucleophiles.

## Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried according to standard procedures [24].  $^1\text{H}$  NMR spectra were recorded using a Bruker WP80 spectrometer with chemical shifts reported relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using either KBr solution cells or NaCl plates.  $\text{CpMoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$  (**10**) was prepared as described previously [17]. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

### *Preparation of $[\text{CpMoCo}_2(\text{CO})_8\text{CCO}][\text{PF}_6]$ (**9**)*

To a solution containing  $\text{CpMoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$  (0.17 g, 0.28 mmol) in propionic anhydride (2.1 ml) was added 65% aqueous  $\text{HPF}_6$  (32  $\mu\text{l}$ , 0.36 mmol) using a micro-syringe. Upon addition of the acid, the color of the solution was transformed from green to brown. Upon stirring, a dark brown precipitate began to form and, after 30 min, ether (5 ml) was added to the reaction mixture to ensure complete precipitation of the salt. The mixture was then filtered under nitrogen pressure and

the salt **9** (0.14 g, 0.20 mmol; 71%) was washed with anhydrous ether and dried in vacuo at room temperature. Infrared (Nujol mull)  $\nu(\text{CO})$  at 2065(m), 2010(s), 1985(s) and 1625(w)  $\text{cm}^{-1}$ . Anal: Found: C, 26.00; H, 1.03.  $\text{C}_{15}\text{H}_5\text{Co}_2\text{F}_6\text{MoO}_9\text{P}$  calcd.: C, 26.19; H, 0.73%.

#### Treatment of **9** with nucleophiles

(a) *MeOH*. To a slurry of **9** (0.0769 g, 0.11 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 ml) was added 1  $\text{cm}^3$  of methanol. The reaction was stirred for 30 min and then poured into 10 ml of water. After extraction with 10 ml of ether, the ether layer was washed with three 10 ml portions of 10% HCl, dried over  $\text{Na}_2\text{SO}_4$  and the ether removed in vacuo to give **11** as the product, m.p. 131–133°C (decomp.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.67(s,3H) and 4.71(s,5H) ppm. IR (cyclohexane):  $\nu(\text{CO})$  at 2090(m), 2080(sh), 2045(sh), 2040(s), 1950(w), 1905(w) and 1685(ester)  $\text{cm}^{-1}$ . Anal: Found: C, 33.08; H, 1.71%.  $\text{C}_{16}\text{H}_8\text{Co}_2\text{MoO}_{10}$  calcd.: C, 33.48; H, 1.41%.

(b) *EtOH*. Using the procedure in (a), the product **12**, m.p. 102–104°C (decomp.) was obtained.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.23(t,3H), 4.27(q,2H) and 4.74(s,5H) ppm. IR (cyclohexane):  $\nu(\text{CO})$  at 2075(m), 2065(m), 2035(s), 2015(s), 1995(s), 1945(w), 1900(w) and 1675(ester)  $\text{cm}^{-1}$ . Anal: Found: C, 34.53; H, 2.06%.  $\text{C}_{17}\text{H}_{10}\text{Co}_2\text{MoO}_{10}$  calcd.: C, 34.72; H, 1.71%.

(c) *Et<sub>2</sub>NH*. The reaction procedure was the same as in (a) except that the reaction mixture was poured into 10 ml of water. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$  and the solvent evaporated under reduced pressure to give **13** as the product.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.97(t,6H), 3.26(q,4H) and 4.71(s,5H) ppm. IR ( $\text{C}_6\text{H}_6$ ):  $\nu(\text{CO})$  at 2080(s), 2030(sh), 1995(sh), 1940(w), 1890(w) and 1580(amide)  $\text{cm}^{-1}$ . Anal: Found: C, 37.43; H, 2.43; N, 2.53.  $\text{C}_{19}\text{H}_{15}\text{Co}_2\text{MoNO}_9$  calcd.: C, 37.10; H, 2.46%; N, 2.28%.

(d) *PhNMe<sub>2</sub>*. The reaction procedure was the same as in (a) but the solvent was removed in vacuo and the residue chromatographed on neutral alumina. Elution with ether/petroleum ether, 30/70, gave the product **14**, which was an oil.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.05(s,6H), 5.42(s,5H) and 6.61–7.90(m,4H,AA'BB') ppm. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  at 2065(s), 2025(sh), 2010(s), 1950(w), 1895(w) and 1605(ketone)  $\text{cm}^{-1}$ . Anal: Found: C, 41.35; H, 2.03; N, 2.23%.  $\text{C}_{23}\text{H}_{15}\text{Co}_2\text{MoNO}_9$  calcd.: C, 41.66; H, 2.28; N, 2.11%.

#### Preparation of $[\text{Co}_3(\text{CO})_9\text{C}]_2$

To a solution containing  $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{CHMe}_2$  (0.24 g, 0.46 mmol) in propionic anhydride (3.4 ml) was added 65% aqueous  $\text{HPF}_6$  (0.1 ml, 1.13 mmol). The reaction mixture was stirred for 30 min at room temperature. Addition of 5 ml of anhydrous  $\text{Et}_2\text{O}$  resulted in the precipitation of small shiny black crystals (0.025 g). An X-ray diffraction study on the product revealed it to be  $[\text{Co}_3(\text{CO})_9\text{C}]_2$ . Subsequently, an IR spectrum on a Nujol mull of the black crystals was in agreement with that reported for  $[\text{Co}_3(\text{CO})_9\text{C}]_2$  in the literature [22].

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