

Mixed metal acylium clusters: A chemical and spectroscopic study

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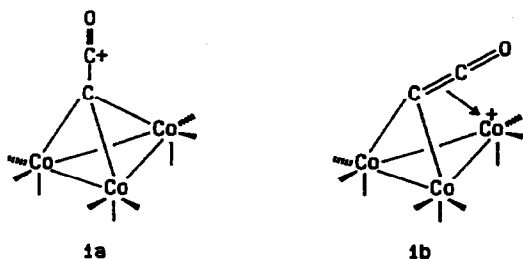
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Abstract

The generation of mixed metal acylium cations $[MCo_2(CO)_6CCO]^+$, $M = (C_5H_5)Mo(CO)_2$, $(C_5Me_5)Mo(CO)_2$ and $(C_5H_5)Ni$, from the parent esters via treatment with HPF_6 in propionic anhydride is described. These cations and also the related $[(C_5H_5)_2Co_3(CO)_4CCO]^+$ cluster react with alcohols to give esters and with indole or pyrrole to give Friedel–Crafts type products. 1H NMR, IR and FAB mass spectroscopic data are reported.

Introduction

The mode of interaction of a ketenylidene fragment, viz. $C=C=O$, with a metal triangle has been the subject of numerous recent investigations. An understanding of the binding of a single carbon monoxide molecule to a surface-bound carbide is of obvious relevance to the mechanistic features of several heterogeneously catalyzed processes. The prototypical organometallic molecule of this type was Seyferth's $[Co_3(CO)_9CCO]^+$ cluster in which the ketenylidene moiety was bonded to a triangle of cobalt atoms, as in **1**. Despite extensive chemical studies of this cation [1,2], it has not yet been possible to obtain crystals of sufficient quality for X-ray diffraction studies and the structures **1a** and **1b** have been envisaged as viable candidates. Recent theoretical and high field NMR spectroscopic studies from this laboratory [3] have indicated that structure **1b** in which there is a direct interaction with a single cobalt vertex is favored and this is also consonant with the facile decarbonylation and carbonylation reactions exhibited by metal clusters of this general type [4,5].



The picture is much clearer with the corresponding anionic clusters, typified by $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$ (**2**), the structures of which have been masterfully elucidated by Shriver and his colleagues [6–9]. In these systems crystallographic evidence is unequivocal and the $\text{C}=\text{C}=\text{O}$ fragment is tilted away from the pseudo three-fold axis unperpendicular to the triangular metal base. Interestingly, X-ray data on the tri-osmium cluster $[\text{H}_2\text{Os}_3(\text{CO})_9\text{C}=\text{C}=\text{O}]$ reveal the ketenylidene moiety to be aligned vertically with respect to the tri-osmium plane [10] and not tilted as in the cases previously discussed.

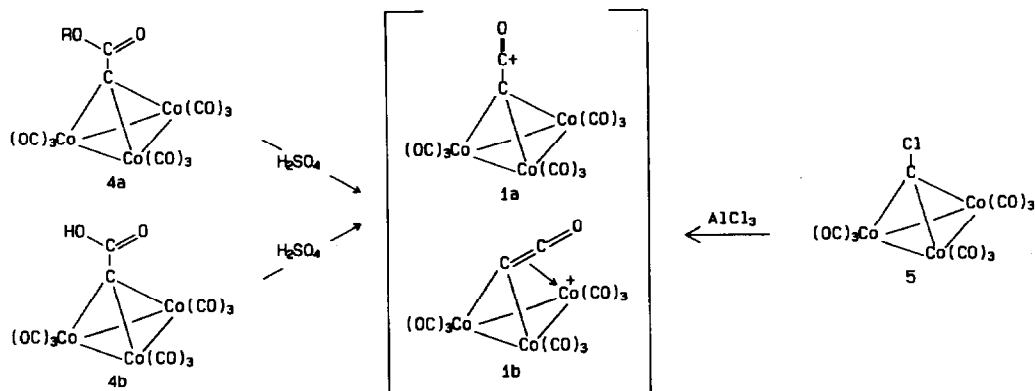
To our knowledge, the only example of a cationic mixed metal ketenylidene cluster is $[(\text{C}_5\text{H}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}]^+$ (**3**). We have reported not only the low temperature ^{13}C NMR spectrum of **3** [3] but also some reactions with nucleophiles [11]. We now describe a general route to such mixed metal species, outline some of their chemistry and point out some future areas of interest.

Results and discussion

The parent cluster cation in the ketenylidene series, i.e., $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$, is readily preparable via two quite different routes. The original synthesis involved the treatment of either the ester **4a** or the carboxylic acid **4b** with strong acid [12]. This is analogous to the well-known hydrolysis mechanism for hindered molecules, such as mesityl esters, which proceeds via an acylium ion [13]. The second route [14] uses a Lewis acid (normally AlCl_3) to remove an apical halogen and thus bring about CO migration from a cobalt carbonyl position, as in **5**. The latter route has the advantage that prior enrichment of the metal carbonyls with ^{13}CO leads to an enrichment of the ketenylidene carbon position with its attendant sensitivity advantages for NMR observation. Unfortunately, thus far, it has proven difficult to obtain mixed metal clusters bearing an apical halogen substituent. The obvious routes which merely substitute an isolobal $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2$ or $(\text{C}_5\text{H}_5)\text{Ni}$ vertex for $\text{Co}(\text{CO})_3$ in $\text{Co}_3(\text{CO})_9\text{CCl}$ lead to decomposition and do not represent a viable synthesis [15,16]. Interestingly, the treatment of $\text{H}_3\text{Ru}_3(\text{CO})_9\text{COMe}$ with BBr_3 is known to yield the analogous bromo cluster [17]. Efforts to generate $\text{CpMoCo}_2(\text{CO})_8\text{CBr}$ from $\text{CpMoCo}_2(\text{CO})_8\text{COMe}$ using this method are being investigated. Consequently, since modification of the readily available $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{R}$ clusters to incorporate a variety of metal vertices is very facile [18,19], we focused our efforts on the ester hydrolysis procedure.

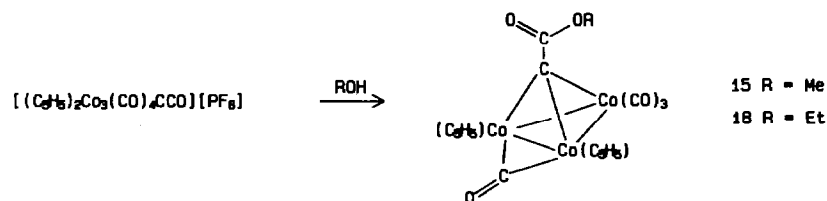
The mixed metal clusters $(\text{C}_5\text{H}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ (**6**), $(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ (**7**), and $(\text{C}_5\text{H}_5)\text{NiCo}_2(\text{CO})_6\text{CCO}_2\text{CHMe}_2$ (**8**) are readily preparable in synthetically useful quantities. The homometallic cluster $(\text{C}_5\text{H}_5)_2\text{Co}_3(\text{CO})_4\text{CCO}_2\text{CHMe}_2$ (**9**) was synthesized in small quantities during preparations of **8**. The appearance of this cluster was not surprising as previous work from this laboratory had identified it as a by-product in this synthesis [15]. Recently the observation of some related clusters as reaction by-products has been reported [20].

The conversion of the neutral clusters to the corresponding acylium cations occurred quite readily when propionic anhydride solutions containing the starting material were treated with HPF_6 . However, the yields of the cations and the time actually required for their generation was found to depend on the starting cluster. For instance, the cation **10** was formed almost instantaneously in 82% yield upon addition of the acid whereas the cation **11** required a longer period of time for



generation and was isolated in only 62% yield. One might speculate that steric factors play an important role in the generation of these cations whereby the more hindered molecules favour the formation of the acylium ions, just as in hindered ester hydrolyses.

Once generated, the salts were subsequently allowed to react with a variety of nucleophiles, as shown in Schemes 1 and 2. While the identity of the cationic intermediates was clearly indicated not only by their mode of generation and spectroscopic properties, but also by their reactivity, attempts were made to obtain analytical data on the cations themselves. To this end they were isolated as their PF₆⁻ salts immediately prior to their analysis. Satisfactory data were obtained for the molybdenum-containing cations **3** and **10** but all attempts to obtain C and H data on **11** and **12** were unsatisfactory. (The values were slightly high indicating possible hydrolysis to the corresponding acids.) The cations react not only with alcohols to give esters but also with relatively electron rich aromatic systems such as pyrrole or indole to give the Friedel–Crafts products. There was no evidence for the formation of the amide derivatives although it is not possible to rule out initial attack at the nitrogen followed by migration to give the observed product. In contrast to the tricobalt cation **1**, the mixed metal systems did not give observable products when treated with ferrocene; perhaps the sterically demanding cyclopentadienyl groups influence the reactivity of these cations.



Scheme 1. Characterization of the tricobalt cation, **12**.

These new clusters were characterized by a variety of techniques including ¹H NMR, IR and elemental analysis but it was found that an extremely useful technique to identify the molecules was Fast Atom Bombardment (FAB) mass spectrometry. With this technique it is possible to detect the high mass parent ions in addition to those arising from the subsequent loss of the carbonyl ligands. A

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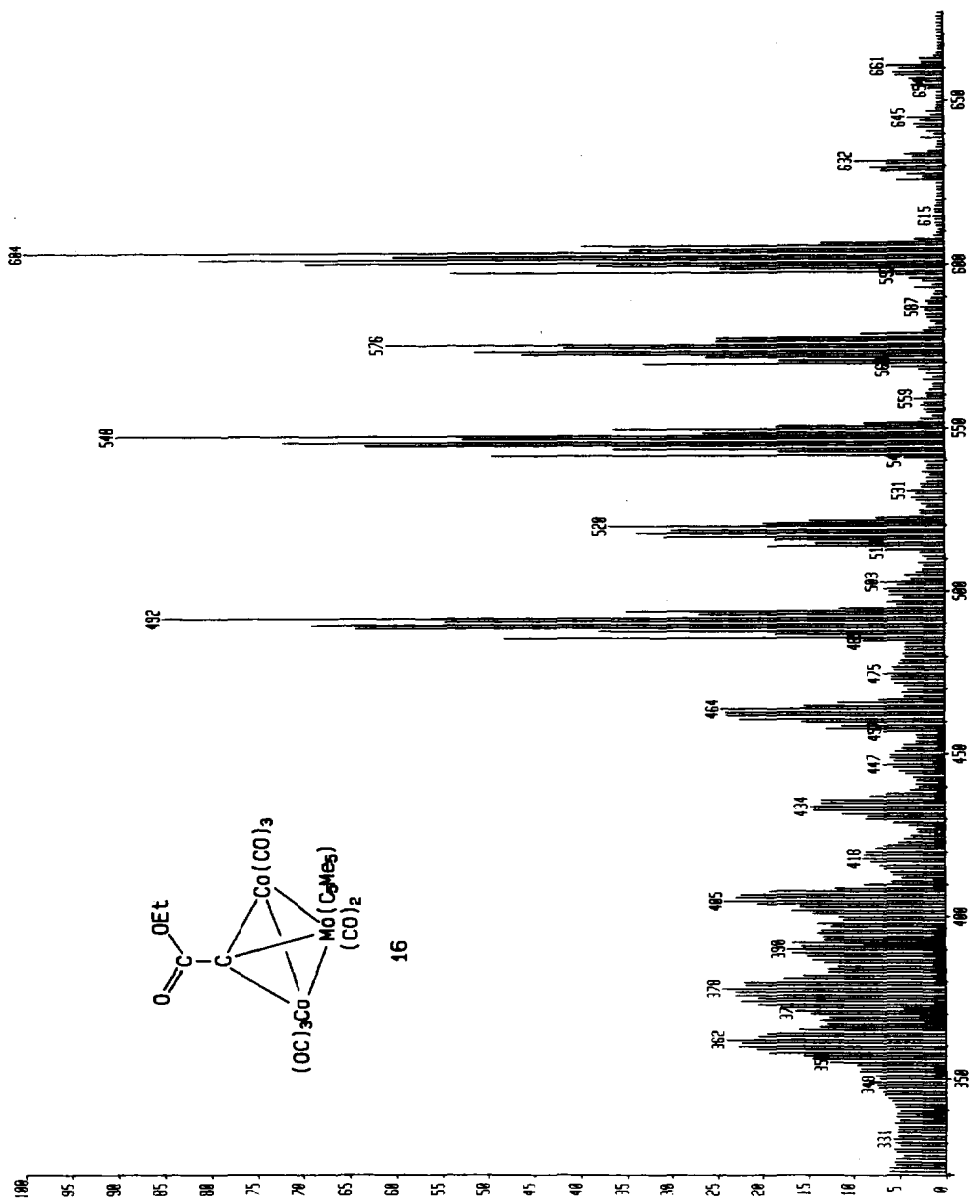
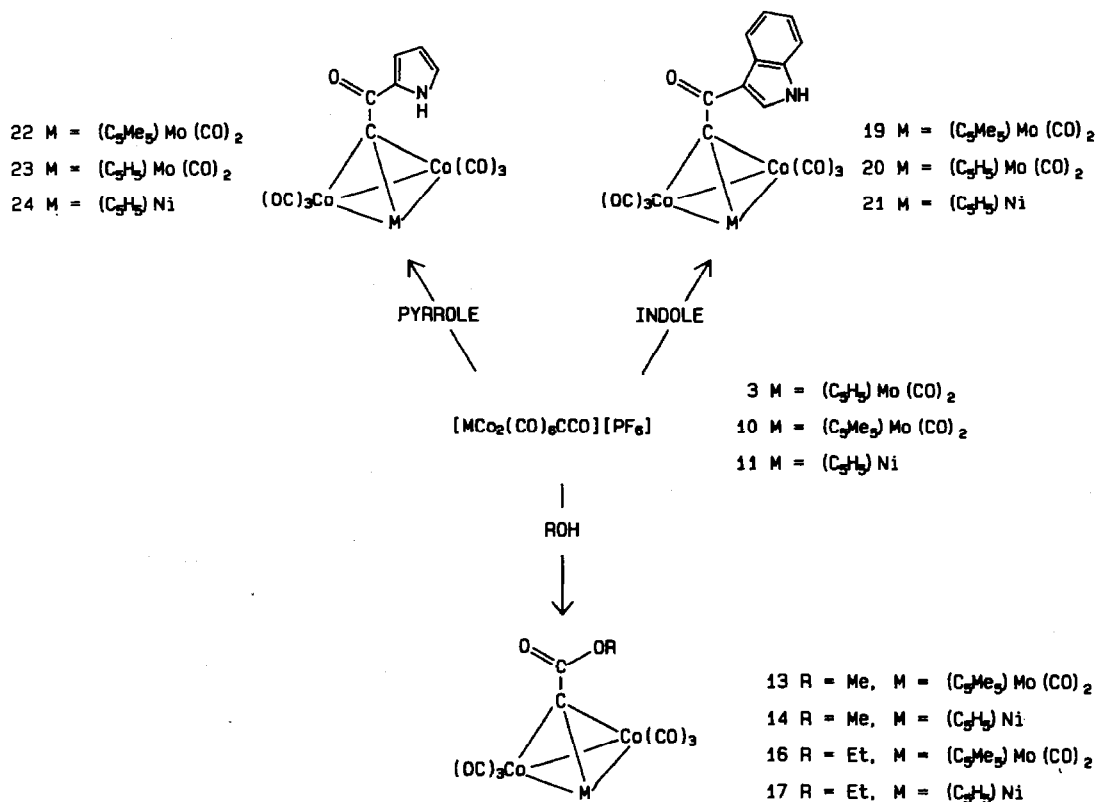


Fig. 1. (a) FAB mass spectrum of $(C_3Me_5)_2MoCo_2(CO)_8CCO_2Et$ (**16**). (b) FAB mass spectrum of $(C_3Me_5)_2MoCo_2(CO)_8CCO_2(C_4H_4NH)$ (**22**).



Scheme 2. Characterization of the mixed metal acylium cations.

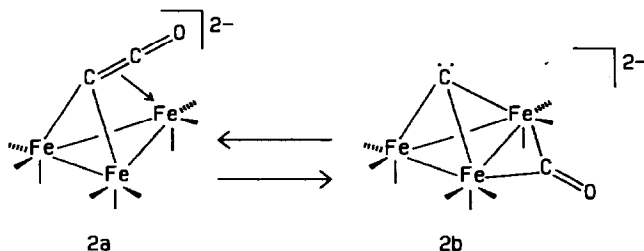
typical set of FAB mass spectra is presented in Fig. 1. The observed isotope patterns compare favourably with the calculated values.

The production of these cationic ketylidene clusters raises several interesting points. First of all, their detailed structures remain unknown. We have already reported the high field ¹³C NMR spectrum of the cation **3** which shows a single carbonyl resonance at room temperature but splits into a 2/6 pattern at -90 °C with chemical shifts of 211.8 and 196.2 ppm, appropriate for carbonyls on molybdenum and cobalt, respectively [3]. A ¹³C NMR study of the cation **10** carried out in this work gave similar results with the carbonyls splitting into a 2/6 ratio at -90 °C having resonances at 228.7 and 195.5 ppm respectively, also indicative of the molybdenum and cobalt bonded carbonyls. This peak pattern is consistent with a molecule of C_s symmetry but does not allow one to decide whether the C=C=O unit is vertical, or tilted toward the molybdenum atom, or even tilted toward the middle of the cobalt-cobalt vector! Hopefully, the observation of unambiguous chemical shifts for the carbons in the ketylidene ligand may allow a distinction between these possibilities. However, these data will be very difficult to obtain without some degree of enrichment of the ¹³C nuclei in the C=C=O fragment. Currently this enrichment can only be realized through an expensive and indirect synthesis.

A preferred method of confirming the structures of these compounds would be to obtain crystals of the cations of sufficient quality for X-ray diffraction studies.

Whereas Seyferth's tricobalt cation dissolved only in nitromethane, cations **3**, **11** and **12** are sparingly soluble in CH_2Cl_2 and cation **10** is completely soluble in methylene chloride. The increase in solubilities is perhaps attributable to the presence of the cyclopentadienyl groups on the periphery of the molecules. The enhanced solubility of these cations may allow for the formation of crystals of high quality; this may provide unequivocal evidence via X-ray crystallography as to the geometry of the ketylidene moiety.

Included in our ^{13}C NMR study was an experiment to determine how the behaviour of the cations, with respect to carbonyl exchange, compared to that of the Shriver's anion **2**. When $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$ (**2**) was stirred under an atmosphere of ^{13}C overnight, both the terminal and ketylidene carbonyls underwent ^{13}C enrichment, as determined by ^{13}C NMR [6]. The enrichment of the apical carbonyl is thought to occur intramolecularly via the intermediate formation of a carbide as in Scheme 3; thus, incorporation of ^{13}C at the iron carbonyl positions provides a route to enrichment of the ketylidene moiety. However, while the $\text{Fe}-\text{CO}/\text{C}-\text{CO}$ interchange is operative on the relatively slow chemical time scale, it is not detectable on the NMR time scale. Thus, even at 50°C the peaks attributable to the ketylidene carbonyl and the CO's bonded to iron show no evidence of exchange.



Scheme 3. Proposed interchange mechanism to account for the incorporation of ^{13}C at the apical carbonyl site in $\text{Fe}_3(\text{CO})_9(\text{CCO})^{2-}$ (**2**).

When the ^{13}C NMR spectrum of $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ enriched at both the metal and ketylidene carbonyls was recorded at 330 K the spectrum obtained was the same as the room temperature spectrum. Two resonances were observed at 191.6 and 168.2 ppm in the ratio 9/1, corresponding to the metal carbonyls and the ketylidene CO. The sharpness of the peak attributed to the apical CO indicated that intramolecular interchange between the acylium CO and the metal carbonyls was slow on the NMR timescale, paralleling Shriver's result for **2**. In order to maximize the chances of observing peak coalescence between two sites for which the activation energy for exchange is high, an 80 MHz FT-NMR instrument was used for the ^{13}C NMR study. The low field is necessary to diminish the frequency separation and thus lower the coalescence temperature.

It was also of interest to determine whether the apical CO would undergo intramolecular exchange with the metal carbonyls on the chemical timescale, however, the experiment was not viable because of the low solubility of **1**. The enhanced solubility of the cation **10** made it the perfect candidate for this experiment and so, after dissolution in CH_2Cl_2 , **10** was stirred in the presence of ^{13}C for seven days. The room temperature ^{13}C NMR spectrum of the cation indicated that enrichment of the metal carbonyls was occurring, as evidenced by a broad resonance at 209.2 ppm; however, no signal was observed for the apical CO. It was

concluded that intramolecular exchange involving the ketylidene carbonyl in the MoCo_2 system was occurring neither on the (relatively fast) NMR timescale nor on the (much slower) chemical timescale. Clearly, such an exchange process is more facile in Shriver's anionic cluster than in the cationic system discussed here.

To conclude, we report the syntheses and chemical reactivity of the mixed metal cations **3**, **10**, **11** and **12**. In general their properties closely resemble those of the parent cation **1**, however, the presence of the bulky organic moieties leads to increased solubility but somewhat decreased reactivity. Nonetheless, they promise to open up many avenues for future investigation.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures [21] before use. ^{13}C NMR spectra were recorded using Bruker WM 250 and WP 80 spectrometers. ^1H NMR spectra were recorded using Bruker WP80 and Varian EM390 spectrometers. Chemical shifts (δ , ppm) reported were referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using either KBr solution cells or NaCl plates. Mass spectra were obtained with a double focusing VG ZAB-E mass spectrometer under positive ion fast atom bombardment (FAB) conditions. 3-Nitrobenzyl alcohol was used as the matrix and xenon was the bombarding species (8 keV). Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

$(\text{C}_5\text{H}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ [19], $(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ [22] and $(\text{C}_5\text{H}_5)\text{NiCo}_2(\text{CO})_6\text{CCO}_2\text{CHMe}_2$ [23] were prepared as previously reported.

*Preparation of $(\text{C}_5\text{H}_5)_2\text{Co}_3(\text{CO})_4\text{CCO}_2\text{CHMe}_2$ (**9**)*

$[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ (0.616 g, 2.03 mmol) and $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{CHMe}_2$ (2.137 g, 4.05 mmol) were stirred in THF (40 cm^3) at room temperature for 14 days. After removal of the solvent, the residue was chromatographed on silica gel. Elution with ether/petroleum ether, 10/90, yielded $(\text{C}_5\text{H}_5)\text{NiCo}_2(\text{CO})_6\text{CCO}_2\text{CHMe}_2$. Increasing the polarity of the eluent to ether/petroleum ether, 50/50 gave **9** (0.088 g, 0.170 mmol, 4.2%) which was a brown solid, m.p. 114–116 °C. ^1H NMR (C_6D_6): δ 5.40(m,1H), 4.74(s,10H) and 1.32(d,6H). IR (cyclohexane): $\nu(\text{CO})$ at 2045(s), 2005(s), 1810(m) and 1680(ester) cm^{-1} . Analysis: Found: 44.27; H, 3.59. $\text{C}_{19}\text{H}_{17}\text{O}_6\text{Co}_3$ calcd.: C, 44.04; H, 3.31%.

Preparation of acylium cations

(a) $[(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}][\text{PF}_6]$ (**10**). Using a microsyringe, 65% aqueous HPF_6 (129 μl , 0.21 mmol) was added to a solution of $(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$ (0.099 g, 0.147 mmol) in propionic anhydride (1.1 cm^3). The colour of the solution changed from green to brown upon addition of the acid and resulted in the immediate formation of a brown precipitate. After allowing the mixture to stir for 20 min, 5 cm^3 of anhydrous ether was added to the reaction mixture to ensure complete precipitation of the salt. The mixture was then filtered under nitrogen pressure and the product, $[(\text{C}_5\text{Me}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}][\text{PF}_6]$ (0.092 g, 0.121 mmol, 82%), was further washed with anhydrous ether and then dried in vacuo at room temperature. IR (CH_2Cl_2): $\nu(\text{CO})$ at 2075(m) 2040(s), 2020(s), 1940(w), 1880(w) and 1650(w) cm^{-1} . Analysis: Found: C, 31.55; H, 2.23. $\text{C}_{20}\text{H}_{15}\text{O}_9\text{PF}_6\text{MoCo}_2$ calcd.: C, 31.69; H, 2.00%.

(b) $[(C_5H_5)MoCo_2(CO)_8CCO][PF_6]$ (**3**). Using the procedure described in (a), the cation (71%) was obtained as a dark brown solid. IR (Nujol mull): $\nu(CO)$ at 2065(m), 2010(s), 1985(s) and 1625(w) cm^{-1} . Analysis: Found: C, 26.00; H, 1.03. $C_{15}H_5O_9PF_6MoCo_2$ calcd.: C, 26.19; H, 0.73%.

(c) $[(C_5H_5)NiCo_2(CO)_6CCO][PF_6]$ (**11**). Using the procedure described in (a), **11** (62%) was obtained as a brown solid. IR (Nujol mull): $\nu(CO)$ at 2070(m), 2040(s), 2000(s) and 1635(w) cm^{-1} .

(d) $[(C_5H_5)_2Co_3(CO)_4CCO][PF_6]$ (**12**). Using the procedure described in (a), the cation (70%) was obtained as a black solid. IR (Nujol mull): $\nu(CO)$ at 2040(s), 1995(m), 1910(m) and 1870(w) cm^{-1} .

Treatment of $[(C_5Me_5)MoCo_2(CO)_8CCO][PF_6]$ with nucleophiles

(a) *MeOH*. To a solution of **10** (0.085 g, 0.112 mmol) in dry CH_2Cl_2 (10 cm^3) was added 1 cm^3 of methanol. This resulted in the immediate formation of a dark green, homogeneous solution. The reaction mixture was stirred for 30 min and then poured into 10 cm^3 of distilled H_2O . After extraction with 10 cm^3 of ether, the ether layer was washed with three 10 cm^3 portions of 10% HCl and then dried over Na_2SO_4 . The ether was subsequently removed in vacuo to give a green solid **13** (97%) as the product, m.p. $> 150^\circ C$. 1H NMR (C_6D_6): δ 3.65(s,3H) and 1.75(s,15H). IR (CH_2Cl_2): $\nu(CO)$ at 2075(m), 2035(s), 2015(s), 1930(w), 1875(w) and 1670(ester) cm^{-1} . Mass spectrum (FAB): m/z (%) 646 (13) $C_{21}H_{18}O_{10}MoCo_2$ (M^+); 618 (15) ($M - CO$) $^+$; 590 (100) ($M - 2CO$) $^+$; 562 (64) ($M - 3CO$) $^+$; 534 (78) ($M - 4CO$) $^+$; 506 (32) ($M - 5CO$) $^+$; 478 (57) ($M - 6CO$) $^+$; 450 (19) ($M - 7CO$) $^+$; 422 (15) ($M - 8CO$) $^+$. Analysis: Found: C, 38.98; H 2.58. $C_{21}H_{18}O_{10}MoCo_2$ calcd.: C, 39.16; H, 2.82%.

(b) *EtOH*. Using the procedure in (a), the product **16** (93%), m.p. $> 150^\circ C$ (decomp.), was obtained as a green solid. 1H NMR (C_6D_6): δ 4.25(q,2H), 1.78(s,15H) and 1.24(t,3H). IR (CH_2Cl_2): $\nu(CO)$ at 2075(m), 2040(s), 2020(s), 1925(w), 1870(w) and 1665(ester) cm^{-1} . Mass spectrum (FAB): m/z (%) 661 (7) ($M + 1$) $^+$; 660 (5) $C_{22}H_{20}O_{10}MoCo_2$ (M^+); 632 (10) ($M - CO$) $^+$; 604 (100) ($M - 2CO$) $^+$; 576 (61) ($M - 3CO$) $^+$; 548 (90) ($M - 4CO$) $^+$; 520 (37) ($M - 5CO$) $^+$; 492 (86) ($M - 6CO$) $^+$; 464 (24) ($M - 7CO$) $^+$. Analysis: Found: C, 39.92; H, 2.85. $C_{22}H_{20}O_{10}MoCo_2$ calcd.: C, 40.15; H, 3.06%.

(c) *Indole*. To a solution of **10** (0.165g, 0.217 mmol) in dry CH_2Cl_2 (10 cm^3) was added indole (0.064 g, 0.546 mmol). The mixture was allowed to stir for 4 h after which time the solvent was removed under reduced pressure and the residue chromatographed on neutral alumina. Elution with hexane/ CH_2Cl_2 , 30/70, gave the product **19** (65%) which was a dark green solid, m.p. $> 160^\circ C$ (decomp.). 1H NMR (CD_2Cl_2): δ 8.52(m,1H), 7.80(m,1H), 7.34(m,3H) and 1.86(s,15H) [24*]. IR (CH_2Cl_2): $\nu(CO)$ at 2080(m), 2040(s), 2020(s), 1995(sh), 1975(sh), 1925(w), 1870(w) and 1560(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 731 (11) $C_{28}H_{21}O_9NMoCo_2$ (M^+); 703 (23) ($M - CO$) $^+$; 675 (46) ($M - 2CO$) $^+$; 647 (43) ($M - 3CO$) $^+$; 619 (54) ($M - 4CO$) $^+$; 591 (100) ($M - 5CO$) $^+$. Analysis: Found: C, 45.88; H, 3.13; N, 1.81. $C_{28}H_{21}O_9NMoCo_2$ calcd.: C, 46.11; H, 2.90; N, 1.92%.

* This and other references marked with asterisks indicate notes occurring in the list of references.

(d) *Pyrrole*. Using the procedure in (c), with hexane/ CH_2Cl_2 , 30/70, as the eluent, **22** (69%) was obtained as a dark green solid, m.p. $> 160^\circ\text{C}$ (decomp.). ^1H NMR (CD_2Cl_2): δ 7.06(m,1H), 6.71(m,1H), 6.24(m,1H) and 1.84 (s,15H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2080(m), 2040(s), 2020(s), 1930(w), 1865(w) and 1550(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 682 (6) ($M+1$) $^+$; 681 (4) $\text{C}_{24}\text{H}_{19}\text{O}_9\text{NMoCo}_2$ (M^+); 653 (11) ($M-\text{CO}$) $^+$; 625 (67) ($M-2\text{CO}$) $^+$; 597 (65) ($M-3\text{CO}$) $^+$; 569 (82) ($M-4\text{CO}$) $^+$; 541 (100) ($M-5\text{CO}$) $^+$; 513 (46) ($M-6\text{CO}$) $^+$; 485 (11) ($M-7\text{CO}$) $^+$. Analysis: Found: C, 42.66; H, 3.01; N, 1.90. $\text{C}_{24}\text{H}_{19}\text{O}_9\text{NMoCo}_2$ calcd.: C, 42.44; H, 2.82; N, 2.06%.

Treatment of $[(\text{C}_5\text{H}_5)\text{MoCo}_2(\text{CO})_8\text{CCO}][\text{PF}_6]$ with nucleophiles

(a) *Indole*. Using the procedure previously described, with hexane/ CH_2Cl_2 , 20/80, as the eluent, **20** (54%) was obtained as a golden brown solid, m.p. $> 150^\circ\text{C}$ (decomp.). ^1H NMR (acetone- d_6): δ 8.50 (m,1H), 8.01(m,1H), 7.40(m,1H), 7.20(m,2H) and 5.60(s,5H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2085(m), 2075(m), 2030(s), 2005(m), 1995(sh), 1995(sh), 1950(w), 1895(w) and 1570(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 661 (42) $\text{C}_{23}\text{H}_{11}\text{O}_9\text{NMoCo}_2$ (M^+); 633 (33) ($M-\text{CO}$) $^+$; 605 (96) ($M-2\text{CO}$) $^+$; 577 (71) ($M-3\text{CO}$) $^+$; 549 (86) ($M-4\text{CO}$) $^+$; 521 (100) ($M-5\text{CO}$) $^+$; 493 (46) ($M-6\text{CO}$) $^+$. Analysis: Found: C, 42.08; H, 1.81; N, 2.42. $\text{C}_{23}\text{H}_{11}\text{O}_9\text{NMoCo}_2$ calcd.: C, 41.91; H, 1.68; N, 2.12%.

(b) *Pyrrole*. Using the procedure previously described, with hexane/ CH_2Cl_2 , 30/70, as the eluent, **23** (66%) was obtained as a brown solid, m.p. $127-129^\circ\text{C}$ (decomp.). ^1H NMR (acetone- d_6): δ 7.12(m,1H), 6.75(m,1H), 6.22(m,1H) and 5.64(s,5H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2080(m), 2040(s), 2020(s), 2000(m), 1950(w), 1900(w) and 1560(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 611 (38) $\text{C}_{19}\text{H}_9\text{O}_9\text{NMoCo}_2$ (M^+); 583 (43) ($M-\text{CO}$) $^+$; 555 (100) ($M-2\text{CO}$) $^+$; 527 (90) ($M-3\text{CO}$) $^+$; 499 (84) ($M-4\text{CO}$) $^+$; 471 (80) ($M-5\text{CO}$) $^+$; 443 (50) ($M-6\text{CO}$) $^+$; 415 (35) ($M-7\text{CO}$) $^+$. Analysis: Found: C, 37.65; H, 1.62; N, 2.56. $\text{C}_{19}\text{H}_9\text{O}_9\text{NMoCo}_2$ calcd.: C, 37.47; H, 1.49; N, 2.30%.

Treatment of $[(\text{C}_5\text{H}_5)\text{NiCo}_2(\text{CO})_6\text{CCO}][\text{PF}_6]$ with nucleophiles

(a) *MeOH*. To a slurry of **11** (0.074g, 0.124 mmol) in dry CH_2Cl_2 was added 1 cm^3 of methanol. The reaction mixture was stirred for 30 min, at which time the solvent was removed in vacuo and the residue chromatographed on silica gel. Elution with ether/petroleum ether, 10/90, gave the product **14** (95%) as a brown solid with m.p. $113-115^\circ\text{C}$ [25*]. ^1H NMR (CDCl_3): δ 5.33(s,5H) and 3.91(s,3H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2080(m), 2045(s), 2020(s) and 1680(ester) cm^{-1} . Mass spectrum (FAB): m/z (%) 480 (20) $\text{C}_{14}\text{H}_8\text{O}_8\text{NiCo}_2$ (M^+); 452 (36) ($M-\text{CO}$) $^+$; 424 (100) ($M-2\text{CO}$) $^+$; 396 (35) ($M-3\text{CO}$) $^+$; 368 (27) ($M-4\text{CO}$) $^+$.

(b) *EtOH*. Using the procedure described in (a), with ether/petroleum ether, 10/90, as the eluent, **17** (89%) was obtained as a brown solid, m.p. $132-133^\circ\text{C}$ (decomp.). ^1H NMR (acetone- d_6): δ 5.45(s,5H), 4.32(q,2H) and 1.37(t,3H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2080(m), 2045(s), 2020(s) and 1670(ester) cm^{-1} . Mass spectrum (FAB): m/z (%) 494 (23) $\text{C}_{15}\text{H}_{10}\text{O}_8\text{NiCo}_2$ (M^+); 466 (28) ($M-\text{CO}$) $^+$; 438 (100) ($M-2\text{CO}$) $^+$; 410 (27) ($M-3\text{CO}$) $^+$; 382 (23) ($M-4\text{CO}$) $^+$; 354 (52) ($M-5\text{CO}$) $^+$. Analysis: Found: C, 36.11; H, 1.94. $\text{C}_{15}\text{H}_{10}\text{O}_8\text{NiCo}_2$ calcd.: C, 36.41; H, 2.04%.

(c) *Indole*. Using the method previously described, with hexane/ CH_2Cl_2 , 10/90, as the eluent, **21** (57%) was obtained as a golden brown solid, m.p. $148-150^\circ\text{C}$

(decomp.). ^1H NMR (acetone- d_6): δ 8.55(m,1H), 8.40(m,1H), 7.51(m,1H), 7.27(m,2H) and 5.52(s,5H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2080(m), 2040(s), 2020(s) and 1575(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 565 (100) $\text{C}_{21}\text{H}_{11}\text{O}_7\text{NNiCo}_2$ (M^+); 537 (38) ($M - \text{CO}$) $^+$; 509 (90) ($M - 2\text{CO}$) $^+$; 481 (82) ($M - 3\text{CO}$) $^+$; 453 (74) ($M - 4\text{CO}$) $^+$; 425 (53) ($M - 5\text{CO}$) $^+$; 397 (44) ($M - 6\text{CO}$) $^+$. Analysis: Found: C, 44.61; H, 2.05; N, 2.19. $\text{C}_{21}\text{H}_{11}\text{O}_7\text{NNiCo}_2$ calcd.: C, 44.57; H, 1.96; N, 2.48%.

(d) *Pyrrole*. Using the method previously described, with hexane/ CH_2Cl_2 , 30/70, as the eluent, **24** (68%) was obtained as a golden brown solid, m.p. 136–138°C. ^1H NMR (acetone- d_6): δ 7.14(m,1H), 7.08(m,1H), 6.27(m,1H) and 5.48(s,5H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2090(m), 2045(s), 2025(s) and 1565(ketone) cm^{-1} . Mass spectrum (FAB): m/z (%) 515 (77) $\text{C}_{17}\text{H}_9\text{O}_7\text{NNiCo}_2$ (M^+); 487 (35) ($M - \text{CO}$) $^+$; 459 (100) ($M - 2\text{CO}$) $^+$; 431 (80) ($M - 3\text{CO}$) $^+$; 403 (61) ($M - 4\text{CO}$) $^+$. Analysis: Found: C, 39.73; H, 1.99; N, 2.99. $\text{C}_{17}\text{H}_9\text{O}_7\text{NNiCo}_2$ calcd.: C, 39.58; H, 1.76; N, 2.72%.

Treatment of $[(\text{C}_5\text{H}_5)_2\text{Co}_3(\text{CO})_4\text{CCO}][\text{PF}_6]$ with nucleophiles

(a) *MeOH*. To a slurry of **12** (0.028g, 0.046 mmol) in 10 cm^3 of dry CH_2Cl_2 was added 1 cm^3 of methanol. After allowing the reaction mixture to stir for 30 minutes the solvent was removed in vacuo and the residue chromatographed on silica gel. Elution with ether/petroleum ether, 15/85, yielded the product **15** (97%) which was a dark green solid [25], m.p. > 140°C (decomp). ^1H NMR (acetone- d_6): δ 4.75(s,10H) and 3.90(s,3H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2040(s), 1995(m), 1990(m), 1800(m) and 1675(ester) cm^{-1} . Analysis: Found: C, 41.32; H, 2.33. $\text{C}_{17}\text{H}_{13}\text{O}_6\text{Co}_3$ calcd.: C, 41.66; H, 2.67%.

(b) *EtOH*. Using the procedure described in (a), with ether/petroleum ether, 15/85, as the eluent, **18** (95%) was obtained as a green solid, m.p. 107–109°C. ^1H NMR (C_6D_6): δ 4.76(s,10H), 4.42(q,2H) and 1.24(t,3H). IR (CH_2Cl_2): $\nu(\text{CO})$ at 2040(s), 1995(s), 1990(m), 1795(w) and 1670(ester) cm^{-1} . Analysis: Found: C, 43.02; H, 2.81. $\text{C}_{18}\text{H}_{15}\text{O}_6\text{Co}_3$ calcd.: C, 42.89; H, 3.00%.

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