

Synthesis of mixed-metal clusters using nickel–molybdenum and nickel–tungsten complexes as cluster building blocks *

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Abstract

Pyrolysis of the heterodinuclear compounds $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ [M = Mo or W] afforded the tetranuclear clusters $\text{Ni}_2\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$ and $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$. The reactions proceed via the isolated coordinatively unsaturated intermediates $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni-W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ respectively. The clusters are believed to contain tetrahedral Ni_2M_2 cores. This contrasts with products obtained when the nickel-cyclopentadienyl species $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ [M = Mo, W] were subjected to thermolysis, affording paramagnetic clusters with Ni_3M tetrahedral metallic cores as the predominant products [M.J. Chetcuti, J.C. Huffman and S.R. McDonald, *Inorg. Chem.*, 28 (1989) 238]. Traces of the cluster $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ have also recently been characterized. The heterobimetallic compounds $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ [M = Mo, W] react with $\text{Co}_2(\text{CO})_8$ yielding a mixture whose constituents' relative proportions are quite sensitive to the reaction conditions. Isolated products include the mixed-metal clusters $\text{Co}_2\text{NiM}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$ (M = Mo, W) and $\text{CoNiW}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ as well as $\text{Co}_3\text{M}(\mu\text{-CO})_3(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $\text{Co}_2\text{W}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ and the dinuclear species $(\text{OC})_4\text{Co-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ (M = Mo, W).

Introduction

A plethora of heterometallic tetranuclear clusters have been characterized and new examples continue to be reported. Trimetallic tetrahedrane type clusters containing both a $\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ (M = Mo, W) moiety and a $\mu_3\text{-RC}$ alkylidyne group are accessible from the carbyne complexes $\text{RC}\equiv\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$, a syn-

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

thetic route of great utility pioneered by Stone and coworkers [1,2]. Nevertheless, despite the abundance of such trimetallic tetrahedral species, many mixed-metal clusters containing tetrametallic and tetrahedral cores remain unknown because of the lack of readily available syntheses. Heterometallic clusters incorporating both early and late transition metals are of interest as the combination of diverse metals in these species may impart interesting reactivity patterns to the cluster towards organic and organometallic reagents. Nickel–molybdenum and cobalt–molybdenum species are of special interest as these metal combinations are vital constituents of industrial hydrodesulfurization and hydrodeamination catalysts.

Recent research by our group has focused on the reactivity of the mixed-metal compounds $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\text{C}_5\text{H}_4\text{Me})$ [**1a**, M = Mo; **1b**, M = W] towards various organic reagents. These compounds combine with alkynes to form complexes of formula $\text{NiM}(\text{CO})_2(\mu\text{-RC}_2\text{R}')(\eta^5\text{-C}_5\text{H}_4\text{Me})(\eta^5\text{-C}_5\text{H}_5)$ [3], which have dimetallatetrahedrane cores. Crossover experiments indicate that metal–metal bond scission does take place in these reactions but is not rate determining: the alkyne effectively reacts with an intact Ni–M species [4]. *Conceptually*, one can assume that an alkyne ligates to an unsaturated Ni–M moiety such as a transiently formed $(\eta^5\text{-C}_5\text{H}_5)\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ or $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}\equiv\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Me})$ species leading to the observed products. These are similar to $\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R})$ species formed in reactions of $\text{Co}_2(\text{CO})_6$ with alkynes.

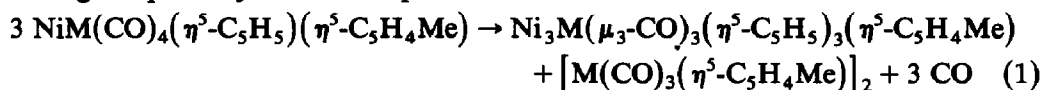
The stability of complexes such as $\text{Co}_3(\text{CO})_9(\mu_3\text{-CR})$ [5,6], $\text{M}_2(\text{CO})_4(\mu\text{-RC}_2\text{R})(\eta^5\text{-C}_5\text{H}_5)_2$ [M = Mo, W] [7,8], $\text{Ni}_2(\mu\text{-RC}_2\text{R})(\eta^5\text{-C}_5\text{H}_5)_2$ [9] and $\text{Co}_2\text{W}(\mu_3\text{-CR})(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)$ [10,11], and the isolobal analogy between RC, $\text{Co}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$ and $\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ [M = Mo, W] units imply that clusters with NiMoCo_2 or NiWCo_2 metallic cores in which $\text{Co}_2(\text{CO})_6$ units span Ni–Mo or Ni–W bonds, in a manner similar to alkyne ligands in dimetallatetrahedrane complexes, might be stable entities. Furthermore, some of these compounds may be accessible by reacting **1a** and **1b** with appropriate sources of molecules isolobal to alkyne moieties.

We recently described the utility of the mixed-metal species $(\text{OC})_4\text{Co-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ (M = Mo, W) as a reagent for synthesizing a series of tetrahedral clusters with $\text{Co}_x\text{W}_{4-x}$ ($x = 1\text{--}3$) metallic cores [12]. Here the use of Ni–Mo and Ni–W heterobimetallic complexes as building blocks in mixed-metal cluster synthesis is explored. Aspects of this work have been communicated [13].

Results and discussion

(a) Thermolysis reactions

We serendipitously discovered that thermolysis of the heterobimetallic species $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ afforded paramagnetic tetranuclear clusters [14]. The stoichiometry of these clusters was not that expected from formal loss of carbonyl ligands and dimerization of the resulting $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}\equiv\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Me})$ units. Instead the thermal decarbonylation of **1a** and **1b** resulted in formation of tetrahedral Ni_3M species $\text{Ni}_3\text{M}(\mu_3\text{-CO})_3(\eta^5\text{-C}_5\text{H}_5)_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, following the pathway shown in eq. 1.



[M = Mo, W]

Table 1

IR data for the new clusters

	Color	Nujol mull	Hexanes
2a	green	2047 (vw) 2003 (w) 1954 (s) 1907 (s) 1899 (m) 1890 (m, sh)	^a 2037 (vw) 2008 (w) 1950 (s) 1901 (s) 1846 (m)
2a*	olive green	1744 (s, br), 1706 (m)	too insoluble for reliable data
2b*	olive green	1949 (s) 1918 (w) 1896 (s) 1887 (m, br)	too insoluble for reliable data
2b'	green	1949 (s) 1921 (s) 1905 (s) 1889 (s)	too insoluble for reliable data
4a	green	2043 (s) 2004 (s) 1996 (s) 1976 (s) 1957 (s) 1942 (s) 1930 (s) 1889 (s) 1835 (s) 1794 (s)	2076 (w) 2060 (s) 2054 (s) 2036 (s) 2027 (s) 2001 (s) 1992 (w) 1982 (w) 1943 (s) 1863 (w) 1778 (w)
4b	green	2054 (s) 2024 (s) 2004 (s, sh) 1997 (s) 1936 (s) 1920 (m, sh) 1864 (s) 1854 (m, sh) 1768 (s) 1741 (s) 1729 (s)	2058 (w, sh) 2051 (m) 2036 (m) 2027 (vs) 1998 (s) 1991 (w, sh) 1981 (vw) 1944 (m) 1902 (vw) 1885 (vw) 1862 (m) 1790 (w) 1771 (s) 1744 (w)
6b	black	2005 (s) 1966 (s) 1910 (s) 1893 (s) 1844 (s) 1811 (s)	^a 2016 (s) 1956 (s) 1915 (s) 1855 (s) 1798 (s) 1787 (s)

^a CH₂Cl₂ solution.

Table 2

¹H NMR data ^a

Complex	C ₅ H ₅	C ₅ Me ₅	
2a*	4.92	2.22	
2b*	5.06	1.77	
	C ₅ H ₄ Me	C ₅ H ₅	C ₅ H ₄ Me
2a	6.00 (4 H)	5.21	2.04
2b'	4.95 (8 H)	1.86 (30 H) ^b	1.96 (6 H)
4a	5.65 (2 H), 5.59 (2 H)	4.94	2.19
4b^c	5.16 (2 H), 4.99 (2 H)	4.84	2.39
6b	5.33 ^d (4 H), 5.27 ^d (2 H), 5.21 ^d (2 H)	5.41	2.22 ^e

^a All spectra were recorded in chloroform-*d*₁; all signals are singlets except the C₅H₄Me resonances which are AA'BB' multiplets. ^b C₅Me₅ resonance. ^c ¹³C NMR spectrum: δ 220 (CO, br.) 106.7 (C1, C₅H₄Me), 9.14 (C₅H₅), 90.8 (C2 and C4, C₅H₄Me), 90.2 (C3 and C5, C₅H₄Me), 13.0 (Me). ^d ABCD type multiplets. ^e Integrates to 6 H relative to C₅H₅ signal.

Thermolysis of the pentamethylcyclopentadienyl nickel species (η^5 -C₅Me₅)(CO)-Ni-M(CO)₃(η^5 -C₅H₅) [**1a***, M = Mo; **1b***, M = W] proceeded differently. Mild thermolysis yielded the paramagnetic compounds (η^5 -C₅Me₅)Ni-M(CO)₃(η^5 -C₅H₅) [M = Mo, W]. Under more vigorous conditions, these species are decarbonylated further, yielding tetranuclear clusters Ni₂Mo₂(CO)₄(η^5 -C₅H₅)₂(η^5 -C₅Me₅)₂, **2a***, and Ni₂W₂(CO)₄(η^5 -C₅H₅)₂(η^5 -C₅Me₅)₂, **2b***, respectively [13].

IR and ¹H NMR data (Tables 1 and 2) are all consistent with these formulations. The ¹H NMR spectrum of **2a*** showed two singlets in a 1 : 3 ratio, at chemical shift ranges characteristic of cyclopentadienyl and pentamethylcyclopentadienyl protons. Solid mull IR spectra show ν (CO) stretches at 1744 and 1706 cm⁻¹—low even for triply bridging carbonyl ligands [15*]. MS and HRMS of this species exhibit parent

* Reference number with asterisk indicates a note in the list of references.

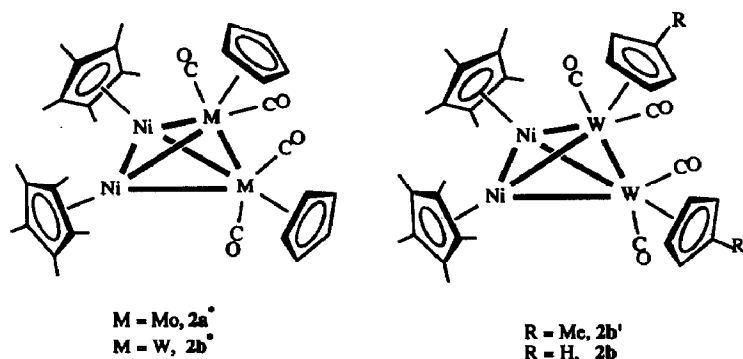


Fig. 1. Structures of the Ni_2M_2 ($M = \text{Mo}, \text{W}$) clusters $2a^*$, $2b^*$, $2b'$ and $2b$. Carbonyl ligands are depicted as terminal though this is not the case here.

ions with the expected m/e ratios of 822 amu and show the successive loss of four carbonyl ligands. Calculated Ni_2Mo_2 isotopic envelopes for a molecule of this formulation are in excellent agreement with those observed for $2a^*$. These data suggest that $2a^*$ is the tetrahedral 60-electron cluster $\text{Ni}_2\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$ (Fig. 1).

The species $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$, $2b^*$, can be similarly prepared and is believed to be a cluster with an isostructural metallic core to $2a^*$, but differing in the disposition of the carbonyl ligands. A solid mull IR spectrum showed four $\nu(\text{CO})$ bands all at terminal or weakly semi-bridging $\nu(\text{CO})$ frequencies. Both $2a^*$ and $2b^*$ are sparingly soluble in most organic solvents and move sluggishly on chromatographic columns, making their purification and the acquisition of good spectroscopic data difficult. They are fairly air-sensitive in solution and decompose slowly in the solid state, even when maintained under nitrogen at -20°C .

To improve the solubility and the quality of the spectroscopic data and to extend the generality of this thermolysis reaction, the methylcyclopentadienyl-tungsten analogue $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ni}-\text{W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $1b'$, was subjected to pyrolysis, yielding the cluster $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\eta^5\text{-C}_5\text{Me}_5)_2$, $2b'$. Spectroscopic data for this more soluble cluster paralleled those of $2b^*$. Resonances for the aromatic methylcyclopentadienyl protons appear as a (single) AA'BB' multiplet in the ^1H NMR of $2b'$, indicating that an effective mirror plane bisects these ligands on the ^1H NMR timescale. IR data for $2b'$ were very similar to those of $2b^*$.

That these two closely related clusters have different carbonyl ligand geometries is interesting. However both species are very sterically congested clusters and minor differences in size and bond strengths between molybdenum and tungsten atoms may tip the balance in favor of strong μ_3 -bridging CO interactions in $2a^*$ compared to the weaker μ_2 -bridges seen in $2b^*$. It is generally recognised that bridging carbonyl ligands are more prevalent among second row metals than in third-row metal complexes.

After complexes $2a^*$, $2b^*$ and $2b'$ were synthesized, we realized that traces of the complex $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$, $2b$, had occasionally been produced during syntheses of $1b$ [16*]. Spectroscopic data for $2b$ indicate that it is isostructural with $2b'$ (Fig. 1) but η^5 -pentamethylcyclopentadienyl groups in $2b'$

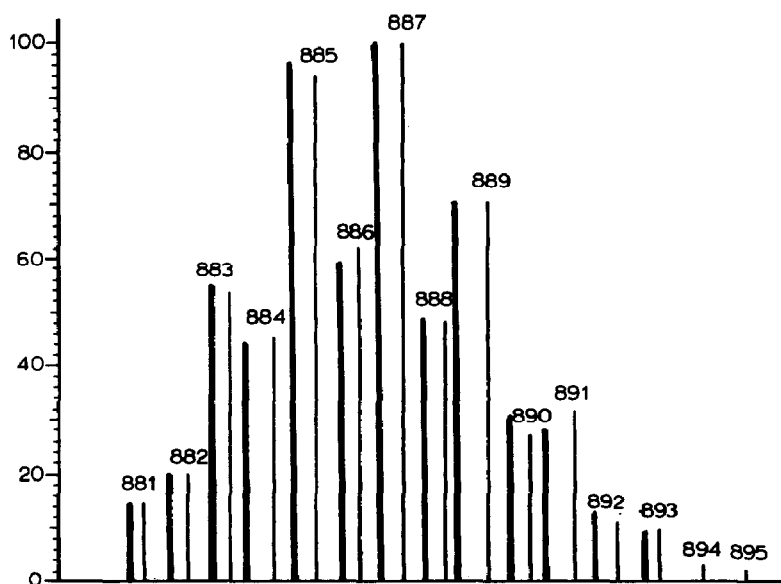


Fig. 2. Theoretical and experimental (bold lines) parent ion isotopomer pattern seen in the mass spectrum of $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$, **2b**.

replace η^5 -cyclopentadienyl ligands in **2b**. Calculated and experimental isotopomer patterns for the MS of the parent ion of **2b** are shown (Fig. 2).

(b) Reactions of **1a** and **1b** with dicobalt octacarbonyl

(i) *Comments.* Dicobalt octacarbonyl is a reactive species that decarbonylates under mild conditions to form $\text{Co}_4(\text{CO})_{12}$ (a fully metallated tetrahedrane). This reaction is formally equivalent to the dimerization of two $(\text{OC})_3\text{Co}\equiv\text{Co}(\text{CO})_3$ units. As $\text{Co}(\text{CO})_3$ groups are isolobal to RC moieties, and $\text{Co}_2(\text{CO})_8$ is known to act as a source of $\text{Co}_2(\text{CO})_6$ in other reactions [10], we surmised that species containing NiMoCo_2 tetrahedral metallic cores might be accessible by reacting $\text{Co}_2(\text{CO})_8$ with **1a** and **1b**.

Dicobalt octacarbonyl reacts with **1a** and **1b** affording various products. In some cases, especially in reactions involving **1b**, the products formed are quite sensitive to the experimental conditions. In addition to the "expected" clusters, other dinuclear species together with new clusters were isolated. Reactions of **1a** with dicobalt octacarbonyl are discussed first.

(ii) *Reaction of $\text{Co}_2(\text{CO})_8$ with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, **1a**.* When solutions of **1a** were added slowly to equimolar solutions of $\text{Co}_2(\text{CO})_8$, the mixture darkened. Chromatography on silica gel afforded four new products in addition to $\text{Co}_2(\text{CO})_8$, the first band eluted off the column. Spectroscopic data indicated that the second band contained two species, that were separated by careful chromatography using pure hexanes as the eluant. These were subsequently characterized spectroscopically as the dimolybdenum species $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2$ and the heterodinuclear complex $(\text{OC})_4\text{Co-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, **3a** [12].

The green cluster $\text{NiMoCo}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$, **4a**, was the third product recovered and was characterized by ^1H NMR and IR spectroscopy and

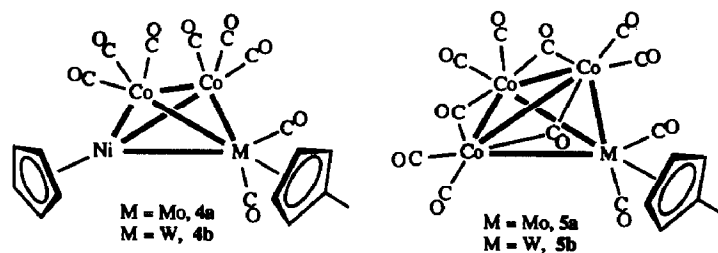


Fig. 3. Structures of clusters 4a, 4b, 5a and 5b. All carbonyl ligands are shown as terminal in 4a and 4b, though IR spectra of these clusters indicate that bridging CO interactions are present.

elemental analysis. The cluster is unstable in solution and decomposes slowly, even in the solid state, affording intractable products and the dimolybdenum species $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2$. No MS data could be obtained, but ^1H NMR data show signals arising from η^5 -cyclopentadienyl and -methylcyclopentadienyl groups. Signal integration indicates that the two groups are in a 1:1 ratio to each other. Aromatic methylcyclopentadienyl ligand resonances appear as an AA'BB' multiplet, indicating an effective mirror plane bisecting this ligand exists on the ^1H NMR time scale.

A low frequency $\nu(\text{CO})$ stretch is observed, in both the solid state and the solution IR spectrum of 4a, that lies in the bridging carbonyl region of the IR spectrum. It appears that at least one carbonyl ligand is bridging. The greater tendency of first row transition metals to support bridging carbonyl groups, coupled with the high electron density on the nickel atom, makes it likely that a CoNi edge is bridged by a carbonyl ligand. The presumed structure of 4a is shown in Fig. 3.

The final band was purple and deposited purple-black crystals of 5a upon workup. The chromatographic mobility, color and solubility of this species were all consistent with 5a being a cluster. ^1H NMR and MS data characterized 5a as $\text{Co}_3\text{Mo}(\mu_2\text{-CO})_3(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})$ (Fig. 3). We reported the synthesis of this compound (and its tungsten analogue) as the major product when the mixed-metal complexes $(\text{OC})_4\text{Co-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$ are treated with $\text{Co}_2(\text{CO})_8$ [12]. The related cyclopentadienyl analogue is known [17] and its structure has been determined [18].

When the order of addition was reversed and a solution of $\text{Co}_2(\text{CO})_8$ was added slowly to 1a, all species reported in the previous section except the dimolybdenum species $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2$ were obtained, albeit in slightly different relative ratios.

(iii) *Reaction of $\text{Co}_2(\text{CO})_8$ with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, 1b.* When $\text{Co}_2(\text{CO})_8$ was added over a two hour period to an equimolar solution of 1b, and the mixture stirred for four hours, three products were isolated. One proved to be the heterodinuclear complex $(\text{OC})_4\text{Co-W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, 3b [12], while the other two complexes were tetranuclear clusters.

The data indicated that one of these species was the mixed-metal cluster $\text{NiWCo}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$, 4b, the tungsten analogue of 4a. Spectroscopic data of this green species mirror those of 4a and are fully in accord with this formulation. However, the lowest energy IR $\nu(\text{CO})$ stretch for 4b (Fig. 4) absorbs at significantly lower energy than the corresponding value for 4a, and in 4b a $\mu_3\text{-CO}$ ligand is suggested, possibly bridging a Co_2Ni face. Other bridging or semi-bridging carbonyl ligands are likely. The MS of 4b shows a parent ion with m/e of 728 and

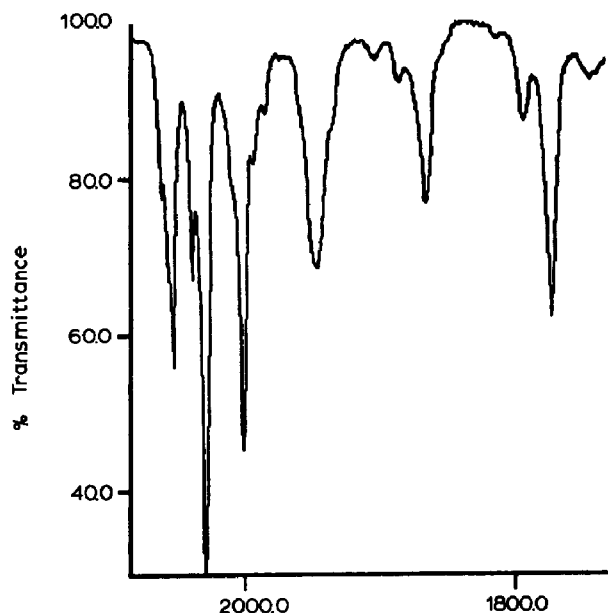


Fig. 4. The IR $\nu(\text{CO})$ spectrum of $\text{Co}_2\text{NiW}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$, **4b**, recorded in hexanes solution. Absorptions are in cm^{-1} .

the successive loss of 8 carbonyl ligands is observed. This cluster is appreciably more stable than its NiMoCo_2 analogue and is formed in higher yield. The $\mu_3\text{-CO}$ ligand in **4b** together with the presence of the tungsten may enhance the thermal and thermodynamic stability of this cluster.

The third product isolated (**6b**) was grey and appeared to contain both nickel and tungsten as its ^1H NMR spectrum contained signals assignable to both η^5 -methylcyclopentadienyl and -cyclopentadienyl groups. Signal integration of these resonances showed that these groups were in a 2:1 ratio respectively. As the aromatic protons of the η^5 -methylcyclopentadienyl group exhibited a (single) ABCD type pattern, a mirror plane bisects the molecule but does not bisect these ligands. The 60 cluster-valence electron count implies a tetrahedral geometry for this species. The large number of $\nu(\text{CO})$ absorptions in the IR spectrum also suggest that cobalt is present and indicated that one or more bridging (or semi-bridging) carbonyl ligands are present in **6b**. A MS could not be obtained for **6b** but elemental analysis is in accord with its formulation as the mixed-metal cluster $\text{CoNiW}_2(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$. Figure 5 shows the presumed structure of **6b**.

Addition of $\text{Co}_2(\text{CO})_8$ to **1b** over a three hour period and stirring of the solution for about thirty 30 minutes led to the formation of **3b**, **4b** and **6b**. The ditungsten species $[\text{W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2$ and $\text{Co}_2(\text{CO})_8$ were also recovered.

Finally, slow addition of $\text{Co}_2(\text{CO})_8$ to **1b** over five hours afforded no homodinuclear products. **6b** was not obtained under these conditions either, but **3b** and **4b** were isolated along with two other clusters. These were characterized as $\text{Co}_3\text{W}(\mu\text{-CO})_3(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})$, **5b**, and $\text{Co}_2\text{W}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$, **7b**, by comparing their IR and ^1H NMR data with those of authentic samples [12]. Their structures are shown in Figs. 3 and 5, respectively. Related Ir_3W [19,20] and Ir_2W_2 [19,21] species are known.

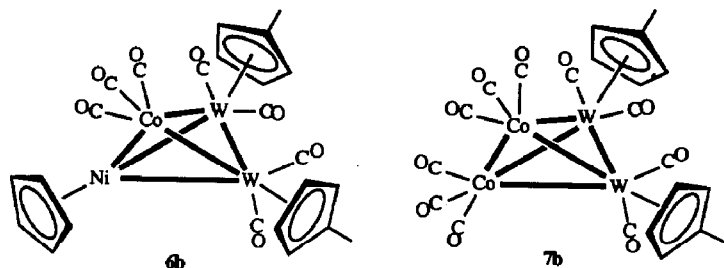


Fig. 5. Structures of clusters **6b** and **7b**. All carbonyl ligands are shown as terminal though IR spectra of these clusters indicate that bridging CO interactions are present.

(c) General comments

The reactions described do give the products expected but their yields (while not optimized) are not high. For the reactions involving $\text{Co}_2(\text{CO})_8$ in particular, other clusters and dinuclear species are frequently observed. Nevertheless, some hitherto inaccessible mixed-metal clusters with tetrahedral metallic cores are now available.

We lack mechanistic data on these reactions. However the product distribution observed and its sensitivity to the reaction conditions makes 17-electron metal carbonyl radical intermediates likely, especially for the complexes that contain η^5 -cyclopentadienyl-nickel groups. Previous work by our group [4] has shown that heteronuclear crossover takes place when solutions of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-W}(\text{CO})_3$ - $(\eta^5\text{-C}_5\text{H}_4\text{Me})$ and $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})\text{Ni-W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ are mixed; we interpreted this crossover leading to the preferential formation of mixed-metal species as indicative of heteronuclear metal-metal bond cleavage. The radical species $\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Mo}, \text{W}$) are also implicated in the thermolysis of **1a** and **1b** to form clusters with Ni_3M cores [14].

A radical pathway is less likely for the η^5 -pentamethylcyclopentadienyl-nickel complexes **2a***, **2b*** and **2b'**. Pyrolyses of these complexes proceed via the isolated intermediate unsaturated species $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni-W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R})$ [$\text{R} = \text{H}, \text{Me}$] respectively [13], which can be considered to have formal $\text{Ni}=\text{M}$ double bonds. Metal-metal bond rupture is less probable here and an associative pathway is indicated for these species.

Conclusions

A series of new mixed-metal clusters with tetrametallic cores are accessible from the heterodinuclear complexes $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R}')$ [$\text{M} = \text{Mo}$ or W ; $\text{R} = \text{H}, \text{R}' = \text{Me}$; $\text{R} = \text{Me}, \text{R}' = \text{H}$]. Thermolysis leads to clusters with tetrahedral Ni_2M_2 cores when $\text{R} = \text{Me}, \text{R}' = \text{H}$. Reaction of the complexes **1a** or **1b** ($\text{R} = \text{H}$; $\text{R}' = \text{Me}$) with $\text{Co}_2(\text{CO})_8$ affords the "expected" clusters $\text{Co}_2\text{NiM}(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$ ($\text{M} = \text{Mo}, \text{W}$) respectively. Other dinuclear and tetranuclear mixed-metal compounds are formed concurrently.

Experimental

(a) General remarks

All manipulations were carried out under a nitrogen atmosphere using Schlenk or vacuum line techniques. Solvents were pre-dried over 4Å molecular sieves. Diethyl

ether, toluene and hexanes were distilled from sodium or sodium benzophenone ketyl. Dichloromethane was distilled over CaH_2 . NMR spectra were recorded on General Electric NT- or GN-300 spectrometers at 20°C . Chloroform- d_1 was the solvent unless stated. IR spectra were recorded on an IBM IR-32 FT spectrometer. MS were obtained on a Finnegan-Matt instrument. All parent ions show the appropriate isotopomer pattern. Elemental analyses were performed by M-H-W Labs, Phoenix, AZ.

(b) *Thermolysis of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($R = \text{H}$, $M = \text{Mo}$; $R = \text{H}$, $M = \text{W}$) affording $2a^*$, $2b^*$ and $2b'$, respectively*

$1a^*$, $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ (439 mg, 1.00 mmol) was refluxed in toluene for 2 d. The solution was concentrated; chromatography on silica gel, using dichloromethane as the eluting solvent, afforded an olive-green band that was pumped to dryness in vacuo. Recrystallization from toluene afforded $\text{Ni}_2\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$, $2a^*$ (145 mg, 35%). MS (m/e , amu) 822 (M^+), 766 ($M - 2 \text{ CO}$) $^+$, 738 ($M - 3 \text{ CO}$) $^+$, 710 ($M - 4 \text{ CO}$) $^+$; HRMS calcd. for $\text{Ni}_2\text{Mo}_2\text{C}_{34}\text{H}_{40}\text{O}_4$: 821.9726. Found: 821.9736. Anal. Found: C, 61.99; H, 5.85. $\text{C}_{34}\text{H}_{40}\text{O}_4\text{Ni}_2\text{Mo}_2$ calcd.: C, 61.68; H, 6.09%.

$\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$ was prepared similarly from $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ni-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$, $1b^*$ (200 mg, 0.36 mmol). The low solubility and sluggish mobility of $2b^*$ on silica gel makes chromatography impractical and this is best omitted. The cluster is most easily obtained by pumping off the toluene and dissolving the residue in dichloromethane. The solution was then placed on a short alumina pad which was rinsed with dichloromethane. After washing away traces of $[\text{Ni}(\mu\text{-CO})(\eta^5\text{-C}_5\text{Me}_5)]_2$ and $[\text{W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]_2$, $2b^*$ was recovered from the alumina pad using methanol. Recrystallization from toluene afforded $2b^*$ (84 mg, 47%). MS (m/e , amu) 998 (M^+). The synthesis of $2b'$ paralleled that of $2b^*$.

(c) *Recovery of $\text{Ni}_2\text{W}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{Me}_5)_2$, $2b$*

Traces of $2b$ are occasionally recovered as a minor side-product during the synthesis of the heterobimetallic species $1b$ [3]. $2b$ is obtained during chromatography of impure $1b$ as a slow moving yellow-green band that elutes with dichloromethane. Yields are very low (< 0.5%). MS (m/e , amu) 886 (M^+).

(d) *Reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $1a$, with $\text{Co}_2(\text{CO})_8$*

(i) *Addition of $1a$ to $\text{Co}_2(\text{CO})_8$.* $1a$ (810 mg, 1.97 mmol) in toluene (20 mL) was added over a ≈ 2 h period, via a pressure equalized dropping funnel, to a solution of $\text{Co}_2(\text{CO})_8$ in toluene (6.2 mL of a 0.32 M solution, 1.98 mmol). The reaction mixture was stirred for a further 2 h, and then pumped dry in vacuum. The solid was dissolved in a hexanes: ether mixture (2:1, 8 mL) and subjected to chromatography on silica gel. Elution with a 2:1 hexanes: ether mixture afforded a dark brown band, later characterized as containing $\text{Co}_2(\text{CO})_8$, and a red band consisting of a mixture of $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]_2$ and $(\text{OC})_4\text{Co-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $3a$. [This mixture was subsequently separated by chromatography, using pure hexanes as the eluting solvent. Multiple hexanes crystallizations yielded pure $3a$ (350 mg, 41% net yield).] A green band containing $\text{NiMoCo}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $4a$, and a purple band containing $\text{Co}_3\text{Mo}(\mu\text{-CO})_3(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})$, $5a$, were eluted with ether. Concentration and crystallizations at -20°C afforded $4a$ (100

mg, 8% net yield) and **5a** (30 mg, 2%) respectively. **4a**. Anal. Found: C, 35.47; H, 2.03. $C_{19}H_{12}O_8Co_2MoNi$ calcd.: C, 35.61; H, 1.89%. No MS of **4a** could be obtained.

(ii) *Addition of $Co_2(CO)_8$ to 1a.* **1a** (370 mg, 0.90 mmol) was placed in a Schlenk tube equipped with a stirrer bar and dissolved in toluene (20 mL). A solution of $Co_2(CO)_8$ in toluene (14.1 mL of a 0.064 M solution; 0.90 mmol) was added dropwise over a 2 h period. The brown solution was stirred for a further 5 h and was then pumped down to dryness. Chromatography under the conditions outlined above afforded $Co_2(CO)_8$, **3a** (135 mg, 35%), **4a** (20 mg, 5%), and **5a** (15 mg, 2%). The complex $[Mo(CO)_3(\eta^5-C_5H_4Me)]_2$ was not recovered.

(e) *Reaction of $(\eta^5-C_5H_5)(CO)Ni-W(CO)_3(\eta^5-C_5H_4Me)$, **1b**, with $Co_2(CO)_8$*

(i) **1b** (525 mg, 1.05 mmol) was dissolved in toluene (20 mL). A solution of $Co_2(CO)_8$ (24.8 mL of a 0.0426 M solution; 1.06 mmol) was added via a pressure equalized dropping funnel over 2 h and the solution stirred for a further 4 h. The solution was then pumped to dryness, was dissolved in a dichloromethane/ether/hexanes mixture (1:1:1) and subjected to chromatography on silica gel. Two distinct bands were collected using hexanes as the eluent: a red solution containing the mixed-metal species $(OC)_4Co-W(CO)_3(\eta^5-C_5H_4Me)$, **3b**, and a green band incorporating the cluster $Co_2NiW(CO)_8(\eta^5-C_5H_5)(\eta^5-C_5H_4Me)$, **4b**. Crystals of **3b** (155 mg, 29%) and **4b** (80 mg, 11%) deposited when the respective solutions were concentrated and placed in a freezer at $-20^\circ C$. A grey band was recovered when ether was used to elute the remaining material. Crystallization of this solution yielded $CoNiW_2(CO)_7(\eta^5-C_5H_5)(\eta^5-C_5H_4Me)_2$, **6b** (10 mg, 1%). **4b**. MS (m/e , amu) 728 (M^+). Successive loss of 1–8 CO ligands was observed. Anal. Found: C, 31.12; H, 1.68. $C_{19}H_{12}O_8Co_2NiW$ calcd.: C, 31.32; H, 1.66%. **6b**. Anal. Found: C, 31.80; H, 1.97. $C_{24}H_{19}O_7CoNiW_2$ calcd.: C, 31.86; H, 2.12%.

(ii) $Co_2(CO)_8$ (7 mL of a 0.132 M toluene solution; 0.924 mmol) was added over a 3 h period to a solution of **1b** (460 mg, 0.922 mmol) in toluene (20 mL). The solution was stirred for 30 min, pumped to dryness, and subjected to chromatography as described above using hexanes as the initial eluting solvent. Bands containing $[W(CO)_3(\eta^5-C_5H_4Me)]_2$, $Co_2(CO)_8$, and **3b** were collected (170 mg, 36% on subsequent crystallization of the hexanes solution). Greyish-green and green bands eluted with ether; crystallization of the green band afforded **4b** (72 mg, 11%). The greyish-green band was separated into an unidentified green and a grey component (**6b**) by a subsequent chromatographic separation, using a hexanes/ether mixture as the eluting solvent. **6b** and the green species were each recovered in ≈ 10 mg quantities ($\approx 1\%$ for **6b**).

(iii) In a third variation, $Co_2(CO)_8$ [18.4 mL of a 0.059 M solution; 1.09 mmol] was added to a stirred solution of **1b** (550 mg, 1.10 mmol) in toluene (15 mL) over 5.5 h. The solution was pumped to dryness, dissolved in a dichloromethane/ether/hexanes mixture (1:1:1) and subjected to silica gel chromatography. Elution with a hexanes rich ether/hexanes solution afforded two bands; subsequent recrystallizations afforded **3b** (200 mg, 35%) and **4b** (120 mg, 15%), respectively. Two other species eluted with a 1:1 hexanes/ether mixture. Crystallization at $-20^\circ C$ eventually yielded $Co_3W(\mu-CO)_3(CO)_8(\eta^5-C_5H_4Me)$, **5b** (10 mg, 0.6%), and $Co_2W_2(CO)_{10}(\eta^5-C_5H_4Me)_2$, **7b** (5 mg, 0.5%), respectively.

Acknowledgments

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