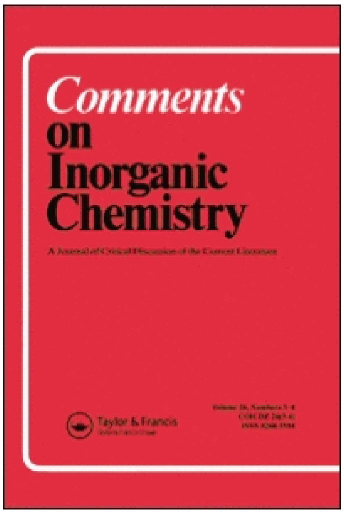

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LIGAND REACTIONS WITH UNSATURATED NICKEL – GROUP 6 COMPLEXES

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The complexes $[(\eta^5-C_5Me_5)Ni-M(CO)_3(\eta^5-C_5H_5)]$ (Ni–M, M=Mo, W) can be considered to contain Ni=Mo or Ni=W double bonds and may be represented as $[(\eta^5-C_5Me_5)Ni{=}M(\mu-CO)(CO)_2(\eta^5-C_5H_5)]$ (Ni=M, M=Mo, W). These species, and their closely related group 6 methylcyclopentadienyl congeners $[(\eta^5-C_5Me_5)Ni{=}M(\mu-CO)(CO)_2(\eta^5-C_5H_4Me]$ (Ni=M, M=Mo, W), have a rich chemistry that stems from their unsaturation. This review relates their discovery, and summarizes the chemistry of these complexes with simple two-electron donor ligands, with alkynes, and with alkenes.

1. INTRODUCTION

Since the early 1990s a central theme of our research in heterobimetallic chemistry has been the study of the unsaturated complexes **1** $[Cp^*Ni-M(CO)_3Cp^{\dagger}]^*$ (M=Mo, W). These complexes have a rich chemistry: they are polar, electronically unsaturated, and are highly reactive. This article summarizes our published work in this area and indicates the direction of future research thrusts in this field. The subject is treated more or less in chronological order, with an account of how the accidental discovery

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Throughout this manuscript, $Cp{=}\eta^5\text{-}C_5H_5$, $Cp'{=}\eta^5\text{-}C_5H_4Me$, $Cp^*{=}\eta^5\text{-}C_5Me_5$, $Cp^{\dagger}$=Cp or Cp′. Cp′ complexes have the same number as corresponding Cp species, but with a prime (′): for example **2a** = $[CpNi(CO)-Mo(CO)_3Cp]$; **2a′** = $[CpNi(CO)-Mo(CO)_3Cp']$.

of paramagnetic tetranuclear clusters, which exhibit temperature dependent spin equilibria, led to the synthesis of the unsaturated complexes **1**. This is followed by a description of their reactions with selected two electron donor ligands, with alkynes, and finally, with alkenes.

2. DISCOVERY, SYNTHESES OF THE COMPLEXES [Cp*Ni–M(CO)$_3$Cp] (1a, M=Mo; 1b, M=W)

2.1. Reactions of the Complexes [CpNi(CO)–M(CO)$_3$Cp′] (Ni–M, M=Mo, W) with 1,5-Cyclooctadiene

Our initial research into heterobimetallic complex chemistry focused on compounds that contained Ni–M (M=Cr, Mo or W) and, to a lesser extent, Co–M (M=Mo, W) bonds. The reported structure of the nickel-chromium complex [CpNi(CO)–Cr(CO)$_3$Cp] (Ni–Cr) indicated the presence of a single metal-metal bond between the two metals.[1] The chemistry of the Ni–Mo and Ni–W complexes [CpNi(CO)–M(CO)$_3$Cp′] (Ni–M, M=Mo, W) with alkynes and with allenes was under investigation at the time, but alkenes had not yet been targeted.[2–5] It was decided to look into the reactions of these species with an alkene.

2.2. "Reactions" of Complexes 1 (Ni–M, M=Mo, W) with 1,5-Cyclooctadiene

Generally, alkene-for-carbonyl substitution reactions are not successful. Alkenes are larger, are weaker σ-donors and π-acceptors than carbonyl ligands, and thus bind less tightly to metal centers for both steric and electronic reasons. However, we thought we had a chance of carrying out such a reaction by using a 1,5-cyclooctadiene (1,5-cod) as the reactant olefin. We believed that the relatively high boiling point of this molecule (bp. 151°C), the potential chelate effect of two olefin moieties, and the use of this diolefin as a solvent would all help promote the entropically favored irreversible CO loss, and might help stack the odds in favor of a reaction. The Ni–Mo complex [CpNi(CO)–Mo(CO)$_3$Cp′] **2a′** was heated in neat 1,5-cod. We envisaged that a possible chemical transformation could be as shown in equation **1**.

$$\begin{aligned}&[\mathrm{CpNi(CO)}\text{–}\mathrm{Mo(CO)_3Cp'}],\ \mathbf{2a'} + 1,5\text{–cod}\\&\quad\longrightarrow[\mathrm{NiMo(CO)_2}(1,5\text{–cod})\mathrm{CpCp'}] + 2\mathrm{CO(g)}\end{aligned}\qquad(1)$$

When **2a′** was dissolved in cod at room temperature and heated, CO loss did indeed ensue, and the initially green reaction mixture gave way to a dark red-brown solution. Two products were separated when the mixture was subjected to chromatography. One of these was the well-known complex $[Mo_2(CO)_6Cp'_2]$ (Mo–Mo), while the other was a dark olive green product, which could be crystallized from a toluene/hexane solvent mixture. This species exhibited an unusual ^1H NMR spectrum, with a strong singlet at $\partial = -4.6$ ppm, in addition to aromatic and aliphatic resonances that could be assigned to a η-C_5H_4Me group.

2.3. The Structure of Complexes 3

The nature of 3 remained enigmatic. By chance, Professor Larry Dahl happened to be an invited lecturer at the University of Notre Dame during the period that we carried out these experiments. He gave a series of talks on paramagnetic triangular clusters of cobalt and nickel with cyclopentadienyl ligands.[6,7] The ^1H chemical shift of the Cp ligands in some of these clusters that exhibited spin-equilibria were observed at negative chemical shifts with respect to TMS. We immediately realized that the signal we had observed at negative chemical shifts could be attributed to Cp ligands attached to a paramagnetic center. A comparison of the integrated intensity of this signal with that of the CH_3 group of the Cp′ ligand (observed at a normal chemical shift for a η^5-Cp′ ligand) revealed a Cp:Cp′ ratio of 3:1.

The chemical shift of this unusual Cp signal was temperature dependent and shifted to larger negative values as the temperature of the sample was raised. In contrast, as the temperature was reduced, this signal moved downfield approaching more "normal" chemical shift values for an η^5-Cp ligand.

A mass spectrum for complex 3 gave a parent peak with an isotopic envelope that was in agreement with the formulation $[Ni_3MoCp_3Cp'(CO)_3]$. A single crystal X-ray structural determination established that 3 is indeed a heterometallic cluster with three triply bridging carbonyl ligands. Two ORTEP diagram views of the structure are shown in Figure 1.[8]

Cluster 3 contains 62 electrons, two more than the 60 expected from applying Wade's rules to a tetrahedral tetrametallic cluster. The two extra electrons are believed to be in an antibonding orbital in the ground state, and this accounts for the asymmetric and very long Ni–Ni distances (2.489, 2.510 and 2.627 Å, respectively) in this cluster. The

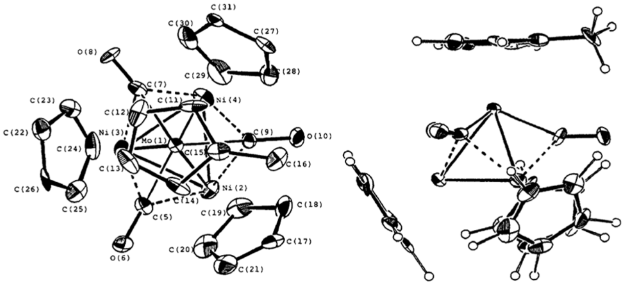


Figure 1. ORTEP diagrams of the cluster $[Ni_3Mo(\mu_3\text{-}CO)_3Cp_3Cp']$, 3. Reprinted with permission from *Inorg. Chem.*, **1989**, *28*, 239 and 240. Copyright **1989**, American Chemical Society.

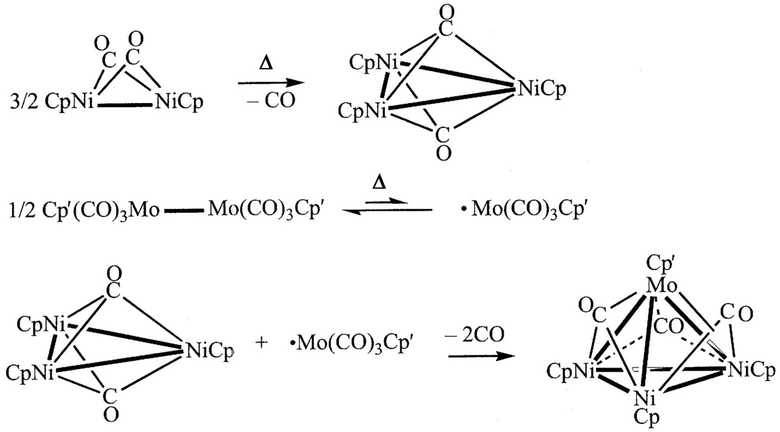
longest Ni–Ni distance is indeed longer than the three Ni–Mo distances, which average 2.594 ± 0.004 Å. The paramagnetic nature of these clusters in solution was demonstrated by variable temperature magnetic measurements using Evan's method.[9,10] The chemical transformations taking place in this reaction are as shown in equation 2.

$$3[CpNi(CO){-}Mo(CO)_3Cp'],\ \mathbf{2a'} \xrightarrow[-3\,CO]{\Delta} [Ni_3Mo(\mu_3{-}CO)_3Cp_3Cp', \mathbf{3} \\ + [Mo_2(CO)_6Cp'_2](Mo{-}Mo) \quad (2)$$

No 1,5-cod containing product is required in this reaction and this di-olefin simply serves as a high boiling solvent. Cluster 3 may also be obtained in another high boiling solvent such as toluene, in the absence of 1,5-cod. Other analogs of 3 with Ni_3W cores, with Cp ligands (and no Cp′) ligands on both metals, or with Cp′ ligands on the nickel atoms and a Cp ligand on the molybdenum have been prepared. Cluster 3 may also be prepared by the thermolysis of the two homometallic dimers, in an entropically driven reaction, as outlined in equation 3.[8]

$$3/2[Ni_2(\mu - CO)_2Cp_2](Ni - Ni) \ + \ 1/2\,[Mo_2(CO)_6Cp'_2](Mo - Mo) \\ \xrightarrow{\Delta} 3 \ + \ 3\,CO \quad (3)$$

We subsequently showed that this reaction proceeds via initial formation of the cluster $[Ni_3(\mu_3{-}CO)_2Cp_3]$,[11,12] by thermolysis of the complex $[Ni_2(\mu{-}CO)_2Cp_2]$ (Ni–Ni). This triangular paramagnetic cluster is attacked by $[Mo(CO)_3Cp']$ radicals that are formed by the slow (reversible) Mo–Mo bond scission in the di-molybdenum complex



Scheme 1. Mechanistic steps leading to the formation of 3.

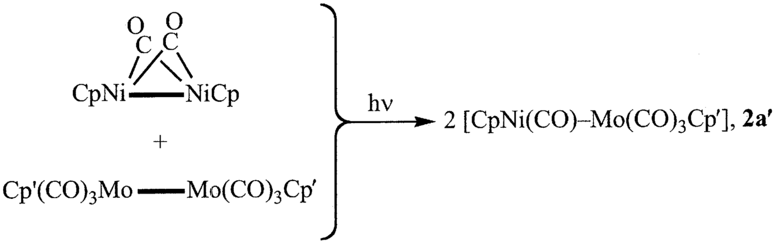
[$Mo_2(CO)_6Cp'2$] (Mo–Mo). The sequence of equations is shown in Scheme 1.

Once the nature of 3 was established, the question of whether a similar cluster with Cp* ligands on the nickel atoms arose. The steric demands of the Cp* ligand made it unlikely that cluster analogs of 3 with Cp* ligands would be produced. The Ni–Ni bonds in the triangular cluster [$Ni_3(\mu{-}CO)_2Cp^*{}_3$] are very long with a mean value of 2.530(3) Å[13] as compared to the 2.389(2) Å found in the analogous Cp cluster [$Ni_3(\mu{-}CO)_2Cp_3$].[12] This reflects the substantial strain present in the Cp* molecule that results from Cp*–Cp* steric interactions. We considered that the capping of this trinickel cluster with a MoCp unit was unlikely. We synthesized the mixed metal complex [Cp*Ni(CO)–$Mo(CO)_3Cp$] to determine what complex would be obtained when this heterobimetallic complex was heated.

3. SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES Cp*Ni–$M(CO)_3Cp$ (1a, M=Mo; 1b, M=W)

3.1. Synthesis of Complexes 1

The complexes of type 2 [$Cp^\dagger Ni(CO){-}M(CO)_3Cp^\dagger$] (M=Cr, Mo, W; $Cp^\dagger$=Cp or Cp′) are readily made by a metal-metal metathesis reaction of the group 6 dimers with the nickel dimer; this reaction is promoted by photolysis in sunlight (Scheme 2).[14]



Scheme 2. Synthesis of the complex [CpNi(CO)–Mo(CO)$_3$Cp′] (2a′).

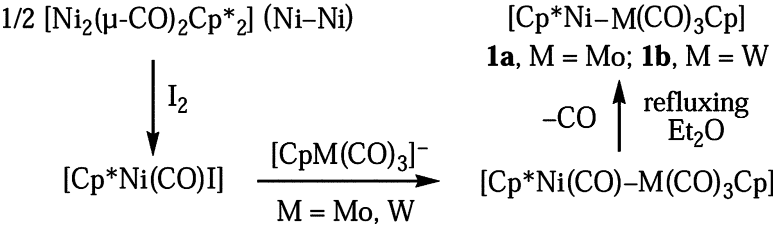
However, this method does not yield the nickel Cp* complexes [Cp*Ni(CO)–M(CO)$_3$Cp] (M=Mo, W). We developed another synthesis of this complex that is outlined below (Scheme 3).[15]

The complex [Cp*Ni(CO)–Mo(CO)$_3$Cp] is dark green. However, when heated gently in refluxing ether or pentane, a deep turquoise color appears that contains complex **1a**. Droplets of this turquoise solution, splashed higher up on the walls of the Schlenk tube, turned green again as the heating was continued, suggesting that the formation of **1a** via mild thermolysis and CO loss from [Cp*Ni(CO)–Mo(CO)$_3$Cp] might be reversible, as shown in equation 4.[15]

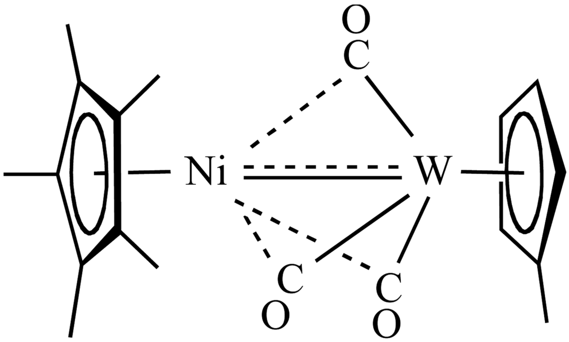
$$\underset{\text{M=Mo, W}}{[\text{Cp}^*\text{Ni(CO)–M(CO)}_3\text{Cp}]} \underset{\text{cool}}{\overset{2}{\rightleftharpoons}} \underset{\textbf{1a}\text{,M=Mo; }\textbf{1b}\text{, M=W}}{[\text{Cp}^*\text{Ni–M(CO)}_3\text{Cp}]} \tag{4}$$

3.2. Structures of Complexes 1 and a More Recent Synthesis

Complex **1a**, and its similarly prepared nickel-tungsten analog **1b**, are paramagnetic in solution, but were fully characterized by elemental analysis and by high resolution mass spectrometry. The structure of **1b′**, the tungsten-methylcyclopentadienyl analog of **1b**, was established by a single



Scheme 3. Synthesis of complexes **1**.



1b′

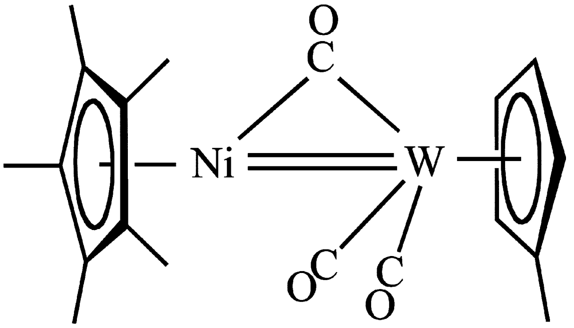
Figure 2. Structure of [Cp*Ni–W(CO)$_3$Cp′], **1b′**.

crystal X-ray diffraction study.[15] This product may be formulated as [Cp*Ni–W(CO)$_3$Cp′]. The geometry of this molecule is shown in Figure 2.

There are two noteworthy points about this structure. Firstly, the complex exhibits startlingly short Ni–W distances of 2.475(2) and 2.457(2) Å for the two independent molecules in the unit cell. These distances are much shorter than the typical values of 2.60–2.75 Å seen in most Ni–W single bonds, and indicate that multiple bond character is present in these metal-metal bonds.

The second significant point concerns the Ni···C_{CO} distances. These are too long to be compatible with μ-CO ligands. The structure of the molecule is distorted with one Ni–C_{CO} distance (per independent molecule) significantly shorter than the other two. [For the two independent molecules in the unit cell, the short Ni···C_{CO} distances are 2.10(1) and 2.13(1) for molecules A and B. The longer Ni···C_{CO} distances in the two independent molecules are 2.36(1); 2.40(2), 2.41(2) and 2.33(2) Å].

In view of these structural observations, the molecule is best represented as shown in Figure 2. However, a limiting form of the structure of complexes **1** that is easier to rationalize and is in accord with the chemistry of these molecules is shown in Figure 3. We will use this limiting representation of molecules **1** in the rest of the discussion of their chemistry. Complexes **1** are extremely air-sensitive and can be pyrophoric in the solid-state. This is in accord with the formally low oxidation state of +1 of the metals in these complexes and their unsaturation.



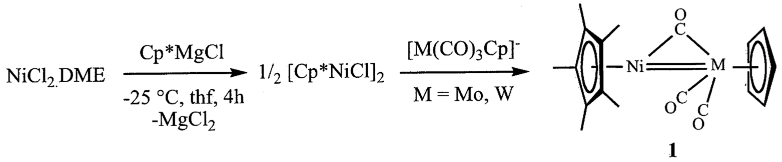
1b′

Figure 3. Double bond representation of the structure of **1b**′.

In view of the proposed multiple bond character of complexes **1**, it was deemed useful to attempt to obtain a high resolution X-ray diffraction study of the Ni–Cr analog, the complex [Cp*Ni–Cr(-–Cr(CO)$_3$Cp], with the goal of studying the electron density in the metal–metal bond. The requirement of an absorption correction, with its inherent errors, for second and third row transition metals ruled out an accurate electron density X-ray study with the nickel–molybdenum or –tungsten complexes.

The synthesis of the nickel-chromium analog to complexes **1** proved to be quite difficult. In contrast to its nickel–molybdenum and –tungsten analogs, the nickel-chromium species is thermally unstable and decomposes rapidly in solution above –30°C. Nevertheless, this complex was synthesized and purified at temperatures below –30°C, and was crystallized from hexanes at –78°C. Dark green crystals suitable for an X-ray diffraction study were harvested and an X-ray diffraction data set was successfully obtained on a single crystal. Unfortunately, the molecule crystallized in the high symmetry space group *R*3 and the Ni–Cr bond was aligned along the crystallographic three-fold axis. The disorder of the two five-membered rings about the crystallographic three-fold axis rendered any accurate electron density measurements moot.[16]

A more recent synthesis of complexes **1** became necessary as [Ni$_2$ (μ-CO)$_2$Cp$^*_2$] (Ni–Ni) is fairly expensive to purchase. The complex is most easily prepared from [Ni(CO)$_4$], and this was our usual route to this complex.[17] Unfortunately, owing to safety concerns, the price of [Ni(CO)$_4$] has become prohibitive in Europe as 450 g of [Ni(CO)$_4$] sells



Scheme 4. Newer synthesis of complexes 1.

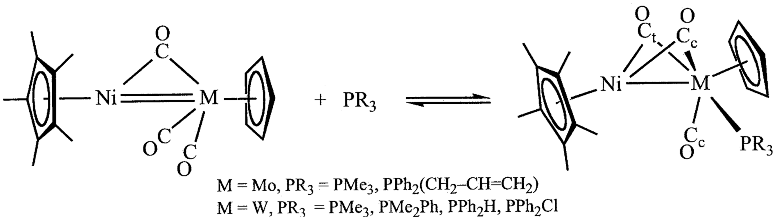
for around 2000 euros. We therefore developed a new synthesis of complex 1 that did not require the use of [Ni(CO)$_4$]. This new method involved the reaction of the 1,2-dimethoxyethane (DME) complex of nickel(II) chloride, NiCl$_2$. DME with Cp*MgCl, followed by reaction of the thermally and photolytically unstable [Cp*NiCl]$_2$ with the group 6 cyclopentadienyl carbonyl anions [M(CO)$_3$Cp]$^-$ (M=Mo, W), as is outlined in Scheme 4.[18]

4. GENERAL CHEMISTRY OF COMPLEXES 1

4.1. Reactions with 2-Electron Donor Ligands

As the representation of complex **1b** depicted in Figure 3 suggests, these complexes are electronically unsaturated. This is reflected in their chemistry with two-electron donor ligands. Carbon monoxide addition to complexes **1** readily regenerates the saturated complexes **2**. In addition, many other two electron donor ligands add on to **1** to give saturated heterobimetallic adducts. Three different types of addition products are seen, depending on the ligand.

4.1.1. Complexes with Group 6 Metal-Bound 2-Electron Donor Ligands. The geometry of the most common addition product of complexes **1** with two electron donors finds the ligand linked directly to the group 6 metal, as shown in Scheme 5.[19] These types of structures are



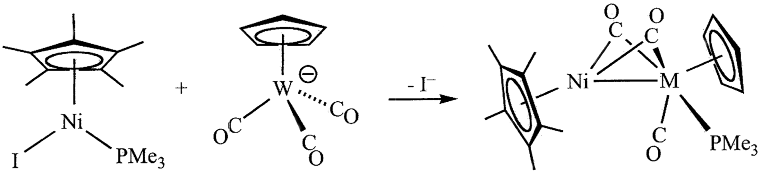
Scheme 5. Reactions of complexes 1 with trialkylphosphine ligands.

commonly observed with trialkylphosphine ligands, such as PMe_3; two of the three carbonyl ligands go into bridging positions. Most reactions were attempted on complex **1b**. The structures of the products were deduced spectroscopically, on the basis of the large $^1J_{WP}$ coupling constants observed for the Ni–W complexes. More recently, the structure of the allyldiphenylphosphine complex was established by X-ray diffraction, and confirmed the previously proposed structure.[20] These additions are often equilibrium reactions; low temperature minimizes the unfavorable entropy change for the addition reaction and hence promotes the formation of the adducts, as is shown in Scheme 5.

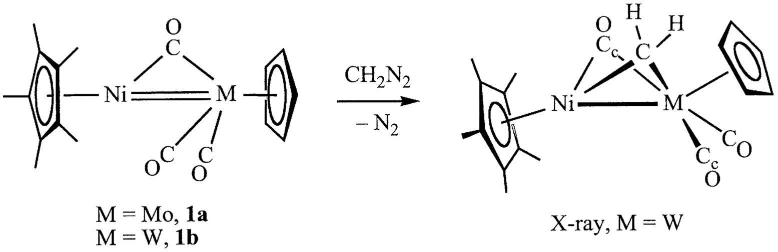
The trialkylphosphine ligands have a distinct preference to bind to the electron-poorer group 6 metal rather than to the nickel atom. The reaction of the nickel PMe_3 complex $[Ni(PMe_3)Cp^*I]$ with $[W(CO)_3Cp]^-$ afforded $[Cp^*Ni(\mu\text{-}CO)_2W(PMe_3)(CO)Cp]$ (Ni–W), in an uncommon example of a phosphine migration reaction, as shown in Scheme 6.[19]

The ^{13}C NMR spectra of complexes with a terminal ligand on the group 6 metal all show that there is rapid bridge-terminal exchange (on the ^{13}C NMR time scale) between the two CO groups that are coordinated *cis*-to the trialkyl-phosphine (i.e., between the bridging carbonyl ligand and the terminal CO group both marked C_cO in Scheme 5). The μ-CO ligand *trans*- to the phosphine (C_tO in the scheme) does not participate in this exchange process. Two signals, in a 2:1 integrated ratio, are observed for all three CO ligands in the ^{13}C NMR spectrum.[19]

4.1.2. Complexes with Bridging 2-Electron Donor Ligands. Molecules that are, or that have the potential to generate, two electron donor ligands may react with complexes **1** to give species in which the ligand is now in a bridging position. This is observed in reactions of the nickel–molybdenum and –tungsten complexes with diazomethane, as shown in Scheme 7. The products, one of which was characterized by single



Scheme 6. A nickel to tungsten PMe_3 migration reaction.



Scheme 7. Reaction of complexes 1 with diazomethane—synthesis of the first reported methylene complexes of nickel.

crystal X-ray diffraction, provided the first reported examples of nickel-methylene complexes[21] (other examples were reported later the same year).[22] The Ni–W distance in the complex [Cp*Ni(μ-CO)(μ-CH_2)W$(CO)_2$Cp] (Ni–W), is 2.5859 (6) Å with Ni–C(H2), and W–C(H2) vectors of length 1.906(5) and 2.185(5) Å, respectively. The complex has a butterfly $NiWC_2$ core with a dihedral angle between the Ni–(μ-CH_2)–W and the Ni–(μ-CO)–W planes of 108°. This small angle hints at the possibility of coupling the CH_2 and CO groups in this species. This has been achieved, indirectly, in a reaction of the [Cp*Ni(μ-CO)(μ-CH_2)W$(CO)_2$Cp] (Ni–W) complex with PhC_2H.[21]

Rapid bridge-terminal exchange on the ^1H and ^{13}C NMR time scales between CO ligands *cis* to the μ-CH_2 ligands (C_cO in Scheme 7) generates an effective mirror plane in the molecule. This leads the CH_2 hydrogen atoms to appear equivalent in the ^1H NMR spectrum. In addition, only 2 CO resonances are seen in the ^{13}C NMR spectrum, a situation analogous to what is observed in the trialkylphosphine adducts.[19,21]

The bright orange complex [Cp*Ni(μ-CO)(μ-SO_2)W$(CO)_2$Cp′] (Ni–W) is obtained when **1b′** is reacted with sulfur dioxide. This complex has a butterfly core geometry analogous to that of the μ-CH_2 adduct (see Figure 4).[23]

Ligands that can reside in both bridging and terminal positions are fluxional. Thus in the tetracarbonyl complex **2** (the result of CO addition to **1**) the CO ligands are fluxional and only one ^{13}C NMR signal is observed for these four carbon atoms, even at –40°C. The situation is similar, but more complex with the ^{t}BuNC adduct [Cp*NiW$(CO)_3$ (^{t}BuNC)Cp] (Ni–W). This species is obtained by simple addition of ^{t}BuNC to complex **1b**; IR evidence suggests that this complex exists as an equilibrating mixture of isomers, in which both bridging and terminal

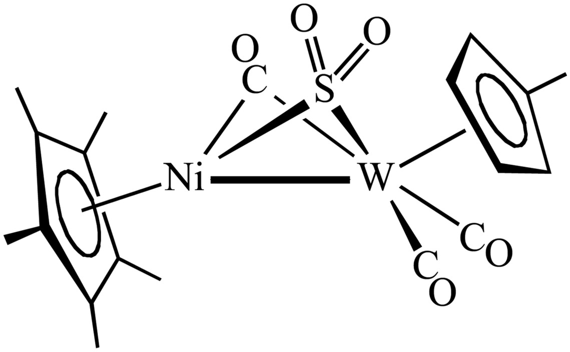


Figure 4. Structure of the μ-SO_2 complex [Cp*Ni(μ-SO_2)(μ-CO)W$(CO)_2$Cp′] (Ni–W).

isocyanide and carbonyl ligands are present. The two isomers are shown in Figure 5.[19]

A bridging ligand of a very different kind is obtained when the complex [$Fe_2(CO)_9$] is reacted with complexes **1**. The Fe(CO)4 fragment, which is isolobal to a CH_2 group, adds on to the Ni=M bonds of **1** to form deep green trinuclear FeMNi clusters (M=Mo, W) of formula [FeMNi(μ_3-CO)(μ_2-CO)$(CO)_5$CpCp*]. The structure of the FeMoNi cluster was established through an X-ray diffraction study. These clusters are tetrahedral and are formally chiral, as the three metals are bridged by a μ_3-CO ligand. The reaction scheme and the structure of the products of these reactions are shown in Scheme 8.

4.1.3. Complexes with Nickel-Bound 2 Electron Donor Ligands.

Complexes with nickel-bound two electron donor ligands have been isolated relatively recently. All known examples are found with primary and secondary amines. However, they may well exist in solution for other N-donors ligands such as pyridine. The structure of a primary amine

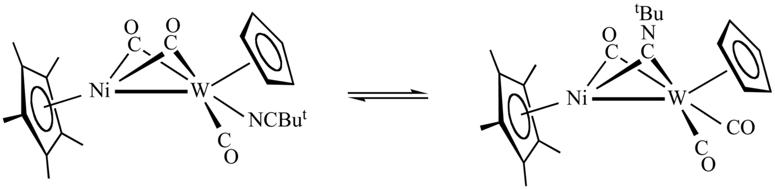
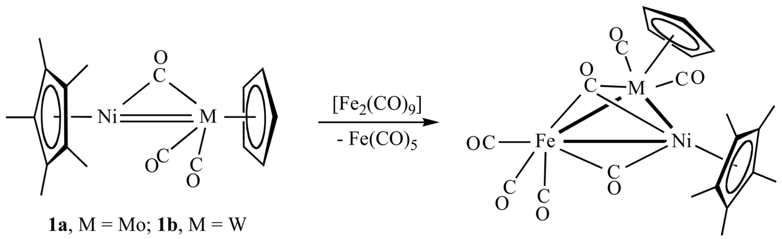


Figure 5. Interconverting isomers of NiW$(CO)_3$(^{t}BuNC)CpCp*.



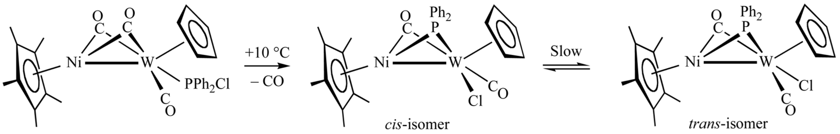
Scheme 8. Addition of an $Fe(CO)_4$ unit across the Ni=M bonds of **1**.

adduct with complex **1a** was established by X-ray diffraction and it conclusively shows that the amine nitrogen atom is directly coordinated to the nickel atom in this species. These reactions are complex, and involve various equilibria. They are under study and are not yet fully understood.

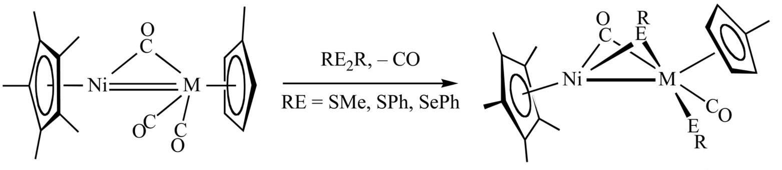
4.2. Oxidative Addition to Complexes 1

Complexes **1** may undergo oxidative addition when reacted with certain ligands. We have observed that both diphenylphosphine and chlorodiphenylphosphine undergo oxidative addition when reacted with the tungsten complex **1b**. The first product, isolated at low temperature is the tungsten-bound chlorodiphenylphosphine adduct as shown previously in Scheme 5. When warmed to ambient temperature, oxidative addition of the $Ph_2P{-}Cl$ bond takes place to give the *cis* oxidation product, in which there is a μ-PPh_2 group and a tungsten-bound terminal chloride moiety. The *cis*-isomer slowly transforms into an equilibrium mixture of *cis* and *trans*-isomers as is shown in Scheme 9. Similar results are obtained with PPh_2H but the oxidative addition products are less stable in this case.[19]

Disulfides (RS_2R, R=Me, Ph) and $PhSe_2Ph$ react via oxidative addition to complexes **1′**. No coordination complexes were ever observed with these chalcogenide ligands, even at –78°C: only products that result



Scheme 9. Addition of PPh_2Cl to **1b**, followed by oxidative addition and product isomerization.



1a′, M = Mo; **1b′**, M = W

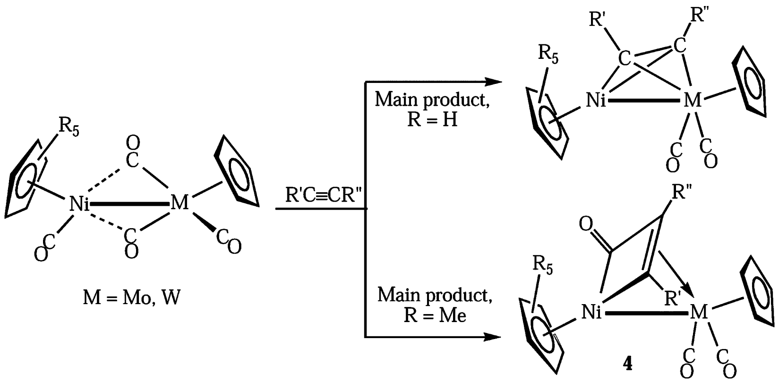
Scheme 10. Oxidative addition of RS–SR and RSe–SeR bonds to complexes **1′**.

from S–S or Se–Se oxidative addition to the dimetal center were obtained. The geometries of these products are similar to those obtained with the group 15 ligands PPh_2X (X=Cl, H). One of the RS (RSe) groups ends up in a terminal position while the other bridges the two metal centers. The bridging and terminal RS or RSe groups undergo site exchange at ambient temperature, but this process can be slowed down at −40°C on the ^{1}H NMR time-scale. The complex [Cp*Ni(μ-CO)(μ-SPh)W(CO)(SPh)Cp′] (Ni–W) was characterized by an X-ray diffraction study. The reactions of **1b′** with these group 16 molecules and the structures of the products are shown in Scheme 10.[24]

4.3. Reactions of Complexes 1 with Alkynes

4.3.1. General Comments. The rich chemistry of the *saturated* complexes [CpNi(CO)–M(CO)$_3$Cp†] (Ni–M, M=Mo, W; Cp=Cp, Cp†) with alkynes[2–5] led us to investigate the reactions of the Cp*Ni analogs with these unsaturated organic hydrocarbons. With CpNi complexes, the products of the alkyne reactions are predominantly μ-alkyne complexes with dimetallatetrahedrane-type geometries. Lesser quantities of metallacycles of type **4** are also obtained, whose relative ratio is alkyne and metal dependant. These results are summarized in Scheme 11.

When the unsaturated complexes **1** are treated with alkynes, much larger percentages of metallacycles of type **4** were obtained. The nickel atom in the Cp*Ni complexes is more electron rich than in its CpNi analogs. The higher electron density on the nickel atom would be more efficiently siphoned off by a metallacyclic CO ligand, so the Cp*Ni metallacyclic complexes **4** (Scheme 11) are stabilized relative to the CpNi species, and are formed in greater quantities. Other products (not shown in this Scheme) are also observed, especially with terminal alkynes. For convenience, the products with terminal alkynes are discussed after a summary of the results with disubstituted alkynes.



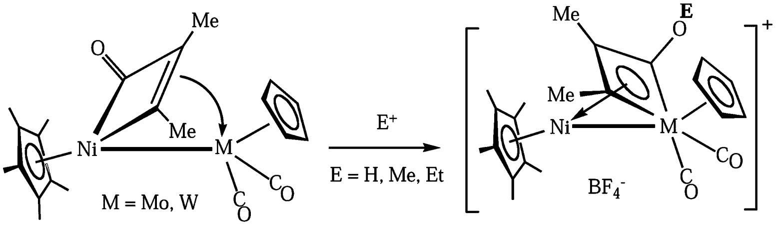
4a, M = M; R = R' = R" = Me
4b, M = W; R = R' = R" = Me

Scheme 11. Reactions of alkynes with saturated Ni–M complexes (M=Mo, W).

4.3.2. Reactions of 1 with Disubstituted Alkynes. Disubstituted alkynes react with **1a** or **1b** to give metallacycles **4a–d** (in some cases exclusively) as shown in Scheme 11.[25] The most commonly used alkyne was MeC_2Me, followed, to a lesser extent, by PhC_2Ph. The metallacycles lose the cyclic CO group when heated, to afford the corresponding dimetallatetrahedrane μ-alkyne complex. Complexes **4** have a rich chemistry, but are completely inert to nucleophiles. Complex **4a**, for example, is totally inert to MeO^-, MeLi and even to TMEDA activated MeLi. However, addition of electrophiles, such as Me^+, Et^+ (in the form of the Meerwein reagents, R_3O^+ BF_4^-, R=Me, Et) or H^+, leads to immediate alkylation or protonation of the oxygen atom of the metallacyclic carbonyl group and affords complexes **5**.[25]

We initially believed that these reactions were simply electrophilic additions onto the acyl-like carbonyl group. This is indeed the case, but as Scheme 12 illustrates, the reactions are accompanied by an isomerization reaction in which the nickelacycle becomes a molybdena- or tungstenacycle. While we have no crystallographic proof of the structures of these cationic species, spectroscopic evidence suggests that the structure is as shown in Scheme 12, with a metalloallylic delocalization in the bridging ring system.

Complexes **5** are cationic and the M–CO bonds are weaker. Substitution of these groups is now possible. In the presence of Me_3NO and iodide ions, one CO ligand is stereospecifically substituted by I^- in



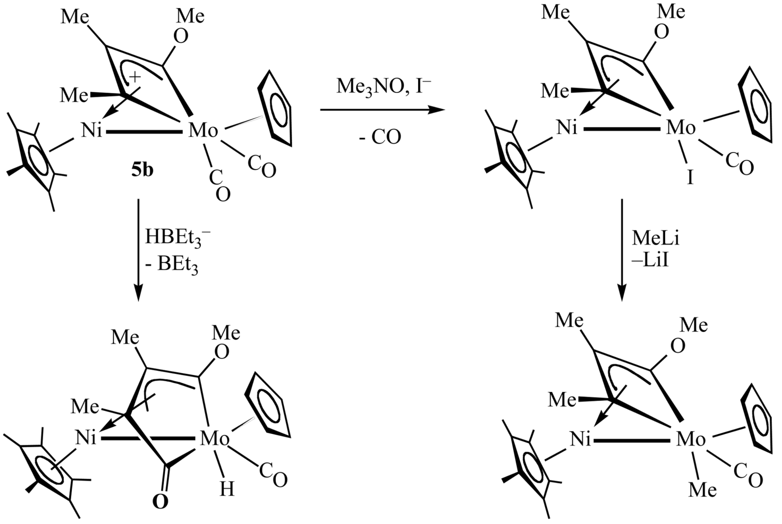
4a, M = Mo
4b, M = W

M = Mo; E = H (**5a**), Me (**5b**), Et (**5c**)
M = W; E = Me (**5d**)

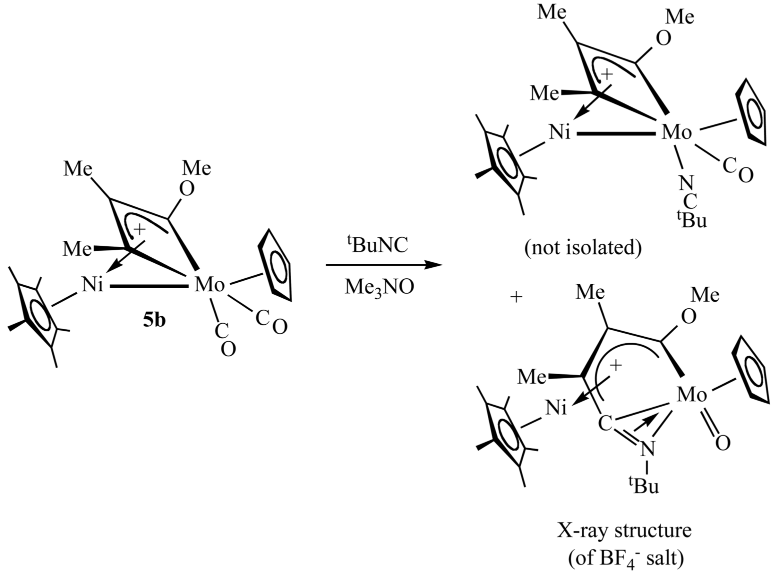
Scheme 12. Electrophilic addition to complexes **4** is accompanied by a ring isomerization.

complex **5b** to give a neutral complex. This species may in turn be alkylated to give a molybdenum bound methyl complex, as is depicted in Scheme 13. The cationic complex **5b** may also be reacted with a source of hydride, which promotes a migratory CO-insertion reaction to give an acyl hydride, in a ring expansion reaction. This is also shown in Scheme 13.[25]

An interesting product was obtained when the substitution of a carbonyl ligand in complex **5b** by a ^{t}BuNC ligand was attempted. The cationic simple substitution product was observed spectroscopically,



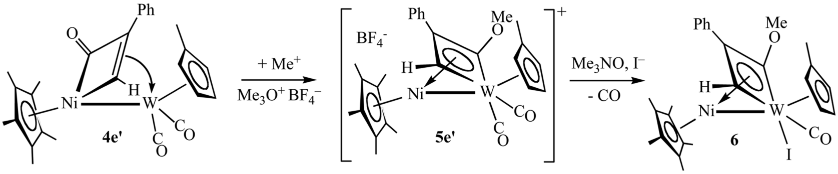
Scheme 13. Chemistry of the molybdenacyclic complex **5b**.



Scheme 14. Reaction of complex **5b** with ᵗBuNC.

but could not be isolated. However a unique oxidation product was isolated that no longer contains a Ni–Mo bond. This species was characterized by an X-ray diffraction study. The molybdenum atom has oxidized and stripped of both CO ligands, and now contains a terminal oxo-ligand. In addition, the isocyanide ligand has added on to the organic ligand to form a larger ring, which the molybdenum remains part of. The ᵗBuN=C bond interacts with the molybdenum atom via both σ and π-interactions, while the carbon atom in this moiety undergoes a bonding interaction with the nickel atom. The structure of this complex and these reactions are summarized in Scheme 14.[25]

4.3.3. Reactions of Complexes 1 with Phenylacetylene. The reactions of complexes **1** with terminal alkynes are similar, but are richer than those of disubstituted alkynes. Their similarity is shown by the formation and reactions of metallacycle **4e′**, obtained from the reaction of phenylacetylene with complex **1b′**, which are analogous to those of complexes **4a–4d**. Complex **4e′** complex may be methylated with Me^+ to give **5e′**. This species, in turn, may undergo an iodide-for-carbonyl ligand substitution, promoted by Me_3NO, to afford the neutral iodide complex **6**



Scheme 15. Alkylation of complex **4e′** followed by an iodide-for-carbonyl ligand substitution.

whose structure was established spectroscopically and via a single crystal X-ray diffraction study. These transformations and the structures of these products, which mirror the reactions with disubstituted alkynes,are shown in Scheme 15. Only one iodide isomer of **6** is obtained, which indicates that the substitution reaction is stereospecific.[26]

In addition to the above-mentioned similarities, there are two major differences in the reactions of complexes **1** with phenylacetylene and with 2-butyne. First, the reactions of PhC_2H with complexes **1** afford more than one metallacycle: in addition to the four-membered metallacycles of type **4** as discussed above, a second complex that contains a five-membered metallacycle ring, 7, is also obtained. The structure of 7 is believed to be that shown in Figure 6. Methylation of both **4e′** and 7 affords the same complex **5e′**.[26]

A second major contrast in reactivity observed between PhC_2H and MeC_2Me with complexes **1** is the tendency of phenylacetylene to give byproducts in which the alkyne has undergone not just alkyne-carbonyl

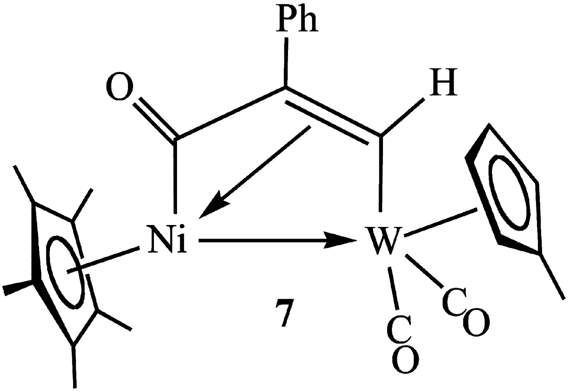


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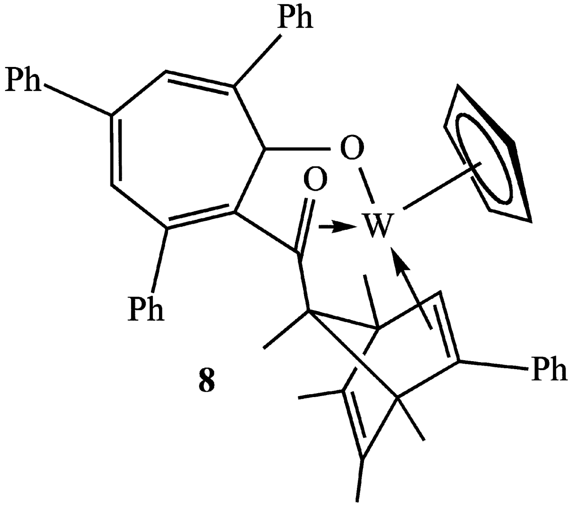
Figure 6. Structure of a five-membered ring obtained from the reaction of **1b′** with PhC_2H.



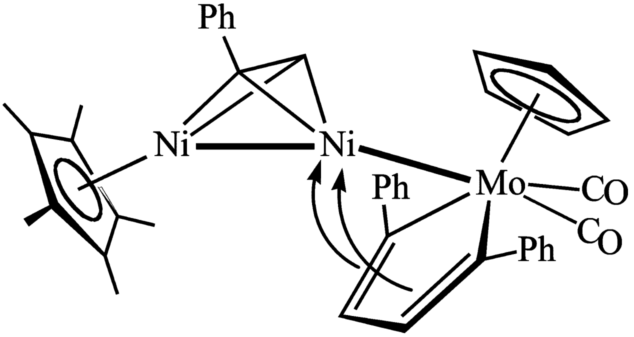
8

Figure 7. Structure of a tungsten ketone complex isolated from the "one-pot" reaction of [Cp*Ni(CO)I], $W(CO)_3Cp]^-$ and excess PhC_2H, at −20°C.

coupling but also alkyne-alkyne coupling. Such alkyne-alkyne coupling has never been observed, to date, with di-substituted alkynes in our systems.

A remarkable side-product that results from such coupling (Figure 7) is the monometallic sixteen-electron π-bound tungsten ketone complex **8** in which *eight* new C–C bonds were formed stereospecifically at −20°C. One of the two R groups of the ketone [RC(O)R′] forms from the head-to tail coupling of three PhC_2H units with a CO group to give a triphenyltropone moiety, which binds through its oxygen atom to the tungsten. The other ketonic group R′ is a nickel derived modified Cp* group that has undergone a Diels-Alder addition reaction with PhC_2H.[27]

The fate of the nickel atom that had lost a Cp* ligand was resolved with the isolation of complex **9** (Figure 8) from the reaction of analogous nickel molybdenum complexes with phenylacetylene. This complex contains a Ni–Ni–Mo trimetallic chain in which the central nickel atom has been stripped of its pendant Cp* ligand. The molecule also contains a μ-PhC_2H ligand that bridges the Ni–Ni bond and two tail-to-tail coupled PhC_2H groups that are σ-bonded to the molybdenum atom to form a molybdenacyclopentadienyl group, that in turn is π-coordinated to the central nickel atom.[28]

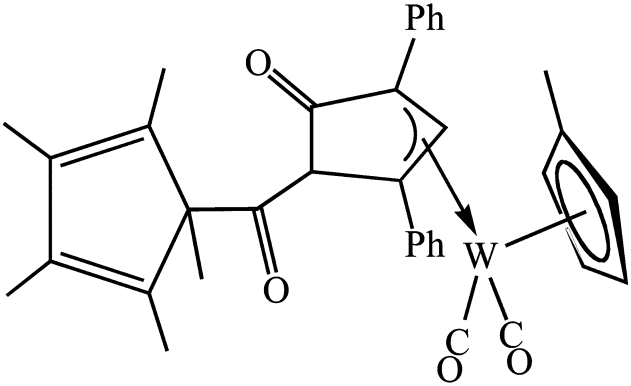


9

Figure 8. A trimetallic Ni_2Mo chain complex isolated from the reaction of 1a with PhC_2H.

More recently, **10** (Figure 9) was isolated. Complex **10** can be considered to be a precursor to the Cp′ analog to complex **8**. The complex is a monometallic tungsten species and also contains a ketone [RC(O)R′] functionality. The ketonic R group is a Cp* ligand while the other functionality, R′, is formed by the coupling of *two* phenylacetylene units (and not *three* as seen in **8**) with a carbonyl ligand to give a five-membered ring. The ketonic CO group is not directly ligated to the tungsten; instead the five-membered ring is bound in an allylic fashion to the tungsten atom.[29]

While a pre-formed metal-metal bond is not necessary, it is noteworthy that complexes **8** and **10** are only ever observed in the presence



10

Figure 9. A tungsten complex, which is a possible precursor to complex 8.

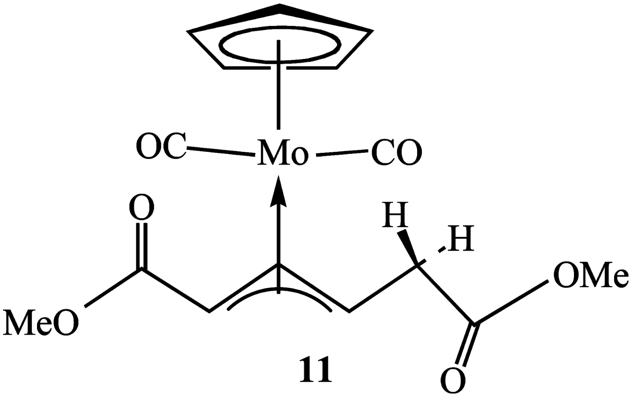
of both nickel and a group 6 element. Despite repeated attempts, no trace of these two complexes was ever observed in the absence of nickel, even though this metal is absent in these products.[27]

4.4. Reactions of Complexes 1 with Alkenes

The lack of reaction of 1,5-cod with the saturated nickel-molybdeum complex **2a′** [CpNi(CO)–M(CO)$_3$Cp′] (Ni–Mo) was discussed at the outset of this review. It was believed that the unsaturated complexes **1** had a much better chance to activate alkenes, especially electron withdrawing ones, which tend to form more stable complexes. The reaction of complex **1** with methylacrylate, CH_2=$CHCO_2Me$, was thus attempted.

When treated with excess methylacrylate, complex **1** reacted slowly to afford a burgundy solution, from which a yellow and a dark brown compound could be isolated following column chromatography. The yellow complex **11** displayed a complicated and not readily assignable ^1H NMR spectrum. However, the absence of Cp* resonances and the light yellow color of this species suggested that in **11** there was no nickel in the complex and that the product was homo- or monometallic. The structure of **11** was established by an X-ray diffraction study, and is shown in Figure 10.[30]

The complex can be described as a Mo(CO)$_2$Cp unit η^3-coordinated to a π-allylic organic ligand. This ligand is formed by the unprecedented



11

Figure 10. The structure of complex 11, an allylic molybdenum complex formed by the tail-to-tail coupling of two methacrylate units.

$$2\,\mathrm{MeO_2C{-}CH{=}CH_2} \xrightarrow{-\,[\mathrm{H}]} \mathrm{MeO_2C{-}CH{\cdots}CH{\cdots}CH{-}CH_2{-}CO_2Me}$$

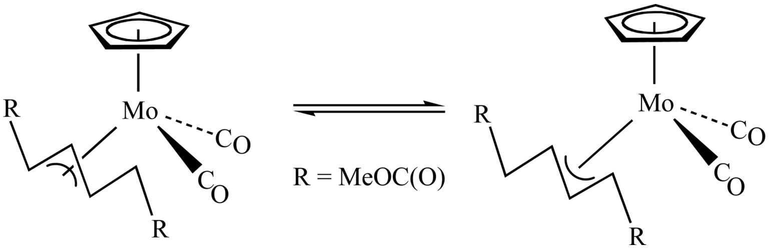
$$\boxed{1\quad 2\quad 3} \qquad\qquad \boxed{1\quad 2\quad 3}{-}\boxed{3'\quad 2'\quad 1'}$$

Scheme 16. Methacrylate transformations that take place in forming complex **11**.

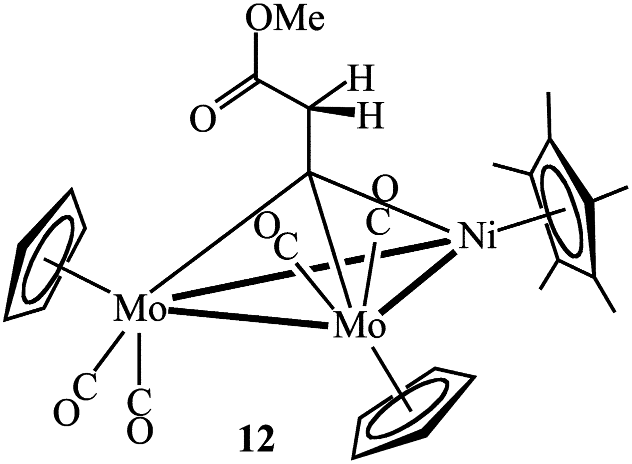
tail-to-tail coupling of two methacrylate groups. The reaction is not just a simple dimerization, but is also a C–H activation reaction since the new allylic ligand has one hydrogen atom less than is found in two $CH_2{=}CHCO_2Me$ molecules. There is also a H-shift during the course of the reaction. The alkene transformations required to produce this allylic ligand are shown in Scheme 16.

The spectrum of **11** is complex and indicates that two isomers are present in solution. These exist in a 5:2 molar ratio at room temperature and were observed by NMR even when a large single crystal of **11** was rapidly dissolved in a deuterated solvent and data was collected in less than 5 minutes total time. We believe that these isomers are the *endo*- and *exo*- complexes as depicted in Scheme 17, with the "V" of the allylic group pointing either towards or away from the Cp ring, as shown.

The second product harvested from this reaction is the dark brown $NiMo_2$ cluster **12** (see Figure 11). This trimetallic species contains the methyacrylate-derived μ_3-alkylidyne ligand CCH_2CO_2Me. An X-ray diffraction established both the nature of this cluster and its asymmetry in the solid state (C_1 symmetry). The Cp groups are oriented differently with respect to the carbyne ligand, and the two molybdenum atoms are inequivalent. This results in different Mo(A) and Mo(B) to other atom distances: for example, the Mo–$C_{\mathrm{alkylidyne}}$ distances are significantly different from each other (2.090 and 2.131 Å).[30]



Scheme 17. *Syn*- and *anti*-forms of complex 11 in equilibrium in solution.



12

Figure 11. The structure of the cluster [NiMo$_2$(μ_3-CCH$_2$CO$_2$Me)(CO)$_4$Cp$_2$Cp*].

This asymmetry is maintained in solution. The ^{1}H NMR spectrum of cluster **12** exhibits two signals for the two inequivalent C_5H_5 rings. The ^{13}C NMR spectrum similarly shows four, not two, CO resonances and two C_5H_5-group signals; the μ_3–carbyne signal is observed at $\delta = 285$ ppm. In addition, four ν(CO) stretches are observed in the solution IR spectrum of this cluster. The formation of this alkylidyne cluster also requires a C–H activation and a hydrogen shift reaction from the methacrylate ligand for it to be transformed into the alkylidyne ligand (Scheme 18).

In addition, as was observed in the case of the molybdenum allylic complex **11**, the reaction stoichiometry to form **12** indicates that the elements of [Cp*NiH] have been lost per mole of cluster formed. The fate of these missing groups in these two parallel reactions has not yet been definitively established, but some experimental pointers suggest where these groups end up. The formation of the free hydrocarbon Cp*H is observed during the course of this reaction, and this probably accounts for a large

$$\mathrm{MeO_2C{-}CH{=}CH_2} \xrightarrow{-\,[\mathrm{H}]} \mathrm{MeO_2C{-}CH_2{-}C}$$

Scheme 18. The methacrylate transformation that takes place in forming complex **11**.

quantity of the Cp* ligand. In addition, both $[Ni_2(\mu\text{-}CO)_2Cp^*{}_2]$ (Ni–Ni) and an uncharacterized blue paramagnetic complex (that may also contain nickel) were obtained in small quantities. These two species, together with decomposition products, may account for the nickel mass balance in this reaction.

While nickel is not present in complexes **11** and **12**, it is apparently necessary for the formation of the complex. When methylacrylate was heated with either the complex $[Mo_2(CO)_6Cp_2]$ (Mo–Mo), with its triply bonded congener $[Mo_2(CO)_4Cp_2]$ (Mo≡Mo), no activation of the methylacrylate ligand was ever observed. No olefin activation was noted either when the dinickel species $[Ni_2(\mu\text{-}CO)_2Cp^*{}_2]$ (Ni–Ni) was refluxed with methylacrylate. These negative results suggest that such activation is unique to the heterobimetallic complex **1**.

More recent research has shown that formation of the cluster **12** requires the presence of the molybdenum dimer $[Mo_2(CO)_6Cp_2]$ (Mo–Mo), which is frequently present either as an impurity in **1a** or as one of its decomposition products. When highly purified samples of **1a** were used, yields of complex **12** were suppressed.

CONCLUSION

This review has outlined some facets of the rich chemistry that complexes **1** exhibit. The reactivity of these unsaturated nickel-molybdenum and –tungsten species stems from two activating effects that to some extent reinforce each other.

The first effect arises from the heterobimetallic nature of these complexes, which leads to a cooperative increase in reactivity due to the different electronic, steric and ligand requirements of the two linked metals. The electron density at the already electron rich nickel center is enhanced by the Cp* ligand, which makes complexes **1** significantly polar, and more reactive.

The second factor that enhances the reactivity of complexes **1** is their unsaturation. Complexes in which there is a multiple bond between two metals in a low formal oxidation state (≤ 1) remain rare, but those that are known exhibit a rich chemistry. A few well known examples include the group 6 complexes $[M_2(CO)_4Cp^\dagger{}_2]$ (M≡M, M–Cr, Mo, W)[31,32] and the group 9 complexes $[M_2(\mu\text{-}CO)_2Cp^*{}_2]$ (M=M, M=Co, Rh, Ir).[33–35] Mixed metal examples of both group 6 metals, namely $[MoW(CO)_4Cp_2]$ (Mo≡W)36 or mixed group 9 metal combinations, for example [RhIr

(μ-CO)$_2$Cp$^*_2$] (Rh=Ir),[35] are also known but are less accessible than complexes 1 and have been less well investigated.

Our investigations into other reactions of 1 with various reagents are ongoing. We are investigating the reactions of complexes 1 with other alkenes, following the unprecedented activation observed with methyacrylate. The reactions of 1 with other 2-electron donor ligands and structural studies of these products are under way, and will be described shortly in other publications.

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REFERENCES

1. Madach, T., K. Fischer, and H. Vahrenkamp, 1980. *Chem. Ber.*, **113**, 3235–44.
2. Azar, M. C., M. J. Chetcuti, C. Eigenbrot, and K. A. Green, 1985. *J. Am. Chem. Soc.*, **107**, 7209–7210.
3. Chetcuti, M. J., C. Eigenbrot, and K. A. Green, 1987. *Organometallics*, **6**, 2298–2306.
4. Chetcuti, M. J. and K. A. Green, 1988. *Organometallics*, **7**, 2450–2457.
5. Chetcuti, M. J., J. C. Gordon, K. A. Green, P. E. Fanwick, and D. Morgenstern, 1989. *Organometallics*, **8**, 1790–1799.
6. Frisch, P. D. and L. F. Dahl, 1972. *J. Am. Chem. Soc.*, **94**, 5082–5084.
7. Sorai, M., A. Kosaki, H. Suga, S. Seki, T. Yohida, and S. Otsuka, 1971. *Bull. Chem. Soc. Jpn.*, **44**, 3364–3371.
8. Chetcuti, M. J., S. R. McDonald, and J. C. Huffman, 1989. *Inorg. Chem.*, **28**, 238–242.

9. Evans, D. F. 1959. *J. Chem. Soc.*, 2003.
10. Evans, D. F., G. V. Fazakerly, and R. F. Phillips, 1971. *J. Chem. Soc. (A)*, 1931.
11. Fischer, E. O. and C. Palm, 1958. *Chem. Ber.*, **91**, 1725–1731.
12. Byers, L. R., V. A. Uchtman, and L. F. Dahl, 1981. *J. Am. Chem. Soc.*, **103**, 1942–1958.
13. Maj, J. J., A. D. Rae, and L. F. Dahl, 1982. *J. Am. Chem. Soc.*, **104**, 3054–3063.
14. Madach, T. and H. Vahrenkamp, 1980. *Chem. Ber.*, **113**, 2675–2685.
15. Chetcuti, M. J., P. E. Grant, P. E. Fanwick, M. J. Geselbracht, and A. M. Stacy, 1990. *Organometallics*, **9**, 1343–1345.
16. Chetcuti, M. J. and R. Welter. Unpublished results.
17. Mise, T. and H. Yamazaki, 1986. In *Organometallic Syntheses*, King, R. B. and J. J. Eisch (eds.), vol. 3, Elsevier, New York, Amsterdam.
18. Braunstein, P., M. J. Chetcuti, and R. Welter, 2002. *C. R. Chimie*, **5**, 67–72.
19. Chetcuti, M. J., K. J. Deck, P. E. Fanwick, J. C. Gordon, and B. E. Grant, 1992. *Organometallics*, **11**, 2128–2139.
20. Boag, N., P. Braunstein, M. J. Chetcuti, S. Clapham, and R. Welter. To be published.
21. Chetcuti, M. J., B. E. Grant, and P. E. Fanwick, 1990. *Organometallics*, **9**, 1345–1347.
22. Baxter, S. and P. T. Wolczanski, 1990. *Organometallics*, **9**, 2498–2509.
23. Bartlone, A. F., M. J. Chetcuti, R. Navarro III, and M. Shang, 1995. *Inorg. Chem.*, **34**, 980–983.
24. Bartlone, A., M. J. Chetcuti, P. E. Fanwick, and K. A. Haller, 1993. *Inorg. Chem.*, **32**, 1435–1441.
25. Chetcuti, M. J., B. E. Grant, and P. E. Fanwick, 1995. *Organometallics*, **14**, 2937–2950.
26. Chetcuti, M. J., B. E. Grant, and P. E. Fanwick, 1996. *Organometallics*, **15**, 4389–4397.
27. Chetcuti, M. J., B. E. Grant, and P. E. Fanwick, 1989. *J. Am. Chem. Soc.*, **111**, 2743–2744.
28. Chetcuti, M. J., L. DeLiberato, P. E. Fanwick, and B. E. Grant, 1990. *Inorg. Chem.*, **29**, 1295–1298.
29. Chetcuti, M. J., P. E. Fanwick, and B. E. Grant, 2001. *J. Organometal. Chem.*, **630**, 215–220.
30. Braunstein, P., M. J. Chetcuti, and R. Welter, 2001. *Chem. Commun.*, 2508–2509.
31. Curtis, M. D. 1987. *Polyhedron*, **6**, 759.
32. Huang, J.-S. and L. F. Dahl, 1983. *J. Organomet. Chem.*, **243**, 57–68.
33. Green, M., R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, 1982. *J. Chem. Soc., Dalton Trans.*, 1309.

34. Cirjak, L. M., R. E. Ginsburg, and L. F. Dahl, 1982. *Inorg. Chem.*, **21**, 940.
35. Bray, A. C., M. Green, D. R. Hankey, J. A. K. Howard, O. Johnson, and F. G. A. Stone, 1985. *J. Organomet. Chem.*, **281**, C12–C16.
36. Curtis, M. D., N. A. Fotinos, L. Messerle, and A. P. Sattelberger, 1982. *Inorg. Chem.*, **22**, 1559–1561.