Reactions of Compounds Containing Ni–Ni, Ni–Mo, and Ni–W Bonds with Allene and 1,1-Dimethylallene. X-ray Diffraction Studies of the π-Allylic Complexes $NiMo(CO)_2\{\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ and $NiMo(\mu\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (Ni–Mo)

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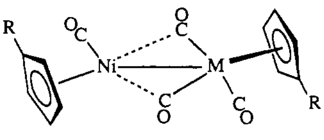
The reactions of the dinickel species $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni) and of the mixed-metal complexes $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4Me)$ [**1a**, M = Mo; **1b**, M = W] with propa-1,2-diene (allene) and 3-methyl-1,2-butadiene (1,1-dimethylallene) are described. When $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni) is treated with allene, the nickel–nickel bond is ruptured and two allene units couple forming the 2,2′-bis(allyl) species $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)Ni(\eta^5\text{-}C_5H_5)$ (**2**). No reaction ensues when the Ni_2 complex is treated 1,1-dimethylallene. **1a** and **1b** react with allene, but the only heterobimetallic product characterized was $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**3**), whose structure was determined by an X-ray diffraction study. Complex **3** contains no metal–metal bond, and the $\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}$ ligand that tethers the two metal centers together, derived from the trimerization of three allene units, is η^3-coordinated in a π-allyl fashion to each metal. Both **2** and **3** exhibit interesting CIMS: when isobutane is used as the ionization gas, a butyl cation adds on to the parent molecule of both species, forming $(M + 57)^+$ ions for both species. 1,1-Dimethylallene reacts with complexes **1a**, **1b**, and $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (**1a′**) to form the 2-nickel-substituted allylic complexes $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}M(CO)_2(\eta^5\text{-}C_5H_4R)$ (Ni–M) [**4a**, M = Mo; **4b**, M = W] and $(\eta^5\text{-}C_5H_4Me)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}Mo(CO)_2(\eta^5\text{-}C_5H_5)$ (Ni–Mo) (**4a′**), respectively. On silica gel, isomerization to the 1-nickel-substituted allyl species $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\mu_2\text{-}CO)M(CO)(\eta^5\text{-}C_5H_4Me)$ (Ni–M) [**5a**, M = Mo; **5b**, M = W] and $(\eta^5\text{-}C_5H_4Me)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\mu_2\text{-}CO)Mo(CO)(\eta^5\text{-}C_5H_5)$ (Ni–M) (**5a′**), respectively, takes place. Complex **4b** reductively eliminates a nickel atom in a side reaction to form an isomeric mixture of 2-substituted 1,3- and 1,4-cyclopentadienyl-1,1-dimethylallyl species $W(CO)_2\{\eta^3\text{-}(CH_2\text{–}C(C_5H_5)\text{–}CMe_2)\}(\eta^5\text{-}C_5H_4Me)$ (**6b**). Related allene derived isomers $W(CO)_2\{\eta^3\text{-}(CH_2\text{–}C(C_5H_5)\text{–}CH_2)(\eta^5\text{-}C_5H_4Me)$ (**6**) were isolated from the reaction of allene with **1b**. Labeling studies using 1,1-dimethylallene-*3*-d_1 or acetic acid-d_1 demonstrated that an effective 1,4-proton shift and not a 1,2-methyl group migration was operative in the isomerization of **4a**-d_1 to **5a**-d_1. In contrast to the reactivity exhibited toward cumulated dienes, neither **1a** nor **1b** reacted with isoprene.

Introduction

A full understanding of the role metals play in promoting carbon–carbon bond formation and hydrocarbon skeletal rearrangements remains elusive despite advances made in di- and polynuclear organometallic chemistry. While synthetically useful reactions have been developed from the interactions of dimetallic systems with hydrocarbons,[1] the outcome of the reaction of a hydrocarbon with a particular dimetallic complex is often unpredictable, especially when dissimilar metals are involved: novel compounds often result or the "expected" species may have a transient existence en route to a new rearranged final product.

The chemistry of the mixed-metal complexes $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4Me)$ [**1a**, M = Mo; **1b**, M = W] with unsaturated hydrocarbons has been the focus of recent research in our group.[2-4] Significant differences are observed between the reactivity of the group 6–group 10 complexes **1a** and **1b** and the chemistry exhibited toward the same reagents by either the dimolybdenum/ditungsten systems $[M(CO)_{2/3}(\eta^5\text{-}C_5H_5)]_2$ or the dinickel compound $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni).[4,5] Reactions of these heterodinuclear species also diverge from those displayed by the isoelectronic diiron species $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$. To date the bulk of our published work has focused on reactions of these and related species with alkynes. Allenes customarily act as $\mu\text{-}\eta^2,\eta^2$-ligands toward



1a, M = Mo; R = H; R′ = Me
1a′, M = Mo; R = Me; R′ = H
1b, M = W; R = H; R′ = Me

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Table I. ^1H NMR Data (δ, ppm; J, Hz)[a]

	C_5H_5	C_5H_4Me[b]	CHH (syn)	CHH (anti)	Me	C_5H_4Me
4a	5.14	4.85, 4.78, 4.68, 4.65	4.22	2.81	2.35, 1.83 (J_{HH} = 0.44)	2.04
4a′	4.94	5.02,[c] 4.95, 4.84	4.29	2.95	2.29, 1.19	1.86
4b	5.13	4.88, 4.83, 4.74, 4.67	4.31	2.89 (J_{WH} = 4.82)	2.44, 1.15	2.18
5a	5.03	4.66,[c] 4.60, 4.51	2.94 (d) (J_{HH} = 1.52)	2.76 (m)	2.15,[d] 1.83	2.01
5a′	4.82	4.98, 4.84, 4.75[c]	3.02 (d) (J_{HH} = 1.37)	2.79 (m)	2.17,[d] 1.83	1.85
5b	5.02	4.71,[d] 4.69, 4.58	2.78	2.77	2.24,[d] 2.00 (J_{WH} = 3.35)	2.13

[a] Spectra recorded in chloroform-d_1. [b] ABCD multiplets. [c] 2 H. [d] Ni–C(*Me*).

Table II. ^{13}C NMR Data (δ, ppm; J, Hz)[a]

	CO	C–CH_2	C_5H_5	C_5H_4Me	C(Me)	CH_2	Me	C_5H_4Me
4a	254.0, 238.7	171.6	93.9	107.2,[b] 94.0, 93.0, 91.7, 90.9	119.0[c]	54.0	32.9, 23.7	13.4
4a′[d]	255.3, 237.3	172.4	91.6	106.6,[b] 96.0, 94.9, 92.7, 90.2	119.5[c]	53.2	32.8, 23.6	12.3
4b[e]	240.2, 227.1 (J_{WC} = 173)	173.7 (J_{WC} = 7)	94.2	105.9,[b] 93.4, 91.8, 89.8, 89.6	110.8[c]	46.2[f]	33.9, 24.6	13.5
5a[d]	262.9 (μ), 229.8	145.6[g]	93.1	107.7,[b] 94.4, 92.6, 92.0, 91.8	101.6	51.1	29.9, 20.4	13.0
5a′	263.4 (μ), 229.3	146.3[g]	92.4	105.6,[b] 94.8, 94.1, 91.9, 90.8	101.2	50.8	29.7, 20.5	12.5
5b	251.3 (μ), 217.0	131.5[g]	93.6	106.6,[b] 93.1, 92.6, 91.1, 89.8	99.8	41.7 (J_{WC} = 9)	29.5, 20.2	13.0

[a] Spectra acquired in choroform-d_1. [b] C(Me). [c] CMe_2. [d] Assigned from ^1H-coupled spectrum. [e] Acetone-d_6. [f] Broad. [g] Ni–C(*Me*).

dimetal compounds, mimicking bridging alkynes in μ-alkyne complexes; an exploration of the reactions of allenes with **1a** and **1b** was therefore of interest.

Reactions of the dimolybdenum species $[Mo(CO)_2(\eta^5\text{-}C_5H_4R)]_2$ (R = H, Me; Mo≡Mo) with allenes have been probed by Chisholm[6] and Curtis:[7] bridging η^2,η^2-allene compounds resulted with allene or monosubstituted allenes, but 1,1-dimethylallene was unreactive toward these metal complexes. Nickel(0) complexes display an interesting reactivity toward allenes,[8] but to our knowledge, reactions of the dinickel complex $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ with allene or 1,1-dimethylallene are not documented. These are reported here, followed by a discussion of the reactions of **1a** and **1b** with these dienes. Some aspects of this work have been communicated.[9]

Results and Discussion

(a) Reaction of Allene and 1,1-Dimethylallene with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni). Allene (1,2-propadiene, $CH_2{=}C{=}CH_2$) reacts slowly with red hexane solutions of this nickel species to afford a dark red compound (**2**). The ^1H NMR spectrum of **2** (Table I) reveals a singlet at δ 5.29 ppm that may be assigned to a η^5-C_5H_5 group; two other singlets are observed at 3.01 and 1.62 ppm, at ranges characteristic of syn and anti protons of π-allylic species. Complex **2** exhibits no ν(CO) absorptions in its IR spectrum.

These spectroscopic results and the EI (electron ionization) MS are in accord with **2** being the 2,2′-bis(π-allyl) complex $Ni_2(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)_2$. [The chemical ionization mass spectrum (CIMS) of **2** is discussed later.] Two allene units are reduced to a "tetramethyleneethane" ligand with the concurrent formal oxidation of a pair of nickel atoms from Ni(I) to Ni(II). A new C–C bond replaces the ruptured Ni–Ni bond present in $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$. The reaction is shown in eq 1.

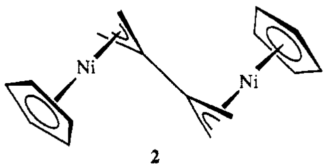

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Table III. IR ν(CO) Data (cm^{-1})

complex	hexanes	Nujol
3	1961 (s), 1891 (s)	1951 (m), 1940 (s), 1888 (w), 1861 (s)
4a	1928 (w), 1809 (s)	1924 (s), 1790 (s)
4a′	1929 (s), 1803 (s)	1934 (s), 1787 (s)
4b	1911 (s), 1811 (s)	1913 (s), 1794 (s)
5a	1948 (s), 1784 (s)	1936 (s), 1757 (s)
5a′	1949 (s), 1782 (s)	1942 (s), 1768 (s)
5b	1944 (s), 1778 (s)	1939 (s), 1755 (s)
6a	1948 (s), 1878 (s)	
6b	1946 (s), 1872 (s)	1943 (s), 1918 (m), 1868 (s), 1840 (m)
6b′	1954 (s), 1881 (s)	

[a] CH_2Cl_2 solution. [b] KBr pellet.

$$[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2 + 2CH_2{=}C{=}CH_2 \rightarrow Ni_2(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)_2 + 2CO \quad (1)$$

The identity of **2** was confirmed by comparing its spectroscopic data with those reported for the independently prepared complex $Ni_2(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)_2$,[10] whose structure has been determined by X-ray diffraction.[11] The manganese[12] and iron[13] complexes $Mn_2(CO)_8(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)$ (no Mn–Mn bond) and $Fe_2(CO)_6(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)$ (Fe–Fe), which contain similar ligands, result when $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$, respectively, are photolyzed with allene.

When $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ was reacted with 1,1-dimethylallene ($Me_2C{=}C{=}CH_2$, 3-methyl-buta-1,2-diene), no complexes containing this ligand could be isolated. The diene was consumed slowly, but nickelocene and the paramagnetic trinickel cluster $[Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3]$[14] were the only new organonickel species characterized.

(b) Reactions of Allene with 1a and 1b. (i) Reaction Description. Molecules of stoichiometry $NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}CH_2{=}C{=}CH_2)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ were *not* iso-

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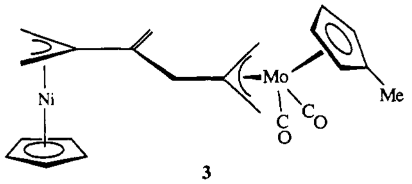
Table IV. Crystal and Data Collection Parameters for 3 and 5a

	3	5a
formula	$C_{22}H_{24}MoNiO_2$	$C_{18}H_{20}MoNiO_2$
fw	475.09	423.10
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	14.104 (1)	9.104 (3)
b, Å	15.444 (2)	15.840 (16)
c, Å	9.952 (1)	11.559 (4)
β, deg	110.558 (8)	94.20 (3)
V, Å^3	2029.6 (7)	1662.3 (9)
Z	4	4
d_{calc}, g cm^{-3}	1.555	1.690
cryst dimens, mm	0.49 × 0.44 × 0.15	0.35 × 0.35 × 0.45
temp, °C	20	25
λ(Mo Kα), Å	0.71073	0.71073
monochromator	graphite	graphite
μ(Mo Kα), cm^{-1}	15.47	18.79
abs corr	empirical	not applied
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
scan method	ω–2θ	θ–2θ
h, k, l limits	0 to 15, −16 to 0, −10 to 10	−11 to 13, 0 to 23, 1 to 17
2θ range, deg	4.00–45.00	3.20–64.0
scan width, deg	0.79 + 0.35 tan θ	0.80 + 0.35 tan θ
programs used	Enraf Nonius SDP	SHELXS
no. of data collcd, no. of unique data	2778, 2778	5509, 5509
no. of data with $I > 3.0\sigma(I)$	2238	3426
no. of variables	235	279
R	0.035	0.039
R_w	0.045	0.043
goodness of fit	1.57	1.32

lated from these reactions. Any heterobimetallic monoallene species resisted characterization and ultimately decomposed yielding intractable products and/or oils. Though the bulk of the allene appeared to oligomerize,[15] a tan species (**3**) was harvested in moderate yield (18%) by reacting **1a** with excess allene under carefully controlled conditions. The corresponding nickel–tungsten complex was not isolated when **1b** was treated with allene, but a yellow oil containing a tungsten species **6** (discussed later) was isolated from this reaction.

The ^1H, ^{13}C NMR (Tables I and II), and IR data (Table III) suggest that **3** can be formulated as $NiMo(CO)_2(C_3H_4)_3(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)$. Four singlets spanning the chemical shift range of δ 2.93–1.76 ppm are observed in its ^1H NMR spectrum. In addition, both AB-type multiplets (centered at 5.35 and 5.29 ppm) and a singlet (at 1.16 ppm) accounting for two hydrogen atoms are seen. Signals for $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5H_4Me$ groups were also noted and the AA′BB′ spin system exhibited by the aromatic $\eta^5\text{-}C_5H_4Me$ protons implies that an effective mirror plane of symmetry is present, at least on the ^1H NMR time scale. EIMS data corroborate the proposed empirical formula. [CIMS data for **3** (cf. **2**) are unusual and will be discussed shortly.] A molecular structure of **3** consistent with these spectroscopic data can be proposed.



3

Table V. Fractional Atomic Coordinates for 3

atom	x	y	z
Mo	0.29976 (3)	0.58224 (2)	0.10968 (4)
Ni	0.12127 (4)	0.33543 (4)	0.47221 (6)
O(1)	0.1214 (3)	0.4525 (3)	−0.0131 (3)
O(2)	0.4077 (3)	0.4103 (3)	0.0971 (5)
C(1)	0.1889 (4)	0.5018 (3)	0.0366 (5)
C(2)	0.3691 (3)	0.4755 (3)	0.1067 (5)
C(11)	0.4023 (4)	0.5822 (3)	0.3481 (5)
C(12)	0.3081 (3)	0.5477 (3)	0.3380 (4)
C(13)	0.2233 (4)	0.6003 (3)	0.2790 (5)
C(21)	0.2047 (4)	0.3704 (4)	0.6718 (5)
C(22)	0.2589 (3)	0.3691 (3)	0.5769 (5)
C(23)	0.2585 (4)	0.2891 (3)	0.5095 (6)
C(31)	0.2983 (3)	0.4561 (3)	0.3832 (4)
C(32)	0.2987 (3)	0.4496 (3)	0.5356 (4)
C(33)	0.3383 (4)	0.5098 (4)	0.6339 (5)
C(101)	0.3946 (4)	0.7044 (3)	0.0784 (5)
C(102)	0.3746 (3)	0.6479 (3)	−0.0383 (5)
C(103)	0.2710 (4)	0.6434 (3)	−0.1111 (5)
C(104)	0.2239 (4)	0.6947 (3)	−0.0405 (5)
C(105)	0.2982 (4)	0.7336 (3)	0.0765 (5)
C(106)	0.4966 (5)	0.7338 (5)	0.1766 (8)
C(201)	−0.0066 (5)	0.4088 (4)	0.3445 (9)
C(202)	0.0282 (4)	0.3590 (5)	0.2552 (6)
C(203)	0.0239 (4)	0.2719 (5)	0.2955 (6)
C(204)	−0.0163 (4)	0.2692 (4)	0.4006 (6)
C(205)	−0.0319 (4)	0.3507 (5)	0.4353 (6)

Table VI. Selected Bond Distances (Å) for 3

Mo–C(1)	1.929 (5)	Mo–C(2)	1.922 (4)
Mo–C(11)	2.305 (4)	Mo–C(12)	2.297 (3)
Mo–C(13)	2.314 (4)	Mo–C(101)	2.396 (4)
Mo–C(102)	2.324 (4)	Mo–C(103)	2.293 (4)
Mo–C(104)	2.296 (4)	Mo–C(105)	2.359 (4)
Ni–C(21)	1.995 (4)	Ni–C(22)	1.924 (4)
Ni–C(23)	1.972 (5)	Ni–C(201)	2.131 (6)
Ni–C(202)	2.128 (5)	Ni–C(203)	2.061 (5)
Ni–C(204)	2.085 (5)	Ni–C(205)	2.073 (5)
O(1)–C(1)	1.182 (5)	O(2)–C(2)	1.167 (5)
C(11)–C(12)	1.402 (6)	C(12)–C(13)	1.393 (6)
C(12)–C(31)	1.504 (5)	C(21)–C(22)	1.408 (6)
C(22)–C(23)	1.405 (6)	C(22)–C(32)	1.480 (5)
C(31)–C(32)	1.519 (5)	C(32)–C(33)	1.322 (6)
C(101)–C(106)	1.498 (6)		
C(Cp)–C(Cp)	1.381 (av)	C(Cp′)–C(Cp′)	1.397 (av)
Ni–C(Cp)	2.096 (av)	Mo–C(Cp′)	2.334 (av)

Table VII. Selected Bond Angles (deg) for 3

C(1)–Mo–C(2)	78.0 (2)	C(1)–Mo–C(11)	121.4 (2)
C(1)–Mo–C(12)	88.6 (2)	C(1)–Mo–C(13)	80.2 (2)
C(2)–Mo–C(11)	82.9 (2)	C(2)–Mo–C(12)	88.1 (2)
C(2)–Mo–C(13)	119.0 (2)	C(11)–Mo–C(12)	35.5 (1)
C(11)–Mo–C(13)	62.3 (2)	C(12)–Mo–C(13)	35.2 (1)
C(21)–Ni–C(22)	42.1 (2)	C(21)–Ni–C(23)	73.4 (2)
C(22)–Ni–C(23)	42.2 (2)	Mo–C(1)–O(1)	177.5 (4)
Mo–C(2)–O(2)	176.2 (4)	Mo–C(11)–C(12)	72.0 (2)
Mo–C(12)–C(11)	72.6 (2)	Mo–C(12)–C(13)	73.1 (2)
Mo–C(12)–C(13)	122.4 (2)	C(11)–C(12)–C(13)	117.3 (4)
C(11)–C912)–C(31)	121.3 (4)	C(13)–C(12)–C(31)	121.3 (4)
Mo–C(13)–C(12)	71.7 (2)	Ni–C(21)–C(22)	66.3 (2)
Ni–C(22)–C(21)	71.6 (2)	Ni–C(22)–C(23)	70.7 (2)
Ni–C(22)–C(32)	119.1 (3)	C(21)–C(22)–C(23)	114.8 (4)
C(21)–C(22)–C(32)	121.5 (4)	C(23)–C(22)–C(32)	123.0 (4)
Ni–C(23)–C(22)	67.0 (2)	C(12)–C(31)–C(32)	113.1 (3)
C(22)–C(32)–C(31)	117.6 (3)	C(22)–C(32)–C(33)	119.2 (3)
C(31)–C(32)–C(33)	123.0 (4)		

(ii) X-ray Structural Determination of 3. A single-crystal X-ray diffraction study of **3** was undertaken to confirm its presumed structure. A tan crystal that was grown from saturated hexanes solution was selected for data collection. Crystal and data collection parameters, atomic positional parameters, and bond lengths and angles are collected in Tables IV–VII. An ORTEP plot of **3** is depicted in Figure 1.

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[15] This allene oligomerization resembles the polymerization of ethyne observed with **1a** or **1b**.[5] Bridging $\eta^2,\eta^2\text{-}C_2H_2$ complexes are isolated only under closely monitored conditions.

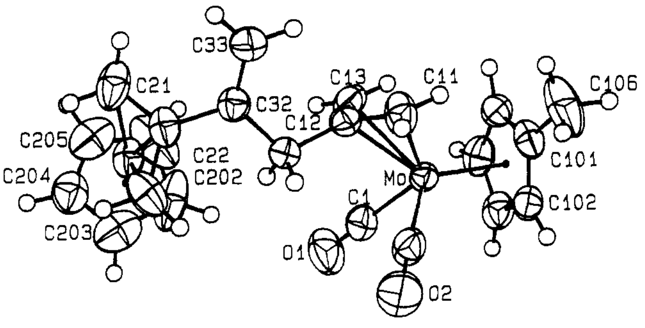

Figure 1. ORTEP plot of $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12})Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**3**). Thermal ellipsoids are shown at the 50% probability level.

The structure of this complex confirmed the prediction made on the basis of spectroscopic data: **3** can be formulated as the heterobimetallic species $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12})Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$. The molecule contains a (η^5-methylcyclopentadienyl)molybdenum dicarbonyl fragment connected to a (η^5-cyclopentadienyl)nickel unit by a bridging $\eta^3,\eta^3\text{-}C_9H_{12}$ group. The C_9H_{12} ligand is derived from the coupling of three allene molecules. It consists of two π-allylic groups, linked at the 2- and 2′-positions to the central and terminal carbom atoms, respectively, of a third C_3H_4 unit. One allylic group is η^3-coordinated to the nickel atom, while the other is similarly bound to the molybdenum atom. The central portion of this moiety contains an uncoordinated olefinic C=C bond [C(33)–C(32) = 1.322 (6) Å]. Other C–C bond lengths in this ligand reflect their single [C(22)–C(32) = 1.480 (5) Å; C(32)–C(31) = 1.519 (5); C(31)–C(12) = 1.504 (5)] or intermediate bond order [allylic C–C bonds are all 1.40 ± 0.01 Å]. There is no metal–metal bond, and only the bridging organic chain tethers the two metals to each other.

The two η^3-allyl blades subtend an angle of 72°. The C(η^3-allyl)–molybdenum bonds are practically identical and range from 2.297 (3) to 2.314 (4) Å. These are typical of values found in other molybdenum π-allyl complexes, though frequently the central carbon atom is significantly closer to the metal.[16] Nickel–η^3-allylic carbon bond lengths span a larger range [1.995 (4), 1.924 (4), and 1.972 (5) Å, respectively, for Ni–C(21), Ni–C(22), and Ni–C(23)] and are similar to those noted for comparable bonds in the 2,2′-bis(allyl) species **2**.[11]

(iii) Chemical Ionization Mass Spectra of Complexes 2 and 3. In contrast to EIMS data, CIMS data of these complexes, acquired by using isobutane as the ionization gas, were unusual. The usual[17] $(M + 1)^+$ ions that stem from isobutane proton transfer were observed in the CIMS of **2** and **3**. Both species also exhibit strong ions with *m/e* ratios of 423 and 533, respectively [$(M + 57)^+$ for each species]. This mass difference corresponds to a C_4H_9 cation: it appears that each species is clustering with C_4H_9 ions to afford the heavier $(M + C_4H_9)^+$ ions noted in the CIMS.

The addition of $C_4H_9^+$ cations to other molecules has been observed in the isobutane CIMS of olefins[18] and alkynes.[19] Few systematic studies of CIMS for organometallic complexes are reported,[20] but clustering phenomena are unusual. The only structural features common to both **2** and **3** are the $(\eta^5\text{-}C_5H_5)Ni\{\eta^3\text{-(2-alkyl)allyl}\}$ groups. As we have never observed $(M + 57)^+$ ions in the CIMS of other $(\eta^5\text{-}C_5H_5)Ni$ species, it is likely that the $Ni\{\eta^3\text{-(2-alkyl)allyl}\}$ functionality is the structural unit that interacts with the $C_4H_9^+$ group.

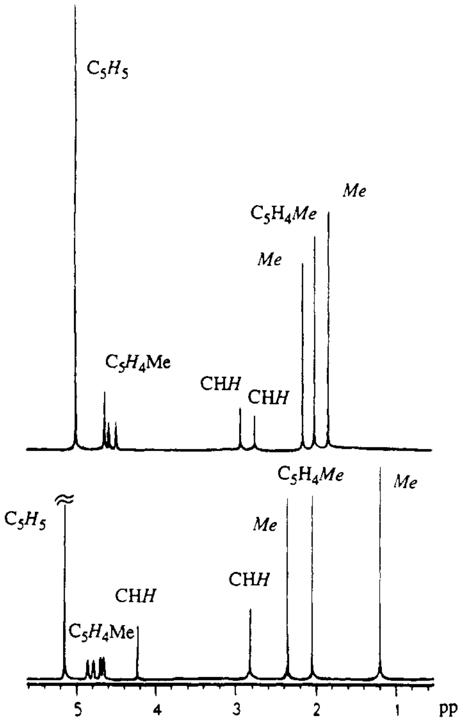

Figure 2. 300-MHz ^1H NMR spectra of **4a** (lower spectrum) and **5a** (upper spectrum). Both spectra are to the same scale.

(iv) Other Comments. The bridging $\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}$ moiety in **3** is reminiscent of the 2,2′-bis(allyl) ligand found in **2**, but an extra allene has effectively inserted into the 2,2′-carbon–carbon bond that links the two π-allylic groups. Nickel compounds catalyze the trimerization of allene to 1,2,4-trimethylenecyclohexane, so it is likely that the allene oligomerization is initiated by the nickel.[21] However allene oligomers are not obtained in the reaction of allene with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$. This indicates that both metals appear to be required. Reductive cleavage of the $\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}$ group off the two metals in **3**, followed by ring closure, would afford 1,2,4-trimethylenecyclohexane. This process has indeed been observed for $Ni\{P(OR)_3\}(\eta^3,\eta^3\text{-}C_9H_{12})$, a species that contains a comparable bis(allyl) ligand.[22,23] Allene could not be induced to further react with **3**.

(c) Reactions of 1,1-Dimethylallene with $(\eta^5\text{-}C_5H_4R)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4R')$ (R = H, Me; R′ = H, Me; M = Mo, W). (i) Reaction with 1a (R = H, R′ = Me, M = Mo). A hexane solution of 1,1-dimethylallene (3-methyl-1,2-butadiene) reacted slowly with **1a** to yield

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[16] Values for the Mo–C(allyl) distances in some molybdenum π-allyl complexes [interior and exterior carbon–molybdenum bond lengths, respectively] are as follows. (a) 2.236 (4), 2.359 (3) Å in $Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$: Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227. (b) 2.200 (3), 2.376 Å (mean) for $Mo(CO)_2(\eta^3\text{-}C_6H_9)(\eta^5\text{-}C_5H_5)$: Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (c) 2.195 (4), 2.366 Å (mean) in $Mo(CO)_2(\eta^3\text{-}C_5H_8R)(\eta^5\text{-}C_5H_5)$: Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.

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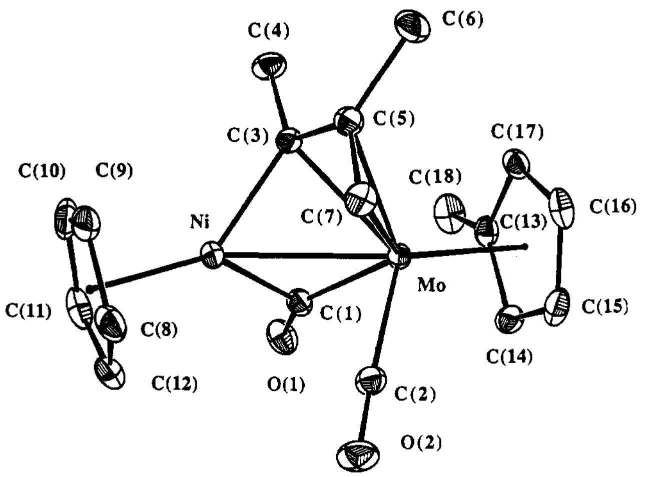
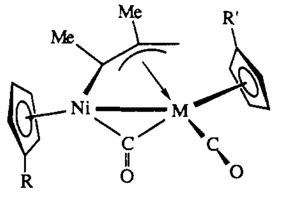


Figure 3. ORTEP plot of NiMo(μ_2-CO)(CO){μ-η^1,η^3-C(Me)–C(Me)–CH$_2$}(η^5-C_5H_5)(η^5-C_5H_4Me) (Ni–Mo) (**5a**). Thermal ellipsoids are shown at the 50% probability level.

a dark solution. Direct crystallization yielded one major product (**4a**), whose ^{1}H NMR spectrum (Table I) showed three singlets in a 1:1:5 ratio. These were assigned to two CH_2 protons and to a η^5-C_5H_5 ligand. Other resonances indicate that a 1,1-dimethylallene ligand (or an isomer of this moiety) and a η^5-C_5H_4Me ligand are also present. The aromatic protons of the methylcyclopentadienyl ligand appear as ABCD type multiplets, implying that complex **4a** contains no symmetry elements (on the ^{1}H NMR time scale). The IR spectrum of this complex exhibits two carbonyl ligand absorptions at ranges characteristic of terminal and semibridging carbonyl ligands.

After the harvesting of **4a**, the mother liquor was subjected to silica gel chromatography to obtain a new crop of crystals. A major brown band and small quantities of a pale yellow band eluted. A new species (**5a**), not originally present, was obtained from the brown band on work up. The same number of unique protons found in **4a** (Figure 2) were noted in the ^{1}H NMR spectrum of **5a** but at different chemical shifts values. The aromatic C_5H_4Me protons afforded an ABCD pattern and singlets attributed to two chemically distinct methyl groups, and two single protons were also noted. Traces of a yellow oil containing **6a** were recovered from the pale yellow band.

MS of **4a** and **5a** exhibit parent ions with the same *m/e* ratios and similar fragmentation patterns. However, the IR spectrum of **5a** indicated that a terminal and a bridging carbonyl ligand are present: in contrast, none of the carbonyl ligands in **4a** are bridging. These data imply that **4a** and **5a** are isomers that have the empirical formula NiMo(CO)$_2$(η^5-C_5H_5)(η^5-C_5H_4Me)(1,1-dimethylallene), but their identities were not immediately apparent. The ^{1}H NMR spectra for both **4a** and **5a** indicate that neither species is an isopropylacetylene (μ-η^2,η^2-HC≡CHMe$_2$) complex. We originally formulated **4a** as NiMo(CO)$_2$(μ-η^2,η^2-CMe$_2$=C=CH$_2$)(η^5-C_5H_5)(η^5-C_5H_4Me) (Ni–Mo). This now appears to be incorrect. Our current view of the structure of **4a**—an isomer of this species—and our reasons for reassigning it are discussed later. The structure of complex **5a** has been established by a single-crystal X-ray diffraction study.



5a: M = Mo; R = H, R' = Me

5a': M = Mo; R = Me, R' = H

5b: M = W; R = H, R' = Me

Table VIII. Fractional Atomic Coordinates for 5a

atom	*x*	*y*	*z*
Mo	−0.08279 (3)	0.25071 (2)	0.29505 (3)
Ni	0.10762 (6)	0.13029 (3)	0.29590 (5)
O(1)	0.0660 (4)	0.1797 (2)	0.5261 (3)
O(2)	−0.2903 (4)	0.0928 (2)	0.2915 (4)
C(1)	0.0359 (4)	0.1899 (2)	0.4265 (4)
C(2)	−0.2116 (5)	0.1497 (3)	0.2922 (4)
C(3)	0.1343 (4)	0.2365 (2)	0.2221 (3)
C(4)	0.2752 (5)	0.2832 (3)	0.2523 (5)
C(5)	0.0369 (5)	0.2583 (3)	0.1265 (3)
C(6)	0.0509 (8)	0.3391 (4)	0.0578 (5)
C(7)	−0.0882 (5)	0.2070 (3)	0.1024 (4)
C(8)	0.0666 (7)	0.0033 (3)	0.2144 (6)
C(9)	0.1953 (8)	0.0412 (3)	0.1796 (6)
C(10)	0.2908 (7)	0.0546 (4)	0.2791 (8)
C(11)	0.2215 (8)	0.0270 (3)	0.3739 (6)
C(12)	0.0805 (7)	−0.0023 (3)	0.3331 (6)
C(13)	−0.0692 (5)	0.3661 (3)	0.4221 (4)
C(14)	−0.2030 (5)	0.3219 (3)	0.4329 (4)
C(15)	−0.2894 (5)	0.3291 (3)	0.3273 (5)
C(16)	−0.2107 (6)	0.3761 (3)	0.2511 (5)
C(17)	−0.0747 (6)	0.3985 (3)	0.3099 (4)
C(18)	0.0485 (7)	0.3835 (4)	0.5168 (6)

Table IX. Selected Bond Distances (Å) for 5a

Mo–Ni	2.577 (2)	Mo–C(1)	2.040 (4)
Mo–C(2)	1.982 (4)	Mo–C(3)	2.216 (4)
Mo–C(5)	2.304 (4)	Mo–C(7)	2.329 (5)
Mo–C(13)	2.342 (7)	Mo–C(14)	2.294 (4)
Mo–C(15)	2.307 (5)	Mo–C(16)	2.339 (5)
Mo–C(17)	2.348 (5)	Ni–C(1)	1.935 (4)
Ni–C(3)	1.910 (4)	Ni–C(8)	2.241 (5)
Ni–C(9)	2.143 (6)	Ni–C(10)	2.074 (6)
Ni–C(11)	2.104 (5)	Ni–C(12)	2.161 (5)
O(1)–C(1)	1.175 (5)	O(2)–C(2)	1.139 (5)
C(3)–C(4)	1.500 (6)	C(3)–C(5)	1.408 (6)
C(5)–C(6)	1.516 (7)	C(5)–C(7)	1.410 (6)
C(13)–C(18)	1.499 (6)		
C(Cp)–C(Cp)	1.393 (av)	C(Cp′)–C(Cp′)	1.405 (av)

Table X. Selected Bond Angles (deg) for 5a

Ni–Mo–C(1)	47.8 (1)	Ni–Mo–C(2)	78.4 (1)
Ni–Mo–C(3)	46.2 (1)	Ni–Mo–C(5)	71.5 (1)
Ni–Mo–C(7)	75.6 (1)	C(1)–Mo–C(2)	84.9 (2)
C(1)–Mo–C(3)	78.3 (2)	C(1)–Mo–C(5)	113.4 (2)
C(1)–Mo–C(7)	123.0 (2)	C(2)–Mo–C(3)	117.0 (2)
C(2)–Mo–C(5)	110.1 (2)	C(2)–Mo–C(7)	76.9 (2)
C(3)–Mo–C(5)	36.2 (1)	C(3)–Mo–C(7)	64.1 (2)
Mo–Ni–C(1)	51.4 (1)	Mo–Ni–C(3)	56.9 (1)
C(1)–Ni–C(3)	88.8 (2)	Mo–C(1)–Ni	80.8 (2)
Mo–C(1)–O(1)	150.2 (3)	Ni–C(1)–O(1)	129.0 (3)
Mo–C(2)–O(2)	177.2 (4)	Mo–C(3)–Ni	76.9 (1)
Mo–C(3)–C(4)	129.2 (3)	Mo–C(3)–C(5)	75.3 (2)
Ni–C(3)–C(4)	117.7 (3)	Ni–C(3)–C(5)	118.3 (3)
C(4)–C(3)–C(5)	122.7 (4)	Mo–C(5)–C(3)	68.5 (2)
Mo–C(5)–C(6)	123.4 (3)	Mo–C(5)–C(7)	73.2 (3)
C(3)–C(5)–C(6)	123.1 (4)	C(3)–C(5)–C(7)	117.8 (4)
C(6)–C(5)–C(7)	118.8 (5)	Mo–C(7)–C(5)	71.3 (2)

(ii) X-ray Diffraction Study of NiMo(μ_2-CO)(CO){μ-η^1,η^3-C(Me)–C(Me)–CH$_2$}(η^5-C_5H_5)(η^5-C_5H_4Me) (Ni–Mo) (5a). Crystals of **5a** were grown from a saturated hexane solution. Crystal and data collection parameters, atomic positional parameters, and bond length and angles are collected in Tables IV and VIII–X. An ORTEP diagram of **5a** is depicted in Figure 3.

5a consists of a (η^5-C_5H_5)Ni–Mo(CO)(η^5-C_5H_4Me) unit spanned by a carbonyl group and a C(Me)–C(Me)–CH$_2$ hydrocarbyl ligand. The organic chain is σ-bonded to the nickel atom via the terminal C(Me) carbon atom and η^3-coordinated in a π-allylic fashion to the molybdenum. The Ni–Mo bond of 2.577 (2) Å is within the spread observed for single nickel–molybdenum bonds.[3]

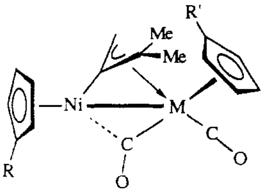
There are various electronically equivalent ways to bond the C(Me)-C(Me)-CH_2 group to two metals: depending on the mode of coordination, complexes incorporating this organic moiety can be considered to be methyl(1-methylvinyl)carbene complexes (with the organic chain represented as C(Me)—C(Me)=CH_2), π-coordinated dimetallacyclopentene species, or 1-metal substituted η^3-1,1-dimethylallyl compounds. **5a** is best described as containing a η^3-(3-nickel)-1,2-dimethylallyl group, on the basis of the geometry of the molecule (in particular the coplanarity of all the heavy atoms in the Ni-C(Me)-C-(Me)-CH_2 fragment). The identical C(3)-C(5) and C-(5)-C(7) bond lengths [1.408 (6) and 1.410 (6) Å, respectively] lend credence to this argument.

The Mo-C(allyl) bonds in **5a** are significantly different from each other, ranging from 2.216 (4) [Mo-C(3)] to 2.304 (4) and 2.329 (5) Å [Mo-C(5), Mo-C(7), respectively]. These values are unexceptional, as wide variations in Mo-C bond lengths have been observed in other species that contain unhindered allyl groups.[16] Steric constraints imposed by anchoring the allyl group to the nickel atom probably play as large a role as electronic factors in affecting the Mo-C bonds in **5a**.

(iii) Reaction of 1,1-Dimethylallene with (η^5-C_5H_4Me)(CO)Ni-Mo$(CO)_3$(η^5-C_5H_5) (1a′) and (η^5-C_5H_5)(CO)Ni-W$(CO)_3$(η^5-C_5H_4Me) (1b). 1,1-Dimethylallene reacts with **1a′** and **1b**, mirroring the behavior of **1a**, to afford **4a′** and **4b**, respectively. ^1H NMR data suggest that these species are analogous to **4a**: pertinent chemical shifts for all species are similar (Table I). A CH*H* proton signal in **4b** exhibits tungsten-183 coupling (J_{WH} = 4.82 Hz).

Complexes **4a′** and **4b** are isomerized on silica gel, affording the compounds (η^5-C_5H_4Me)Ni{μ-η^1,η^3-C(Me)-C-(Me)-CH_2}(μ_2-CO)Mo(CO)(η^5-C_5H_5) (Ni-Mo) (**5a′**) and (η^5-C_5H_5)Ni{μ-η^1,η^3-C(Me)-C(Me)-CH_2}(μ_2-CO)W-(CO)(η^5-C_5H_4Me) (Ni-W) (**5b**), respectively. Spectroscopic data indicate that these species are isostructural with **5a**. Furthermore, one of the C(Me)-C(Me)-CH_2 methyl groups of **5b** exhibits a small ^{183}W-^1H coupling (J_{WH} = 3.35 Hz). Minor quantities of a complex (**6b**) were also isolated following the silica gel chromatography of **4b**.

(iv) Structures of Complexes 4a, 4a′, and 4b and of Compounds 6 and 6b. When we communicated the transformation of **4a** to **5a**,[9] we formulated **4a** as a μ-η^2,η^2-1,1-dimethylallene species. We now believe that this was incorrect. Data suggest that **4a** is best represented as (η^5-C_5H_5)Ni{μ-η^1,η^3-C(CMe_2)(CH_2)}Mo$(CO)_2$(η^5-C_5H_4Me) (Ni-Mo), in which a (2-nickel)allyl group η^3-coordinated to the group 6 metal and a nickel-group 6 metal bond are present.[24] The complexes (η^5-C_5H_4Me)Ni{μ-η^1,η^3-C-(CMe_2)(CH_2)}Mo$(CO)_2$(η^5-C_5H_5) (Ni-Mo) (**4a′**) and (η^5-C_5H_5)Ni{μ-η^1,η^3-C(CMe_2)(CH_2)}W$(CO)_2$(η^5-C_5H_4Me) (Ni-W) (**4b**) have similar structures. Our rationale for reassigning them is described here.



4a: M = Mo; R = H, R′ = Me

4a′: M = Mo; R = Me, R′ = H

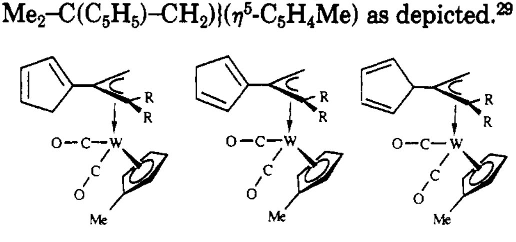
4b: M = W; R = H, R′ = Me

Allene, 1-methylallene, and 1,3-dimethylallene all react with $[Mo(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (Mo≡Mo), affording the μ-η^2,η^2-allene species $Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}CHR{=}C{=}CHR)(\eta^5\text{-}C_5H_5)_2$[7] (R = H and/or Me). The dinickel compound $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ also combines with allene, affording complex **2**, which contains π-allylic groups. 1,1-Dimethylallene does not react with either of these dimolybdenum or dinickel complexes. These results suggest that a CMe_2=C group π-complexed to either a nickel or a molybdenum atom is unlikely in **4a**.

More evidence that **4a** should not be formulated as a η^2,η^2-1,1-dimethylallene species stems from a comparison of ^1H NMR spectroscopic data of the bridging organic groups in **4a**, **4a′**, and **4b** with those of allene ligands in other π-η^2,η^2-allene complexes. Significant ^1H-^1H coupling is seen between CH_2 protons of coordinated ligands in the latter species ($^2J_{HH} \approx$ 2-5 Hz).[25-27] In contrast, minimal geminal coupling (unresolved, $J_{H\text{-}H}$ < 0.5 Hz) is noted in **4a**, **4a′**, and **4b** and resonances for the two chemically distinct CH_2 protons appear as singlets in ^1H NMR spectra of each complex. This small $^2J_{HH}$ coupling is characterized of coordinated π-allylic CH_2 protons, where values of 0-2 Hz (typically ≤1 Hz) are observed.[28] In complexes **2** and **3**, there is no resolvable ^1H-^1H coupling between the allylic protons, and even in the constrained species **5a**, **5a′**, and **5b**, values observed for $^2J_{HH}$ are only 1.5, 1.4, and <0.5 Hz, respectively.

Finally, the structures of compounds **6** and **6b** corroborate those proposed for **4**. Complex **6b** is a yellow oil formed from the slow ambient temperature decomposition of **4b**; **6** is isostructural, with physical and spectroscopic properties similar to those of **6b**, and was isolated from the reaction of allene with **1b**. Each compound shows two ν(CO) IR bands in solution. Complex **6b** was best characterized, and its spectroscopic data are presented.

The MS of **6b** shows a parent ion with an isotopic envelope characteristic of a compound that contains a single tungsten atom. The ^1H NMR data for **6b** are intricate: though the spectrum is broad, it suggests that two (or more) compounds are present. The more informative ^{13}C NMR spectrum indicates the presence of three species. Four sets of three signals (all in an approximate 2:1:0.4 ratio) are exhibited in the chemical shift range of noncoordinated olefinic carbon atoms. Three sets of resonances (in the same ratio) are assigned to three η^5-C_5H_4Me groups and to three allylic groups. Data are consistent with **6b** being a mixture of the 2-substituted 1,3-, 1,4-, *and* 2,4-cyclopentadienyl-1,1-dimethylallyl isomers of $W(CO)_2$-{η^3-(CMe_2-C(C_5H_5)-CH_2)}(η^5-C_5H_4Me) as depicted.[29] The



1,3 – Isomer 1,4 – Isomer 2,4 – Isomer

6 : R = H
6b: R = Me

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(24) Bridging 2-metalloallyl species have been noted in some iron complexes: (a) Ben Shoshan, R.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1968**, 247. (b) Davis, R. E. *J. Chem. Soc., Chem. Commun.* **1968**, 248.

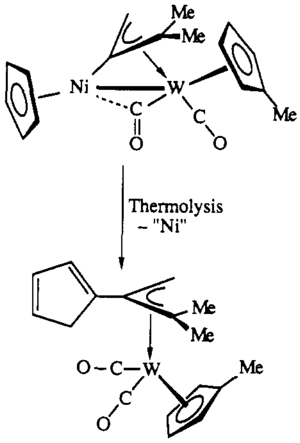
(25) Geminal ^1H-^1H coupling constants of 2.6, 4.7, and 2.4 Hz, respectively, are observed in the complexes $Mn_2(CO)_8(\mu\text{-}\eta^2,\eta^2\text{-}CH_2{=}C{=}CH_2)$,[13] $Mn_2(CO)_8(\mu\text{-}\eta^2,\eta^2\text{-}CMe_2{=}C{=}CH_2)$,[26] and $Mo_2(CO)_4\{\mu\text{-}\eta^2,\eta^2\text{-}CH_2{=}C{=}CH(OMe)\}(\eta^5\text{-}C_5H_4Me)_2$.[7] The smallest ^1H-^1H coupling seen in the complex $Fe_2(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}CH_2{=}C{=}CH_2)(\eta^5\text{-}C_5H_5)_2$[27] is 2.4 Hz.

(26) Kreiter, C. G.; Leyendecker, M.; Sheldrick, W. S. *J. Organomet. Chem.* **1986**, *302*, 217.

(27) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1986**, *5*, 585.

(28) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 177.

Scheme I. Reductive Elimination of a Nickel Atom from 4b To Afford 6b with Only One of the Cyclopentadienyl Isomers of 6b Being Shown

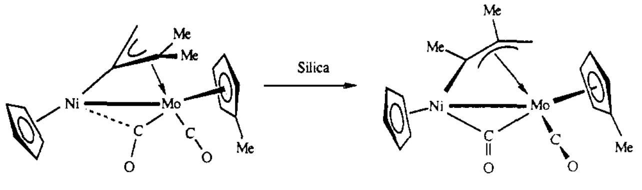


isomeric ratio is time-invariant, which implies that the isomers are in dynamic equilibrium.[30] **6** is believed to be an equivalent mixture of 1,3- and 1,4- and 2,4-cyclopentadienyl isomers of the allene-derived species W(CO)$_2${η^3-(CH$_2$-C(C$_5$H$_5$)-CH$_2$)}(η^5-C$_5$H$_4$Me). For both **6** and **6b**, the 2,4-cyclopentadienyl isomer (the least abundant isomer in each case) is not evident in ^{1}H NMR spectra—its signals are too weak or overlap those of the other more plentiful species.

When complex **4a** is heated in hexane, an isomeric mixture (**6a**), that builds up slowly over a 10-day period, appears to be the molybdenum analogues of **6b**.[31] These isomers are formed in small quantities when **1a** is reacted with 1,1-dimethylallene. Reductive cleavage of the nickel-(η^5-C$_5$H$_5$) and nickel-{η^3-C(CMe$_2$)(CH$_2$)} bonds in **4a**, followed by elimination of a nickel atom and formation of a C$_5$H$_5$-C(CMe$_2$)(CH$_2$) bond, would afford Mo(CO)$_2${η^3-(CMe$_2$-C(C$_5$H$_5$)-CH$_2$)}(η^5-C$_5$H$_4$Me) (**6a**). This thermolysis is more easily envisaged if complex **4a** contains η^3-allyl-molybdenum groups rather than η^3-allyl-nickel moieties. **6b** may similarly form from reductive elimination of a nickel atom from NiW(CO)$_2${μ-η^1,η^3-C(CMe$_2$)(CH$_2$)}(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (**4b**) in similar fashion (Scheme I). A parallel mechanism may account for the formation of **6**, though in this case the allene complex akin to **4b** has not been characterized or observed.[32]

On balance, the data suggest that, rather than η^2,η^2-1,1-dimethylallene ligands, **4a**, **4a′**, and **4b** contain 2-nickel-substituted μ-η^1,η^3-C(CMe$_2$)(CH$_2$) allylic groups as shown, resulting from oxidative addition of 1,1-dimethylallene to the dimetal system. The semibridging carbonyl ligand compensates for the formally 17-electron nickel atom. An alternative formulation with a group 6 substituted μ-η^1,η^3-C(CMe$_2$)(CH$_2$) ligand η^1-ligated to the group 6 metal at the C(2) carbon and η^3-coordinated to the nickel atom (with a dative M→Ni bond) is electronically feasible, but the proposed structure better fits the data. Minimal ^{183}W-^{13}C coupling (J_{WC} = 7 Hz) is observed to the central allylic carbon atom in the ^{13}C NMR spectrum of **4b**, similar to that noted for a tungsten-carbon π-interaction (J_{WC} = 9 Hz for the allylic CH$_2$ carbon atom in **5b**). A sizable coupling would be expected for a molecule that contains a tungsten-carbon σ-bond.[33]

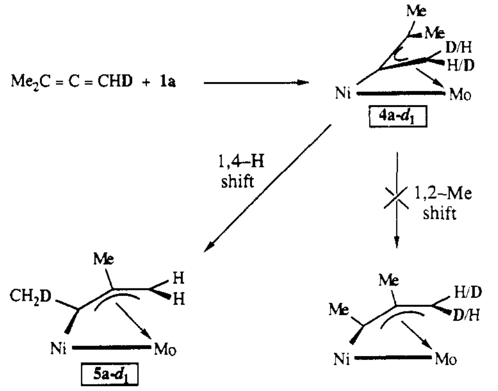
Scheme II. Isomerization of 4a to 5a on Silica Gel



4a

5a

Scheme III. Reaction of 1a with Me$_2$C=C=CHD To Afford 4a-*d*$_1$ and the Subsequent Transformation of 4a-*d*$_1$ on Silica Gel To Form 5a-*d*$_1$ with the Product Obtained Indicating That an Effective 1,4-Proton Shift Is Operative [Ni = Ni(η^5-C$_5$H$_5$); Mo = Mo(CO)$_2$(η^5-C$_5$H$_4$Me)]



(v) Mechanistic Pointers of the Rearrangement of 4a to 5a. The atoms in 1,1-dimethylallene have undergone a change in their connectivity in going from the free diene to **4a** and finally to **5a**, as shown in Scheme II. As the C-C and C-H bonds present in the free diene appear to be maintained in **4a**, a structural rearrangement takes place in the **4a**/**5a** isomerization. A 1,2-methyl group migration can account for the CMe$_2$-C-CH$_2$ to C(Me)-C(Me)-CH$_2$ ligand transformation. The nickel atom *does not* remain bonded to the same carbon atom in this process.

An *effective* 1,4-proton shift, from one of the methyl groups to the CH$_2$ carbon atom, also can lead to the final product **5a**, and indeed, acid-base proton-transfer chemistry is not unprecedented on silica. In this latter mechanism, the nickel atom remains σ-coordinated to the same carbon atom during the conversion of **4a** to **5a**. A labeling study using 1,1-dimethylallene-*3*-*d*$_1$ was undertaken to distinguish between these two pathways.

1,1-Dimethylallene-*3*-*d*$_1$ reacts with **1a** affording **4a**-*d*$_1$. This species exists as a mixture of isotopomers, in which

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(29) The related pentamethylcyclopentadienyl species W(CO)$_2${η^3-(CH$_2$-C(C$_5$Me$_5$)-CH$_2$)}(η^5-C$_5$H$_4$Me) was characterized from the reaction of (η^5-C$_5$Me$_5$)Ni-W(CO)$_3$(η^5-C$_5$H$_4$Me) with allene. This compound displays a far simpler ^{1}H NMR spectrum than **6b**: a mirror plane of symmetry is present and there is no cyclopentadiene H-H coupling here. In addition, no sigmatropic shifts are operative and only one isomer—the 2-allyl-substituted 1,2,3,4,5-pentamethylcyclopentadienyl species—exists. The unambiguous characterization of this species helped us elucidate the structures of both **6b** and **6b′**: Chetcuti, M. J.; Grant, B. G. Manuscript in preparation.

(30) The isomers probably interconvert via 1,5-sigmatropic shifts: Ashe, A. J., III. *J. Am. Chem. Soc.* **1970**, *93*, 1233.

(31) This species is not definitively characterized: its ^{1}H and ^{13}C NMR spectra are complicated. Data suggest that **6a** consists of six closely related and interconverting isomers. These may be a mixture of *endo*- and *exo*-allyl rotamers of the 1,3-, 1,4-, and 2,4-cyclopentadienyl isomers of Mo(CO)$_2${η^3-(CMe$_2$-C(C$_5$H$_5$)-CH$_2$)}(η^5-C$_5$H$_4$Me). Only two (slightly broad) ν(CO) bands are observed in the IR spectrum of **6a**.

(32) It is noteworthy that, in addition to ions corresponding to the expected loss of CO and other ligands, ions with *m*/*e* ratios that correspond to the loss of a single nickel atom are also seen in MS of **4a**, **4a′**, and **4b**.

(33) For a series of μ-η^1,η^2-alkenyl species in which the alkenyl carbon atom is σ-bonded to a tungsten atom, J_{WC} = 73-79 Hz.[5] For the ^{13}C NMR spectrum of a Ni-(μ-CH$_2$)-W species, J_{WC} = 38 Hz for the CH$_2$ group: Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345.

the deuterium atom is statistically distributed between the syn and anti positions of the π-1,1-dimethylallyl ligand. Complex **4a**-d_1 generated the monodeuterated species **5a**-d_1 when passed through a silica gel column.

A 1,2-methyl group migration would retain the CHD group present in the two isomers of **4a**-d_1 in the final product **5a**-d_1. This species would consist of an isomeric mixture in which the deuterium atoms are in syn and anti geometries relative to the central methyl group. In contrast, an effective 1,4-proton shift would afford a *single* isomer incorporating CH_2D and CH_2 groups (Scheme III). These outcomes are readily differentiated by NMR spectroscopy. The ^1H NMR spectrum of **5a**-d_1 showed that a single isomer had formed. A multiplet centered at 2.13 ppm and integrating to two protons had replaced the methyl group at δ 2.15 ppm present in **5a**. This is consistent with a CH_2D group in **5a**-d_1 and indicates that an effective 1,4-proton shift rather than a 1,2-methyl migration is operative.[34]

Isomerizations of metal-ligated hydrocarbyl groups on silica surfaces have been previously reported.[35,36] The effective 1,4-proton migration observed here probably occurs via an acid–base reaction. Further experiments support this. Complex **4a** is inert to base: no reaction was observed with sodium methoxide or trimethylamine. Intractable products resulted with strong acids such as trifluoroacetic acid, and **4a** was inert to a methanolic ammonium chloride solution. A solution of acetic acid in methanol slowly induced the isomerization reaction. This suggests that the first step in the rearrangement of the $Me_2C{=}C{=}CH_2$ ligand is protonation and not deprotonation, as expected on an acidic silica medium. Stirring a solution of **4a** with a suspension of silica gel also converts **4a** to **5a** in high yield.

When **4a** was reacted with a methanol-d_1 solution of acetic acid-d_1, the compound formed was **5a**-d_1. Moreover, when **4a**-d_1 was treated with methanolic acetic acid, the product was also **5a**-d_1. These experiments confirm that the rearrangement occurs by a proton-transfer mechanism and not a methyl group migration. The proton-transfer reaction here is intermolecular and not intramolecular, and this is also likely to be the case on a silica surface.

(d) Other Reactions. The transformation of **4a**/**4b** to **5a**/**5b**, respectively, appears to be irreversible. The protonation of **5a** or **5b** with trifluoroacetic acid did not lead to isolable cationic species. Similarly, treatment of these compounds with $HBF_4{\cdot}Et_2O$ resulted in decomposition and intractable products. The complexes yield messy oils when treated with strong bases, and we were unable to isolate pure materials from these reactions. Finally, **5a** is inert to trimethylphosphine. This suggests that the formulation of **5a** as a metalloallyl species appears to be correct as regards both its structure and its reactivity. Trimethylphosphine might displace the coordinated olefin if the hydrocarbyl ligand in **5a** had substantial μ-C(Me){C(Me)=CH_2} (vinylcarbene) character.

In contrast to cumulated dienes, **1a** and **1b** were unreactive toward the few other dienes we attempted. Paramagnetic clusters resulted when these compounds were treated with 1,5-cyclooctadiene, but the diene only functioned as a thermolysis solvent and the clusters were diene free.[37] Isoprene did not react with **1a**; the heterobimetallic complex was recovered unchanged.

(e) General Comments. In all the experiments reported here, the products that stem from the reactions of Ni–Ni, Ni–Mo, or Ni–W metal–metal-bonded species with the allene and 1,1-dimethylallene are substituted dinuclear π-allyl complexes; there is a pronounced tendency for the cumulated dienes to isomerize to (formally negatively charged) π-allylic ligands on ligation to these species. Most of the discussed reactions can be viewed as formal oxidative additions of the allene ligands to the dimetal centers—coordinated η^2,η^2-allene complexes are not formed. Each metal undergoes a formal *single* increase in oxidation state [Ni(I) → Ni(II); Mo(I)/W(I) → Mo(II)/W(II)].

The high electron density at the nickel center may provide some of the driving force for these reactions. When Ni–Mo and Ni–W systems are treated with 1,1-dimethylallene, the hydrocarbyl ligand formed is η^3-coordinated to the group 6 metal and η^1-linked to the nickel atom. The organic moiety acts as a formal 3-electron donor to the group 6 metal and as a 1-electron donor to the nickel atom rather than vice versa. The observation that the allene ligands always react or couple at the central carbon atom of the cumulated diene suggests that radicals may trigger these reactions.[8]

The chemistry of the Ni–Ni species $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ toward allenes is clearly different from that of the group 6–group 10 heterodinuclear complexes, though π-allyl complexes are obtained in each case. Reactions of the mixed-metal species contrast even more drastically with those exhibited by Mo–Mo compounds toward cumulated dienes and furnish another definitive example of novel reaction pathways that are exhibited by mixed-metal complexes.

Conclusions

The reaction of allene and 1,1-dimethylallene with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni) and with the heterodinuclear complexes $(\eta^5\text{-}C_5H_4R)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4R')$ (R = H, Me; R′ = H, Me; M = Mo, W) have been probed. The dinickel complex only reacts with allene, affording the 2,2′-bis(π-allyl) compound $Ni_2(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)_2$. No mixed-metal species was isolated from reactions of the nickel–tungsten complex $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ with allene, but the compound $NiMo(CO)_2(\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12})(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)$, which contains a trimerized allene moiety and no metal–metal bond, was obtained in moderate yields when allene was reacted with $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$. The complexes $(\eta^5\text{-}C_5H_4R)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4R')$ (R = H, Me; R′ = Me, H; M = Mo, W) react with 1,1-dimethylallene to afford the (2-nickel)-substituted π-allyl complexes $(\eta^5\text{-}C_5H_4R)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}M(CO)_2(\eta^5\text{-}C_5H_4R')$ (Ni–M) and not the $\mu\text{-}\eta^2,\eta^2\text{-}Me_2C{=}C{=}CH_2$ species previously formulated. These species isomerize to $(\eta^5\text{-}C_5H_4R)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\mu_2\text{-}CO)M(CO)(\eta^5\text{-}C_5H_4R')$ (Ni–M), respectively, when subjected to silica gel chromatography. A deuterium labeling study, using $Me_2C{=}C{=}CHD$, indicates that the conversion of $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$ to $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\mu_2\text{-}CO)Mo(CO)(\eta^5\text{-}C_5H_4Me)$ proceeds via an effective 1,4-hydrogen shift rather than a 1,2-methyl migration.

Experimental Section

(a) General Remarks. All manipulations were carried out by using Schlenk or vacuum-line techniques under a nitrogen atmosphere. Solvents were predried over 4-Å molecular sieves and were distilled over sodium (toluene), sodium benzophenone

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[34] The conclusions of this deuteration labeling experiment also hold if the structure of **4a** contains a $\mu\text{-}\eta^2,\eta^2\text{-}Me_2C{=}C{=}CH_2$ ligand, as originally proposed.[9]

[35] Eisenstadt, A.; Efraty, A. *Organometallics* **1982**, *1*, 1100.

[36] Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164.

[37] Chetcuti, M. J.; Huffman, J. C.; McDonald, S. R. *Inorg. Chem.* **1989**, *28*, 238.

ketyl (diethyl ether and hexanes), or CaH_2 (dichloromethane). Trifluoroacetic acid, $LiAlD_4$, methanol-d_1, and acetic acid-d_1 (99+%) were used as received from Aldrich. Syntheses of **1a**, **1a′**, and **1b** have been described.[3]

NMR spectra were obtained on a Magnachem A-200, General Electric NT-300, or General Electric GN-300 spectrometer at 20 °C in chloroform-d_1 unless otherwise stated. $Cr(acac)_3$ (0.01–0.05 M) was used for the ^{13}C NMR spectra as a shiftless relaxation reagent. IR spectra were recorded on an IBM IR-32 FT instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Mass spectra were obtained on a Finnegan-Matt instrument in the EI or CI mode. All parent ions show the appropriate isotopomer pattern for that species. Complexes **2** and **3** are moderately soluble in hexanes; all compounds **4** and **5** are sparingly soluble, while complexes **6** are very soluble in this solvent. All species are soluble in toluene, ether, chloroform, and dichloromethane.

(b) Synthetic Data. (i) Reaction of Allene with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni) To Afford $Ni_2(\mu\text{-}\eta^3,\eta^3\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)_2$ (2). $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (304 mg, 1.0 mmol) was dissolved in hexanes (40 mL) in a Schlenk tube, and the solution was frozen in a liquid-nitrogen bath. The tube was evacuated and warmed to ambient temperature and allene was introduced. The solution was stirred for 1 week, concentrated, and then subjected to silica gel chromatography. **2** and $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ eluted as one red band. Careful fractional crystallization afforded small quantities (8 mg, 2%) of **2**. Poor yields reflect low conversions of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ to **2**, as the bulk of the recovered material was unreacted $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$. ^1H NMR data matched reported values.[10] EIMS: m/e 326 (M^+). CIMS (isobutane): m/e 383 $[(M + C_4H_9)]$, 327 $[(M + H)^+]$, 326 (M^+).

(ii) Reaction of 1,1-Dimethylallene with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (Ni–Ni). $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (303 mg, 1.0 mmol) was stirred with 1,1-dimethylallene (0.1 mL, ≈5 mmol) for 1 week, after which IR absorptions assignable to the ligand were no longer present. Additional 1,1-dimethylallene (0.1 mL, ≈5 mmol) was added and the reaction stirred for a further 20 days. The only metallic species isolated and characterized after chromatography were traces of $Ni(\eta^5\text{-}C_5H_5)_2$, and the complexes $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ and $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$.

(iii) Reaction of Allene with $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1a) To Form $NiMo(CO)_2\{\mu\text{-}\eta^3,\eta^3\text{-}C_9H_{12}\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (3). **1a** (411 mg, 1.0 mmol) was dissolved in hexanes (20 mL) in a Schlenk tube, and the solution was frozen in a liquid-nitrogen bath. The mixture was evacuated, warmed to ambient temperature, and charged with allene (≈7 mmol) and stirred magnetically. A noticeable color change (green to red-brown) was evident after 3 h, but the reaction was allowed to proceed for a total of 18 h. The solution was concentrated. Chromatography on alumina, using hexanes as the eluting solvent, afforded traces of yellow and red bands and a major brown band, which was eluted with a hexanes/ether mixture (20:1). Crystallization yielded orange brown crystals of **3** (85 mg, 18%). ^1H NMR: δ 5.35 and 5.29 (m, br, 2 H, AB spin system, $C{=}CH_2$), 5.31 (5 H, C_5H_5), 5.15 and 5.09 (m, 4 H, AA′BB′ spin system, C_5H_4Me), 2.93 (2 H, CH*H*, syn), 2.90 (2 H, CH*H*, syn), 2.61 (2 H, C*H*H, anti), 1.88 (3 H, C_5H_4Me), 1.76 (2 H, C*H*H, anti), 1.16 ppm (2 H, $C\text{–}CH_2\text{–}C$). $^{13}C\{^1H\}$ NMR (assigned from ^1H-coupled spectrum): δ 241.0 (*C*O), 150.2 ($C{=}CH_2$), 111.7 ($C{=}CH_2$), 108.4 [C(1), C_5H_4Me], 106.63 $[C(CH_2)_2]$, 106.60 $[C(CH_2)_2]$, 92.1 (2 C, C_5H_4Me), 89.1 (C_5H_5), 87.4 (2 C, C_5H_4Me), 42.4 ($C\text{–}CH_2\text{–}C$), 41.9 (2 C, CH_2), 37.2 (2 C, CH_2), 14.1 ppm (C_5H_4Me). EIMS: m/e 476 (M^+), 448 $[(M - CO)^+]$, 420 $[(M - 2CO)^+]$ and 418 (envelopes overlap). CIMS: m/e 533 $[(M + C_4H_9)^+]$. Anal. Calcd for $C_{22}H_{24}MoNiO_2$: C, 55.62; H, 5.09. Found: C, 55.46; H, 5.16.

(iv) Reaction of Allene with $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (1b). Under conditions similar to those employed for **1a**, no heterodinuclear products analogous to **3** could be isolated from the reactions of **1b** with allene. However, variable amounts of a yellow oil that contained $W(CO)_2\{\eta^3\text{-}(CH_2\text{–}C(C_5H_5)\text{–}CH_2)\}(\eta^5\text{-}C_5H_4Me)$ (**6**) were isolated in ≤5% yields. Spectroscopic data for isomers **6** (assignments are tentative owing to the spectra's complexity, the limited sample quantity, and similar (or overlapping) chemical shift resonances for the isomers) are as follows. ^1H NMR (acetone-d_6, ppm): δ 6.45–6.36, 6.17–6.14, and 6.08–6.04 (br m, $CH{=}$), 5.48, 5.34, and 5.27–5.29 (br m, C_5H_4Me *and* $CH{=}$), 3.30 and 3.17 (br m, aliphatic CH_2, minor isomer), 3.14 and 2.84 (br m, aliphatic CH_2, major), 3.06 (br m, C*H*H syn, both isomers), 2.80 (br m, C*H*H anti, both isomers), 1.63 (Me, major), 1.58 (Me, minor). ^{13}C NMR (chloroform-d_1): δ 230.1, 229.6, 228.9 (CO's in a 2.0:0.4:1 ratio), 147.1, 146.7, 145.8, 145.6, 145.3, 136.5, 133.5, 131.8, 131.7, 131.6, 131.3, 130.4, 125.9, 124.7, 123.7 (olefinic C's), 109.0, 107.2, 107.0, 106.8, 106.6, [C(1), C_5H_4Me, and C(2) allylic carbons), 95.7, 95.5, 95.4, 93.6 [aromatic C_5H_4Me's except C(1)], 90.5, 90.3, 90.0, 88.8, 84.84, 84.75, 84.6, 41.0, 40.7, 40.3 (CH_2, aliphatic), 27.5 (allyl CH_2, J_{WC} = 15.8), 27.3 (allyl CH_2, J_{WC} = 16.5), 14.2, 14.0 (Me). MS: m/e 424 (M^+), 396 $[(M - CO)^+]$, 368 $[(M - 2CO)^+]$, and 366 (envelopes overlap). HRMS (^{184}W): m/e 424.0655 ($C_{16}H_{16}WO_2$ requires m/e 424.0662).

(v) Reaction of 1,1-Dimethylallene with 1a To Afford $NiMo(CO)_2\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (Ni–Mo) (4a) and $NiMo(\mu_2\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (Ni–Mo) (5a). **1a** (500 mg, 1.2 mmol) and 1,1-dimethylallene (0.5 mL, ≈5.0 mmol) were dissolved in hexanes/toluene (1:1, 20 mL). The Schlenk tube was frozen in liquid nitrogen, evacuated, and warmed to ≈35 °C, and the solution was stirred for 2 days. Solvents were removed, the residue was dissolved in hexane, and the mixture filtered through a Celite pad. Crystallization of the brown solution (−20 °C) afforded dark brown crystals of **4a** (176 mg, 0.41 mmol). The mother liquor was subjected to silica gel chromatography: elution with a hexanes/ether mixture (20:1) followed by hexane crystallization yielded traces of a bright yellow band containing **6a** and a brown band from which **5a** (22 mg, 0.051 mmol) was crystallized. Combined yields (**4a** and **5a**): 195 mg (38%). Spectroscopic data for **4a** are as follows. MS: m/e 424 (M^+), 396 $[(M - CO)^+]$, 368 $[(M - 2CO)^+]$ and 366 (envelopes overlap), 300 $[(M - 2CO - Me_2C{=}C{=}CH_2)^+]$. HRMS ($^{60}Ni$, ^{100}Mo): m/e 427.984 ($C_{18}H_{20}MoNiO_2$ requires m/e 427.984). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 50.97; H, 4.87. Spectroscopic data for **5a** are as follows. MS: m/e 424 (M^+), 396 $[(M - CO)^+]$. HRMS (^{60}Ni, ^{100}Mo): m/e 427.9836 ($C_{18}H_{20}MoNiO_2$ requires m/e 427.984). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 51.14; H, 5.00. Despite a simple IR spectrum (Table III), the ^1H and ^{13}C NMR spectra of **6a** are extremely complex and uninterpretable. Certain resonances (e.g. two sets of three CO signals with very similar chemical shifts but different intensity ratios) suggested the presence of six isomers.

(vi) Reaction of 1,1-Dimethylallene with $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (1a′) To Afford $NiMo(CO)_2\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)$ (Ni–Mo) (4a′) and $NiMo(\mu_2\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\eta^5\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)$ (Ni–Mo) (5a′). This procedure mirrored that used to synthesize **4a** and **5a**. Combined yields (**4a′** and **5a′**): 29%. Spectroscopic data for **4a′** are as follows. MS: m/e 424 (M^+), 396 $[(M - CO)^+]$, 368 and 366 (envelopes overlap) $[(M - 2CO)^+$ and $(M - Ni)^+$, respectively], 300 $[(M - Me_2C{=}C{=}CH_2 - 2CO)^+]$. HRMS ($^{60}Ni$, ^{98}Mo): m/e 425.985 ($C_{18}H_{20}MoNiO_2$ requires m/e 425.983). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 51.36; H, 4.87. Spectroscopic data for **5a** are as follows. MS: m/e 424 (M^+), 396 $[(M - CO)^+]$, 368 $[(M - 2CO)^+]$ and 366 (envelopes overlap), 300 $[(M - 2CO - Me_2C{=}C{=}CH_2)^+]$. HRMS ($^{60}Ni$, ^{98}Mo): m/e 425.9850 ($C_{18}H_{20}MoNiO_2$ requires m/e 425.9825). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 50.90; H, 4.95.

(vii) Reaction of 1b with 1,1-Dimethylallene. Formation of $NiW(CO)_2\{\mu\text{-}\eta^1,\eta^3\text{-}C(CMe_2)(CH_2)\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (Ni–Mo) (4b), $NiW(\mu_2\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)\text{–}C(Me)\text{–}CH_2\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (Ni–W) (5b), and $W(CO)_2\{\eta^3\text{-}(CH_2\text{–}C(C_5H_5)\text{–}CMe_2)\}(\eta^5\text{-}C_5H_4Me)$ (6b). The syntheses and colors of **4b** and **5b** paralleled those of **4a** and **5a** (reactants were stirred for 1 day at 25 °C and not at 35 °C). Spectroscopic data for **4b** are as follows. MS: m/e 510 (M^+), 482 $[(M - CO)^+]$, 454 $[(M - 2CO)^+]$ and 452 (envelopes overlap), 386 $[(M - 2CO - Me_2C{=}C{=}CH_2)^+]$. HRMS ($^{58}Ni$, ^{184}W): m/e 510.0305 ($C_{18}H_{20}NiWO_2$ requires m/e 510.0312). Anal. Calcd for $C_{18}H_{20}NiWO_2$: C, 42.32; H, 3.95. Found: C, 42.28; H, 4.05. Spectroscopic data for **5b** are as follows. MS: m/e 510 (M^+), 482 $[(M - CO)^+]$, 454 $[(M - 2CO)^+]$ and 452 (envelopes overlap), 386 $[(M - 2CO - Me_2C{=}C{=}CH_2)^+]$. HRMS ($^{58}Ni$, ^{184}W): m/e 510.0310 ($C_{18}H_{20}NiWO_2$ requires m/e 510.0312). Anal. Calcd for $C_{18}H_{20}NiWO_2$: C, 42.32; H, 3.95. Found: C, 43.50; H, 4.41.

Spectroscopic data for **6b** are as follows. MS: *m/e* 452 (M$^+$), 424 [(M − CO)$^+$], 394, 379. HRMS (^{184}W): *m/e* 452.0972 ($C_{18}H_{20}WO_2$ requires *m/e* 452.0976). ^{1}H NMR (chloroform-d_1): 6.55–6.16 (m, C*H*=), 5.23–4.75 (m, CH= and C$_5$*H*$_4$Me), 3.36 and 3.23 (m, aliphatic C*H*$_2$, minor isomer), 3.17 and 3.15 (m, aliphatic C*H*$_2$, major), 2.83 (d, C*H*H syn, minor, J_{HH} = 4.3 Hz), 2.77 (d, C*H*H syn, minor, J_{HH} = 4.1 Hz), 2.17 (s, major, C$_5$H$_4$*Me*), 2.16 (minor, C$_5$H$_4$*Me*), 2.04 (br Me, minor, *and* C*H*H anti, both isomers), 1.96 (Me, major), 1.53 (Me, minor), 1.35 (s, Me, major).

(viii) Thermolysis of 4a To Afford Mo(CO)$_2${η^3-(CH$_2$–C(C$_5$H$_5$)–CMe$_2$)}(η^5-C$_5$H$_4$Me) (6a). Complex **4a** was heated in refluxing hexanes. The thermolysis was monitored by IR spectroscopy. After 14 days about two-thirds of **4a** had been converted to **6a**. In a separate experiment, the hexanes pyrolysis of **4a** for 21 days afforded **6a** as the only product with observable ν(CO) bands.

(ix) Synthesis of 4a-d_1 and 5a-d_1. 1,1-Dimethylallene-*3*-d_1 was prepared as reported in the literature:[38] no undeuterated material was observed by ^{1}H NMR spectroscopy. The diene was reacted with **1a** as outlined previously, and **4a**-d_1 was obtained by direct crystallization. Signal integration of the ^{1}H NMR spectrum indicated that there was no deuterium discrimination between the two methylene positions (0.5 H each) or loss of label. The mother liquor was subjected to silica gel chromatography, and the major band containing **5a**-d_1 was collected and crystallized from hexanes. Combined yields of **4a**-d_1 and **5a**-d_1: 33%. ^{1}H NMR data for **4a**-d_1: δ 4.21 (s, 0.5 H), 2.80 (s, 0.5 H) ppm (cf. 4.22 and 2.81 for **4a**). Other resonances are as for **4a**. ^{1}H NMR data for **5a**-d_1: spectrum as for **5a** except for a signal at δ 2.761 (1 H, d of t, $^2J_{HH}$ = 1.50 Hz, $^5J_{HH}$ = 0.71 Hz) and one at 2.133 (m, 2 H, C*H*$_2$D) that replaces the Me signal at δ 2.15 ppm.

(x) Conversion of 4a to 5a by Reaction with Methanolic Acetic Acid. **4a** (40 mg) was dissolved in methanol (8 mL), and acetic acid (≈100 mL) was added. The solution was stirred magnetically and monitored by IR spectroscopy. Significant quantities of **5a** had formed after a 2.5-h period, and after 18 h, **4a** was totally consumed. The presence of **5a** was confirmed by ^{1}H NMR spectroscopy.

(xi) Rearrangement of 4a to 5a with Silica Gel. Silica gel (1.00 g, 60 mesh) was added to a hexanes/ether solution (20 mL, 9:1) of **4a** (212 mg, 0.50 mmol). The suspension was stirred for 24 h, and the silica was filtered off. Concentration afforded crystals of **5a** (150 mg, 71%).

(xii) Reaction of 4a with Acetic Acid-d_1. **4a** (50 mg) was added under nitrogen to a freeze–thaw–degassed solution of acetic acid-d_1 (100 mg) in methanol-d_1 (9 mL). The solution was stirred for 36 h at ambient temperature till all IR bands assignable to **4a** had vanished. The mixture was pumped down to dryness, and residue was dissolved in hexanes/ether, and the mixture was passed through an alumina column. Crystallization and subsequent ^{1}H NMR spectroscopy revealed that >95% of the product was **5a**-d_1 with traces of **5a** also being present.

(xiii) Reaction of 4a-d_1 with Acetic Acid. **4a**-d_1 (50 mg) was added under nitrogen to a freeze–thaw–degassed solution of acetic acid (80 mg) in methanol (10 mL), which was allowed to stir for 18 h. The residue after solvent removal was extracted with hexanes and purified by passing the solution through a short alumina pad. Crystallization and subsequent ^{1}H NMR spectral analysis revealed that the product was, within NMR detection limits, pure **5a**-d_1.

(xiv) Attempted Reaction of 4a with PMe$_3$. PMe$_3$ (0.1 mL of a 1.3 M Et$_2$O solution, ≈0.13 mmol) was added to a solution of **4a** (30 mg, 0.071 mmol) in hexanes (10 mL). There were no changes in the solution IR spectra after 2 days. The solution was concentrated and deposited crystals that were shown to be **4a** by ^{1}H NMR spectroscopy.

(c) X-ray Diffraction Studies. (i) Structural Characterization of NiMo(CO)$_2${μ-η^3,η^3-C$_9$H$_{12}$}(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (3). An orange crystal of **3**, grown from hexanes solution, was mounted in a random orientation in a glass capillary tube on a CAD 4 Enraf-Nonius diffractometer. Refinement of 25 reflections in the range $21 \leq \theta \leq 23°$ led to the cell constants and an orientation matrix. The systematic absences *h*0*l*, *l* = 2*n*, and 0*k*0, *k* = 2*n*, indicated the space group $P2_1/n$. After a correction for Lorentz and polarization effects, an empirical absorption correction was applied.[39] The molybdenum atom was located from a Patterson map; other non-hydrogen atoms were located with DIRDIF and in succeeding difference Fourier syntheses. While hydrogen atoms were located and added to structure factor calculations, their positions were not refined. Anomalous dispersion effects[40] were included in F_c (values were of Cromer).[41] Calculations were performed on a VAX computer with SDP/VAX software.[42] Refinement converged at R = 0.035 and R_w = 0.045.

(ii) Structural Characterization of NiMo(μ_2-CO)(CO){μ-η^1,η^3-C(Me)–C(Me)–CH$_2$}(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (Ni–Mo) (5a). A brown crystal of **5a** was selected from a batch grown from hexanes solution and mounted on a CAD4 Enraf-Nonius diffractometer. Crystal and data collection parameters are tabulated in Table IV. Cell parameters were obtained from least-squares refinement of 25 reflections with $24 \leq \theta \leq 30°$. Four standard reflections were monitored every 60 min of X-ray exposure, but no intensity decay was observed. The solution of this structure was not straighforward: MULTAN-78 failed to lead to a solution of the structure and while the heavy metal atoms were located from a Patterson map, DIRDIF did not reveal any further motif. After further efforts the solution of this structure appeared doubtful (Indeed, **5a′** was synthesized to determine its structure instead). However the acquisition and utilization of the program SHELXS allowed the structure to be solved by using Patterson methods and subsequent Fourier syntheses. All hydrogen atoms were located and refined isotropically. No absorption correction was applied, but data were corrected for anomalous dispersion effects.[40,41] Refinement converged at R = 0.039 and R_w = 0.043.

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Supplementary Material Available: Full listings of bond distances, bond angles, anisotropic thermal parameters for nonhydrogen atoms, and positional parameters for hydrogen atoms for **3** and **5a** (14 pages); tables of structure factor amplitudes for **3** and **5a** (28 pages). Ordering information is given on any current masthead page.

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