The difference in Ti–C(η^7) and Ti–C(η^5) separations results in the Ti atom also fractionally disordered about the center of inversion. As a result, the Ti–C(η^7) distances are shorter as expected. Due to the proximity of the disordered carbon atoms, refinement of the rings was very poor. No hydrogen atoms were included. Final position parameters for **5** are given in Table IV.

Several diffuse peaks near a center of inversion were observed in a difference Fourier map for **6**. Analysis of these positions revealed a toluene molecule in four different positions (two related by the center of inversion). One position [C(41)] was common to both unique orientations and was given an occupancy of 0.5. Another position [C(50)] corresponded to an aryl carbon atom on one side of the inversion center and a methyl group on the other side and was also given an occupancy of 0.5. The remaining ten carbon atoms were given occupancies of 0.25. Due to the proximity of the carbon atom positions, the refinement was poor. In the final cycles, each group of six ring atoms was idealized and only the isotropic thermal parameters were allowed to refine. The hydrogen atoms (except for those associated with the toluene molecule) were included in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Final positional parameters for **6** are given in Table V.

Acknowledgment. We are grateful to Fina Oil and Chemical Co., Sekisui Chemical Co., and the donors to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research program. We also wish to thank Prof. Helmut Alt and Mr. Daniel Mallin for assistance in obtaining the mass and NMR spectra. The National Science Foundation Chemical Instrumentation Program provided funds used to purchase the diffractometer (N.I.U.).

Supplementary Material Available: Full tables of bond distances and angles, H atom coordinates, thermal parameters, and least-squares results (11 pages); listings of structure factors (9 pages). Ordering information is given on any current masthead page.

Protonation of Nickel–Molybdenum and Nickel–Tungsten Alkyne Complexes with Trifluoroacetic Acid Affording μ-η^1,η^2-Alkenyl Species: X-ray Structure of NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$)

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Protonation of the heterodinuclear bridging alkyne complexes NiM(CO)$_2$(μ-η^2,η^2-RC$_2$R′)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (M = Mo, RC$_2$R′ = MeC$_2$Me; M = W, RC$_2$R′ = HC$_2$H, MeC$_2$Me, *n*-PrC$_2$H, PhC$_2$H) with trifluoroacetic acid affords the neutral alkenyl complexes NiM(CO)$_2$(μ-η^1,η^2-(*E*)-CR=CHR′)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$), in which the alkenyl ligand is σ-bonded to the group 6 metal and π-bonded to the nickel atom. In some cases, the alkenyl complexes are in equilibrium with the alkyne species: the position of the equilibrium depends on the particular complex and on the solvent. Proton addition is regio- and stereospecific: isomers obtained result from Markovnikov addition to the alkyne. The nickel–tungsten isomer containing the alkenyl ligand μ-η^1,η^2-C(Ph)=CH$_2$, resulting from Markovnikov addition, can be thermally isomerized to the anti-Markovnikov isomer NiW(CO)$_2$(μ-η^1,η^2-(*E*)-CH=CHPh)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$). Deuteration of the nickel–tungsten ethyne, 1-pentyne, or phenylacetylene complexes with trifluoroacetic acid-d_1, afforded (*Z*)-alkenyl-d_1 species. However, the 2-butenylnickel–molybdenum complex exists as an equilibrium mixture of *E* and *Z* isomers, and the complex NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-C(Ph)=CHD)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) eventually afforded a mixture of *Z* and *E* isomers when allowed to stand in solution. The complexes have been characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and elemental analysis. An X-ray diffraction study was carried out on **2a**, NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$). Crystals of **2a** (C$_{19}$H$_{19}$F$_3$NiO$_4$W) belong to the monoclinic space group $P2_1/n$ (No. 14) with a = 8.3710 (7) Å, b = 27.609 (5) Å, c = 9.045 (1) Å, β = 109.210 (7)°, and Z = 4.

Introduction

We have been investigating the chemistry of the group 6–group 10 cyclopentadienyl–carbonyl complexes NiM(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) with reactive hydrocarbon ligands. The mixed-metal species react with alkynes affording the bridging alkyne complexes NiM(CO)$_2$(μ-η^2,η^2-RC$_2$R′)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (M = Mo, W).[1] Mechanistic details of these reactions have been reported.[2] The protonation of these alkyne complexes was of interest in order to establish whether this would be a viable route to mixed-metal alkenyl complexes.

Protonation of homodinuclear bridging alkyne complexes to afford μ-η^1,η^2-alkenyl species has been observed for dimolybdenum complexes,[3,4] and an uncommon in-

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Table I. ^{1}H NMR Data^a (ppm, in Acetone-d_6)

complex	C_5H_5	$C_5H_4Me^b$	C_5H_4Me	R(1)	R(2)	R(3)
1	5.13	5.42,^{c} 5.46^c	2.12	5.91^d	5.91^d	
3	5.10	5.38, 5.48 (3 H)	2.12	0.92,^{e} 1.45,^{f,h} 2.81,^{f,i} 3.05^{f,j}	6.06^{f,g}	
1a	5.35	4.83, 5.52, 5.83 (2 H)	1.92	8.24	5.07	3.55
2a	5.21	4.64, 4.68, 5.43, 5.78	1.89	1.52	2.48	4.08
2a′^{k}	5.02	5.29, 5.42, 5.54, 5.74	1.97	1.57	2.22	4.40
3a	5.31	4.56, 4.83, 5.69, 5,85	1.88	0.91,^{l} 1.23,^{f,m} 1.58,^{f,m} 1.82,^{f,n} 3.65^{f,o}	4.96	3.08
3b	5.27	4.77, 4.89, 5.41, 5.79	1.93	7.74	0.93,^{p} 1.08,^{f,q} 1.47,^{f,q} 1.56,^{f,r} 4.32^{f,r}	5.28
4a	5.45	4.69, 4.92, 5.72, 5.85	1.65	7.0–7.2^f	4.72	3.50
4b	4.99	4.88 (2 H), 5.65, 5.91	1.96	8.59	7.0–7.5^f	5.21
5a	5.28	4.35, 4.49, 5.27, 5.71	1.80	1.48	2.59	3.90
5b	5.24	4.44, 4.92, 4.99 (2 H)	1.77	1.26	4.03	2.46

^{a} Singlets observed unless stated; coupling constants are in Hz. ^{b} ABCD spin system. ^{c} AA′BB′ spin system. ^{d} $^2J_{WH}$ = 3.6. ^{e} t, MeCH$_2$CH$_2$, $^3J_{HH}$ = 7.4. ^{f} Multiplet. ^{g} $^4J_{HH}$ = 0.8, 0.9. ^{h} MeCH_2CH$_2$, $^3J_{H(Me)\text{-}H}$ = 7.4; $^3J_{HH}$ = 7.5. ^{i} EtCHH, $^4J_{HH}$ = 0.8; $^3J_{HH}$ = 15.1. ^{j} EtCHH, $^4J_{HH}$ = 0.9; $^3J_{HH}$ = 7.5; $^2J_{HH}$ = 15.1. ^{k} CH_3CO$_2$: δ = 2.61 ppm, $^4J_{WH}$ = 3.6. ^{l} t, MeCH$_2$CH$_2$, $^3J_{HH}$ = 7.3. ^{m} MeCH_2CH$_2$, J_{HH} = 4.7, 6.0, 7.3, 10.3, 10.7. ^{n} EtCHH, $^4J_{HH(2)}$ = 0.6; $^3J_{HH}$ = 6.0, 10.7; $^2J_{HH}$ = 12.1. ^{o} EtCHH, $^3J_{HH}$ = 4.7, 10.3; $^2J_{HH}$ = 12.1. ^{p} t, MeCH$_2$CH$_2$, $^3J_{HH}$ = 7.2. ^{q} MeCH_2CH$_2$. ^{r} EtCH_2.

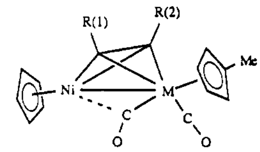
tramolecular hydrogen atom transfer from a dimethylamido to a μ-ethyne ligand yielding a complex containing a bridging vinyl species has been observed in a ditungsten complex.[5] Diiron and diruthenium compounds containing C(R)C(R′)C(O) ligands derived from alkynes may also be protonated to give μ-η^1,η^2-alkenyl complexes:[6] these species are also obtained from reactions of allenes.[7] Related iron species are accessible by the thermal rearrangement of cationic dinuclear μ-alkylidyne compounds.[8] The protonation of a dirhodium allene species afforded a complex containing a bridging propenyl ligand.[9]

Homo-[10] and heteronuclear[11] clusters containing alkenyl ligands have been prepared, but dinuclear examples are not as prevalent. Complexes containing μ-alkenyl ligands, occasionally with associated bridging hydride ligands are known, some of which result from the C–H activation of ethylene. A recent report describes the synthesis of diruthenium complexes containing two bridging vinyl ligands.[12] Dirhenium compounds with μ-alkenyl and μ-H ligands have been synthesized by photolysis,[13] and ditantalum[14] and dirhodium species containing both ligands are known.[15,16]

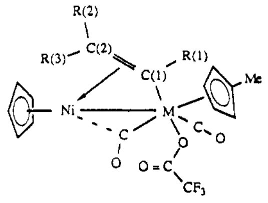
Heterodimetallic bridging alkenyl complexes are recognized but are less common. Cobalt–iron μ-η^1,η^2-alkenyl species have been prepared[17] by reacting mono- or dinuclear iron compounds with $Co_2(CO)_8$ and iron–ruthenium compounds are known.[18] Stone and co-workers have treated species containing bridging alkylidyne ligands with various reagents including Tebbe's reagent and diazomethane affording molybdenum–iron,[19] tungsten–iron,[20] tungsten–platinum,[21,22] and tungsten–titanium[22] complexes containing μ-η^1,η^2-alkenyl ligands. An iron–manganese species containing a bridging alkenyl ligand has been isolated from the reaction of diazomethane with a mixed-metal cluster.[23] Isomeric bonding modes of the bridging alkenyl group to the dissimilar metals are possible in these

Chart I. Numbering and Labeling Scheme Used in the Text and in the NMR Tables for the Alkyne and Alkenyl Complexes

Complex	R(1)	R(2)	M
1	H	H	W
2	Me	Me	W
3	n-Pr	H	W
4	Ph	H	W
5	Me	Me	Mo



Complex	R(1)	R(2)	R(3)	M
1a	H	H	H	W
1a-(Z)-d_1	H	H	D	W
1a-(E)-d_1	H	D	H	W
2a	Me	Me	H	W
^{a}2a′	Me	Me	H	W
3a	n-Pr	H	H	W
3a-(Z)-d_1	n-Pr	H	D	W
3b	H	n-Pr	H	W
4a	Ph	H	H	W
4a-(Z)-d_1	Ph	H	D	W
4a-(E)-d_1	Ph	D	H	W
4b	H	Ph	H	W
5a	Me	Me	H	Mo
5b	Me	H	Me	Mo



^{a} 2a′ contains a CO_2CH_3 group instead of a CO_2CF_3 group.

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Table II. ^{13}C NMR Data[a] (ppm, in acetone-d_6)

complex CO	C(=O)CF$_3$	C$_5$H$_5$	C$_5$H$_4$Me	C(1)	C(2)	R(1)	R(2)	C$_5$H$_4$*Me*
1[a] 222.7 (172)[b]		91.8	109.0 (*C*Me), 89.8, 87.9	74.8 (31)[b,c]	74.8 (31)[b,c]			13.9
3 226.0 (177),[b] 222.2 (172)[b]		92.7	109.8 (CMe), 91.6, 90.8, 89.3, 88.9	80.2	92.6 (44)[b]	14.4 (Me), 25.9 (*Me*CH$_2$), 36.2 (EtCH$_2$)		14.2
1a 241.9 (134),[b] 221.6 (133)[b]	162.0 (36),[d] 114.7 (290)[e]	94.4	119.2 (CMe), 92.3, 91.5, 84.6, 86.1	161.7 (73)[b]	73.2 (24)[b,f]			13.6
2a 243.7 (127),[b] 223.0 (129)[b]	161.4 (36),[d] 114.4 (290)[e]	95.0	118.3 (CMe), 92.5, 90.9, 86.0, 83.4	171.5 (74)[b]	92.9 (8)[b]	23.8	22.5	12.8
3a 243.8 (136),[b] 222.8 (131)[b]	162.0 (37),[d] 115.0 (291)[e]	95.1	120.0 (*C*Me), 92.6, 89.4, 87.2, 84.2	182.2 (75)[b]	76.2 (7)[b]	14.6 (Me), 26.7 (Me*C*H$_2$), 46.9 (Et*C*H$_2$)		13.2
4a 240.0, 222.5	162.2 (38),[d] 114.7 (292)[e]	95.7	121.1 (*C*Me), 92.7, 90.1, 88.0, 84.8	176.4	72.7 (28)	151.3, 130.2 (2 C), 127.1 (2 C), 126.0		13.3
4b 241.6, 221.5	not seen	95.5	120.1 (*C*Me), 92.4, 92.0, 86.3, 84.5	151.1 (79)[b]	94.3 (9)		145.8, 129.5 (2 C), 127.5, 127.0 (2 C)	13.6
5a 255.6, 228.6	162.0 (37),[d] 116.3 (292)[e]	95.3	121.2 (*C*Me), 95.0, 92.6, 91.4, 89.3	186.2	85.5	23.7	23.0	13.1
5b not seen, 236	162.0 (37),[d] 114.2 (292)[e]	94.1	119.4 (*C*Me), 93.8, 92.2, 91.0, 89.6	178.9	85.6	24.2	21.1[g]	12.9

[a] Chloroform-d_1. [b] J_{WC} (Hz). [c] $^1J_{CH}$ = 210 Hz. [d] *C*(=O)CF$_3$, J_{CF} (Hz). [e] C(=O)*C*F$_3$, J_{CF} (Hz). [f] For **1a**–d_1, $^1J_{CD}$ = 24.3 Hz. [g] R(3).

and other heterodimetallic systems, but there appears to be a strong preference as to which metal is σ-bonded or π-bonded to the alkenyl ligand: isomers differing in the bonding mode of the alkenyl ligand to the same pair of distinct metals have not been observed, even when the metals belong to the same group in the periodic table.[18]

This work describes the preparation of new nickel–tungsten alkyne bridged complexes and the reactions of these species and others of general formula $NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (M = Mo, RC_2R' = MeC_2Me, PhC_2H; M = W, RC_2R' = HC_2H, MeC_2Me, *n*-PrC_2H, PhC_2H) with trifluoroacetic acid. We were interested in establishing whether bridging alkenyl ligands would be obtained on protonation and if so, whether the ligand would end up being π-bonded to the nickel atom or to the group 6 metal. In addition, the stereochemistry of the alkenyl group was of interest. Curtis and co-workers[3] have reported anti-Markovnikov addition in the alkenyl protonation products of the dimolybdenum alkyne bridged complexes $Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}RC_2H)(\eta^5\text{-}C_5H_5)_2$. To our knowledge, no heterodinuclear alkenyl complexes have been formed by direct protonation of the corresponding bridging alkyne complex.

Results

I. Synthesis and Protonation of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}HC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (1).

The ethyne complex $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}HC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (1) was prepared by reacting the compound $NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ with ethyne for a controlled time period. Prolonged reaction times with excess ethyne led to uncharacterized products and careful monitoring of reaction conditions was required to isolate 1. The structure of the red-brown product was determined spectroscopically (Tables I and II) and is shown in Chart I (which also contains the numbering scheme for the other complexes and the labeling system used for the NMR tables). Complex 1 is analogous to other alkyne-bridged nickel–tungsten complexes prepared by our group.[1,2]

An ethereal solution of 1 reacted with excess trifluoroacetic acid to give a yellow-brown solution. No products were eluted when this solution was passed through an alumina column, but direct crystallization from diethyl ether afforded crystals of a new species (**1a**). **1a** is attacked by chloroform and is sparingly soluble in benzene or toluene but is soluble in acetone-d_6.

Table III. ^{1}H–^{1}H and ^{183}W–^{1}H Coupling Constants (Hz) of the Alkenyl Complexes' Vinylic Protons

complex	$J_{H(1)-H(2)}$	$J_{H(1)-H(3)}$	$J_{H(2)-H(3)}$	$J_{W-H(1)}$	$J_{W-H(2)}$	$J_{W-H(3)}$
1a	8.7	14.7	1.0	7.9	9.2	3.7
2a		0.9[a]	6.2[a]			3.3
2a′		<0.4	4.9[a]			*b*
3a	0.6[c]		1.2		8.6	3.4
3b		13.5		7.2		*b*
4a			0.6		8.7	3.5
4b		14.0		7.6		*b*
5a		0.9[a]	6.3[a]			
5b[a]	0.3[a]		6.3[a]			

[a] J_{Me-H}. [b] Not observed. [c] $J_{EtCH\mathit{H}-H}$.

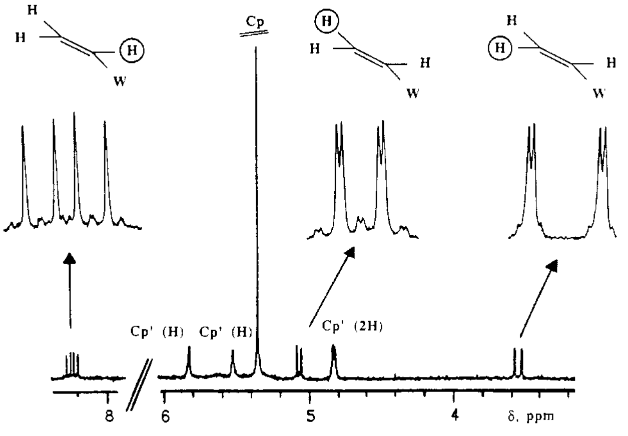


Figure 1. The olefinic region of the 300-MHz ^{1}H NMR spectrum of $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**1a**). Note the ^{1}H–^{1}H and ^{183}W–^{1}H couplings for the alkenyl protons and the ABCD-type pattern observed for the $\eta\text{-}C_5\mathit{H}_4Me$ (Cp′) resonances.

On the basis of the spectroscopic data and C/H microanalysis, **1a** is believed to be the complex $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$, having the structure shown in Chart I. ^{1}H NMR spectra of acetone-d_6 solutions of **1a** (Tables I and III) revealed AMX-type resonances with the multiplets centered at δ = 8.24, 5.07, and 3.55 ppm (Figure 1). The chemical shifts of the signals can be unequivocally assigned to the H(1) H(2), and H(3) protons, respectively, of a coordinated vinyl group. In addition the cis, trans, and gem coupling constants of 8.7, 14.7, and 1.0 Hz, respectively, are in the range noted for other vinylic species. Each signal was flanked by tungsten-183 satellites.

Resonances assigned to a cyclopentadienyl and a methylcyclopentadienyl group were also observed, suggesting that both metals were present. The ABCD-type pattern for the aromatic methylcyclopentadienyl protons indicated a lack of symmetry for the molecule on the ^{1}H NMR time scale; this feature was noted in the ^{1}H NMR spectrum of every alkenyl complex prepared.

The ^{13}C NMR spectrum of **1a** revealed resonances from the C(1) and C(2) vinylic carbon atoms at $\delta = 161.7$ and 73.2 ppm that were assigned from proton-coupled ^{13}C experiments. These signals exhibit markedly different ^{183}W satellites, arising from ^{183}W–^{13}C coupling, of 73 and 24 Hz. IR spectra of **1a** showed three carbonyl absorptions at 2003, 1825, and 1697 cm^{-1} assigned to a terminal, a semibridging carbonyl group and a trifluoroacetate ligand, respectively. The complex showed no molecular ion in its mass spectrum.

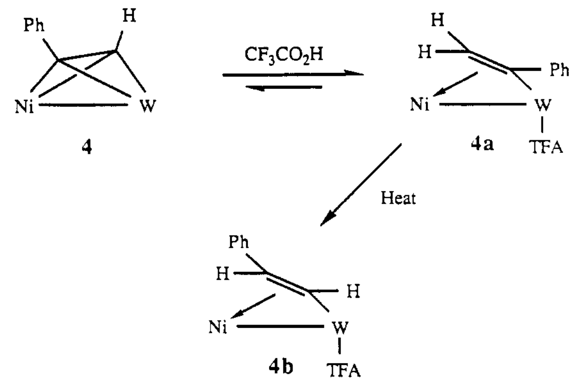
The asymmetric ^{183}W–^{13}C couplings observed for the vinylic C(1) and C(2) carbon atoms suggested that the complex contained a tungsten σ-bound vinyl ligand: a tungsten π-bound alkenyl species would exhibit substantially smaller and more similar ^{183}W couplings to C(1) and C(2).[24] Electron counting arguments also suggest that the ligand is coordinated to the tungsten atom.

II. Protonation of Other Nickel–Tungsten Alkyne Complexes. (i) Protonation of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$. Protonation of alkyne complexes may, in principle, lead to (*E*)- and (*Z*)-alkenyl isomers[25] and to structural isomers for unsymmetrical alkynes. However, the 2-butyne complex $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (**2**) afforded only one isomer of the 2-butenyl species $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}C(Me){=}CHMe)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**2a**) when treated with trifluoroacetic acid. This reaction was monitored by ^{1}H NMR spectroscopy in benzene-d_6; no intermediate metal hydride species or other isomer was detected at any stage in this reaction. Pertinent spectroscopic data (Tables I–III) for **2a** parallel data for **1a** and the two species are believed to have similar structures. The ^{1}H NMR data indicate that a C(Me)=CHMe group is present. The C(1) carbon of the butenyl ligand resonates at $\delta = 171.5$ ppm, a low-field signal possibly indicating some carbenoid character for this carbon atom.

Reaction of ethereal solutions of **2** with $HBF_4{\cdot}Me_2O$ led to the immediate formation of a yellow brown precipitate, that darkened when allowed to stand and resisted purification or characterization. ^{1}H NMR spectra of this insoluble, presumably ionic, species are broad and featureless, and the product is either paramagnetic or readily decomposes to paramagnetic products.

(ii) Protonation of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}\textit{n}\text{-}PrC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (3). Protonation of **3**, a new complex prepared in similar fashion to **1**, yields only one isomer.

Scheme I. Schematic Diagram Showing the Protonation Products of 4 (TFA = CO_2CF_3)



^{1}H NMR data suggest that the alkenyl complex may be formulated as $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}C(\textit{n}\text{-}Pr){=}CH_2)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**3a**). There is no evidence of any other protonated species, and a low-field signal, characteristic of monosubstituted μ-vinyl C*H*=CHR protons,[26] is absent. The large difference (1.83 ppm) observed in the chemical shift of the two hydrogen atoms of the *n*-Pr methylene group α to the coordinated double bond results in an essentially first-order spectrum for each multiplet. The two protons exhibit different coupling constants to the two adjacent methylene group hydrogen atoms; one of these two hydrogen atoms exhibits a small coupling to the alkenyl H(2) proton.

(iii) Protonation of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (4). Treatment of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (**4**) with trifluoroacetic acid afforded $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}C(Ph){=}CH_2)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**4a**). ^{1}H NMR spectra of solutions of **4a** in acetone-d_6 always exhibited signals arising from **4**. This was a source of considerable frustration and repeated purification attempts till it was shown that solution of analytically pure crystals of **4a** also exhibited resonances assignable to **4**. Spectra of toluene-d_8 solutions of **4a**, in which the complex is sparingly soluble, showed no detectable quantities of **4**. Complexes **3a** and **4a** result from formal Markovnikov addition to the coordinated alkyne.

In general only one isomer of **4a** was obtained at ambient temperatures, but in one instance another species, believed to be the anti-Markovnikov adduct $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHPh)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**4b**), having the phenyl group and the tungsten atom in an anti orientation, was also observed in solution. This species could not be isolated free of **4a** and **4**, but ^{1}H NMR spectra of this mixture revealed a signal at $\delta = 8.32$ ppm, characteristic of species having a hydrogen atom on the C(1) alkenyl carbon atom, and other resonances that could be assigned to **4b**.

As **4b** was inadvertently obtained in one instance, an attempt was made to see whether this isomer was accessible by heating solutions of **4a**. Toluene-d_8 solutions of pure **4a** that were heated in a sealed ^{1}H NMR tube darkened and deposited a dark insoluble material within a few hours. After a 2-day period, ^{1}H NMR spectra of the resultant solution showed resonances that could be assigned to **4b**, together with those arising from other uncharacterized decomposition products. A ^{1}H NMR spectrum of the sparingly soluble material was obtained by

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[24] No ^{183}W satellites are reported in the ^{13}C NMR spectrum for the tungsten π-bound alkenyl C(1) and C(2) carbon atoms in the complexes $TiW(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}C(R){=}CH_2)(\eta\text{-}C_5H_5)_3$ (R = Me, *p*-tolyl).[22] In contrast, ^{183}W–^{13}C coupling of $\approx$60 Hz is observed for the C(1) carbon atom of the tungsten σ-bound alkenyl ligands in the complexes $FeW(\mu\text{-}CO)(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHR)(\eta^5\text{-}C_5Me_5)$ and $FeW(\mu\text{-}CH_2)(CO)_5(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHR)(\eta^5\text{-}C_5Me_5)$ (R = *p*-tolyl).[20]

[25] When the substituents (including the group 6 metal) linked to C(1) and C(2) with the greatest atomic mass are in a cisoid geometry, that isomer is designated the *Z* isomer.

[26] The protons on the C(1) carbon in the iron–tungsten alkenyl complexes[20] resonate at $\delta = 8.14$ and 8.30, respectively. Protons on the C(1) carbon of bridging alkenyl ligands in other complexes also resonate at low field.[3,6a]

using acetone-d_6 as the solvent. The material was spectroscopically pure **4b**, showing that the anti-Markovnikov product was accessible by thermolysis of **4a**. Solutions of **4b** in acetone-d_6 show no detectable quantities of the alkyne complex **4**. These results are shown in Scheme I. Complex **3a** similarly isomerizes to the anti-Markovnikov species $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CH(n\text{-}Pr)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (**3b**) when heated.

III. Protonation of Nickel–Molybdenum Alkyne Complexes. While there is some IR evidence for its presence in solution, we were unable to isolate the nickel–molybdenum ethyne bridged complex. When the phenylacetylene-bridged species $NiMo(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ was treated with trifluoroacetic acid in diethyl ether, no pure product could be isolated. There is spectroscopic evidence for the formation of several alkenyl isomers, but the isomer mixture could not be isolated free from the bridging phenylacetylene species.

The nickel–molybdenum 2-butyne bridged complex $NiMo(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (**5**) was protonated with trifluoroacetic acid giving a mixture of **5a** and **5b**, both isomers of $NiMo(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}C(Me){=}CHMe)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$. The isomers are obtained in a 2:1 ratio respectively, and the more abundant isomer (**5a**) may be obtained pure by fractional crystallization. **5b** has never been obtained free of **5a**.

5a and **5b** are believed to be the *E* and *Z* isomers, respectively, the *Z* isomer having the methyl groups trans to each other. The 2-butenyl ligand is believed to be σ-coordinated to the molybdenum in each case. The chemical shifts of the cyclopentadienyl ligands in both isomers are almost identical (δ = 5.28 and 5.24 ppm), suggesting that there are no substantial differences in coordination around the nickel atoms in the two isomers.[27] An isomer having the 2-butenyl ligand σ-coordinated to the nickel would be expected to have a substantially different ^1H NMR cyclopentadienyl chemical shift from the isomer having a nickel π-coordinated butenyl ligand.

Large and small coupling constants of 6.3, 0.9 Hz and 6.3, 0.3 Hz are observed for the alkenyl C*H*Me protons in the ^1H NMR spectra of the two complexes, typical of C*H*(*Me*)=CMe and C*H*(Me)=C*Me* coupling constants and ruling out a $\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CMe_2$ ligand. A larger $J_{H\text{-}Me}$ W-coupling is predicted[28] for the *E* isomer, and on this (rather tentative) basis, the more abundant isomer (**5a**) is believed to be the *E* isomer.

IV. ^{183}W–^1H Coupling Constants in Assigning the Stereochemistry of the Nickel–Tungsten Alkenyl Complexes. The ^1H NMR spectra of the alkenyl complexes reveal characteristic chemical shifts and proton–proton coupling constants for the vinylic protons (Tables I and III). In addition, satellites arising from ^{183}W–^1H coupling are observed for the vinylic protons in all the alkenyl complexes, as shown in the ^1H NMR spectrum of **1a** (Figure 1). The magnitude of this coupling may be a useful tool in stereochemical assignments. In complex **1a** when the protons may be unambiguously assigned from ^1H–^1H coupling constants and chemical shift data, $^3J_{WH_{trans}}$ = 9.2 Hz while $^3J_{WH_{cis}}$ = 3.7 Hz. Assignments based solely on $^3J_{WH}$ for the two alkenyl protons in both **3a** and **4a** are in agreement with assignments based on chemical shift and coupling constant data. For **2a**, where there is only one vinylic proton, $^3J_{WH}$ = 3.3 Hz, indicative of a cis tungsten–proton geometry (*E* isomer). The alkenyl proton resonates at δ = 4.08 ppm, a value more typical of a proton cis rather than trans to the tungsten atom. A subsequent X-ray structural characterization of **2a** confirmed our assignment.

V. Solution Stability and Equilibria Involving the Alkenyl Complexes. Acetone-d_6 solutions of **1a**, **2a**, and **3a** are stable in solution at room temperature over at least a few days. However, when analytically pure samples of **4a** are dissolved in acetone-d_6, ^1H NMR signals of the alkyne complex **4** are present, even when spectra are taken immediately after dissolution. Complex **4** and trifluoroacetic acid are in equilibrium with **4a** in acetone-d_6, as shown in eq 1.

$$\begin{gathered}NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me) + CF_3CO_2H \rightleftharpoons \\ NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}C(Ph){=}CH_2)(\eta^5\text{-}C_3H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)\end{gathered}$$

$$K = \frac{[\text{alkenyl complex}]}{[\text{alkyne complex}][CF_3CO_2H]} \tag{1}$$

The equilibrium is established quickly: ratios of **4**:**4a** obtained from ^{13}C NMR spectra are in agreement with values obtained from ^1H NMR data. From the initial quantity of **4a** used and the integrated ratios of **4**:**4a** observed from NMR experiments, an approximate value of the equilibrium constant *K* (**4a**) can be calculated and is found to be 150 ± 30 M^{-1} at 20 °C in acetone-d_6.

Acetone-d_6 solutions of the isomeric mixture of **5a** and **5b** slowly revert back to **5**. A similar equilibrium is in effect here, but the equilibrium constant is smaller here than for **4a**. Solutions of **5a** initially generate an equilibrium mixture of **5a**/**5b**: trifluoroacetic acid and **5** are formed subsequently, over a 3-day period. For the other alkenyl species, the equilibrium lies (within the ^1H NMR detection limit) completely to the right in acetone-d_6, implying that values of the equilibrium constants are $\geq$5000 M^{-1} at 20 °C for each of these species.

Parallel equilibria may be established in diethyl ether and toluene-d_8, but if so, values for the equilibrium constants are much larger in these solvents. No detectable quantities of **4** are observed when **4a** is dissolved in toluene-d_8. While the two- to threefold excess of trifluoroacetic acid present does help to drive the equilibrium reaction to the right in diethyl ether, complexes **4a** and **5a**/**5b** mixture may be isolated pure from this solvent in high yields. Polar species such as trifluoroacetic acid are solvated to a greater extent in polar solvents, and this solvation may govern the dependence of the equilibrium constant on the solvent.

VI. Deuteration Studies. Protonation of all the alkyne complexes except **5** afforded only one isomer at ambient temperatures. The stereochemistry of the reaction was probed by analyzing the monodeuterated products obtained from treating complexes **1**, **3**, and **4** with trifluoroacetic acid-d_1.

Deuteration of **1** and **3** yielded the isomers $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(Z)\text{-}CH{=}CHD)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ [**1a**-(*Z*)-d_1] and $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(Z)\text{-}C(n\text{-}Pr){=}CHD)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ [**3a**-(*Z*)-d_1], respectively. Both isomers have the deuterium atom and the tungsten atom in a syn orientation. The reactions proceed with high stereoselectivity: apart from traces of protio impurities, these isomers were the only species detected by ^1H NMR spectroscopy. An interesting feature of the ^1H NMR spectra of these monodeuterated derivatives is the slight difference observed between the chemical shifts

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(27) The ^1H NMR chemical shift of nickel bound cyclopentadienyl ligands are relatively sensitive to the groups that are coordinated to the nickel atom. There is a chemical shift different of 0.01 and 0.04 ppm, respectively, for the two pairs of complexes $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_4Me)$ (M = Mo, W).[2]

(28) Barfield, M.; Chakrabarti, B. *Chem. Rev.* **1969**, *69*, 757–778.

Table IV. Crystal Data and Data Collection Parameters

formula	$C_{19}H_{19}F_3NiO_4W$
fw	610.92
space group	$P2_1/n$ (No. 14)
a, Å	8.3710 (7)
b, Å	27.609 (5)
c, Å	9.045 (1)
β, deg	109.210 (7)
V, Å^3	1974.0 (8)
Z	4
d_{calcd}, g cm^{-3}	2.056
cryst dimen, mm	0.79 × 0.65 × 0.57
temp, °C	20
radiatn, Å	Mo Kα, 0.71073
monochromator	graphite
μ(Mo Kα), cm^{-1}	69.57
abs corrctn method	empirical
transmissn (max, min, av)	0.7, 1.10, 0.96
diffractometer	Enraf-Nonius CAD-4
scan method	ω–2θ
h,*k*,*l* limits	0 to 9, 0 to 29, –9 to 9
2θ range, deg	4.00–45.00
scan width, deg	0.65 + 0.35 tan θ
takeoff angle, deg	2.80
programs used	Enraf-Nonius SDP
F_{000}	1176.0
weighing factor	0.040
data collected, unique data	2639, 2639
data with $I > 3.0\sigma(I)$	2211
no. of variables	253
largest shift/esd in final cycle	0.08
R	0.030
R_w	0.043
goodness of fit	1.604

of the $CH_2{=}CR-$ group and its corresponding $C\mathit{HD}{=}CR-$ isotopomer. An upfield shift of ≈0.01 ppm is observed for the signals of the C*HD* group as compared to those arising from the CH_2 group.

Results stemming from the deuteration of **4** were more complex. Following deuteration by a solution of trifluoroacetic acid-d_1 in diethyl ether, the isomer isolated was $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(Z)\text{-}C(Ph){=}CHD)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ [**4a**-(*Z*)-d_1]. This was crystallized in high yield and purity. A ^{1}H NMR spectrum in acetone-d_6, obtained within minutes of dissolution, showed that the solution contained almost exclusively the *Z* isomer and the alkyne complex **4**, in ≈5:1 molar ratio. In a separate NMR tube experiment, trifluoroacetic acid-d_1 was added in a 1:1 molar ratio to an acetonitrile-d_3 solution[29] of **4**: the ^{1}H NMR spectrum, recorded immediately, showed a spectrum identical to that of **4a**-(*Z*)-d_1 crystallized from diethyl ether.

Within 2 h, partial isomerization to $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}C(Ph){=}CHD)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ [**4a**-(*E*)-d_1] had taken place. After a 10-h period, the ratio of the two alkenyl isomers **4a**-(*Z*)-d_1 and **4a**-(*E*)-d_1 was 1:1 while the molar ratio of the two alkenyl isomers to **4** remained ≈5:1.

When solutions of **3a**-d_1 are maintained at ambient temperatures, their ^{1}H NMR spectra are invariant for at least 6 h (the time-period monitored). No change is observed in spectra of **1a**-d_1 after a few days. However, some isomerization of **1a**-(*Z*)-d_1 to **1a**-(*E*)-d_1 was observed after allowing a solution of **1a**-(*Z*)-d_1 to stand for 7 weeks in a sealed NMR tube. The ratio of **1a**-(*Z*)-d_1 to **1a**-(*E*)-d_1 was ≈4.5:1 after this time period. No deuterium was detected on the C(1) carbon,[30] and no ^{1}H NMR signals arising from the alkyne complex **1** were observed.

Table V. Atomic Positional Parameters and Isotropic Thermal Parameters for 2a

atom	*x*	*y*	*z*	*B*, A^2
W	–0.04722 (3)	0.39024 (1)	0.30564 (3)	2.742 (7)
Ni	–0.1061 (1)	0.31995 (4)	0.4736 (1)	3.04 (2)
F(1)	0.4151 (8)	0.4667 (2)	0.8285 (7)	7.9 (2)
F(2)	0.436 (1)	0.3915 (2)	0.807 (1)	14.3 (3)
F(3)	0.4913 (8)	0.4379 (4)	0.6490 (9)	10.8 (3)
O(1)	–0.4074 (7)	0.3457 (2)	0.2046 (7)	5.0 (2)
O(2)	–0.2530 (7)	0.4607 (2)	0.4544 (7)	5.6 (2)
O(3)	0.0977 (8)	0.4432 (3)	0.6786 (7)	5.7 (2)
O(4)	0.1822 (7)	0.4059 (2)	0.4964 (6)	3.9 (1)
C(1)	–0.2667 (9)	0.3566 (3)	0.2594 (9)	3.7 (2)
C(2)	–0.167 (1)	0.4360 (3)	0.4125 (9)	3.9 (2)
C(11)	0.114 (1)	0.4313 (3)	0.1671 (9)	4.4 (2)
C(12)	0.058 (1)	0.3860 (3)	0.099 (1)	5.1 (2)
C(13)	–0.120 (1)	0.3857 (4)	0.042 (1)	5.0 (2)
C(14)	–0.177 (1)	0.4307 (4)	0.081 (1)	5.1 (2)
C(15)	–0.031 (1)	0.4579 (3)	0.159 (1)	4.9 (2)
C(16)	0.294 (1)	0.4468 (5)	0.235 (1)	7.4 (3)
C(17)	0.010 (1)	0.2261 (3)	0.354 (1)	4.6 (2)
C(18)	–0.0491 (9)	0.2782 (3)	0.3111 (8)	3.5 (2)
C(19)	0.0584 (8)	0.3179 (3)	0.3579 (7)	2.7 (1)
C(20)	0.246 (1)	0.3089 (3)	0.439 (1)	4.3 (2)
C(21)	–0.016 (1)	0.3211 (5)	0.2726 (1)	6.9 (3)
C(22)	–0.144 (1)	0.3516 (4)	0.671 (1)	5.8 (2)
C(23)	–0.279 (1)	0.3273 (5)	0.591 (1)	6.9 (3)
C(24)	–0.240 (1)	0.2789 (4)	0.583 (1)	9.4 (3)
C(25)	–0.063 (1)	0.2759 (4)	0.673 (1)	8.9 (3)
C(31)	0.200 (1)	0.4275 (3)	0.626 (1)	3.8 (2)
C(32)	0.387 (1)	0.4302 (4)	0.729 (1)	5.6 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table VI. Selected Bond Distances (Å) for 2a

W–Ni	2.6096 (8)	O(1)–C(1)	1.157 (8)
W–O(4)	2.161 (4)	O(2)–C(2)	1.141 (8)
W–C(1)	1.977 (7)	O(3)–C(31)	1.190 (8)
W–C(2)	2.045 (8)	O(4)–C(31)	1.279 (8)
W–C(19)	2.173 (6)	C(17)–C(18)	1.53 (1)
Ni–C(1)	2.206 (7)	C(18)–C(19)	1.393 (9)
Ni–C(18)	2.045 (6)	C(19)–C(20)	1.517 (9)
Ni–C(19)	1.986 (5)	C(31)–C(32)	1.53 (1)
W–C(Cp′)	2.314	Ni–C(Cp)	2.100
C(CF$_3$)–F	1.30		

VII. X-ray Structure of $NiW(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}C(Me){=}CHMe)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(CO_2CF_3)$ (2a).

In order to confirm the structures of the alkenyl complexes, an X-ray diffraction study of **2a** was undertaken. The 2-butenylnickel–tungsten complex was selected to confirm the presumed stereochemistry of the 2-butenyl ligand to provide a direct comparison of structural parameters in **2a** to those of the alkyne complex $NiW(CO)_2(\mu\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)_2$ whose structure has been previously reported.[1] The tungsten atom in **2a** has undergone a formal increase in oxidation state to W(III), from W(I) in **2**.

Crystals of **2a** were grown from diethyl ether. Table IV summarizes the data collection parameters; lists of atomic coordinates, bond lengths, and bond angles are tabulated in Tables V, VI, and VII, respectively. An ORTEP plot of **2a** is shown in Figure 2.

The structure of the complex is in accord with spectroscopic predictions. The molecule contains a nickel–tungsten bond of 2.6096 (8) Å, a normal nickel–tungsten single bond length (Table VIII). This bond is straddled

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(29) Signals arising from the H(3) alkenyl proton fortuitously resonate at the same chemical shift as one of the ABCD type multiplets of the C_5H_4Me resonances in acetone-d_6. This reaction was thus monitored in acetonitrile-d_3, a solvent which behaved similarly to acetone-d_6 but made the reaction easier to follow.

(30) The effect of a $CD{=}CH_2$ group would be manifested by the far smaller cis- and trans HD coupling to the H(2) and H(3) protons as compared to the respective H–H coupling.

Table VII. Selected Bond Angles (deg) for 2a

Ni–W–O(4)	88.4 (1)	W–C(1)–O(1)	163.1 (6)
Ni–W–C(1)	55.5 (2)	Ni–C(1)–O(1)	119.8 (5)
Ni–W–C(2)	88.2 (2)	W–C(2)–O(2)	170.7 (6)
Ni–W–C(19)	48.0 (1)	N–C(18)–C(17)	118.7 (5)
O(4)–W–C(1)	141.5 (2)	Ni–C(18)–C(19)	67.5 (3)
O(4)–W–C(2)	86.8 (2)	C(17)–C(18)–C(19)	122.7 (6)
O(4)–W–C(19)	79.6 (2)	W–C(19)–Ni	77.6 (2)
C(1)–W–C(2)	79.8 (3)	W–C(19)–C(18)	118.8 (4)
C(1)–W–C(19)	84.1 (2)	W–C(19)–C(20)	122.5 (5)
C(2)–W–C(19)	133.9 (2)	Ni–C(19)–C(18)	72.1 (3)
W–Ni–C(1)	47.6 (2)	Ni–C(19)–C(20)	122.5 (4)
W–Ni–C(18)	82.4 (2)	C(18)–C(19)–C(20)	118.7 (6)
W–Ni–C(19)	54.4 (2)	O(3)–C(31)–O(4)	130.7 (7)
C(1)–Ni–C(18)	81.1 (3)	O(3)–C(31)–C(32)	117.7 (7)
C(1)–Ni–C(19)	83.0 (2)	O(4)–C(31)–C(32)	111.5 (7)
C(18)–Ni–C(19)	40.4 (3)	C(12)–C(11)–C(16)	125.9 (8)
W–O(4)–C(31)	129.1 (4)	C(15)–C(11)–C(16)	127.7 (8)
W–C(1)–Ni	77.0 (2)		

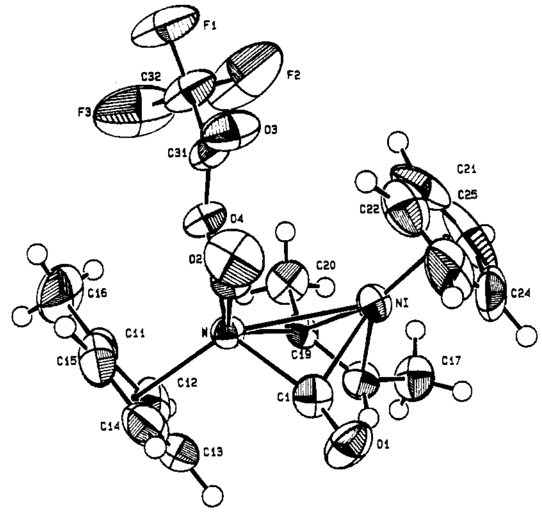

Figure 2. ORTEP diagram of NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)═CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (**2a**). Ellipsoids are drawn at the 50% probability level.

by a η^1,η^2-butenyl ligand that is σ-bonded to the tungsten atom and π-bound to the nickel atom. The W–C(19) bond of 2.173 (6) Å is typical of W(III)–C(alkyl) σ-bonds; nickel–carbon bonds of 1.986 (5) Å and 2.045 (6) Å to C(19) and C(20) respectively are in the range observed for nickel–olefin complexes.[31]

The tungsten atom is coordinated to both a terminal and a semibridging carbonyl ligand (W–C(1)–O(1) = 163.1 (6)°; Ni–C(1) = 2.206 (7) Å) and to a trifluoroacetate ligand that is terminally bound to the tungsten atom. The nickel–tungsten, tungsten–oxygen (trifluoroacetate), and tungsten–carbon (terminal carbonyl) bonds are all close to perpendicular to each other.

The methyl groups in the butenyl ligand are in a cis orientation, as suggested by the ^{1}H NMR data (the isomer obtained is the *E* isomer). The coordinated olefinic C═C bond distance is 1.393 (9) Å. This is typical of values observed for other bridging alkenyl complexes,[32] and shows significant occupancy of the olefinic π^* orbitals compared to ethylene where a 1.335 (3) Å C═C bond distance is observed.[33] Bond lengths in **2a** are marginally longer than comparable values observed for the alkyne-bridged complex NiW(CO)$_2$(μ-MeC$_2$Me)(η^5-C$_5$H$_5$)$_2$ (Table IX).

Table VIII. A Listing of Nickel–Tungsten Bonds Reported in the Literature

complex	Ni–W bond length (Å)	ref
NiW(CO)$_2$(μ-η^2,η^2-MeC$_2$Me)-(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)	2.624 (1); 2.628 (1)	1
NiW(CO)$_3$(PPh$_3$)$_2$(η-C$_5$H$_5$)	2.584 (3)	40
NiW$_2$(CO)$_4$(η-CC$_6$H$_4$Me-4)$_2$-(η-C$_5$H$_5$)$_2$	2.582 (1); 2.586 (1)	41
NiW(CO)$_2$(η-η^1,η^2-C(Me)═CHMe)(CO$_2$CF$_3$)(η-C$_5$H$_5$)-(η-C$_5$H$_4$Me)	2.6096 (8)	this work
NiW(μ-CO)$_3$(η-C$_5$Me$_5$)-(η-C$_5$H$_4$Me)^a	2.475 (2); 2.457 (1)	42
[Ni$_3$W$_2$(CO)$_{16}$]$^{2-a}$	3.10	43
Ni$_2$Pt$_2$W$_4$(μ_3-CPh)(CO)$_8$(η-C$_5$H$_5$)$_4$	2.634 (4); 2.657 (4)	44
[Ni$_2$Pt$_2$W$_4$(μ_2-CR)(μ_3-CR)(μ-CO)-(CO)$_7$(η-C$_5$H$_5$)$_4$]·CH$_2$Cl$_2$^{b}	2.654 (4); 2.716 (4) 2.644 (5); 2.684 (5)	44

^{a} Electron-deficient species. ^{b} R = C$_6$H$_4$Me-4.

Table IX. A Comparison of Selected Structural Parameters for 2 and 2a^a

	2	2a	
Ni–W	2.6098 (8)	2.624 (1)	2.628 (1)
W–C(18)	nonbonding	2.157 (7)	2.154 (7)
W–C(19)	2.173 (6)	2.096 (7)	2.079 (7)
Ni–C(18)	2.045 (6)	1.946 (7)	1.945 (7)
Ni–C(19)	1.986 (5)	1.958 (6)	1.948 (7)
C(18)–C(19)	1.393 (9)	1.335 (10)	1.343 (11)
W–C(2)–O(2)	163.1 (6)	161.8 (7)	164.9 (7)

^{a} Bond lengths in Å; bond angles in deg.

Discussion

I. Alkenyl Ligand Coordination to the Two Metals. The conversion of the alkyne complexes into neutral alkenyl species is the result of net oxidative addition of trifluoroacetic acid to the alkyne species. Protonation of the nickel–molybdenum or nickel–tungsten alkyne bridged species invariably results in complexes having the alkenyl ligands π-bound to the nickel atom and σ-bonded to the group 6 metal atoms. Isomers containing alkenyl groups that are π-bound to the tungsten or molybdenum atoms and σ-bound to nickel atoms never been observed. The group 6 rather than the group 10 metal has undergone a *formal* increase in its oxidation state. When the stabilities of Ni(II) and Mo(III) or W(III) species are compared, this can be rationalized: while tungsten(III) and molybdenum(III) complexes are well established, Ni(III) species are uncommon in the absence of chelating or macrocyclic nitrogen donor ligands.[34]

II. The Alkenyl Isomer Distribution. (i) Mechanism of Protonation. The conversion of the bridging alkyne complexes to alkenyl species may proceed through the initial protonation of the metal–metal bond, followed by rapid migration of the proton to a bridging alkyne carbon atom and coordination of a trifluoroacetate ligand. There is no evidence for any intermediate hydride species in our system, but there is precedent for the conversion of an alkyne-bridged dinuclear complex into a species

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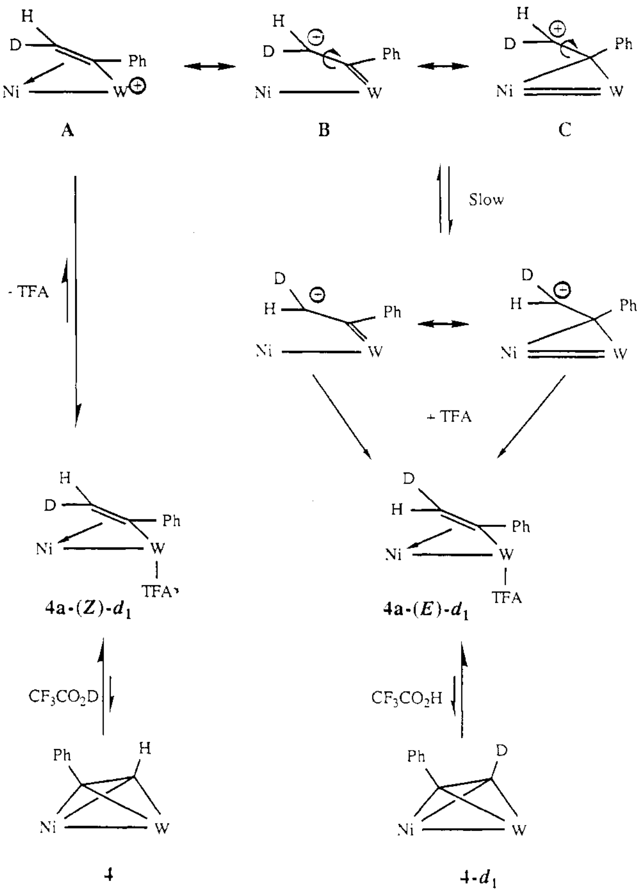
(31) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, London, 1974; Vol. 1, Chapter V, pp 244–327 and references cited therein.

(32) In the osmium cluster species Os$_3$(CO)$_{10}$(μ-H)(μ-η^1,η^2-CH═CH$_2$) and Os$_4$(CO)$_{11}$(μ-H)(μ-η^1,η^2-CH═CH$_2$), respectively, values of 1.396 (4) and 1.36 (2) Å have been reported.[10] The C═C distances in some dinuclear species are 1.38 (2) Å for [Mo$_2$(CO)$_4$(H$_2$O)(μ-η^1,η^2-CH═CHPh)(η^5-C$_5$H$_5$)$_2$]$^+$BF$_4^-$;[3] 1.40 (2) Å for Fe$_2$(μ-CO)$_2$(CO)$_2$(μ-η^1,η^2-CH═CH$_2$)(η-C$_5$H$_5$)$_2$;[6b] 1.407 (8) Å for Rh$_2$(CO)$_2${μ-η^1,η^2-C(Me)═CH$_2$}(η^5-C$_9$H$_7$)$_2$,[9] and 1.40 (2) Å for CoFe(CO)$_6${μ-η^1,η^2-C(CO$_2$Me)═CH(CO$_2$Me)}.[17] The C═C distance in the *cis*-2-butenyl ligand in the complex Rh$_2${P(O-*i*-Pr)$_3$}$_4$(μ-H){μ-η^1,η^2-(*Z*)-C(Me)═CHMe} is 1.40 (1) Å.[15]

(33) Kutchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906–911.

(34) (a) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988**, *32*, 241–295 and references cited therein.

Scheme II. A Possible Mechanism for the Scrambling of the Deuterium Label in 4a-(*Z*)-d_1 Affording a 1:1 Mixture of 4a-(*Z*)-d_1 and 4a-(*E*)-d_1 (TFA = CO_2CF_3)



containing a bridging alkenyl ligand,[35] via an isolated intermediate containing a cationic bridging hydride ligand. This mechanism is in accord with our observations.

Electrophilic attack by a proton migrating from the protonated metal-metal bond would afford an alkenyl species having the proton and the group 6 metal in a mutually cis conformation, in agreement with our results and with literature reports where electrophilic attack on metal polyene or polyenyl complexes in most cases affords endo addition products.[36]

(ii) A Possible Isomerization Mechanism for the (*Z*)- and (*E*)-Alkenyl Species. Our results indicate that the initial products isolated from the diethyl ether/trifluoroacetic acid mixture are alkenyl species having the added proton or deuteron syn to the group 6 metal. Isomerization and partial deprotonation to regenerate the alkyne complexes may subsequently take place in acetone-d_6 in some cases [**4a**-(*Z*)-d_1 $\rightleftharpoons$ **4a**-(*E*)-d_1 $\rightleftharpoons$ 4; **5a** $\rightleftharpoons$ **5b** $\rightarrow$ **5**].

Apart from possible deuterium isotope effects, there is no thermodynamic driving force for the isomerization of **4a**-(*Z*)-d_1 to **4a**-(*E*)-d_1. A mechanism applicable to the isomerization of **4a**-(*Z*)-d_1 and to other alkenyl complexes is shown in Scheme II. Loss of the trifluoroacetate ligand from **4a** would afford a unsaturated cationic alkenyl species (A), whose charge could be delocalized on to the alkenyl C(2) carbon atom affording B, containing a 16-electron nickel atom and a tungsten alkylidene group. An alternative cationic structure (C) contains a formal Ni–W double bond. Rotation of the H–C$^+$–D blade about the now single C(1)–C(2) bond in B or C by 180° would result in deuterium scrambling between the cis and trans positions relative to the tungsten in **4a**-d_1. Loss of a proton from this cation would regenerate the original alkyne complex 4.

The scrambling of the deuterium label, coupled with the alkenyl complex–alkyne complex equilibrium (eq 1) should result in the formation of a terminal alkyne complex enriched in deuterium. This has been observed for complex 4: the **4a**-(*Z*)-d_1 $\rightleftharpoons$ **4a**-(*E*)-d_1 scrambling process and eq 1 lead to 4-d_1 being formed. The presence of this species may be inferred by ^{1}H NMR signal integration: a decrease in the ratio of the terminal alkyne proton in 4 relative to the cyclopentadienyl resonance of the 4 and **4a**-d_1 mixture is observed as the isomerization proceeds.

The facility by which these complexes form cationic alkenyl species may account for the isomeric distribution of some of the neutral alkenyl species. A trapping experiment has provided circumstantial evidence that cationic alkenyl species may be formed in solution. Addition of acetic acid, *which does not react with **2***, to an acetone-d_6 solution of **2a** afforded the acetate complex NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$Me) (**2a**).[37] Attack of the more nucleophilic acetate anion on the positive tungsten center may rationalize the formation of **2a′**.

Large equilibrium constants for the protonation reaction lead to a kinetically controlled *Z*/*E* and Markovnikov/anti-Markovnikov alkenyl isomer distribution that is "locked in" because of the reaction's lack of reversibility at ambient conditions. This is the case for complexes **1a**–**3a**. Alkenyl species that readily isomerize also generate observable concentrations of the corresponding alkyne complexes when dissolved in acetone-d_6.

Formation of cationic alkenyl species from the neutral complexes is dependent on both steric congestion around the group 6 metal and the M–O bond strength. Steric congestion on the tungsten or molybdenum atom would be increased by bulky substituents on C(1) and relieved by dissociation of the trifluoroacetate anion. This rationalizes why the isomerization of **4a**-(*Z*)-d_1 to the *E* isomer is faster than the corresponding isomerization of **1a**-(*Z*)-d_1 and also explains why an equilibrium mixture of **5a** and **5b** is obtained when **5** is protonated, whereas only one 2-butenyl isomer is observed for **2a**. Bonds to second-row metals are generally regarded as being weaker than those to third-row metals, and dissociation of a trifluoroacetate ligand is more facile from **5a** than from **2a**.[38] Protonation of **2** affords the *E* isomer of **2a** (W and H cis), and the stronger W–O bond presumably prevents ready isomerization to a thermodynamic mixture of *Z* and *E* isomers, via a cationic alkenyl intermediate. While in our systems and many others,[21,22] alkenyl isomers having the R(1) and R(2) groups in a cis orientation are more stable, there are cases when both are observed, and steric factors appear to control the relative proportions of each isomer.[15]

The equilibrium described by eq 1 shifts in the direction of the alkyne complexes and trifluoroacetic acid in polar donor solvents. These solvents stabilize and solvate the

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(35) Boag, N. M.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1281–1282.

(36) 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; Chapter VIII, pp 433–458.

(37) The methyl protons of the acetate ligand exhibit tungsten-183 coupling of 3.6 Hz clearly indicating ligation of the acetate group to the tungsten atom.

(38) A 1:1 mixture of *Z* and *E* isomers of Mo$_2$(CO)$_4$(μ-η^1,η^2-CH=CHD)(η-C$_5$H$_5$)$_2$(CO$_2$CF$_3$) was also obtained when the dimolybdenum complex Mo$_2$(CO)$_4$(μ-η^2,η^2-HC$_2$H)(η-C$_5$H$_5$)$_2$ was deuterated with trifluoroacetic acid-d_1.[3]

cationic alkenyl species and the ionized trifluoroacetic acid. While no traces of **4** are detectable by ^{1}H NMR spectroscopy when **4a** is dissolved in toluene-d_8, **4** is present when **4a** is dissolved in acetone-d_6.

(iii) Markovnikov and Anti-Markovnikov Addition. The alkenyl isomers obtained initially result from net Markovnikov addition of a proton to the alkyne. There is a choice of carbon atoms onto which the proton can migrate, and proton transfer to the less highly substituted and less hindered carbon atom of the alkyne, resulting in Markovnikov addition, is kinetically favored. However, steric interactions between the group 6 metal's ancillary ligands are maximized when an alkyl or aryl ligand is present on the C(1) alkenyl carbon and the migration of a proton from a cationic μ-hydride species to the more substituted carbon would generate a more thermodynamically stable product. Once formed, this species would not dissociate back to the alkyne complex. The isomerization of **4a** to the anti-Markovnikov product **4b** can be thermally induced, and acetone-d_6 solutions of **4b** do not show detectable quantities of **4** in their ^{1}H NMR spectra.

Conclusions

Protonation of the bridging alkyne complexes NiM(CO)$_2$(μ-η^2,η^2-RC$_2$R′)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (M = Mo, RC$_2$R′ = MeC$_2$Me; M = W, RC$_2$R′ = HC$_2$H, MeC$_2$Me, *n*-PrC$_2$H, PhC$_2$H) with trifluoroacetic acid affords the alkenyl complexes NiM(CO)$_2$(μ-η^1,η^2-C(R)=CHR′)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) having the alkenyl ligand η^1-bound to the group 6 metal and η^2-coordinated to the nickel atom. A terminal trifluoroacetate ligand is coordinated to the molybdenum or tungsten atom. The structures of the alkenyl complexes were established by ^{1}H and ^{13}C NMR spectroscopy and by an X-ray diffraction study on a single crystal of NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (**2a**).

The protonation reactions are stereospecific and were studied by using trifluoroacetic acid-d_1: Markovnikov addition isomers having the incoming proton or deuteron in a syn orientation relative to the tungsten atom are formed initially. Subsequent scrambling of the deuteron may occur. The complex **4a**, NiW(CO)$_2$(μ-η^1,η^2-C(Ph)=CH$_2$)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) may be thermally isomerized into the anti-Markovnikov isomer NiW(CO)$_2$(μ-η^1,η^2-(E)-CH=CHPh)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$). A possible mechanism for the isomerization reactions is given.

Experimental Section

General Remarks. All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk or vacuum line techniques. Solvents were predried over 4-Å molecular sieves. Toluene, hexanes, and diethyl ether were distilled over sodium or sodium benzophenone ketyl. Dichloromethane was distilled over CaH$_2$. Trifluoroacetic acid and trifluoroacetic acid-d_1 (99 atom %) were obtained from Aldrich and were used as received. They syntheses of NiM(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (M = Mo, W) and of complexes **2**, **4**, and **5** have been described previously.[1]

NMR spectra were obtained on a Magnachem A-200, a Nicolet NT-300, or a General Electric GN-300 spectrometer at 20 °C using acetone-d_6 as the solvent unless otherwise stated. For the ^{13}C NMR spectra, Cr(acac)$_3$ was added at a concentration of 0.01–0.05 M, as a shiftless relaxation reagent. IR spectra were recorded on an IBM IR-32 FT instrument; absorptions are in reciprocal centimeters. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Synthesis of NiW(CO)$_2$(μ-η^2,η^2-HC$_2$H)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (1). Ethyne was bubbled slowly through a green solution of NiW(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (250 mg, 0.501 mmol) in hexane ($\approx$20 mL) for 15–20 min till the solution turned orange-brown. The solution was then concentrated and purified by centrifugal chromatography on a silica gel coated plate using hexanes as eluent. The product was eluted off as a dark orange-brown band. Concentration and crystallization at −20 °C afforded brown microcrystals of **1** (166 mg, 70%). IR (ν(CO), hexanes): 1984 (s), 1951 (s), 1920 (s), 1844 (s) cm^{-1}. MS: M$^+$, (M − CO)$^+$, (M − 2CO)$^+$, (M − 2CO − HCCH)$^+$. HRMS (based on ^{60}Ni and ^{186}W): calcd 471.984; found 471.984.

Synthesis of NiW(CO)$_2$(μ-η^2,η^2-*n*-PrC$_2$H)(η-C$_5$H$_5$)(η-C$_5$H$_4$Me) (3). A degassed Schlenk tube equipped with a magnetic stirrer bar was charged with NiW(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me) (250 mg, 0.501 mmol) and 10 mL of freshly distilled hexane. 1-Pentyne (0.12 mL, 1.20 mmol) was added via syringe, and the green solution partially evacuated and stirred overnight. The now red-brown solution was concentrated to $\approx$5 mL and purified by centrifugal chromatography on silica, using hexanes as the eluent. One major brown band was collected. The concentrated solution was pumped to dryness affording **3** as an oily brown spectroscopically pure solid in >70% yield. (Repeated attempts at crystallization, even at −78 °C, failed owing to the high solubility of **3**: the only solid products recovered through attempted crystallization were impurities or decomposition products). IR (ν(CO), hexanes): 1973 (s), 1956 (m), 1937 (s), 1910 (s), 1841 (s) cm^{-1} MS: M$^+$ 512, (M − CO)$^+$, (M − 2CO)$^+$, (M − 2CO − HCCH)$^+$. HRMS (based on ^{60}Ni and ^{186}W): calcd 512.0333; found 512.0332.

Protonation of 1 To Give NiW(CO)$_2$(μ-η^1,η^2-CH=CH$_2$)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (1a). Trifluoroacetic acid (0.25 mL, 3.25 mmol) was added to a solution of **1a** (472 mg, 1.00 mmol) in diethyl ether (15 mL) and the mixture maintained in an ice bath. Within a few hours, the solution turned yellow-brown. After being allowed to stand for a 3-day period, the solution was concentrated and cooled to −20 °C, and brown crystals were deposited (513 mg, 88%). Anal. Calcd for C$_{17}$H$_{15}$F$_3$NiO$_4$W: C, 35.05; H, 2.59. Found: C, 35.26; H, 2.40. IR (ν(CO), dichloromethane): 2003 (s), 1825 (s), 1696 (s, CF$_3$CO$_2$). IR (Nujol): 2006 (s), 1820 (s) 1697 (s, CF$_3$CO$_2$) cm^{-1}.

Protonation of 2 To Give NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (2a). NiW(CO)$_2$(μ-η^2,η^2-MeC$_2$Me)(η-C$_5$H$_5$)(η-C$_5$H$_4$Me) (**2**) (497 mg, 1.00 mmol) was placed in a degassed Schlenk tube, dissolved in $\approx$15 mL of freshly distilled diethyl ether, and placed in an ice-filled Dewar flask. Trifluoroacetic acid (0.23 mL, 3.00 mmol) was syringed into the brown solution under nitrogen and the mixture partially evacuated and kept at 0 °C. The solution turned yellow-brown over a 3-day period. Concentration and cooling to −20 °C afforded dark yellow crystals of **2a** (550 mg, 90%). Anal. Calcd for C$_{19}$H$_{19}$F$_3$NiO$_4$W: C, 37.38; H, 3.14. Found: C, 37.40; H, 3.25. IR (ν(CO), dichloromethane): 1998 (s), 1959 (sh), 1813 (s), 1717 (s, CF$_3$CO$_2$), 1699.5 (s, CF$_3$CO$_2$) cm^{-1}. IR (Nujol): 2013 (s), 2005 (s), 1812 (s), 1702 (s, CF$_3$CO$_2$) cm^{-1}.

Protonation of 3 To Give NiW(CO)$_2$(μ-η^1,η^2-C(*n*-Pr)=CH$_2$)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (3a). **3a** was prepared following the procedure outlined for **1a** and **2a**. A color change was noted within a few hours of addition of the trifluoroacetic acid. Yield: 528 mg, 92%. Anal. Calcd for C$_{20}$H$_{21}$F$_3$NiWO$_4$: C, 38.44; H, 3.39. Found: C, 38.38; H, 3.60. IR (ν(CO), dichloromethane): 2000 (s), 1812 (s), 1698 (s, CF$_3$CO$_2$) cm^{-1}. IR (Nujol): 1994 (s), 1807 (s), 1793 (s, sh), 1690 (s, CF$_3$CO$_2$).

Protonation of 4 Affording NiW(CO)$_2$(μ-η^1,η^2-C(Ph)=CH$_2$)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (4a). The synthesis of **4a** reflects that of **2a**, with a gradual color change being observed over a 3-day period after addition of the trifluoroacetic acid to **4**. Solid samples of **4a** may be obtained analytically pure, but spectra of solutions of **4a** in donor solvents show signals arising from **4**. Yield: 514 mg, 78%. Anal. Calcd for C$_{23}$H$_{19}$F$_3$NiO$_4$W: C, 41.92; H, 2.91. Found: C, 41.87; H, 2.77. IR (ν(CO), dichloromethane): 2002 (s), 1834 (s), 1695 (s, CF$_3$CO$_2$) cm^{-1}. IR (Nujol): 1994 (s), 1817 (s), 1684 (s, CF$_3$CO$_2$). [In one instance, following apparently identical procedures, ^{1}H NMR spectra of the product in acetone-d_6 exhibited resonances arising from small quantities (ca. 10%) of NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-CH=CHPh)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (**4b**) in addition to signals from **4a** and **4**].

Thermal Transformation of 4a into NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-CH=CHPh)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (4b). **4a** ($\approx$25 mg) was dissolved in toluene-d_8 (0.8 mL). The solution was added to a degassed ^{1}H NMR tube, which was then sealed under nitrogen and heated to 75 °C in an oil bath for 2 days. A dark insoluble material deposited inside the tube. A ^{1}H NMR spectrum of the toluene-d_8 solution revealed resonances arising from complex **4b**. The tube was cracked open and the solution syringed off and placed in a new ^{1}H NMR tube. The toluene was blown off under a rapid nitrogen stream and the resulting solid material dissolved in acetone-d_6, in which it was more soluble. A spectrum of this solution only revealed resonances arising from **4b**.

Protonation of 5 To Give NiMo(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (5a) and NiMo(CO)$_2$(μ-η^1,η^2-(Z)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$CF$_3$) (5b). The isomeric mixture of **5a**/**5b** was prepared in similar fashion to **2a**. Yield: 450 mg, 86%. **5a**:**5b** ≈ 2:1. IR (ν(CO), dichloromethane): 2015 (s), 1808 (s), 1691 (s, CF$_3$CO$_2$) cm^{-1}. IR (Nujol): 2026 (s), 1807 (s), 1693 (s, CF$_3$CO$_2$) cm^{-1}. Anal. Calcd for C$_{19}$H$_{19}$F$_3$MoNiO$_4$: C, 43.51; H, 3.65. Found: C, 42.07; H, 3.65.

Deuteration Experiments. ^{1}H NMR data (in ppm) are given for the vinylic resonances of the *Z* and *E* monodeutero isomers. J_{HD} values are 1/6 those of corresponding J_{HH} values and are not given. Chemical shifts in parentheses are those of small quantities of the corresponding protio isomer impurity. All experiments were carried out in a degassed Schlenk tube: a representative preparation of **1a**-(*Z*)-d_1 is given in full here.

Preparation of NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-CH=CHD)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CF$_3$CO$_2$) (1a-*d*$_1$). **1** (118 mg, 0.25 mmol) was dissolved in 10 mL of diethyl ether in a degassed Schlenk tube. The solution was cooled in an ice bath, and trifluoroacetic acid-d_1 (48 μL, 0.625 mmol) was added using a microsyringe. The Schlenk tube was placed in an ice bath for 3 days, after which the now yellow black solution was concentrated to a few milliliters in vacuo and placed in a freezer at −20 °C to effect crystallization of **1a**-(*Z*)-d_1 (130 mg, 89%). Very slow deuterium scrambling takes place when **1a**-(*Z*)-d_1 is dissolved in acetone-d_6. After a 7-week period, the ratios of **1a**-(*Z*)-d_1 to **1a**-(*E*)-d_1 were ≈4.5:1. ^{1}H NMR: **1a**-(*Z*)-d_1, δ 5.056 (5.066) [C*H*(2)D=CH]; **1a**-(*E*)-d_1, δ 3.544 (3.553) [C*H*(3)D=CH].

Preparation of NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-C(*n*-Pr)=CHD)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CF$_3$CO$_2$) (3a-(*Z*)-*d*$_1$). **3** (60 mg, 0.117 mmol) was treated with trifluoroacetic acid-d_1 (20 μL, 0.26 mmol) yielding **3a**-(*Z*)-d_1 (66 mg, 90%). **3a**-(*Z*)-d_1: ^{1}H NMR δ 4.952 (4.963) [C*H*(2)D=C(*n*-Pr)].

Preparation of NiW(CO)$_2$(μ-η^1,η^2-(*Z*)-C(Ph)=CHD)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CF$_3$CO$_2$) (4a-(*Z*)-*d*$_1$). The procedure mirrors that of **1a**-(*Z*)-d_1. Yield: 82%. When **4a**-(*Z*)-d_1 was dissolved in acetone-d_6, scrambling of the label to give a 1:1 mixture of **4a**-(*Z*)-d_1 and **4a**-(*E*)-d_1 took place within 10 h. ^{1}H NMR: **4a**-(*Z*)-d_1, δ 4.696 (4.708) [C*H*(2)D=CPh]; **4a**-(*E*)-d_1, δ 3.468 (3.477) [C*H*(3)D=CPh].

Reaction of 2a with Acetic Acid Affording NiW(CO)$_2$(μ-η^1,η^2-(*E*)-C(Me)=CHMe)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)(CO$_2$Me) (2a′). **2a** (15 mg, 0.023 mmol) was dissolved in acetone-d_6 (≈0.6 mL) and placed in a ^{1}H NMR tube. Acetic acid (3.5 μL, 0.062 mmol) was added: an ^{1}H NMR spectrum obtained immediately after addition showed that no reaction had occurred. A spectrum, obtained after a 36-h period, showed resonances assignable to **2a** and **2a′** and to an unidentified organic product.

X-ray Diffraction Study of 2a. Crystal data and data collection parameters are tabulated in Table IV. Yellow brown crystals of **2a** were grown from diethyl ether solutions at −20 °C, and a single crystal was selected and mounted on an Enraf-Nonius CAD 4 diffractometer. Unit-cell parameters were based on 25 reflections with $21.9 < \theta < 22.5$. Three standard reflections were monitored every 5000 s of beam time; no decay was observed.

The structure was solved by direct methods and an empirical absorption correction was applied.[39] No correction for extinction was applied, and hydrogen atoms were not refined: their positions were calculated by using idealized geometries and a C–H bond distance of 0.95 Å. For hydrogen atoms of the methyl groups, one atom was located in a Fourier difference map, its position idealized and the remaining hyrogen atomic positions calculated. Refinement converged at $R = 0.030$ and $R_w = 0.043$.

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Registry No. 1, 121011-38-9; **1a**, 121029-31-0; **1a**-(*Z*)-d_1, 121011-40-3; **1a**-(*E*)-d_1, 121054-48-6; **2**, 110512-13-5; **2a**, 121011-41-4; **2a′**, 121011-42-5; **3**, 121011-39-0; **3a**, 121011-43-6; **3a**-(*Z*)-d_1, 121011-44-7; **3b**, 121029-32-1; **4**, 110512-17-9; **4a**, 121011-45-8; **4a**-(*Z*)-d_1, 121011-46-9; **4a**-(*E*)-d_1, 121054-49-7; **4b**, 121011-47-0; **5**, 99280-72-5; **5a**, 121011-48-1; **5b**, 121054-50-0; NiMo(CO)$_2$(μ-η^2,η^2-PhC$_2$H)(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me), 110512-09-9; NiW(CO)$_4$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me), 110512-11-3.

Supplementary Material Available: Full listings of bond distances, bond angles, anisotropic thermal parameters for nonhydrogen atoms, and positional parameters for hydrogen atoms (9 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Simple Functional Siloles. 3,4-Dimethylsiloles with Si–F, Si–O, or Si–N Bonds and Other Silicon-Substituted Derivatives

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Stable 1-alkoxy (RO = MeO, ^{i}PrO) and 1-dialkylamino (R$_2$N = Et$_2$N) 1,3,4-trimethylsiloles have been prepared from 1,3,4-trimethylsilole (**1**). The 1-fluoro derivative appears to be less stable, and the synthesis of the 1-chloro derivative failed. 1-*n*-Butyl-, 1-allyl-, and 1-phenylsiloles have also been prepared from **1** and 1-phenyl-3,4-dimethylsilole (**2**) by Si–H substitution using lithium reagents, which can give a second substitution on the exocyclic Si–R bond. The low-temperature reaction of potassium hydride with **1** and **2** did not allow the chemical characterization of corresponding silacyclopentadienide anions.

Having obtained the first stable simple siloles with a silicon–hydrogen bond,[1] the functionalization of these metalloles on the heteroatom appeared possible either by direct substitution of the hydrogen atom or via the cor-

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