Reactions of unsaturated nickel-molybdenum and nickel-tungsten complexes with diazomethane: x-ray diffraction study of the .mu.2-methylene compound (.eta.5-C5Me5)Ni(.mu.2-CH2)(.mu.2-CO)W(CO)2(.eta.5-C5H5)(Ni-W)

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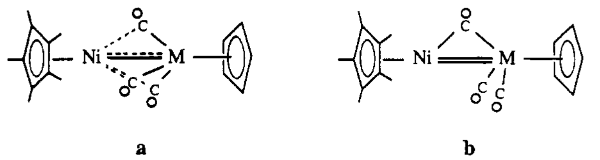

Figure 2. Alternative representations of **2b**.

and are isoelectronic with the 32-electron complexes $Fe_2(\mu_2\text{-}CO)_3(\mu\text{-}C_5R_5)_2$ (R = H, Me).[19] These diiron species contain two unpaired electrons residing in an e-type HOMO, which stems from the C_3 symmetry axis present.

The broad or absent ^1H NMR signals for **2b** and **2b′** suggest that both complexes are paramagnetic in solution. Preliminary data indicate that crystals of **2b** are paramagnetic ($\mu = 2.7 \pm 0.2\ \mu_B$ from 175 to 270 K; μ decreases below 175 K).[20] Even if **2b** has a singlet ground state, a small HOMO–LUMO gap may result in the thermal population of the LUMO at ambient temperature. In contrast, samples of **2b′** appear to be diamagnetic: the inherent asymmetry of this species destroys the pseudo C_3 axis presumably present in **2b**. Startlingly different magnetic behavior between $\eta\text{-}C_5H_5$ and corresponding $\eta\text{-}C_5H_4Me$ complexes is not unprecedented.[21]

2b reacts with PhC_2H, affording the μ-alkyne complex $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta\text{-}C_5H_5)$(*Ni–W*), the nickelacyclobutenone species $(\eta\text{-}C_5Me_5)Ni\{\mu\text{-}C(O)C(H)C(Ph)\}W(CO)_2(\eta\text{-}C_5H_5)$(*Ni–W*), and other products. Prolonged thermolysis of **2a** and **2b** led to irreversible CO loss, yielding the 60-electron tetrahedral clusters $Ni_2M_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2$ (**3a**, M = Mo; **3b**, M = W) and not Ni_3M species (Scheme I).[22] The ^1H NMR spectra of **3a** and **3b** indicate an effective mirror plane of symmetry is present on the NMR time scale.[23]

Parts a and b of Figure 2 depict alternative representations of **2b**. The Ni=W bond shown in Figure 2b, suggested by the short Ni–W bond in **2b′**, is useful in rationalizing the chemistry of **2a** and **2b**. Addition of CO to **2a** and **2b** quantitatively regenerated **1a** and **1b**, respectively, illustrating the unsaturation of these species.[24] Both compounds add a methylene group across the Ni=M bond when treated with diazomethane, yielding Ni–Mo and Ni–W μ-CH_2 species.[25]

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Supplementary Material Available: Tables of crystal data and data collection parameters, positional parameters for hydrogen and non-hydrogen atoms, bond lengths and angles, thermal parameters for non-hydrogen atoms, and VT ^1H NMR data for **2b′** (18 pages); a structure factor listing (22 pages). Ordering information is given on any current masthead page.

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[19] (a) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561. (b) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174. (c) Hooker, J. K.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022. The species $M_2(\mu\text{-}CO)_3(\eta\text{-}C_nR_n)_2$(*M≡M*) (M = Cr, R = H, n = 6; M = Mn, Re, R = Me, n = 5; M = Fe, R = H, Me, n = 4)[19d–g] and $CoM(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_4Me_4)$(*Co=M*) (M = Mo, W)[19h] have similar structures. (d) Klüfers, P.; Knoll, L.; Reiners, C.; Reiss, K. *Chem. Ber.* **1985**, *118*, 1825. (e) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27. (f) Bernal, I.; Korp, J. D.; Herrmann, W. A.; Serano, R. *Chem. Ber.* **1984**, *117*, 434. (g) Fischler, I.; Hildenbrand, K.; Koerner von Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 54. (h) Härter, P.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 839.

[20] Measurements were obtained on a SQUID magnetometer. Data are complicated by the high oxygen sensitivity of **2b** and **2b′** and are not very accurate, thus, no diamagnetic correction was attempted. Some field dependence, arising from attendant paramagnetic and/or ferromagnetic impurities, was noted, and more precise readings are planned.

[21] Pulliam, C. R.; Englert, M. H.; Dahl, L. F. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; American Chemical Society: Washington, DC, 1985; INOR 387.

[22] **2a** (439 mg, 1.00 mmol) was refluxed in toluene for 2 days. Concentration of the solution followed by chromatography on silica gel, with dichloromethane as the eluting solvent, afforded an olive green band that was pumped to dryness in vacuo. Recrystallization from toluene afforded **3a** (~145 mg, 35%). **3b** was prepared similarly.

[23] Spectroscopic data for **3a**: ^1H NMR (chloroform-*d*, ppm) δ 4.92 (10 H, C_5H_5), 2.22 (30 H, C_5Me_5); IR (ν(CO), cm^{-1}, THF) 1957 (m), 1913 (m, br); MS (*m/e*, amu) 822 $(M)^+$, 766 $(M - 2CO)^+$, 738 $(M - 3CO)^+$, 710 $(M - 4CO)^+$; HRMS calcd for $Ni_2Mo_2C_{34}H_{40}O_4$ 821.9726, found 821.9736. Spectroscopic data for **3b**: ^1H NMR (chloroform-*d*) δ 5.06 (10 H, C_5H_5), 1.77 (30 H, C_5Me_5); IR (ν(CO), cm^{-1}, Nujol) 1949 (s), 1918 (w), 1896 (s), 1887 (m, br); MS (*m/e*, amu) 998 $(M)^+$.

[24] Other unsaturated complexes such as $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$(*Mo≡Mo*),[2] $Fe_2(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_2$,[19a] and $CoM(\mu\text{-}CO)_3(\eta\text{-}C_4Me_4)(\eta\text{-}C_5H_5)$ (M = Mo, W)[19h] also add CO, forming the corresponding saturated species.

[25] The preparation, structure, and preliminary chemistry of the complex $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CH_2)(\mu\text{-}CO)W(CO)_2(\eta\text{-}C_5H_5)$ are described in: Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics*, following communication in this issue.

Reactions of Unsaturated Nickel–Molybdenum and Nickel–Tungsten Complexes with Diazomethane: X-ray Diffraction Study of the μ_2-Methylene Compound $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CH_2)(\mu_2\text{-}CO)W(CO)_2(\eta^5\text{-}C_5H_5)$(*Ni–W*)

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Summary: The compounds $(\eta^5\text{-}C_5Me_5)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$ (M = Mo, W) react with diazomethane, affording the first fully characterized nickel methylene complexes. The structure of $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CH_2)(\mu_2\text{-}CO)W(CO)_2(\eta^5\text{-}C_5H_5)$(*Ni–W*) was established by X-ray diffraction. 2-Butyne reacts with the Ni–W μ-methylene complex by effectively inserting into the Ni–CH_2 bond to generate $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CO)\{\mu_2\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}W(CO)(\eta^5\text{-}C_5H_5)$.

The species $(\eta^5\text{-}C_5Me_5)(CO)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$ (M = Mo, W) reversibly lose CO, affording the unsaturated complexes $(\eta^5\text{-}C_5Me_5)Ni\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$ (**1a**, M = Mo; **1b**, M = W).[1] Diazomethane reactions with **1a** or **1b** were of interest as unsaturated dinuclear compounds frequently add CH_2 groups, yielding μ-methylene complexes when treated with this reagent,[2] and limited numbers of such species are recognized.[3] The rich chemistry nickel compounds exhibit toward unsaturated hydrocarbons,[4] coupled with the role alkylidene complexes play in organic syntheses[5] and olefin polymerizations,[6] olefin metathesis,[7] and Fischer–Tropsch chemistry,[7d] suggests that new μ-

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[1] Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E.; Geselbracht, M. J.; Stacy, A. M. *Organometallics*, preceding communication in this issue.

[2] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159 and references cited therein. Diazoalkane complexes are occasionally isolated.

methylene species are worthy synthetic targets.

Diazomethane reacts instantaneously with **1a** at −78 °C, affording a brown product (**2a**) in high yield. **1b** similarly affords **2b**.[8] No nitrogen quadrupolar broadening is observed for the signals assigned to the $C\mathrm{H}_2$ carbon atoms of these species in ^{13}C NMR spectra, implying that μ-CH$_2$ and not diazomethane ligands are present. Analytical and spectroscopic data[9] also suggest **2a** and **2b** can be formulated as $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}(\mu_2\text{-CH}_2)(\mu_2\text{-CO})\text{M(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$-(*Ni–M*) (**2a**, M = Mo; **2b**, M = W), making **2a** and **2b** the first nickel methylene complexes isolated.[10] However, spectral data for these compounds exhibit unusual features: (1) In ^{1}H NMR spectra, the $\mathrm{C}H_2$ protons of **2a** and **2b** resonate at uncharacteristically high field shifts (δ 4.78 and 4.08 ppm, respectively)[11] compared to the shifts for other metal–metal-bonded μ_2-methylene complexes.[12] (2) ^{13}C NMR chemical shifts for the $C\mathrm{H}_2$ carbon atoms (δ 87.9 (**2a**), 57.2 ppm (**2b**)) are also peculiar.[13] (3) While the ^{13}C–^{1}H coupling of the CH$_2$ group (144 Hz) lies in the normal range of μ-CH$_2$ ligands in other such complexes,[2] tungsten-183 coupling to these nuclei is small. The ^{1}H NMR spectrum of **2b** reveals no ^{183}W–^{1}H coupling, and the ^{183}W–^{13}C coupling of 39 Hz is less than values seen in other tungsten μ-CHR species.[14,15] (4) IR spectra for both species display six ν(CO) bands for these presumably tricarbonyl compounds.

^{1}H NMR chemical shifts exhibited by the $\mathrm{C}H_2$ groups of these species may be characteristic of nickel–methylene complexes, none of which have hitherto been isolated, and are possibly related to the high electron density on the nickel atoms.[16] Nevertheless, an X-ray diffraction study was deemed necessary to unambiguously establish the structure of **2a** or **2b**.

A crystallographic study determined that **2b** is indeed $(\eta\text{-C}_5\text{Me}_5)\text{Ni}(\mu_2\text{-CH}_2)(\mu_2\text{-CO})\text{W(CO)}_2(\eta\text{-C}_5\text{H}_5)$;[17] an ORTEP plot is shown in Figure 1. A single nickel–tungsten bond of 2.5689 (6) Å[18] is present, spanned by a methylene ligand and a carbonyl group. The Ni–CH$_2$ distance is 1.906 (5) Å, a typical Ni–C single-bond value. The W–C(1) distance of 2.185 (5) Å lies within the fairly large range observed in bridging alkylidene complexes of tungsten.[19] The NiWC$_2$ molecular core is arranged in a butterfly geometry with the Ni–W bond forming the hinge and the CO and CH$_2$ groups in wingtip positions. The angle subtended by the Ni–C(O)–W and Ni–C(H$_2$)–W planes is small (108.8°).

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(3) Other heterodinuclear μ-methylene complexes include: (a) Theopold, K. H.; Bergman, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 2489. (b) Davis, R. E.; Gadol, S. M. *Organometallics* **1982**, *1*, 1607. (c) Arsenault, G. J.; Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2255. (d) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706. (e) Macklin, P. D.; Mirkin, C. A.; Viswanathan, N.; Williams, G. D.; Geoffroy, G. L. *J. Organomet. Chem.* **1987**, *334*, 117. (f) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853. (g) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.

(4) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. II.

(5) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Spring Valley, CA, 1987; pp 783–823.

(6) (a) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 502. (b) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (c) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (d) Reference 5b, pp 577–608.

(7) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Feldman, J.; Murzdek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260 and references cited therein. (c) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346. (d) Reference 5b, p 654–656, 794–796 and references cited therein.

(8) CH$_2$N$_2$ (5 mL of a ~0.3 mM Et$_2$O solution, ~1.5 mmol) was added to a −78 °C solution of **1a** (439 mg, 1.0 mmol) in THF (35 mL). An instantaneous color change (deep blue to brown) and effervescence ensued. After the mixture was warmed to 20 °C, solvents were removed (into an acetic acid trap to destroy excess CH$_2$N$_2$). The residue was dissolved in hexane; chromatography on silica gel and elution with a hexane–ether (5:1) mixture afforded traces of **1a** and a dark band that yielded dark brown crystals of **2a** (~320 mg, 70%) from hexane. **2b** (prepared similarly from **1b**) moves sluggishly on silica gel; chromatographic purification is best omitted. **1b** (527 mg, 1.0 mmol) afforded **2b** (410 mg) in 76% yield.

(9) Spectroscopic data for **2a**: ^{1}H NMR (benzene-d_6) δ 4.78 (2 H, $\mathrm{C}H_2$), 4.47 (5 H, C_5H_5), 1.89 (15 H, C_5Me_5); ^{13}C NMR (benzene-d_6) δ 101.0 ($C_5\mathrm{Me}_5$), 90.9 ($C_5\mathrm{H}_5$), 87.9 ($C\mathrm{H}_2$), 9.2 (C_5Me_5) CO resonances absent; IR (ν(CO), hexane, cm^{-1}) 2047 (w), 2021 (m), 1986 (vs), 1938 (s), 1792 (s), 1688 (w). Anal. Calcd for NiMoC$_{19}$H$_{22}$O$_3$: C, 50.38; H, 4.90; N, 0.00. Found: C, 50.18; H, 5.00; N, 0.00. Spectroscopic data for **2b**: ^{1}H NMR (benzene-d_6) δ 4.43 (5 H, C_5H_5), 4.08 (2 H, $\mathrm{C}H_2$), 1.94 (15 H, C_5Me_5); ^{13}C NMR (benzene-d_6, J in Hz, 20 °C) δ ~237 (CO, br), 100.5 ($C_5\mathrm{Me}_5$), 89.1 ($C_5\mathrm{H}_5$), 57.2 ($C\mathrm{H}_2$, $J_{\mathrm{WC}} = 38$, $J_{\mathrm{CH}} = 144$), 9.09 (C_5Me_5, $J_{\mathrm{CH}} = 125$); ^{13}C NMR (acetone-d_6, J in Hz, −40 °C) δ 238.1 (CO), 217.0 (CO), other resonances essentially the same; IR (ν(CO), hexane, cm^{-1}) 2022 (m), 2012 (w), 1984 (s), 1932 (vs), 1777 (s), 1683 (w); MS (m/e, amu) 541 (M)$^+$, 513 (M − CO)$^+$, with the correct NiW isotopic envelope. Anal. Calcd for NiWC$_{19}$H$_{22}$O$_3$: C, 42.19; H, 4.10; N, 0.00. Found: C, 42.18; H, 4.17; N, 0.00.

(10) Nickel–carbene complexes (terminal or bridging) are not common. Examples include the following: (a) $\mathrm{Ni_3(CO)_3\{\mu_2\text{-}C(OMe)Ph\}_3}$: Fischer, E. O.; Beck, H. J. *Angew. Chem., Int. Ed.* **1970**, *9*, 72. (b) $\mathrm{Ni(CO)_3\{C(OEt)(NEt_2)\}}$: Fischer, E. O.; Kreissl, F. R.; Winkler, E.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 588. (c) $\mathrm{Ni(CO)_3\{\overline{CN(Me)CH_2CH_2N}(Me)\}}$: Lappert, M. F.; Rye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172. (d) $(\eta^5\text{-}\mathrm{C_5H_5})\overline{\mathrm{Mn(CO)_2\{\mu\text{-}C(OMe)(Ph)\}Ni}}\mathrm{(PPh_3)_2}$: Berry, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1601. A transient nickel–diazomethane species has been observed: Bogdanović, B.; Kröner, M.; Wilke, G. *Justus Liebigs Ann. Chem.* **1966**, *699*, 1. Many molybdenum and tungsten alkylidene and carbene complexes are known, including a tungsten methylene complex.[11]

(11) μ-$\mathrm{C}H_2$ protons typically resonate at δ 6.0–11.0 ppm in ^{1}H NMR spectra.[2] The $\mathrm{C}H_2$ protons of the complex $[\mathrm{W(CH_2)(PMe_3)_4Cl}]^+\mathrm{CF_3SO_3}^-$ exhibit a ^{1}H NMR chemical shift of δ 0.16 ppm at 25 °C, but this species exhibits unusual fluxional behavior and can be regarded as being in dynamic equilibrium with an alkylidyne hydride species: Schrock, R. R.; Holmes, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 4599.

(12) Such shifts are observed for complexes lacking metal–metal bonds. For example, ^{1}H NMR $\mathrm{C}H_2$ chemical shifts in a series of A-frame Pd species span the 1.6–2.5 ppm range: Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(13) $C\mathrm{H}_2$ carbon atoms resonate at δ 100–210 ppm in ^{13}C NMR spectra.[2] To our knowledge, high-field ^{13}C NMR chemical shifts for μ-CH$_2$ groups are found elsewhere only in a series of Os$_3$ clusters. (a) $\mathrm{Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}}$, δ 25.8: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. (b) $\mathrm{Os_3(\mu\text{-}CH_2)(CO)_{11}}$, δ 62.5: Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (c) $\mathrm{Os_3Pt(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2}$, δ 76.5: Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 2228. (d) $\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9\{P(C_6H_{11})_3\}(C_6H_{11}NC)}$, δ 58.6: Farrugia, L. J. *Organometallics* **1989**, *8*, 2410.

(14) $J_{\mathrm{WC}} = 100 \pm 6$ Hz for a series of μ_2-benzylidene tungsten–osmium clusters: Chi, Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1987**, *6*, 301.

(15) Values similar to those of **2b** are observed in tungsten μ-carbene species. In the complex $\mathrm{(OC)_5\overline{W\{\mu\text{-}C(OMe)Ph\}Pt}(cod)}$, $J_{\mathrm{WC}} = 41$ Hz: Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1593.

(16) Electron-rich ligands have been noted to shift $\mathrm{C}H_2$ ^{1}H NMR signals upfield.[2] The d^{10} nickel atoms, ligated to η^5-C$_5$Me$_5$ groups in both complexes, are particularly electron-rich.

(17) A crystal of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}(\mu_2\text{-CH}_2)(\mu_2\text{-CO})\text{W(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$ (**2b**, dimensions 0.63 × 0.52 × 0.47 mm), grown from hexane solution, belonged to the triclinic space group $P\bar{1}$ (No. 2) at 20 °C, with $a = 8.518$ (2) Å, $b = 10.280$ (1) Å, $c = 10.719$ (1) Å, $\alpha = 89.26$ (1)°, $\beta = 87.24$ (1)°, $\gamma = 79.18$ (1)°, $V = 920.9$ Å^3, and $Z = 2$. Of the 4204 unique data, 3675 with $I > 3\sigma(I)$ were used to refine the 217 variables. An empirical absorption correction was applied, together with corrections for Lorentz and polarization effects. The structure was solved with use of SHELX-86. Heavy atoms were refined anisotropically. Hydrogen atoms, located and added to F_c listings, were not refined; their thermal parameters were set at 1.3 times the values of their attached carbon atoms. Refinement converged at $R(F_o) = 0.039$ and $R_w(F_o) = 0.053$. The large crystal size and imperfect absorption correction applied led to larger than desirable electron density artifacts near the tungsten atom.

(18) Most bridged Ni–W single bonds average 2.60 ± 0.03 Å: Chetcuti, M. J.; Fanwick, P. E.; Gordon, J. C.; Green, K. A.; Morgenstern, D. *Organometallics* **1989**, *8*, 1790.

(19) W–μ-C values span the 2.18 (2)–2.29 (1) Å range in a series of W$_2$(μ-CHR) species: (a) Levisalles, J.; Rudler, H.; Dahan, F.; Jeannin, Y. *J. Organomet. Chem.* **1980**, *188*, 193. (b) Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* **1987**, *323*, 353.

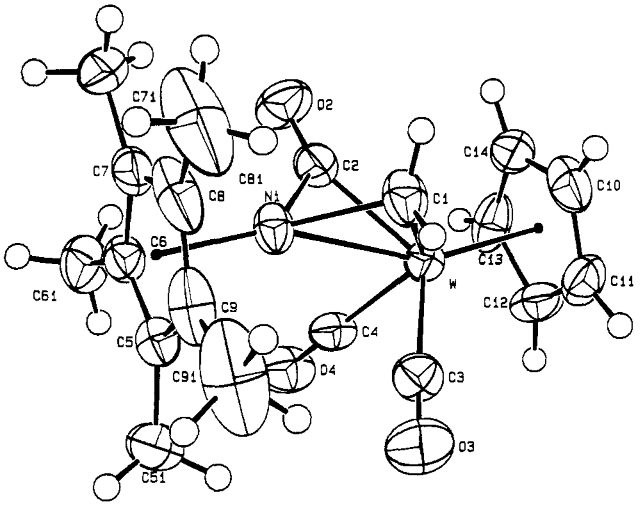
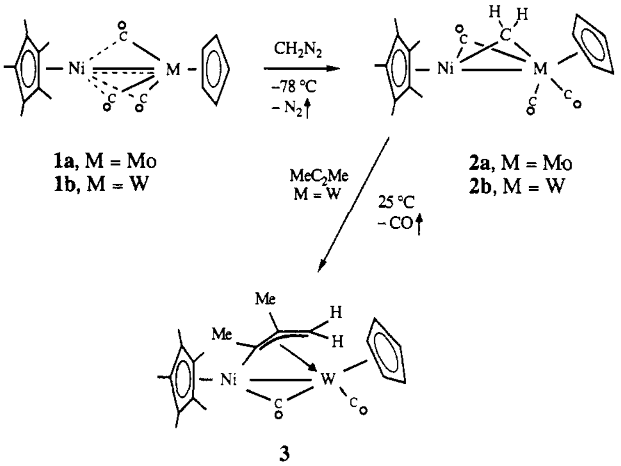


Figure 1. ORTEP diagram of $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CH_2)(\mu_2\text{-}CO)W(CO)_2(\eta^5\text{-}C_5H_5)$(*Ni–W*) (**2b**) (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ni–W = 2.5689 (6); Ni–C(1) = 1.906 (5); W–C(1) = 2.185 (5); Ni–C(2) = 1.916 (6); W–C(2) = 2.073 (6); Ni–C(1)–W = 77.5 (2); Ni–W–C(1) = 46.4 (1); Ni–C(2)–W = 80.1 (2); Ni–W–C(2) = 47.3 (1).

Scheme I. Reactions of 1a and 1b with Diazomethane and the Effective Insertion of MeC_2Me into the Ni–CH_2 Bond of 2b, Affording 3



1a, M = Mo
1b, M = W

2a, M = Mo
2b, M = W

3

Nickel and tungsten atoms are linked to η^5-C_5Me_5 and η^5-C_5H_5 groups respectively, and two terminal carbonyl ligands complete the tungsten atom's coordination sphere.

The CH_2 protons of **2b** (and **2a**) resonate as singlets in ^{1}H NMR spectra even at –70 °C, at variance with what is expected if the solid-state structure of **2b** is maintained in solution. However, ^{13}C NMR data establish the fluxionality of **2b**. At ambient temperatures a single broad CO signal is seen; at –40 °C it sharpens considerably and another CO resonance appears. A bridge–terminal carbonyl exchange process operative in **2b** may render the CH_2 protons equivalent.

Preliminary data indicate **2a** and **2b** are reactive species. Alkynes frequently insert into metal–carbon bonds of terminal or bridging alkylidene complexes, generally affording vinyl carbene species or their derivatives.[5a,20] **2b** forms $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CO)\{\mu_2\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}W(CO)(\eta^5\text{-}C_5H_5)$(*Ni–W*) (**3**) under very mild conditions when treated with 2-butyne. This species stems from the effective alkyne insertion into the nickel and not the tungsten–CH_2 bond of **2b** (Scheme I).[21] **3** is best regarded as a nickel-substituted π-allyl complex[22] in which the three allylic carbon atoms are coordinated to the tungsten atom. Its structure was deduced by the close correspondence of its spectral features[23] to those of the structurally characterized species $(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}CO)\{\mu_2\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}Mo(CO)(\eta^5\text{-}C_5H_4Me)$(*Ni–Mo*), which was prepared by a different synthetic route.[24] Further reactivity studies of **2a** and **2b** are underway.

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Supplementary Material Available: Tables of crystal data and data collection parameters, atomic coordinates for non-hydrogen and hydrogen atoms, thermal parameters for non-hydrogen atoms, and bond lengths and angles of **2b** (10 pages); a structure factor listing (26 pages). Ordering information is given on any current masthead page.

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[20] For a recent example and list of leading references in this field, see: Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

[21] **2b** (161 mg, 0.298 mmol) was dissolved in hexane (15 mL), 2-butyne (32 μL, ~4 mmol) was added, and the solution was stirred overnight. The mixture was then filtered, concentrated, and cooled to –20 °C, affording crystals of **3** (85 mg, 50%). IR spectra of the mother liquor indicated that the main carbonyl-containing species present in solution was unreacted **2b**.

[22] The C(Me)C(Me)CH$_2$ fragment can bond in three electronically equivalent but structurally different μ-η^1,η^3 modes in dimetal systems—as a vinyl carbene, as part of a dimetallacyclopentene species, or as a metal-substituted allyl. The structural characteristics of each class are outlined in a report of a similar diiron species: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803.

[23] Spectroscopic data for **3**: ^{1}H NMR (benzene-d_6) δ 4.29 (5 H, C_5H_5), 2.83 (d, H, CH*H*, J_{HH} = 2.1 Hz), 2.58 (d, H, C*H*H, J_{HH} = 2.1 Hz), 2.00 (3 H, Me), 1.85 (15 H, C_5Me_5), 1.56 (3 H, Me, J_{WH} = 3.6 Hz); ^{13}C NMR (benzene-d_6) δ 253.2 (μ-CO), 216.3 (CO), 125.2 (CMe), 100.2 (C_5Me_5), 98.2 (CMe), 90.1 (C_5H_5), 37.6 (CH_2), 27.2 (Me), 20.3 (Me), 9.4 (C_5Me_5); IR (ν(CO), hexane, cm^{-1}) 1930 (s), 1759 (μ-CO, s); MS (*m/e*, amu) 566 (M)$^+$, with the correct NiW isotopic envelope. Anal. Calcd for $NiWC_{23}H_{28}O_3$: C, 46.60; H, 4.98. Found: C, 46.85; H, 5.00.

[24] Chetcuti, M. J.; McDonald, S. R.; Rath, N. P. *Organometallics* **1989**, *8*, 2077.

Isolation and Structure of the Fluxional Phosphine Complex (η^3-PR$_3$)Mo(CO)$_3$ (R = 2,4,6-Trimethoxyphenyl)

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Summary: We report the synthesis of the novel fluxional molecule (η^3-TMPP)Mo(CO)$_3$ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) from a reaction between (C_7H_8)Mo(CO)$_3$ and TMPP. A single-crystal X-ray study revealed that the molecule is comprised of a Mo(0) center ligated by three carbonyl ligands and a TMPP ligand in a facial bonding mode. The metal–ether interactions from the pendant methoxy groups are quite labile. Variable-temperature ^{1}H NMR spectra in toluene-d_8 and CD_2Cl_2 reveal that a low-energy intramolecular exchange process is occurring.

We have been engaged in a broad study of the coordination chemistry of a versatile new phosphine ligand with transition metals possessing d^n configurations (n = 2–10). The tertiary phosphine ligand is tris(2,4,6-trimethoxy-

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