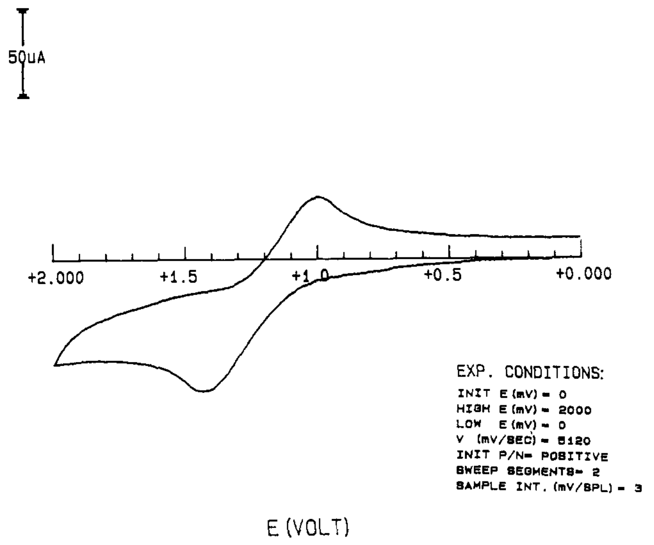

Figure 2. Cyclic voltammogram of $Ru(O)(CH_2SiMe_3)_4$ in CH_2Cl_2, 0.1 M $[NBu_4][BF_4]$.

mation does not allow us to distinguish between isomers due to the distortion from square-pyramidal geometry observed in the crystal structure of 4 or to rotational isomers about the $Os\text{-}CH_2SiMe_3$ bond.

The electronic natures of 4 and 5 were probed with UV–visible spectroscopy and electrochemical techniques. Both complexes had intense charge-transfer transitions for the metal–oxo moiety and relatively weak d to d transitions.[15] Each of these complexes exhibited a one-electron-oxidation wave by cyclic voltammetry, Osteryoung square-wave voltammetry, and coulometry.[16] In $Os(O)(CH_2SiMe_3)_4$, the oxidation wave is found at 1.19 V vs Ag/AgCl in methylene chloride. The oxidation is reversible with equal anodic and cathodic currents and a peak to peak separation of 72 mV. The oxidation wave of the ruthenium complex at 1.20 V is quasi-reversible with approximately equal anodic and cathodic currents only at fast scan rates (2000–5000 mV/s) and a peak to peak separation of 400 mV. Neither complex exhibited reversible reduction waves.

Now that the ruthenium and osmium complexes $M(O)(CH_2SiMe_3)_4$ have been prepared and characterized, we have series of complexes for these metals that differ only in the nature of the multiply bonded heteroatom ligand. Studies on the comparative reaction chemistry of these complexes is now underway.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant No. CHE 88-07707) in support of this work. Spectra were obtained on NMR instruments purchased through grants from the National Institutes of Health and the National Science Foundation (Grant Nos. NIH PHS 1532135, NIH 1531957, and NSF CHE 85-14500).

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles (8 pages); a table of final observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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[15] Ultraviolet and visible spectra were recorded on a Perkin-Elmer Lambda 3 UV–vis spectrometer. UV–vis for $Os(O)(CH_2SiMe_3)_4$ (CH_2Cl_2, 5.6×10^{-5} M, nm): 233 (ϵ = 19 000), 386 (ϵ = 23), 476 (ϵ = 16), 500 (ϵ = 18). UV–vis for $Ru(O)(CH_2SiMe_3)_4$ (CH_2Cl_2, 5.9×10^{-4} M, nm): 236 (ϵ = 4900), 514 (ϵ = 390).

[16] Electrochemical experiments were performed on a BAS 100 electrochemical analyzer, with Pt working and auxiliary electrodes and an Ag/AgCl reference electrode. Methylene chloride solutions were 0.1 M in $[NBu_4][BF_4]$ and 10^{-3}–10^{-4} M in sample.

Unsaturated Mixed-Metal Complexes: Syntheses of $(\eta\text{-}C_5Me_5)Ni\text{-}M(CO)_3(\eta\text{-}C_5H_5)$ (M = Mo, W) and X-ray Diffraction Study of $(\eta\text{-}C_5Me_5)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_4Me)$

Michael J. Chetcuti* and Brian E. Grant

Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, Indiana 46556

Phillip E. Fanwick

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Margaret J. Geselbracht and Angelica M. Stacy

Department of Chemistry
University of California at Berkeley
Berkeley, California 94720

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Summary: Mild thermolysis of $(\eta\text{-}C_5Me_5)(CO)Ni\text{-}M(CO)_3(\eta\text{-}C_5H_5)$ (M = Mo, W) afforded the paramagnetic coordinatively unsaturated species $(\eta\text{-}C_5Me_5)Ni\text{-}M(CO)_3(\eta\text{-}C_5H_5)$. Irreversible decarbonylation to the tetrahedral clusters $Ni_2M_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2$ occurred on prolonged heating. The compound $(\eta\text{-}C_5Me_5)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_4Me)$ was characterized by an X-ray diffraction study: short nickel–tungsten distances of 2.475 (2) and 2.457 (2) Å for the two independent molecules in the unit cell indicate multiple Ni–W bond character.

Coordinatively unsaturated metal species display a rich chemistry, and their study is of great interest. Dinuclear complexes of this type often contain multiple metal–metal bonds and may be classified into two groups. Molecules in which the metals have formal oxidation states ≥II are found in one set.[1] The other group contains metal in lower formal oxidation states; π-acid ligands such as $\eta\text{-}C_5H_5$ and CO are generally present. Few molecules exist in this class, and except for the compounds $[M(CO)_2(\eta\text{-}C_5R_5)]_2$ ($M{\equiv}M$, M = Cr, Mo, W; R = H, Me)[2] and $[M(\mu_2\text{-}CO)(\eta\text{-}C_5Me_5)]_2$ ($M{=}M$, M = Co, Rh, Ir),[3] their chemistry has not been probed in depth.[4] Mixed-metal multiply bonded compounds are rare in both sets: examples include a few group 6[5] species and the group 9 complexes $CoM(\mu_2\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ ($Co{=}M$, M = Rh, Ir).[3,6] In most cases the metals

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[1] (a) Walton, R.; Cotton, F. A. In *Multiple Bonds between Metal Atoms*; Wiley-Interscience: New York, 1982. (b) Cotton, F. A.; Walton, R. *Struct. Bonding* **1985**, *62*, 1. (c) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21.

[2] (a) Curtis, M. D. *Polyhedron* **1987**, *6*, 759. (b) For a summary of earlier work, see: Curtis, M. D. In *Reactivity of Metal-Metal Bonds*; ACS Symposium Series 155; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; p 221.

[3] (a) Schore, N. E.; Illenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 255, 256; **1977**, *99*, 1781. (b) Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21. (c) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 193. (d) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1309.

[4] Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101.

[5] (a) $MoW(^tBuCO_2)_4(Mo\overset{4}{-}Mo)$: Katovic, V.; Templeton, J. L.; Hoxmeier, R. J.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 5300. (b) $CrMo(MeCO_2)_4(Cr\overset{4}{-}Mo)$: Garner, D. C.; Senior, R. G.; King, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3526. (c) MoW(2-hydroxy-6-methylpyridine)$_4$-$(Mo\overset{4}{-}W)$: Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1978**, *17*, 3237. (d) $MoW(CO)_4(\eta\text{-}C_5H_5)_2(Mo{\equiv}Mo)$: Curtis, M. D.; Fotinos, N. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, *22*, 1559.

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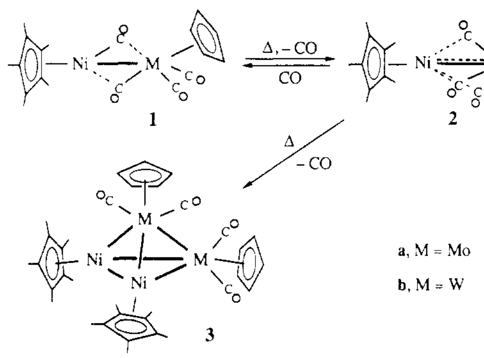
Scheme I



belong to the same group in the periodic table. The syntheses of multiply bonded Ni–Mo and Ni–W species are described here.

Thermolysis of (η-C_5H_5)(CO)Ni–M(CO)$_3$(η-C_5H_4Me) (M = Mo, W)[7] affords the clusters $Ni_3M(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_3(\eta\text{-}C_5H_4Me)$.[8] However, the Ni–Ni bonds in the cluster $Ni_3(\mu_3\text{-}CO)_2(\eta\text{-}C_5Me_5)_3$[9] are very long, reflecting the substantial steric strain present. We doubted that pyrolysis of (η-C_5Me_5)(CO)Ni–M(CO)$_3$(η-C_5H_5) (**1a**, M = Mo; **1b**, M = W)[10] would yield the even more congested tetrahedral $Ni_3M(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_3$ species.

Green solutions of **1b** turn Mediterranean blue when refluxed gently,[11] and pyrophoric crystals of **2b** deposit on cooling. **1a** is similarly decarbonylated to **2a**.[12] No ^1H NMR signals were noted for **2b**, but its MS spectrum exhibits a parent peak whose *m/e* ratio and NiW isotopic envelope are in accord with **2b** being the complex (η-C_5Me_5)Ni–W(CO)$_3$(η-C_5H_5) (Scheme I). Its IR spectrum exhibited a single ν(CO) stretch at 1828 cm^{-1} in methylcyclohexane. The radically different IR spectrum observed in THF suggests that this solvent ligates to **2b** in solution, possibly forming the metastable coordinatively saturated species NiW(THF)(CO)$_3$(η-C_5H_5)(η-C_5Me_5).

An X-ray data set was collected for **2b**, but disorder prevented the location of the atoms. The structure of the related species (η-C_5Me_5)Ni–W(CO)$_3$(η-C_5H_4Me) (**2b′**),[13] established by X-ray diffraction,[14] consists of a tripodal W(CO)$_3$(η-C_5H_4Me) group interacting asymmetrically with a (η-C_5Me_5)Ni unit (Figure 1) via three semibridging CO ligands and a Ni–W bond. The Ni–W bonds of 2.475 (2) and 2.457 (2) Å for the two independent molecules in the unit cell are short and indicate significant multiple-bond character: single Ni–W bonds average 2.60 ± 0.03 Å.[15] One Ni–C_{CO} interaction (2.12 Å, average) is longer than found for typical Ni–$C_{\mu_2\text{-}CO}$ distances, while the other two are very long (2.38 Å, average).[16] The dienyl rings are close to parallel and eclipse each other, more so in one molecule than in the other. (Cp*$_{centroid}$–Ni–W–Cp′$_{centroid}$ torsion angles are 22 and 27°.)

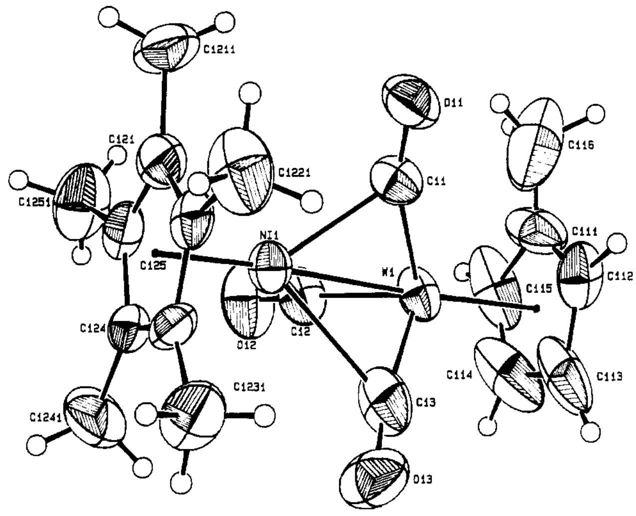


Figure 1. ORTEP diagram (30% probability ellipsoids) for one of the two independent molecules of **2b′**, (η-C_5Me_5)Ni-W-(CO)$_3$(η-C_5H_4Me). Key bond lengths (Å) and angles (deg) for molecule A, followed by equivalent parameters of molecule B, are as follows: Ni–W = 2.475 (2), 2.457 (2); W–C(11) = 1.97 (1), 1.91 (2); W–C(12) = 1.96 (2), 1.93 (2); W–C(13) = 1.91 (2), 1.88 (2); Ni–C(11) = 2.10 (1), 2.13 (2); Ni–C(12) = 2.36 (1), 2.40 (2); Ni–C(13) = 2.41 (2), 2.33 (2); W–C(11)–O(11) = 159 (1), 162 (1); W–C(12)–O(12) = 168 (1), 170 (1); W–C(13)–O(13) = 171 (2), 168 (1).

M(CO)$_3$(η^5-C_5H_5) groups, in compounds in which both the carbonyl carbon atoms and the group 6 metals interact with one or more metal fragments,[17] are isolobal with η^5-C_5H_5 ligands.[18] **2a** and **2b** are isolobal with nickelocene

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(6) (a) Green, M.; Hankey, D. R.; Howard, J. A. K.; Louca, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 757. (b) Herrmann, W. A.; Barnes, C. E.; Serrano, R.; Koumbouris, B. *J. Organomet. Chem.* **1983**, *256*, C30.

(7) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298.

(8) Chetcuti, M. J.; Huffman, J. C.; McDonald, S. R. *Inorg. Chem.* **1989**, *28*, 238.

(9) Maj, J. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054.

(10) Chetcuti, M. J.; Fanwick, P. E.; Grant, B. E. *J. Am. Chem. Soc.* **1989**, *111*, 2743.

(11) **1b** (555 mg, 1 mmol) was refluxed in hexane (30 mL) for 3 h. Cooling (−20 °C) caused crystals of **2b** to deposit; further concentration afforded a second crop (369 mg, 70%). Spectroscopic data for **2b**: IR (ν(CO), cm^{-1}, THF) 1953 (s), 1904 (m), 1821 (s); IR (ν(CO), cm^{-1}, methylcyclohexane) 1828 (s); MS (*m/e*, amu) 526 (M)$^+$, 442 (M − 3CO)$^+$; HRMS calcd for $NiWC_{18}H_{20}O_3$ 526.0255, found 526.0239; UV/vis (λ_{max}, nm (ϵ)) 603.8 (3400).

(12) Syntheses of **1a** and **2a** mirror those of **1b**[10] and **2b**.[11] Spectroscopic data for **1a**: ^1H NMR (benzene-d_6, ppm) δ 4.63 (5 H, C_5H_5), 1.77 (15 H, C_5Me_5); ^{13}C NMR (benzene-d_6) δ 230.7 (CO), 104.7 (C_5Me_5), 92.2 (C_5H_5), 9.5 (C_5Me_5); IR (ν(CO), cm^{-1}, hexane) 1990 (m) 1933 (s), 1868 (m, br), 1796 (w); MS (*m/e*, amu) M$^+$ not seen, 440 (M − CO)$^+$, 412 (M − 2CO)$^+$, 384 (M − 3CO)$^+$, 356 (M − 4CO)$^+$. Spectroscopic data for **2a**: MS identical with MS of **1a**; HRMS calcd for $NiMoC_{18}H_{20}O_3$ 439.9811, found 439.9815; IR (ν(CO), cm^{-1}, hexane) 1837.

(13) The synthesis of **2b′** from (η-C_5Me_5)(CO)Ni–W(CO)$_3$(η-C_5H_4Me) (not isolated) paralleled that of **2b**. Spectroscopic data for **2b′**: ^1H NMR (benzene-d_6, ppm) δ 5.4, 9.5 and 13.0 (all v br); IR (ν(CO), cm^{-1}, hexane) 1827; MS (*m/e*, amu): 540 (M)$^+$; HRMS calcd for $NiWC_{19}H_{22}O_3$ 540.048, found 540.043.

(14) Crystal data at 20 °C for a crystal of **2b′**, $NiWC_{19}H_{22}O_3$, grown from hexane at −20 °C: $a = 8.209$ (1) Å, $b = 25.272$ (3) Å, $c = 18.066$ (2) Å, $\beta = 91.440$ (8)°, $V = 3746$ (1) Å^3, $Z = 8$, $d_{calcd} = 1.918$ g cm^{-3}, space group $P2_1/n$ (No. 14), Mo K_α radiation, $\mu = 72.9$ cm^{-1}. An empirical absorption correction was applied. Of the 5024 unique data, 3135 with $I > 3.0\sigma(I)$ were used in the refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen positional parameters were calculated with use of idealized geometries; isotropic thermal parameters for hydrogen atoms were set at 1.3 times the isotropic parameters of their attached carbon atoms. Refinement converged at $R(F) = 0.042$ and $R_w(F) = 0.050$. (Thermal parameters for some carbon atoms of one Cp′ group indicate significant thermal motion and/or some disorder for this ligand.)

(15) One example of an unbridged Ni–W single bond has been reported.[15a] This lies in the middle of the range of all the other (non-electron-deficient) bridged Ni–W bonds noted. (a) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *Organometallics* **1985**, *4*, 1138. (b) Chetcuti, M. J.; Fanwick, P. E.; Gordon, J. C.; Green, K. A.; Morgenstern, D. *Organometallics* **1989**, *8*, 1790. (c) Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 763. (d) Reference 7.

(16) In each molecule the shortest Ni–C_{CO} bond is to the CO ligand closest to the methyl group.

(17) Examples are known for di-,[17a,b] tri-,[17c] and tetranuclear species:[8,17d,e] (a) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Dalton Trans.* **1984**, 1693. (b) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675. (c) Werner, H.; Kraus, H.-J.; Thometzek, P. *Chem. Ber.* **1982**, *115*, 2914. (d) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410. (e) Bender, R.; Braunstein, P.; Jud, J.-M. *Inorg. Chem.* **1983**, *22*, 3394.

(18) Hofmann, P.; Schmidt, H. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 837. HOMO's of the M(CO)$_3$(η^5-C_5H_5) group have a_1 and e symmetry, display z^2, $x^2 - y^2$, and xy character at the metal atom, and contain bonding contributions from carbonyl ligand π^* orbitals.

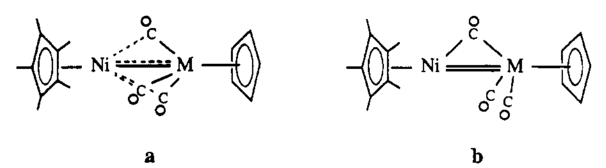

Figure 2. Alternative representations of **2b**.

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 $\mu\text{-}CH_2$ species.[25]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the University of Notre Dame, and to the National Science Foundation (Grant No. CHE 8615556) for the MICROVAX computer and Enraf-Nonius CAD4 diffractometer.

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 $M_2(\mu\text{-}CO)_3(\eta\text{-}C_nR_n)_2(M{\equiv}M)$ (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 $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2(Mo{\equiv}Mo)$,[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*)

Michael J. Chetcuti* and Brian E. Grant

Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, Indiana 46556

Phillip E. Fanwick

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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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 $Ni\text{-}CH_2$ 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.