The lack of formation of dodecatriene having deuterium bonded to the terminal carbon atoms upon reaction of **2** with DCl (eq 3) apparently rules out a simple deuteriolysis of the Pd–C bond in this case. The deuterium in this reaction is found exclusively at C-3 and C-10 of the triene suggesting either that the reaction with acid is preceded by a rearrangement similar to that shown in eq 5 or, alternatively, that the acid attacks the allylic double bond directly.

Registry No. **1**, 96165-40-1; **2** (R = Me), 96193-93-0; **2** (R = *i*-Pr), 96165-41-2; **2** (R = Cy), 96165-42-3; $PdCl_2(Me_2PC_2H_4PMe_2)_2$, 15559-64-5; $PdCl_2((i\text{-}Pr)_2PC_2H_4P(Pr\text{-}i)_2)_2$, 96165-43-4; $PdCl_2(Cy_2PC_2H_4PCy_2)_2$, 96165-44-5; $[Pd(dba)_2]$, 32005-36-0; [Pd(bpy)(dba)], 52462-56-3; $Me_2PC_2H_4PMe_2$, 23936-60-9; $(i\text{-}Pr)_2PC_2H_4P(i\text{-}Pr)_2$, 87532-69-2; $Cy_2PC_2H_4PCy_2$, 23743-26-2; *cis*-1,6,11-dodecatriene, 96165-45-6; butadiene, 106-99-0; dodecatetraene, 33637-94-4; *n*-dodecane, 112-40-3.

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Preparation, Structure, and Properties of Paramagnetic, Heterobinuclear Complexes Containing Nickel and Molybdenum or Tungsten. X-ray Crystal Structure of $[NiW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$

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Summary: New paramagnetic complexes $[MNi(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo, W) have been characterized and studied by ESR spectroscopy, EHMO calculations, and cyclic voltammetry; the structure of crystalline $[NiW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ has been determined by X-ray diffraction.

Current interest in heteronuclear derivatives containing both early and late transition metals[1,2] prompts us to report new, neutral, paramagnetic binuclear complexes of nickel with molybdenum or tungsten. Binuclear derivatives containing nickel bonded to a range of metals (e.g., Cr, Mo, W, Mn, Fe, Co)[1,3] are known, but these are all diamagnetic and mainly contain the entity $Ni(\eta\text{-}C_5H_5)$. Also, the diamagnetic complexes $[MnNi\{\mu\text{-}C(OMe)Ph\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$[4] and $[NiW_2(\eta\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$[5] have been reported by Stone and co-workers. Several higher nuclearity heteroclusters containing nickel exist[1,6] including a few paramagnetic systems.[7] However, although the neutral d^9 Ni(I) complexes $[NiXL_3]$ (L = phosphorus ligand) are well established,[8] the incorporation of such a center into a simple bimetallic complex has not been reported.

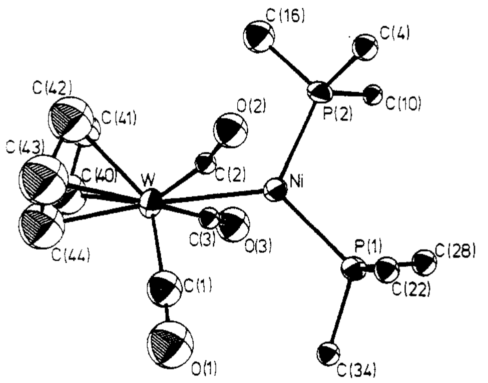

Figure 1. X-ray crystal structure of $[NiW(CO)_3(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**2**). Apart from the carbon atoms bonded to phosphorus, the remaining phenyl group carbons have been omitted for clarity. Some important geometrical parameters: W–Ni = 2.584 (3) Å, W–C(1) = 1.87 (3) Å, W–C(2) = 1.924 (20) Å, W–C(3) = 1.958 (21) Å, Ni–P(1) = 2.270 (7) Å, Ni–P(2) = 2.277 (7) Å, Ni–C(2) = 2.071 (20) Å, Ni–C(3) = 2.050 (21) Å; C(2)–W–C(3) = 103.2 (9)°, Ni–W–C(1) = 87.0 (9)°, Ni–W–C(2) = 52.2 (6)°, Ni–W–C(3) = 51.4 (6)°, W–Ni–P(1) = 121.01 (20)°, W–Ni–P(2) = 127.72 (19)°.

Reaction of $Na[M(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W) with $[NiCl_2(PPh_3)_2]$ in tetrahydrofuran at ambient temperature (2–10 min), followed by addition of water, filtration, and careful washing of the resulting solid with acetone gives crude product $[MNi(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$, which may be recrystallized from dichloromethane–hexane {M = Mo (**1**), ca. 20%; M = W (**2**), 53%}. Both **1** and **2** form deep green crystals, moderately stable on short exposure to air but very air-sensitive in solution. In these syntheses Ni(II) is reduced to a formal Ni(0) state, although, with the heterometallic Ni–M bond, the Ni may be considered to be analogous to Ni(I) in complexes $[NiXL_n]$; other products isolated from the reaction mixtures include $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W), $[Ni(CO)_2(PPh_3)_2]$ (**3**) and $[Ni\{W(CO)_3(\eta\text{-}C_5H_5)\}_2(PPh_3)_2]$ (**4**).[9]

The IR spectra[9] of **1** and **2** suggest the presence of bridging and terminal carbonyl groups. ^1H and ^{31}P NMR investigations of these complexes afforded either broad-

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(9) Anal. Calcd $C_{44}H_{35}O_3P_2MoNi$ (**1**): C, 63.80; H, 4.26; P, 7.48. Found: C, 63.69; H, 4.36; P, 7.56. Anal. Calcd $C_{44}H_{35}O_3P_2NiW$ (**2**): C, 57.68; H, 3.85; P, 6.76; Ni, 6.4; W, 20.1. Found: C, 57.51; H, 3.94; P, 6.61; Ni, 6.9; W, 20.9. Anal. Calcd $C_{52}H_{40}O_6P_2NiW_2$ (**4**): C, 50.0; H, 3.22. Found: C, 49.0; H, 3.45. IR spectra (ν(CO), cm^{-1}): (**1**) 1891, 1779, 1739 (Nujol); (**2**) 1895, 1770, 1730 (Nujol), 1892, 1769, 1741 (CH_2Cl_2); (**4**) 1935, 1917 (sh), 1870, 1840 (Nujol). ESR spectra (2-methyltetrahydrofuran, 10 °C): (**1**) g_{iso} = 2.118, $A_{iso}(^{31}P)$ = 7.49, 5.49 mT; (**2**) g_{iso} = 2.128, $A_{iso}(^{31}P)$ = 7.63, 5.89 mT.

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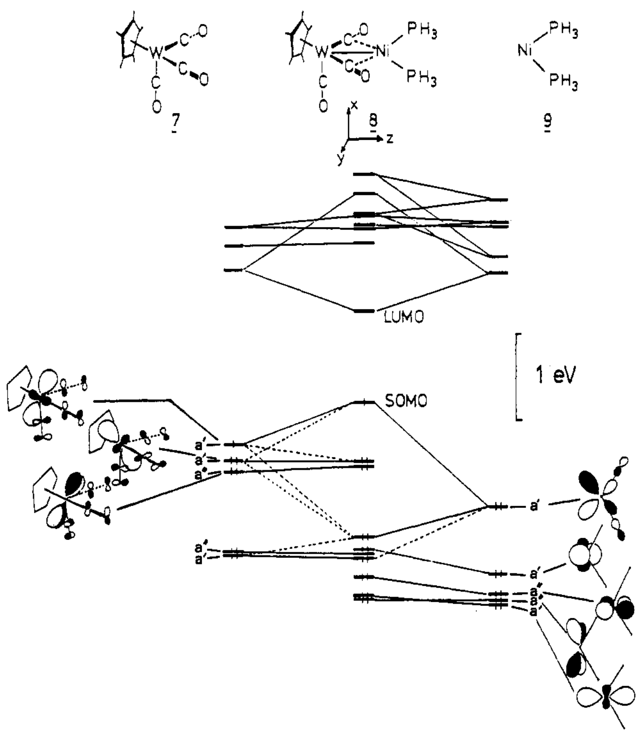

Figure 2. Interaction diagram for complex **9**. (Orbital correlations derived by using program FMO.)

ened resonances or the absence of signals and a determination of the magnetic susceptibility of **2** in benzene by Evans' method[10] gave $\mu_{eff} = 2.2 \pm 0.2\ \mu_B$ (22 °C). Both **1** and **2** in solution exhibit ESR spectra (dd)[9] showing coupling of the unpaired electron to two inequivalent ^{31}P nuclei; any coupling to $^{95/97}Mo$ or ^{183}W, respectively, is obscured by the line widths of the signals ($\Delta\omega_{1/2} \approx 2$ mT), but this must be relatively small. ESR spectra of frozen solutions have also been analyzed in terms of three anisotropic *g* tensors with coupling to two inequivalent ^{31}P nuclei.

A crystal of **2** was subjected to X-ray analysis.[11] The molecular structure so determined (Figure 1) shows normal η^5-coordination of the cyclopentadienyl group to tungsten and typical Ni–PPh_3 interactions with Ni–P distances intermediate between those in **3**[12] and in $[NiBr(PPh_3)_3]$.[8c] The carbonyl groups approach linear coordination to W; C(1)–O(1) is terminal to W but both C(2)–O(2) and C-(3)–O(3) interact with Ni and may be considered to be "semibridging". The bridging Ni–C separations are longer than in $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$,[3a,13] significantly shorter than in $[CrNi(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_2]$,[3a] and comparable to those in $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$[5] (**5**). The nickel atom is virtually in the plane of the $W(\mu\text{-}CO)_2$ unit (angle W–C(2)–Ni/W–C(3)–Ni = 171.4°), and **2** is structurally analogous to the red/orange isomer of $[CuW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$[14] (**6**). The Ni–W distance [2.584 (3) Å] is consistent with a significant metal–metal interaction, being shorter by ca. 0.2 Å than Cu–W in **6**[14] and comparable to Ni–W in **5**—some multiple-bond character was suggested in this latter complex.[5]

To understand better the metal–metal interaction in complexes **1** and **2** and in related binuclear complexes $[MM'(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo, W; M′ = Rh, Cu)[14] which have increasing number of valence shell electrons M′ = Rh < Ni < Cu, we have carried out EHMO calculations.[15,16] Figure 2 shows the interaction diagram of fragments $[W(CO)_3(\eta\text{-}C_5H_5)]$ (**7**) and $[Ni(PH_3)_2]$ (**8**) to form $[NiW(CO)_3(PH_3)_2(\eta\text{-}C_5H_5)]$ (**9**), in idealized C_s symmetry. The frontier orbitals of both fragments are related to previously described systems.[17,18] The SOMO of **9** is antibonding with respect to fragments **7** and **8**; it has a′ symmetry and is composed mainly of W and Ni d_{xz} orbitals with delocalization on to CO groups and a little on to P atoms consistent with the low $A_{iso}(^{31}P)$ values in the ESR spectrum of **2**. Overall, the EHMO study shows no strong, direct Ni–W bonding, and **7** and **8** appear to be held together by a combination of relatively weak Ni–W and C–Ni interactions (reduced orbital overlap populations: Ni–W, 0.134; C(2)/C(3)–Ni, 0.240). Comparable studies on complex **6** also indicate negligible Cu–W and weak C–Cu interactions. These results reflect similar theoretical studies of binuclear bridged systems in which minimal direct metal–metal bonding has been proposed.[18,19]

The antibonding nature of the SOMO of **9** suggests that ready oxidation of complex **2** might occur. Cyclic voltammetric studies of **2** in CH_2Cl_2 show an essentially reversible one-electron oxidation at $E_{1/2} = -0.15$ V.[20] The primary product $[NiW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ is electronically related to $[RhW(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$.[14] Further irreversible oxidation of **2** occurs at higher potentials.

In solution, complexes **1** and **2** decompose on contact with air with the rupture of the binuclear unit. The only identifiable nickel product is **3**, and this suggests an unsymmetrical cleavage of the $M(CO)_2Ni$ systems. Photolysis (λ > 300 nm) of **1** in the absence of air but in the presence of nitrosodurene (CH_2Cl_2, −40 °C) forms the paramagnetic nitroxide with solution ESR parameters identical with those assigned to species $[Mo(\dot{N}OC_6Me_4H\text{-}4)(CO)_n(\eta\text{-}$

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(11) Crystal data for complex **2**: $C_{44}H_{35}NiO_3P_2W$, M_r = 916.2, monoclinic space group $P2_1/c$ (No. 14), *a* = 17.873 (9) Å, *b* = 10.156 (6) Å, *c* = 21.249 (7) Å, β = 105.05 (3)°, *U* = 3725 Å^3, *Z* = 4, D_{calcd} = 1.634 g cm^{-3}, *F*(000) = 1820, μ(Mo Kα) = 38.98 cm^{-1}, crystal dimensions ca. 0.2 × 0.3 × 0.08 mm. [ω–2θ scans, θ < 23°, Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (λ = 0.71069 Å)]. The structure was solved by standard Patterson-Fourier difference map methods. Least-squares refinement, using anisotropic temperature factors for the W, Ni, and P atoms only, reduced the conventional *R* factor to a current value of 0.072 (R_w = 0.114) for 2896 absorption corrected intensity data [$I > 2.5\sigma(I)$]. The comparatively high current *R* factor results from (i) the weakness of the data set [only 2896 out of 5122 unique reflections had $I > 2.5\sigma(I)$] probably arising from the thinness of the data crystal (<0.1 mm) and (ii) the failure of absorption corrections to account for several residual peaks (>1 e Å^{-3}) close to the W atoms; the C and O atoms of the carbonyl ligands could not consequently be refined anisotropically.

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(20) At platinum microelectrodes in CH_2Cl_2 (18 °C) and 0.1 M $NBu_4[PF_6]$, scan rate = 0.05 V s^{-1} ($E_{1/2}$ vs. SCE). ($E_{1/2}$ for $[Fe(\eta\text{-}C_5H_5)_2]^+/[Fe(\eta\text{-}C_5H_5)_2]$ = 0.385V.)

$C_5H_5)]$ ($n \leq 3$);[21] again cleavage of the metal–metal system must occur.

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Registry No. 1, 96109-94-3; 2, 96109-95-4; 3, 13007-90-4; 4, 96109-96-5; 9, 96109-97-6; $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, 12091-64-4; $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$, 12091-65-5; $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, 12107-35-6; $Na[W(CO)_3(\eta\text{-}C_5H_5)]$, 12107-36-7; $[NiCl_2(PPh_3)_2]$, 14264-16-5.

Supplementary Material Available: Listings of positional and thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes for 2 (21 pages). Ordering information is given on any current masthead page.

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Uranium–Carbon Multiple-Bond Chemistry. 5.[1] Carbon–Oxygen Bond Cleavage in a Uranium Phosphonium Enolate Manganese Complex

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Summary: Upon heating, the carbon–oxygen bond in $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$ can be cleaved to form $Cp(OC)_2MnC{\equiv}CPMe_2Ph$, **3**. Crystals of **3** belong to space group $P2_1/c$, with unit cell parameters of a = 10.611 (2) Å, b = 18.603 (3) Å, c = 8.193 (2) Å, β = 102.55 (2)°, Z = 4, and V = 1578.7 (6) Å^3. The structure of **3** shows it to be a phosphonium acetylide.

We have proposed[1,2] that coordinated carbon monoxide can be activated by reaction with the uranium–carbon multiple bond in $Cp_3U{=}CHPMePhR$[3-5] (**1a**, R = Me; **1b**, R = Ph), where Cp = $\eta\text{-}C_5H_5$, Me = CH_3, and Ph = C_6H_5. An example[2] of this is a carbonyl coupling which results in allyl formation during the reaction of 1 with $[CpFe(CO)_2]_2$. We postulated[2] that the initial step of this process is the insertion of a terminal carbonyl into the uranium–carbon multiple bond. In the previous paper of this series[1] such an insertion was documented in a reaction of $CpMn(CO)_3$ with **1a** which produces $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$, **2**. We argued that the organouranium compound had activated the carbon–oxygen bond by decreasing its bond order through the strong tendency of U(IV) to accept electrons from oxygen. In this communication we report that the carbon–oxygen bond in **2** can be *cleaved* under fairly mild conditions to form a complex, $Cp(OC)_2MnCCPMe_2Ph$, **3**, containing a zwitterionic phosphonium acetylide ligand. The overall reaction is the *formation of a new carbon–carbon triple bond accompanied by the deoxygenation of a terminal carbonyl.*

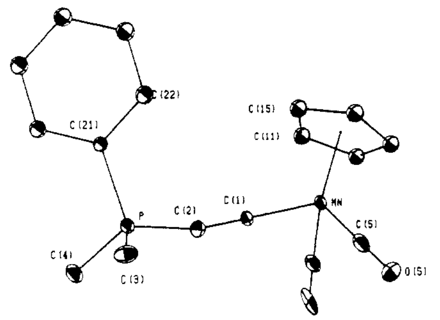
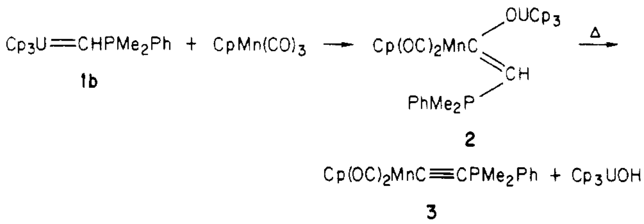


Figure 1. An ORTEP drawing of $Cp(OC)_2MnCCPMe_2Ph$, **3**. Some important bond distances (Å) and angles (deg): Mn–C(1) = 1.895 (5), Mn–C(5) = 1.744 (7), Mn–C(6) = 1.742 (6), C(1)–C(2) = 1.221 (7), P–C(2) = 1.683 (6); Mn–C(1)–C(2) = 179.6 (4), P–C(2)–C(1) = 166.6 (5).

As previously described[1] an equimolar mixture of **1b** and $CpMn(CO)_3$ in THF produced **2**. After evaporation of the THF, the remaining red-brown solid was dissolved in toluene, refluxed for 1 h, and filtered. Upon addition of an equal volume of heptane and cooling to room temperature, translucent yellow crystals of **3** formed in 55% yield.[6]



The structure of **3**, belongs to the monoclinic space group $P2_1/c$, with unit cell parameters of a = 10.611 (2) Å, b = 18.603 (3) Å, c = 8.193 (2) Å, β = 102.55 (2)°, Z = 4, and V = 1578.7 (6) Å^3, was determined by X-ray diffraction.[7] An ORTEP drawing is shown in Figure 1; a summary of crystal and data collection parameters and listings of bond distances and angles, positional and thermal parameters, and the observed and calculated structure factors can be found as supplementary material.

The molecular structure of **3** reveals a zwitterionic phosphonium acetylide ligand coordinated to $Cp(OC)_2Mn$. The $MnC{\equiv}CP^+R_3$ unit is rare, the only other structure determination being $Br(OC)_4MnC{\equiv}CPPh_3$,[8,9] **4**. A Re analogue of **4**,[9] $(OC)_5WC{\equiv}CPPh_3$,[10] and $(CH_3C_5H_4)(OC)_2MnC{\equiv}CPMe_3$,[11] **5**, have also been synthesized. As expected for an acetylide, the Mn–C(1)–C(2) angle, 179.6

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(3) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* 1981, *20*, 2466–2470.
(4) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* 1981, *103*, 3589–3590.
(5) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* 1983, *2*, 869–871.

(6) NMR (C_6D_6, chemical shifts in ppm from Me_4Si): CH_3P 1.90 (6 H, d, J_{PCH} = 14.0 Hz); Cp 4.43 (5 H, s); Ph 7.60 (1 H, m), 7.93 (2 H, m), 8.08 (2 H, m). IR (Nujol mull, 1800–2000 cm^{-1}): 1972 vs, 1887 vs, 1852 vs. Two of these IR bands will arise from CO stretches and the third from the C≡C stretch. The assignment of a particular vibration to a specific frequency is not certain.[9,11]
(7) A single crystal was mounted in a glass capillary and sealed under nitrogen. X-ray data was collected by using a Syntex P$\bar{1}$ diffractometer and processed as previously described.[21] The structure was solved with SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976, using Patterson methods to locate the uranium, followed by refinements and Fourier maps to locate the remaining atoms. The Cp and Ph groups were refined as rigid bodies with H atoms included, using the standard parameters included in SHELX-76.
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