# Synthesis and Structural Characterization of the Complex [NiMo(CO)₂{μ-η²,η²-C(Me)C(Me)C(O)}-(η-C₅H₅)(η-C₅H₄Me)]

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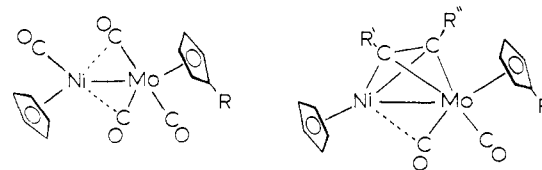
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Reactions of alkynes with di- and polynuclear metal complexes continue to be an active research area.[1,2] Most studies have focused on homometallic species, where it is hoped that a fuller understanding of these systems will shed light on important catalytic processes. However, the potential of mixed-metal complexes in catalysis is even greater owing to the different electronic, steric, and ligand requirements of dissimilar metals and the possibility of synergic effects in bonding and activating organic substrates. We have initiated a study of various simple mixed-metal carbonyl species and their reactions with alkynes and other organic molecules. The reactions of Ni–Mo complexes with alkynes generate, in addition to bridging alkyne complexes, unusual metallacyclobutenone rings observed previously only in homometallic systems. CO loss in these rings occurs readily and is reversible in one case.

Treatment of the mixed-metal complexes [NiMo(CO)₄(η-C₅H₅)(η-C₅H₄R)](Ni–Mo) [1a, R = H; 1b, R = Me][3] with 2-butyne or 2-pentyne at 25 °C for 2–4 h affords a varying ratio of two main products that may be separated by chromatography on alumina (Figure 1). One of the two sets of products obtained are the alkyne-bridged metal–metal bonded complexes [NiMo-(CO)₂(μ-η²,η²-R'CCR'')(η-C₅H₅)(η-C₅H₄R)](Ni–Mo) [2a, R = H; R',R'' = Me; 2b, R,R',R'' = Me; 3, R = H, R' = Me, R'' = Et],[4] which appear to have a "dimetallatetrahedrane-type" structure.[5,6] Complexes 2a and 2b are obtained in minor quantities, but 1a affords a 40% yield of 3, with 2-pentyne.

In addition to 2a, complex 4a is obtained as the major product when 1a is reacted with 2-butyne. Complex 1b yields almost exclusively 4b, with small quantities of 2b. However, 1a reacts with 2-pentyne, affording, in addition to 3, a mixture of what are believed to be two isomers, 5a and 5b, in a close to 1:1 molar ratio. 5a and 5b are not readily separated by chromatography or by fractional crystallization.

Complexes 4a, 4b, 5a, and 5b are believed to have similar structures on the basis of their spectroscopic data.[7] In addition

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(2) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffmann, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794–6805. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806–6815, 6815–6826.

(3) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675–2685. The methylcyclopentadienyl complex 1b was made analogously.

(4) IR (Nujol mulls) (2a) 1902 (s), 1807 (s), (2b) 1917 (s), 1818 (s), (3) 1972 (s), 1939 (s), 1914 (s), 1852 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) (1a) δ 5.32 (s, 5 H, C₅H₅), 5.09 (s, 5 H, C₅H₅), 2.53 (s, 6 H, MeCCMe), (2b) 5.43–5.23 (m, 4 H, C₅H₄Me), 5.07 (s, 5 H, C₅H₅), 2.51 (s, 6 H, MeCCMe), 2.01 (s, 3 H, *Me*Cp), (3) 5.36 (s, 5 H, C₅H₅), 5.10 (s, 5 H, C₅H₅), 2.76–2.80, 2.96–3.00 (m, 2 H, CH₃C*H₂*), 2.58 (s, 3 H, CH₃C≡), 1.15 (t, 3 H, C*H₃*CH₂, ³*J*(H–H) = 7 Hz). Rotation of the alkyne about the metal–metal bond⁵ may equivalence the two Me groups in 2a,b. Low-temperature NMR [–95 °C, (CD₃)₂CO] slightly broadened the alkyne Me resonances in 2a,b but did not "significantly decrease" this dynamic behavior. MS: M⁺, (M – CO)⁺, (M – 2CO)⁺, (M – R'C₂R'')⁺ observed for 2a,b and 3.

(5) A compound similar to complexes 2a,b and 3 has been prepared (Jaouen, G.; Marinetti, A.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 225–227) by reacting Cp₂Ni with Mo₂(CO)₆Cp₂ and the alkyne PhC₂CO₂-*i*-Pr in hot toluene.

(6) The structure of the complex [NiW(CO)₂(μ-MeC₂Me)(C₅H₅)₂], with spectroscopic properties similar to 2a, has been established through an X-ray diffraction study. The structure shows an alkyne bridge perpendicular to the Ni–W bond [Ni–W = 2.624 (1) and 2.628 (1) Å; two independent molecules in the unit cell] and a CO ligand semibridging to the Ni atom. Full details will be published shortly.



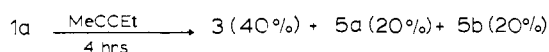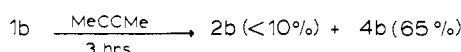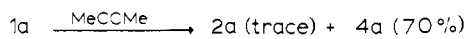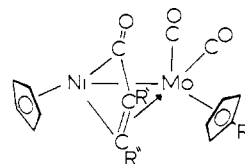**Figure 1.** Reactions of complexes 1a and 1b with 2-butyne and 2-pentyne.



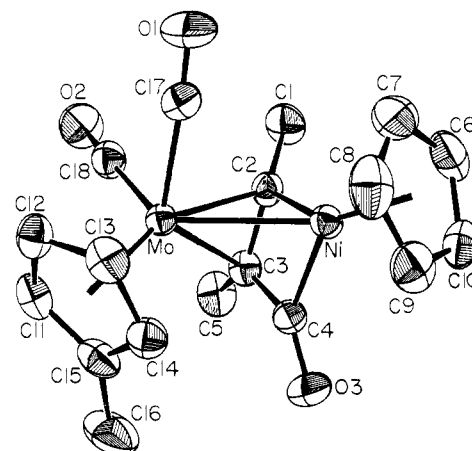**Figure 2.** ORTEP view of complex 4b, [NiMo(CO)₂{μ-η²,η²-C(Me)C-(Me)C(O)}(η-C₅H₅)(η-C₅H₄Me)]. Ellipsoids are shown at the 50% probability level. Pertinent bond distances (Å) and angles (deg): Mo–Ni = 2.5859 (2); Mo–C(2) = 2.179 (2); Mo–C(3) = 2.290 (2); Ni–C(2) = 1.912 (2); Ni–C(4) = 1.927 (2); C(2)–Ni–C(4) = 69.92 (7); Ni–C-(4)–C(3) = 94.4 (1); C(2)–C(3)–C(4) = 99.9 (1); C(17)–Mo–C(18) = 81.70 (8); MeCp centroid–Mo–Ni = 118.1; Cp centroid–Ni–Mo = 143.5.

to showing two terminal ν(CO) bands in the IR spectrum, they exhibit a ketonic CO stretch absorbing around 1650 cm⁻¹. However, these complexes show the same mass spectra as that of their corresponding alkyne complexes 2a, 2b, or 3. In order to determine the structure of these complexes, crystals of 4b were grown from hexane and an X-ray structural determination was carried out.[8]

(7) IR (Nujol mulls) (4a) 1983 (s), 1927 (s), 1658 (ms), (4b) 1979 (s), 1941 (s), 1646 (ms), (5a,b) 1984 (s), 1931 (s, br), 1927 (sh), 1659 (sh), 1648 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) (4a) 5.36 (s, 5 H, C₅H₅), 5.22 (s, 5 H, C₅H₅), 2.68 (s, 3 H, MeCCO), 1.26 (s, 3 H, *Me*CCMeCO), (4b) 5.3–5.1 (m, 4 H, C₅H₄), 5.20 (s, 5 H, C₅H₅), 2.65 (s, 3 H, MeCCO), 2.08 (s, 3 H, *Me*C₅H₄), 1.20 (s, 3 H, *Me*CCMeCO), (5a) 5.36 (s, 5 H, C₅H₅), 5.20 (s, 5 H, C₅H₅), 2.69 (s, 3 H, MeCCO), 1.7–1.7 (m, 2 H, C*H₂*Me), 0.88 (t, 3 H, *Me*CH₂, ³*J*(CH) = 7 Hz), (5b) 5.33 (s, 5 H, C₅H₅), 5.24 (s, 5 H, C₅H₅), 2.55–2.45 (m, 2 H, CH₂Me), 1.43 (t, 3 H, *Me*CH₂, ³*J*(CH) = 7 Hz), 1.22 (s, 3 H, *Me*CCEt); MS M⁺ only observed (weak signal) for 5a,b. 4a,b only show (M – CO)⁺ as highest peak.

The structure **4b** is shown in Figure 2. It contains a Ni–C-(O)–C(Me)–C(Me) metallacyclobutenone ring that is π-bonded to the molybdenum through carbons C(2) and C(3). This ring is close to planar, the maximum deviation of any atom from the mean square plane NiC(2)C(3)C(4) being 0.055 Å. The $\mu$-$\eta^2,\eta^2$-1,3-$\sigma$/2,3-$\pi$ bonding mode of the C(R)C(R)C(O) ligand has been observed in only a few other cases, all involving homonuclear metals.[9]

In complex **4b**, the Mo–C(2) and Mo–C(3) bonds are unequal [Mo–C(2) = 2.179 (2) Å; Mo–C(3) = 2.290 (2) Å]. Asymmetric π-bonding of the C(R)–C(R) fragment to the metal has been reported[10-12] in all structurally characterized complexes of this type. In each case, as occurs here, the significantly longer M–C bond occurs for that carbon atom bonded to the ketonic CO. The Ni–Mo bond length of 2.5859 (2) Å is in the same range observed for other simple Ni–Mo single bonds.[14]

Complexes **4a**, **5a**, and **5b** are believed to have similar structures to **4b**.[17] All the compounds lose CO slowly when allowed to stand in solution at ambient temperatures, over a period of 1–2 days. The yields of complexes **4a**, **4b**, **5a**, and **5b** from reactions of the complexes **1a** and **1b** with alkynes are thus time-dependent and decrease with time significantly. Clean conversion into the corresponding alkyne complex **2a**, **2b** or **3** is observed when samples of **4a**, **1b**, or **5a,b** are heated in a sealed NMR tube. The complexes **5a** and **5b** are not regenerated by bubbling CO through solutions of **3** under ambient conditions. However, **4a** is formed by bubbling CO through toluene solutions of **2a** at 25 °C.

Bubbling CO through solutions of **4b** for 12 h does not afford **4b**. It is not clear to us why a nickelacyclobuteone π-bonded to Mo rather than molybdenacyclobutenone π-bonded to Ni is obtained. However, the carbonyl ligand may be required by the nickel to reduce its electron density. In this regard it is interesting to note that in the alkyne complexes, a carbonyl ligand on the Mo appears to semibridge to the Ni, rather than remain terminal.

Subtle electronic and steric factors appear to have drastic effects on the ease of formation and stability of the π-bonded metallacycle. We have been able to synthesize Ni–Cr and Ni–W analogues to complexes **2a**, **2b**, and **3** similarly, but have not yet observed the formation of any Ni–Cr or Ni–W complex of a structure similar to **4a,b** or **5a,b**. Further studies are in progress.

**Supplementary Material Available:** Complete listings of atomic positional and thermal parameters and bond distances and angles for compound **4b** (3 pages). Ordering information is given on any current masthead page.

# On the Stability of Cubic P₈

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The stable molecular form of elemental phosphorus, which occurs in white phosphorus, is the $P_4$ tetrahedron, which undergoes considerable ring strain due to the 60° valence angles at all atoms. In some polymerized modifications such as black or red phosphorus, the valence angles are closer to nonhybridized values. Indeed, in black phosphorus, which is directly derived from a simple cubic system, the angles at the phosphorus atoms are 102° and 96°; in red phosphorus, they are 101°. The question of whether or not the cubic $P_8$ molecule could be stable has been put forward several times. Such a structure would give 90° angles at all phosphorus atoms and should induce reduced ring strain.

Fluck, Pavlidou, and Janoschek have calculated $P_8$ ($O_h$) to be less stable than $2P_4$ by 47 kcal/mol, using the experimental P–P bond length (2.21 Å) of $P_4$ in both molecules.[1] In a previous work we have optimized the geometry of $P_8$ with a double-$\zeta$ basis set.[2] In this way, $P_8$ was found to be more stable than $2P_4$ by 10 kcal/mol but we already suggested that this result might be reversed by including d orbitals in the basis set, which should favor the more compact and constrained $P_4$ systems. Halevi, Bock, and Roth recently reported a MNDO study in which all geometries were optimized and which gives $P_8$ more stable than $2P_4$ by 68 kcal/mol.[3] These authors show neatly that the simplest $D_{3d}$ coupling $2P_4 \rightleftharpoons P_8$ is forbidden in the ground state. However, as pointed out by Kutzelnigg,[4] both an ab initio SCF calculation with d orbitals in the basis set and a calculation of the force field, in order to demonstrate that $P_8$ is a real minimum on the potential surface, are still needed. These two points are the main object of the present report. Possible ways of reaching this intermediate by coupling two electronically excited $P_4$ molecules will be also examined.

Ab initio effective core potential SCF calculations were performed with the PSHONDO algorithm,[5] using double-$\zeta$ (DZ) and

(8) Crystal data for complex **4b**, at 21 °C: a = 9.075 (2) Å, b = 12.416 (3) Å, c = 14.873 (3) Å; β = 97.72 (1)°, Z = 4, $d_{calcd}$ = 1.748 g cm⁻³, Mo Kα, space group $P2_1/n$ (No. 14). Of the 5677 unique reflections, 4342 with $F_o^2 > 3\sigma F_o^2$ was used in the refinement. R(F) = 0.024; $R_w$(F) = 0.030. Full details will be reported at a later date.

(9) Three other examples of the $\mu$-$\eta^2,\eta^2$-bonding mode of the C(R)C(R)-C(O) ligand have been structurally characterized. These are the complexes [Rh₂($\mu$-CO)|$\mu$-$\eta^2,\eta^2$-C(O)C₂(CF₃)₂}($\eta$-C₅Me₅)₂],[10] [W₂(CO)₄{$\mu$-$\eta^2,\eta^2$-C-(O)C₂(CO₂Me)₂}($\eta$-C₅H₅)₂],[11] and [Pt₂{$\mu$-$\eta^2,\eta^2$-C(O)C₂Ph₂}($\eta$-C₅H₅)₂].[12] Isomeric bonding modes, with the terminal C(R) and C(O) groups of this ligand bonded to two *different* Fe atoms or two *distinct* Ru atoms, are known.[13]

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(14) Ni–Mo = 2.651 and 2.557 Å in the complex MoNi₂($\mu_3$-CPh)-(CO)₂($\eta$-C₅H₅)₂,[15] 2.622 Å in the related complex CoMoNi($\mu_3$-CMe)-(CO)₅($\mu$-C₅H₅)₂,[15] and 2.616 (2) Å in the alkyne-bridged species FeMoNi-(CO)₅($\mu$-PhC₂CO₂-i-Pr)($\eta$-C₅H₅)₂.[16]

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(17) Two other isomeric forms of **5a,b**, with a molybdenacyclobutenone ring π-bonded to the nickel cannot be ruled out. However, based on the similar spectroscopic and chromatographic behavior of **5a** and **5b** to **4a**, and in view of the structure of **4b**, we believe that the assigned structures are more likely.

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(5) The PSHONDO program results from inclusion of pseudopotentials[6] in the HONDO program.[7] These pseudopotentials have now been introduced into the version of HONDO that contains the calculation of analytical energy gradient in both RHF and UHF schemes.[8]

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