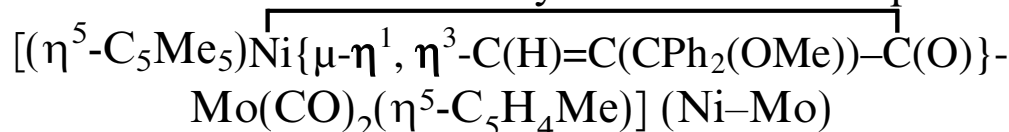


Note

Reactions of nickel-group 6 complexes with a bulky terminal alkyne to afford alkyne–carbonyl coupled products: X-ray structure of the heterobimetallic nickelacyclobutenone complex



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Abstract

The nickel–molybdenum complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}=\text{Mo(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ can be considered to contain a partially dative nickel–molybdenum double bond. This complex reacts with the bulky terminal alkyne $\text{HC}\equiv\text{CCPh}_2(\text{OMe})$ (DPMP) to afford the alkyne–carbonyl coupled metallacyclic product $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}\{\mu\text{-CH=CR-C(O)}\}\text{Mo(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ (**3c**, R = CPh₂(OMe), Ni–Mo) regioselectively and exclusively. No traces of a nickel–molybdenum μ -alkyne complex, analogous to similar complexes isolated with less bulky alkynes, were observed. The structure of complex **3c** was established via a single crystal X-ray diffraction study. It exhibits the same connectivity as that observed with a related complex formed with the smaller but-2-yne, but some significant differences are observed between the two structures. Reactions of the nickel–molybdenum and -tungsten species $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}=\text{M(CO)}_3(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo, W) with DPMP proceeded analogously and afforded similar products.
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1. Introduction

Many research groups have been interested in alkyne reactions with mixed metal complexes, in particular those that involve carbon–carbon coupling [1–6]. We share these interests and have been studying the reactions of $[\text{Cp}^{\text{a}}\text{-Ni(CO)-M(CO)}_3\text{Cp}^{\text{b}}]$ (M = Cr, Mo, W; Cp^a = Cp, Cp*⁺; Cp^b = Cp, Cp')¹ and, more recently, of the unsaturated tri-

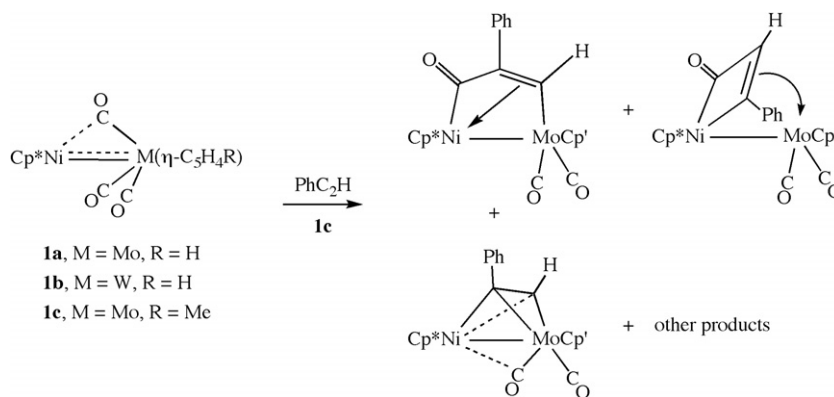
carbonyl complexes **1** $[\text{Cp}^{\text{a}}\text{Ni}=\text{M(CO)}_3\text{Cp}^{\text{b}}]$ (Cp^a = Cp, Cp'; M = Mo, W) [7] with alkynes [8–16]. (Complexes **1** are represented with Ni=M double bonds but the real situation is more complex; a better representation is shown in Scheme 1. The metal–metal bond is partially dative). The major products isolated from reactions of nickel–(group 6 metal) complexes with alkynes are nickelacyclobutenone species, in which the alkyne has coupled with a carbonyl group ligand, and this unit is bonded to the group 6 metal [8,9,13,14].

The reactivity pattern of phenylacetylene, a terminal alkyne, is significantly different from that of internal alkynes, such as 2-butyne. Other reactions, in which multiple

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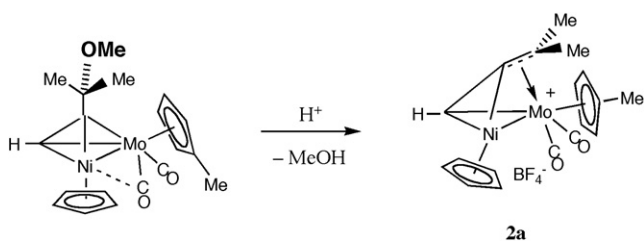
¹ Throughout this manuscript, Cp = $\eta^5\text{-C}_5\text{H}_5$, Cp' = $\eta^5\text{-C}_5\text{H}_4\text{Me}$, Cp* = $\eta^5\text{-C}_5\text{Me}_5$, Cp⁺ = Cp or Cp'.

Scheme 1. Complexes **1** and the reaction of phenylacetylene with **1c**.

alkyne–alkyne, alkyne–carbonyl and alkyne–Cp*H couplings occur, were observed with this alkyne [10,12]. When phenylacetylene was reacted with Ni=Mo and Ni=W complexes **1**, three different metallacycles, were isolated as the major products, as shown in Scheme 1 for complex **1c** [14].

We decided to react complexes **1**, [Cp*Ni=M(CO)₃(η-C₅H₄R)] (**1a**, R = H, M = Mo; **1b**, R = H, M = W; **1c**, R = Me, M = Mo) with the bulky terminal alkyne HC₂-CPh₂(OMe) (3,3-diphenyl-3-methoxy-prop-1-yne, DPMP) for two principal reasons. Firstly, we wanted to determine whether a more sterically demanding terminal alkyne would narrow the product distribution from that seen when phenylacetylene reacts with the Ni=Mo heterobimetallic complex **1c**. The presumed structures of the two metallacyclic complexes obtained from the reaction of **1c** with phenylacetylene are shown in Scheme 1. The geometries of these complexes were deduced spectroscopically, but we were keen to confirm the structure of one or more DPMP analogs of these products by an X-ray diffraction study [14].

The second reason for choosing this particular alkyne is related to some of our recent work on metal-stabilized carbocations. The synthesis and some reactions of the carbocationic complexes [CpNi(μ-η², η²-HC₂CMe₂)M(CO)₂Cp']⁺ (Ni–M: **2a**, M = Mo; **2b**, M = W) were recently described. The nickel–molybdenum cation is formed by the protonation of an alkoxy–alkyne complex; subsequent loss of methanol, as shown in Scheme 2 affords complex **2a** [15].



Scheme 2. Formation of metal-stabilized carbocations by protonation of a μ-alkoxy-alkyne complex.

Complexes **2** are unstable at room temperature and decompose rapidly enough in solution that a ¹³C NMR spectrum could not be obtained. We reasoned that we might be able to stabilize these carbocationic complexes (i) by increasing the electron density on the nickel atom and (ii) by stabilizing the cation via resonance delocalization. The electron density could be increased on the nickel atom by replacing the Cp group with a Cp* ligand and this would help counterbalance the formal positive charge. Replacement of the CMe₂ group in complexes **2** with a CPh₂ group would also allow possible resonance stabilization of the cationic charge. The protonation of such a Cp* nickel–molybdenum μ-DPMP complex should then result in loss of MeOH to yield a stabilized HC₂CPh₂⁺ carbocation.

2. Results and discussion

The reaction of DPMP with complex **1a** was relatively slow but after 3 h, the deep blue green color of **1a** had given way to an orange brown solution. Following solution work-up and chromatography on an alumina column (see Section 3.1), red-brown crystals of complex **3a** were isolated as the *only* isolated alkyne-containing product. The nickel–tungsten complex **1b** reacted with DPMP to afford **3b** and the Cp*Ni=MoCp' complex **1c** afforded **3c**. The spectroscopic data of all three products were similar (see Section 3.1) and indicated that complexes **3** had similar structures. The spectroscopic data of complex **3c** are discussed here and are consistent with the structure

[Cp*Ni{μ-η¹, η³-C(H)=C(R)-C(O)}Mo(CO)₂Cp'] (Ni–Mo) shown in Fig. 2.

The ¹H NMR data revealed that **3c** contained Cp', Cp* and DPMP groups in a 1:1:1 ratio. The aromatic Cp' proton resonances exhibited an ABCD type multiplet, indicative of a lack of an effective mirror plane of symmetry in the molecule. The ¹³C NMR spectra of solutions of **3c** corroborated these results, and in addition, showed the presence of three CO groups. The IR spectrum of **3c** exhibited three ν(CO) peaks: two corresponded to terminal and semi-bridging metal carbonyl stretches (1951 and

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