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Structure of an η^1 Nickel *O*-Enolate: Mechanistic Implications in Catalytic Enyne Cyclizations

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Received November 22, 2000

Summary: Two metallacycles derived from the oxidative cyclization of nickel(0) with an alkynyl enal have been isolated and fully characterized. The metallacycles obtained possess an η^1 nickel O-enolate motif within the metallacyclic framework.

Enynes have proven to be versatile substrates in an impressive variety of metal-catalyzed processes involving a broad range of early and late transition metals.[1] The classes of reactions that involve metal-catalyzed functionalization of enynes include cycloisomerizations,[2] reductive cyclizations,[3] alkylative cyclizations,[4] carbonylative cyclizations,[5] and various cycloadditions,[6] among others. Many mechanisms have been proposed in these classes of reactions, but the formation of metallacycles from the oxidative cyclization of an enyne with a low-valent catalyst is commonly invoked as a key step.

Early studies by Wilke demonstrated that diene oligomerizations proceeded via the formation of bis(allyl)nickelacycles,[7] and a comprehensive study of structurally simpler nickel metallacycles was carried out by Grubbs.[8] Numerous more recent reports described the isolation and structure determination of various nickelacycles, but none of these were related to enyne cyclizations.[9] There is indeed a real paucity of mechanistic and structural insight into the conversion of enynes to reactive late-transition-metal metallacycles. Remarkably, to our knowledge, no example of a well-characterized nickel or palladium enyne-derived metallacycle has previously been reported.[10,11] This is surprising, given the extraordinary synthetic importance of palladium- and nickel-catalyzed cyclizations of enynes and related polyunsaturated substrates.

Our group has recently contributed to the area of late-metal-catalyzed enyne cyclizations.[12] These reports have included a variety of nickel-catalyzed or -promoted processes involving alkynyl enones, such as alkylative cyclizations,[13a] reductive cyclizations,[13a] [2 + 2 + 2] cycloadditions,[13b] [3 + 2] alkylative cycloadditions,[13c] and [2 + 1] oxidative cycloadditions.[13c] The intermolecular versions of several of these processes have been extensively developed by Ikeda.[12b] Whereas several mechanisms may be envisioned for these processes, the formation of a reactive nickel metallacycle has emerged as the most reasonable mechanistic model on the basis of the data obtained to date. Our most recent studies demonstrated that treatment of equimolar quantities of Ni(COD)$_2$ and tetramethylethylenediamine (tmeda) with an alkynyl enone afforded a complex in situ that demonstrated reactivity consistent with the proposed metallacycle.[13c] However, no direct evidence for formation of the proposed nickel metallacycle was initially obtained.

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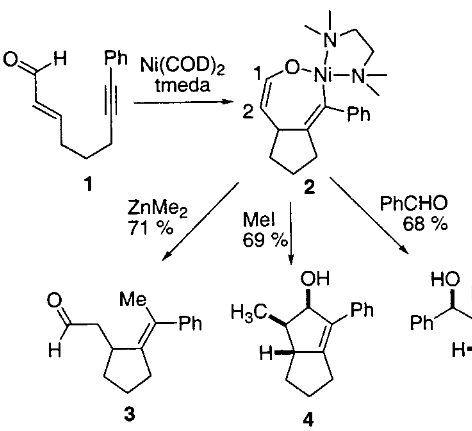
10.1021/om0010013 CCC: $20.00
Publication on Web 01/09/2001

Scheme 1. Structure and Reactivity of Metallacycle 2[a]



[a] ^{1}H NMR (CD_2Cl_2): C(1)−H (δ 5.6), C(2)−H (δ 3.5). ^{13}C NMR (CD_2Cl_2): C(1) (δ 153), C(2) (δ 101). IR (Nujol): 1577, 1450 cm^{-1}.

To prepare such a metallacycle, alkynyl enal **1** was treated with a stoichiometric quantity of $Ni(COD)_2$ and tmeda (Scheme 1). A deep red solution resulted, and upon concentration, filtration, and recrystallization with hexane/THF, a red crystalline solid was obtained. Single-crystal X-ray analysis of the crystalline solid **2** was carried out, and the molecular structure is the η^1-(O)-bound tautomer of the metallacycle proposed in catalytic cyclizations (Figure 1).[14] A square-planar geometry is observed, and the Ni−O−C bond angle of 125° clearly demonstrates the η^1 nature of the enolate. The metallacycle was further characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis, and NMR assignments were rigorously made utilizing 2D techniques. The η^1(O)-bound solution structure was confirmed by the data provided in Scheme 1. The O-bound structure is unusual, since most classes of late-metal enolates exist as the C-bound tautomers. The extensive studies from Bergman and Heathcock with a variety of mid- and late-metal enolates clearly document this trend, and enolates of nickel were reported in their study to be η^1(C)-bound.[15] Significantly, in the NMR spectra of nickel *C*-enolates, the carbon and protons α to the carbonyl appeared at δ −8.0 to 13.6 (^{13}C) and δ 0.75−1.88 (^{1}H), compared with the analogous signals for complex **2**, which appeared at δ 101 (^{13}C) and δ 3.5 (^{1}H). Complex **2** is the first example of a nonconjugated η^1(O)-bound nickel enolate,[16] although η^1(O)-bound enolates of palladium and copper have been proposed on the basis of spectroscopic evidence.[17] The corresponding bipyridine complex **6** was also prepared, and its structural and spectroscopic properties were directly analogous to those of complex **2** (Figure 2).[14]

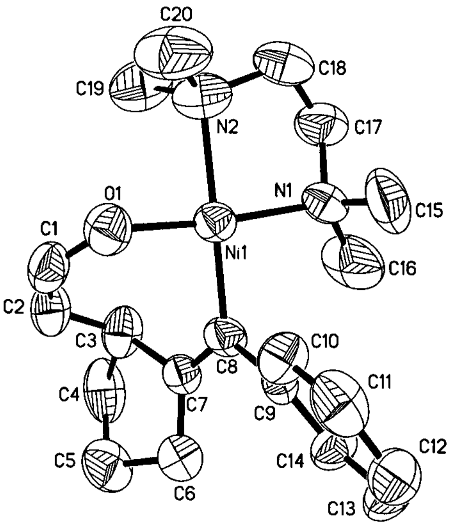


Figure 1. X-ray crystal structure of metallacycle **2**. Selected bond lengths (Å) and angles (deg): Ni−O = 1.852(6), O−C1 = 1.316(10), C1−C2 = 1.298(11), C2−C3 = 1.508(11), C7−C8 = 1.357(10) C8−Ni = 1.897(7); O−Ni−C8 = 91.3(3), O−Ni−N2 = 88.9(3), N2−Ni−N1 = 85.6(3), N1−Ni−C8 = 94.3(3), Ni−O−C1 = 124.7(5), O−C1−C2 = 132.1(8), C1−C2−C3 = 126.0(8).

Isolation of a metal complex tells nothing about its kinetic competence in a catalytic pathway, but the isolation of **2** and **6** does clearly demonstrate that metallacycles are accessible from the oxidative cyclization of Ni(0) with enals and alkynes. Furthermore, complex **2** was observed to demonstrate reactivity that closely parallels the nickel-catalyzed and nickel-promoted chemistry of alkynyl enal **1**. For instance, treatment of complex **2** with dimethylzinc affords a 71% isolated yield of aldehyde **3**, in direct analogy to the catalytic alkynyl enone/organozinc couplings that we

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[14] X-ray crystal data for **2**: 0.2 × 0.2 × 0.1 mm^3, monoclinic, *C*2/*c*, a = 33.224(15) Å, b = 7.712(3) Å, c = 32.863(14) Å, β = 90.748(9)°, V = 8419(6) Å^3, ρ(calcd) = 1.178 g cm^{-3}, 2θ(max) = 56°, λ = 0.710 73 Å. A total of 1650 CCD frames were collected at room temperature, yielding 60 870 reflections, of which 9971 were independent. Refinement was carried out on I on all reflections in SHELX-97, with absorption corrections fron SADABS and calculated hydrogen positions. R1 = 0.082 and wR2 = 0.217 for the final R indices ($I > 2\sigma(I)$); when weak reflections are included, R1 = 0.232 and wR2 = 0.251. There is an additional ill-defined solvent region that could not be reasonably assigned. X-ray crystal data for **6**: 0.2 × 0.1 × 0.1 mm^3, monoclinic, $P2_1/n$, a = 10.5385(7) Å, b = 16.4647(12) Å, c = 12.4162(9) Å, β = 113.689(1)°, V = 1972.9(0.4) Å^3, ρ(calcd) = 1.391 g cm^{-3}, 2θ(max) = 56°, λ = 0.710 73 Å. A total of 1650 CCD frames were collected at room temperature, yielding 14 397 reflections, of which 4686 were independent. Refinement was carried out on I on all reflections in SHELX-97, with absorption corrections fron SADABS; hydrogen atoms were observed and refined. R1 = 0.033 and wR2 = 0.050 for the final R indices ($I > 2\sigma(I)$); when weak reflections were included, R1 = 0.133 and wR2 = 0.059. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 150892 and 150893. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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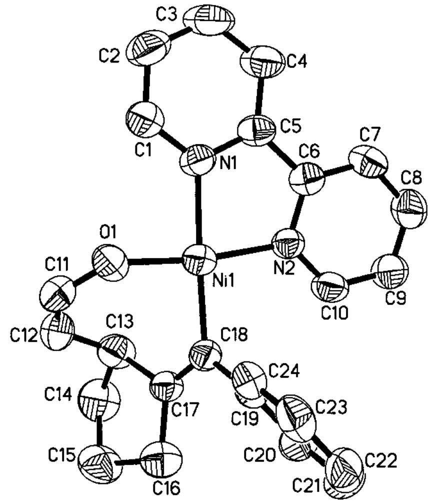

Figure 2. X-ray crystal structure of metallacycle **6**. Selected bond lengths (Å) and angles (deg): Ni−O = 1.8347(17), O−C11 = 1.319(3), C11−C12 = 1.324(4), C12−C13 = 1.493(4), C17−C18 = 1.333(3), C18−Ni = 1.897(2); O−Ni−C18 = 92.13(8), O−Ni−N1 = 89.62(8), N1−Ni−N2 = 82.35(9), N2−Ni−C18 = 95.87(9), Ni−O−C11 = 127.5(2), O−C11−C12 = 130.6(3), C11−C12−C13 = 125.8(3).

extensively developed (Scheme 1).[13a,b,18] Likewise, alkylative cycloadditions of **2** with methyl iodide and benzaldehyde proceeded in direct analogy to the one-pot procedures recently developed[13c] to allow the efficient production of **4** and **5** in 69% and 68% yields, respectively.

It must be stressed that isolation of nickel metallacycle **2** does not rigorously demonstrate its involvement in the catalytic organozinc-promoted cyclizations. However, we are unaware of any other mechanistic alternative that is fully consistent with the very diverse manifolds of reactivity demonstrated in alkynyl enone cyclizations. This study now provides the first direct precedent for formation of a metallacycle derived from oxidative cyclization of an alkynyl enone. We cannot rule out the possibility that metallacycle **2** cycloreverts to a nickel(0) alkynyl enal complex which could then proceed by an alternative mechanism to products **3**−**5**. However, treatment of complex **2** with an excess of tmeda does not result in recovery of alkynyl enone **1** as might be expected if the cyclization were reversible. Indeed, we have obtained no evidence to date that indicates that the formation of **2** is reversible, although we are continuing to investigate this possibility.

In summary, we have demonstrated that an alkynyl enal, upon treatment with Ni(COD)$_2$ and tmeda or bipyridine, is converted to a Ni(II) metallacycle with a highly unusual η^1(O)-enolate ligand structure. In addition to elucidating the structural characteristics of the key intermediate proposed in the alkynyl enone cyclizations developed in our laboratory, the metallacycles prepared in this study serve as excellent structural models for many synthetically important catalytic processes developed in other laboratories.[12b,19]

Acknowledgment. This work was supported by the National Science Foundation and by a Camille Dreyfus Teacher-Scholar Award to J.M.

Supporting Information Available: Text providing full experimental details, figures giving ^{1}H and ^{13}C NMR spectra, and tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0010013

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