2924 *Organometallics* **1998,** *17,* 2924−2925

Formation of a Substituted Tetrahydrofuran by Formal [2 + 2 + 1] Coupling of an Oxygen Atom with Two Olefins at a Nickel Center

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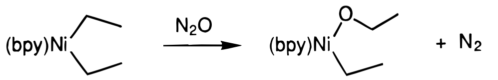
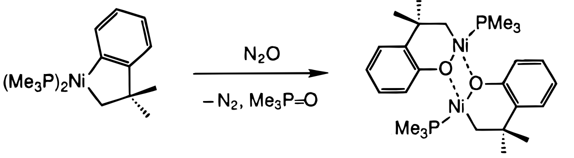
Received March 12, 1998

*Summary: Formation of the tetrasubstituted tetrahydrofuran exo-trans-endo-3-oxapentacyclo[9.2.1.1.^{5,8}0.^{2,10}0^{4,9}]-pentadeca-6,12-diene (**5**) has been accomplished by the coupling of an oxygen atom (from nitrous oxide) with two olefins (norbornadiene) at a Ni center. The reaction proceeds via a nickelacyclopentane complex (**2**) that is subsequently oxidized by N_2O to give an isolable oxanickelacyclohexane (**3**). Oxidation of **3** with iodine results in formation of the C−O bond of **5** (47% isolated yield) via C,O-reductive elimination.*

Nitrous oxide (N_2O) can be a potent but selective reagent for oxygen atom transfer to organometallic complexes. For example, we have previously reported that N_2O can be used to insert an O atom into a Zr−C bond of complexed diphenylacetylene in $(\eta\text{-}C_5Me_5)_2Zr(C_2Ph_2)$ to give an oxametallacyclobutene complex, $(\eta\text{-}C_5Me_5)_2\overline{Zr(OCPh{=}C}Ph)$, which is susceptible to further synthetic elaboration at the remaining Zr−C(Ph) bond.[1] Metal-mediated reactions of N_2O with alkenes to give analogous oxametallacyclobutane complexes or free epoxides have not been reported. Recently we have demonstrated that nitrous oxide reacts with a variety of organonickel complexes via O-atom insertion into Ni−alkyl or Ni−aryl bonds to give new alkoxide or aryloxide products, examples of which are shown in eqs 1 and 2.[2,3]



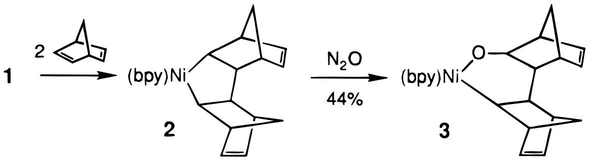
(1)



(2)

Since it is well-established that strained-ring olefins can be catalytically cyclodimerized or cyclotrimerized using Ni(0) complexes or atoms,[4,5] we have investigated the possibility of taking advantage of Ni(0)-based chemistry to effect the coupling of two olefins with the O atom of nitrous oxide in a novel, potentially catalytic route to tetrahydrofurans.

In a classic study, Binger and co-workers showed that under mild conditions the strained-ring olefins 3,3-dimethylcyclopropene, methylenecyclopropane, and norbornadiene react with (bpy)Ni(cod) (**1**; bpy = 2,2′-bipyridine, cod = 1,5-cyclooctadiene) to undergo cycloaddition with formation of isolable nickelacyclopentane complexes that are catalysts for cyclodimerization of the olefins.[6] Thus, **1** reacts with norbornadiene to give, in high yield, the nickelacyclopentane **2** exclusively as the *exo,trans,endo* isomer (eq 3).[5,6]



(3)

We now report that when benzene solutions of **2** are stirred at 55 °C for 3 days under a nitrous oxide atmosphere, dinitrogen is evolved and the oxanickelacyclohexane derivative **3** can be isolated as a royal blue, microcrystalline solid in 44% yield (eq 3). We do not observe evidence of secondary oxidation at the remaining Ni−C bond to give a bis(alkoxide) complex. The characterization of **3** follows from its ^1H and $^{13}C\{^1H\}$ NMR spectra, CHN elemental analyses, and reactivity (see below). Spectral data for **3** are similar to those for the unsubstituted metallacycle $(bpy)\overline{Ni(OCH_2CH_2CH_2\text{-}CH_2})$ (**4**), which has been characterized by X-ray crystallography,[2a] and moreover, the spectral data indicate that **3** is formed as a single isomer.

Whereas **2** reacts with excess norbornadiene at elevated temperatures (90 °C) to reductively eliminate the *exo,trans,endo*-norborornadiene dimer and enter into a catalytic cycle for olefin cyclodimerization,[5,6] **3** is inert toward simple thermal reductive elimination with C−O bond formation in the presence or absence of norbornadiene. This is consistent with our general observation that thermolysis of a (bpy)Ni(OR)(R′) complex does not result in ether elimination but, rather, β-H elimination

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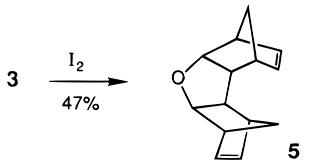
S0276-7333(98)00182-4 CCC: $15.00

occurs when a β-H is sterically accessible. For **3**, β-H elimination is not observed, presumably because constraints imposed by the ligand's cyclic structure prevent the β-hydrogens from interacting with Ni.

Treatment of a benzene solution of **3** with iodine (eq 4) results in an immediate bleaching of the blue color with elimination of the tetrasubstituted tetrahydrofuran *exo-trans-endo*-3-oxapentacyclo[9.2.1.1.^{5,8}0.^{2,10}0^{4,9}]pentadeca-6,12-diene (**5**), which can be isolated in 47% yield upon chromatographic workup (silica gel; eluent hexane/ethyl acetate, 100:3). As judged by ^{1}H NMR, ^{13}C NMR, and gas chromatography, only a single isomer, the *exo,trans,endo* isomer, of **5** is produced in this reaction.



(4)

Oxidatively induced reductive-elimination reactions from alkylnickel(II) amido complexes that form cyclic amines in high yields (e.g., pyrrolidines and indolines) are well-established, with one-electron oxidation of Ni(II) to Ni(III) (using O_2 or ferrocenium) being the trigger to the reductive-elimination event.[7] We have also recently reported that 4,4-dimethylchroman, *o*-C_6H_4-$CMe_2CH_2CH_2O$, is formed by oxidatively induced O,C-reductive elimination on exposure of (bpy)$NiOCH_2CH_2$-CMe_2-*o*-C_6H_4 to oxygen or (1,1′-diacetylferrocenium)silver tetrafluoroborate.[8] However, reasonable yields of **5** are only obtained using I_2 as the oxidant (not Cp_2Fe^+ or O_2). This suggests that this reaction might involve I_2 addition to **3** to give a Ni(IV) intermediate which undergoes direct O,C-reductive elimination to give **5**.[9] Alternatively, **5** could be formed by iodinolysis of the Ni−C bond of **3** to give an alkyl iodide, followed by intramolecular nucleophilic substitution with ring closure,[10] although the observed isomeric selectivity argues against this latter pathway.

In summary, we have demonstrated the formal [2 + 2 + 1] coupling of an oxygen atom (from nitrous oxide) with two olefins at a nickel center which, upon oxidation with I_2, gives the tetrasubstituted tetrahydrofuran **5**. Work is currently underway to elucidate factors that might favor *thermally* induced O,C-reductive elimination in this system, analogous to that recently reported for Pd phosphine complexes,[11] which would obviate the requirement for chemical oxidation of the Ni complex to effect O−C bond formation.

Experimental Section

General Procedures. Reactions were carried out using standard high-vacuum and Schlenk techniques using dry, air-free solvents. NMR spectra were recorded using a GE Ω-500 spectrometer in C_6D_6 solution at ambient temperature, as noted. ^{1}H NMR spectra were recorded at 500 MHz, and ^{13}C{^{1}H} NMR spectra were recorded at 125.77 MHz. Electron impact mass spectra were recorded on a VG Analytical, LTD 70-70 EQ double-focusing mass spectrometer. Elemental analyses were carried out by Desert Analytics (Tucson, AZ). The nickelacyclopentane **2** was prepared according to the literature method.[5,6]

Preparation of (bpy)Ni($OC_{14}H_{16}$) (3). A 0.35 g sample of **2** (0.94 mmol) and 10 mL of benzene were placed in a round-bottomed flask attached to a swivel-frit assembly. The solution was stirred under N_2O (1 atm) at 55 °C for 3 days, after which the solution was filtered and the filtrate was taken to dryness under vacuum. The resulting solid was washed with petroleum ether (3 × 5 mL), and the blue product was collected on a filter frit to give 0.16 g (44%) of microcrystalline **3**. Anal. Calcd for $C_{24}H_{24}N_2ONi$: C, 69.4; H, 5.83; N, 6.75. Found: C, 69.5; H, 6.01; N, 6.55. ^{1}H NMR (500 MHz, C_6D_6): δ 1.24 (d,1 H, CH), 1.60 (d, 1 H, CH), 1.70 (m, 2 H, CH_2), 1.87 (d, 1 H, CH), 2.72 (dd, 1 H, CH), 2.83 (s, 1 H, CH), 2.95 (s, 1 H, CH), 3.18 (m, 2 H, CH_2), 3.64 (s, 1 H, CH), 4.75 (dd, 1 H, CH), 6.40−9.52 (m, 12 H, bpy & CH). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 34.2, 42.5, 46.4, 47.6, 51.8, 52.7, 53.0, 53.6, 54.9, 78.1, 118.9, 121.0, 124.9, 125.7, 133.2, 135.2, 135.9, 136.8, 137.4, 148.1, 149.3, 149.7 (two resonances obscured by solvent).

Preparation of *exo-trans-endo*-3-Oxapentacyclo[9.2.1.1^{5,8}.0^{2,10}.0^{4,9}]pentadeca-6,12-diene (5). A 0.12 g sample of **3** (0.31 mmol) and 10 mL of benzene were placed in a round-bottomed flask, to which iodine (0.08 g, 0.31 mmol) was added under an argon counterflow. There was an immediate color change from blue to brown. The solution was stirred for 30 min at ambient temperature and filtered, and the filtrate was evaporated using a rotary evaporator. The residue was chromatographed on silica gel (eluent hexane/ethyl acetate, 100:3) to give **5** (0.03 g, 47%) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 1.07 (d, 1 H, CH*H*), 1.41 (d, 1H, CH*H*), 1.60 (d, 1 H, CH*H*), 1.64 (s, 1 H, CH), 1.65 (d, 1 H, CH*H*), 1.98 (m, 1 H, CH), 2.39 (s, 1 H, CH), 2.60 (s, 1 H, CH), 2.80 (s, 1 H, CH), 2.88 (s, 1 H, CH), 4.18 (d, 1 H, CH), 4.96 (dd, 1 H, CH), 5.73 (m 1 H, CH), 6.00 (m, 2 H, CH), 6.20 (m, 1 H, CH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 45.4, 46.6, 47.1, 48.7, 49.1, 49.5, 49.6, 51.1, 91.9, 93.7, 134.4, 135.6, 135.9, 140.5. EIMS: *m*/*e* 200 (M^+).

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-9505692) for financial support of this research.

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