Nickeladihydrofuran. Key intermediate for nickel-catalyzed reaction of alkyne and aldehyde†

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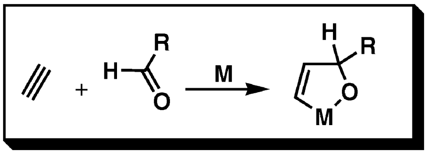
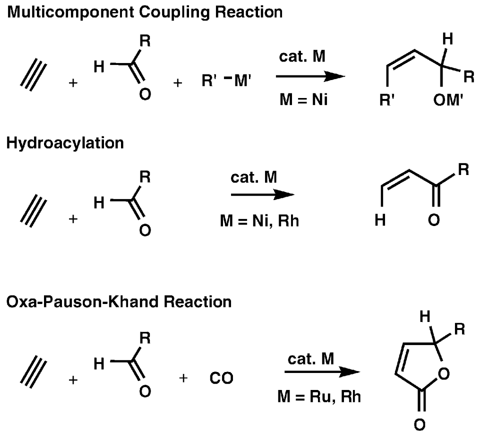
The formation of a nickeladihydrofuran by oxidative cyclization of an alkyne and an aldehyde with nickel(0) has been demonstrated; the transformation of the nickeladihydrofuran into an enone by decomposition, a lactone by carbonylation and an allylic alcohol by treatment with $ZnMe_2$ suggests that nickeladihydrofuran is an important key intermediate in a variety of catalytic reactions.

The oxidative cyclization of an alkyne and an aldehyde with a transition metal can simultaneously form a carbon–carbon bond, a carbon–metal bond and a metal–oxygen bond to generate a metaladihydrofuran (Scheme 1).[1] Therefore, a metaladihydrofuran can potentially act as a key intermediate in a late transition metal-catalyzed reaction involving carbon–carbon bond formation between an alkyne and an aldehyde, such as a multi component coupling reaction,[2] a hydroacylation reaction[3] and an oxa-Pauson–Khand reaction[4] (Scheme 2). In fact, it is believed that a nickeladihydrofuran is the key intermediate in a nickel-catalyzed multicomponent coupling reaction. Nickeladihydrofuran also is a possible reaction intermediate in the nickel-catalyzed hydroacylation reaction, although an acyl nickel hydride generated by the oxidative addition of an aldehyde to nickel(0) has been proposed as the likely reaction intermediate.[3a] However, the presence or absence of alkyl metals is the only difference between a nickel-catalyzed multicomponent coupling reaction and a nickel-catalyzed hydroacylation reaction. Thus, it is logical that both nickel-catalyzed reactions could proceed *via* the same key intermediate nickeladihydrofuran. Herein we report the formation of the nickeladihydrofuran by the oxidative cyclization of an alkyne and aldehyde with nickel(0) for the first time. Moreover, the transformation of the nickeladihydrofuran into an enone, a lactone and an allylic alcohol also is reported.



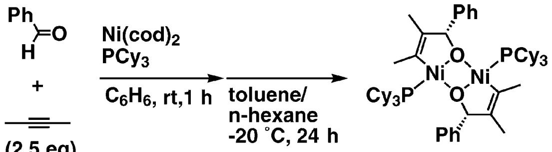
Scheme 1 Oxidative cyclization of alkyne and aldehyde.



Scheme 2 C–C Bond formation with alkyne and aldehyde.

The reaction of PhCHO and 2-butyne (2.5 eq.) with $Ni(cod)_2$ and PCy_3 in C_6D_6 for 1 h generated the expected nickeladihydrofuran (**1**) as a dimer in 50% NMR yield.‡ This dimeric structure might be required to form a 16-electron square-planar structure (see later). However, the nickeladihydrofuran **1** decomposed slowly in C_6D_6 at room temperature. Thus, **1** was isolated in 40% yield by reprecipitation from a toluene–*n*-hexane solution (1 : 3) of a concentrated reaction mixture at −20 °C. A single crystal suitable for X-ray crystallography§ was obtained by recrystallization from THF–*n*-pentane at −20 °C (Scheme 3).[5] The molecular structure of **1** in Fig. 1 shows the square-planar dimeric structure around nickel. The spatial relation of two phenyl groups is *cis*. The bond length between C1 and C2 is in the range of normal carbon–carbon double bond lengths. As an example of oxidative cyclization of a carbonyl group and an alkyne with nickel(0), the reaction of carbon dioxide and an alkyne with nickel(0) to give a nickelalactone had been reported.[6] Although it is very important work in this field, the nickelalactone can not act as a key intermediate in mutlicomponent coupling reactions as well as hydroacylation reactions.

Under carbon monoxide pressure (5 atm), **1** underwent carbonylation to give the corresponding unsaturated γ-lactone



1 40%

Scheme 3 Formation of nickeladihydrofuran.

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† Electronic supplementary information (ESI) available: General procedure and spectral data for all new compounds. See DOI: 10.1039/b717261c

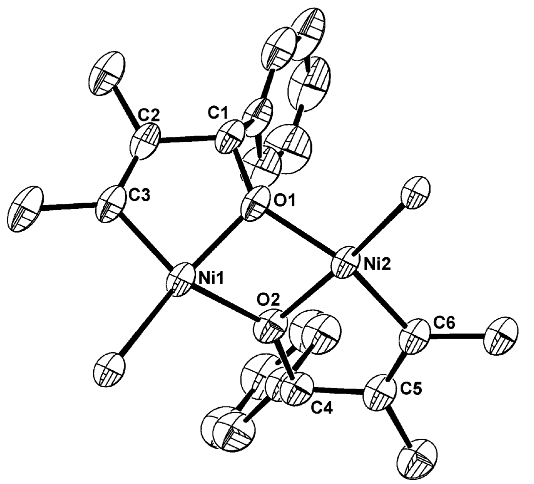
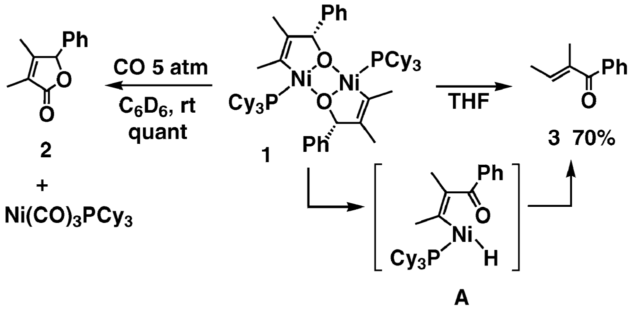


Fig. 1 Molecular structure of **1** with thermal ellipsoids at the 30% probability level. H atoms, cyclohexyl groups on the phosphorous atoms, and solvents are omitted for clarity.

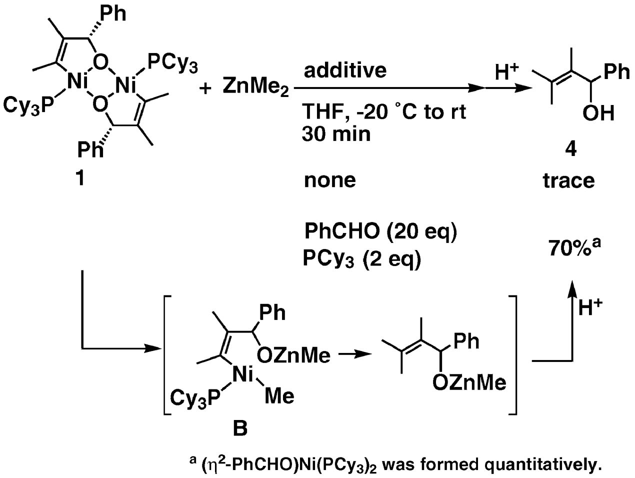


Scheme 4 Transformation into enone and lactone.

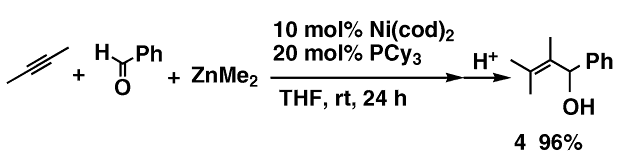
(**2**) quantitatively (Scheme 4),[7] which is consistent with the structure confirmed by X-ray crystallography. The formation of lactone **2** from **1** is a very rare example, since only one previous example of the formation of a lactone by the carbonylation of an isolated metaladihydrofuran complex has been reported.[1o] Formally, lactone **2** is an oxa-Pauson–Khand reaction product of 2-butyne and PhCHO with carbon monoxide, which suggests that a similar metaladihydrofuran could be a key intermediate in a late transition metal-catalyzed oxa-Pauson–Khand reaction.

The dimer complex **1** decomposed slowly at room temperature in THF to give an enone (**3**) in 70% isolated yield, which corresponds to the hydroacylation product of 2-butyne with PhCHO (Scheme 4). The formation of **3** might proceed as follows: The β-hydrogen elimination from **1** generates a nickel hydride intermediate (**A**) followed by reductive elimination to give **3**. These observations suggest that a nickeladihydrofuran can be a key intermediate in the nickel-catalyzed hydroacylation reaction, although it has been regarded as an unlikely reaction intermediate.[3a]

The reaction of **1** with $ZnMe_2$ in THF at −20 °C for 30 min resulted in a complicated mixture, in which a trace amount of the expected allylic alcohol (**4**) was observed (Scheme 5). On the other hand, it was confirmed that a three-component coupling reaction of 2-butyne, PhCHO with $ZnMe_2$ in the presence of a catalytic amount of $Ni(cod)_2$ (10 mol%) and PCy_3 (20 mol%), proceeded smoothly to give **4** in 96% isolated yield (Scheme 6). In a catalytic cycle, a generated nickel(0) species might be immediately trapped by unreacted substrates. Thus, the stoichiometric reaction was carried out in the presence of excess amounts of PCy_3 and PhCHO. In the presence of PCy_3 (2 eq.) and PhCHO (20 eq.) at −20 °C, the reaction proceeded slowly (Scheme 5). At the end of the reaction, the formation of $(\eta^2\text{-PhCHO})Ni(PCy_3)_2$ was observed quantitatively in the ^{31}P NMR spectra.[8] The expected allyloxyzinc was confirmed as the corresponding alcohol **4** (70%). These results indicate that the three-component coupling reaction of alkyne, aldehyde and alkylmetals might also proceed *via* a nickeladihydrofuran followed by reductive elimination. The stabilization of the generated nickel(0) species by the coordination of a substrate also is crucial for the achievement of a catalytic cycle.



Scheme 5 Reaction of nickeladihydrofuran with $ZnMe_2$.



Scheme 6 Catalytic reaction.

In conclusion, the formation of a nickeladihydrofuran by the oxidative cyclization of an alkyne and an aldehyde with nickel(0) was demonstrated for the first time. The transformation of the nickeladihydrofuran into an enone by decomposition, a lactone by carbonylation and an allylic alcohol by treatment with $ZnMe_2$ suggests that nickeladihydrofuran is an important intermediate in a variety of catalytic reactions.

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Notes and references

‡ *Selected spectral data* for **1**: H NMR (400 MHz, THF-d_8, −20 °C): δ 0.81 (s, 6H, $-NiC(CH_3){=}C(CH_3)-$), 1.09 (s, 6H, $-NiC(CH_3){=}C(CH_3)-$), 1.1–2.4 (m, 66H, *Cy*), 4.23 (s, 2H, –NiOC*H*Ph–), 7.20 (t, *J* = 6.8 Hz, 2 H, *p-Ph*), 7.28 (t, *J* = 6.8 Hz, 4 H, *m-Ph*), 7.85

(t, J = 7.2 Hz, 4 H, *o-Ph*). ^{31}P NMR (109 MHz, THF-d_8): δ 31.9 (s). ^{31}C NMR (100 MHz, THF-d_8, −20 °C): δ 12.7 (s, –NiC-(CH_3)=C(CH_3)–), 14.7 (s, *Cy*), 21.6 (s, *Cy*), 23.6 (s, *Cy*), 23.7 (–NiC(CH_3)=C(CH_3)–), 27.5 (br s, *Cy*), 29.0 (br s, *Cy*), 32.7 (s, *Cy*), 90.4 (s, –NiO*C*HPh–), 126.2 (d, J = 27.0 Hz, –Ni*C*(CH_3)=C(CH_3)–), 128.7 (s, *p-Ph*), 129.0 (s, *m-Ph*), 129.7 (s, *o-Ph*) 148.6 (s, *ipso-Ph*), 150.7 (s, –NiC(CH_3)=*C*(CH_3)–). Anal. Calc. for $C_{58}H_{90}Ni_2O_2P_2$: C, 69.75; H, 9.08. Found: C, 69.32; H, 9.08%.

§ *Crystal data* for **1**·C_5H_{12}·C_4H_8O: M = 1142.91, black, monoclinic, $C2/c$ (no. 15), a = 49.179(3), b = 13.9696(8), c = 20.1131(11) Å, β = 110.2380(15)°, V = 12964.8(13) Å, D_c = 1.171 g cm^{-3}, T = 0 °C, R_1 = 0.0585 [$I > 2\sigma(I)$], wR_2 = 0.1712 (all data). CCDC 655569. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717261c

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