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$AlMe_3$-Promoted Oxidative Cyclization of η^2-Alkene and η^2-Ketone on Nickel(0). Observation of Intermediate in Methyl Transfer Process

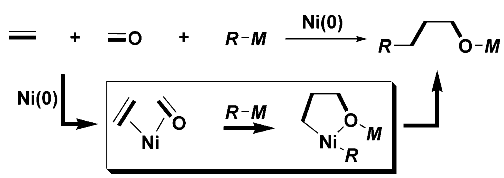
Sensuke Ogoshi,* Mizu Ueta, Tomoya Arai, and Hideo Kurosawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Received June 28, 2005; E-mail: ogoshi@chem.eng.osaka-u.ac.jp

Ketones and aldehydes can be employed as one of the two π components in the nickel-catalyzed three-component coupling, with alkylmetals as the third component (Scheme 1).[1] The oxidative cyclization on nickel(0) to give a nickelacycle intermediate was assumed as a key step. However, so far, only scattered studies on the oxidative cyclization on nickel(0) have been reported. Recently, we reported a spontaneous oxidative cyclization of η^2:η^2-enalnickel and the acceleration of the cyclization by the addition of Me_3SiOTf as a Lewis acid.[2] Montgomery and Schlegel suggested that $ZnMe_2$ can play a dual Lewis basic/Lewis acidic role in the nickel-catalyzed coupling reaction of enone and alkyne with $ZnMe_2$ based on their experimental and computational study.[3] Here, we report that $AlMe_3$ promotes oxidative cyclization of an η^2:η^2-2-allylacetophenone- or η^2:η^2-2-allylbenzophenone nickel complex to lead to the formation of a nickelahydrofuran, having a significant interaction between nickel and an aluminum−methyl bond. Moreover, the catalytic application of this oxidative cyclization is also reported.

Scheme 1. Nickel-Catalyzed Three-Component Coupling Reaction



The reaction of 2-allylacetophenone (**1a**) or 2-allylbenzophenone (**1b**) with $Ni(cod)_2$ and PCy_3 gave an η^2:η^2-1,5-enonenickel complex (**2a**, **2b**) quantitatively (Scheme 2).[4] ^1H, ^{13}C, and ^{31}P NMR spectra indicate that both C═C and C═O bonds coordinate to Ni(0) in η^2-fashion. The molecular structure of **2b** was also confirmed by the X-ray diffraction analysis, showing that all of the atoms expected to participate in the oxidative cyclization (Ni, C1, C2, C10, O) are on the same plane and the atom distance between C2 and C10 is 2.7 Å (Figure 1). Neither **2a** nor **2b** was converted into the nickelacycle by heating at 60 °C or by addition of Me_3SiOTf, which was efficient for the oxidative cyclization of the aldehyde analogues on nickel(0).[2]

The reaction of **2a** or **2b** with $AlMe_3$ in C_6D_6 proceeded very rapidly to give a deep-orange solution of cyclized compound **3a** or **3b** (quantitative).[5] Both complexes **3a** and **3b** could be isolated, and the molecular structure of **3b** confirmed by X-ray diffraction analysis shows a unique nickelacycle structure having a bridging methyl group (Figure 2; C2−C10 1.536(8) Å, Ni−C1 1.925(6) Å, Ni−O 1.893(4) Å, Ni−C17 2.292(6) Å, Al−C17 2.037(7) Å, Al−C18 1.970(6) Å, Al−C19 1.961(9) Å, Ni−Al 2.691(1) Å, Al−O 1.796(5) Å, <Ni−C17−Al 76.6(2)°, <Ni−O−Al 93.7(2)°). This structure is very intriguing because the bond sequence Ni−C4−Al−O−Ni could be regarded as a nice model for the transmetalation.[6] The bridging methyl group and the other two methyl groups exchange one another very rapidly in a solution at room temperature

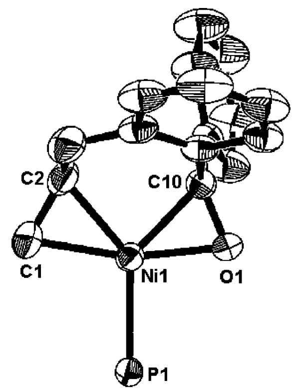


Figure 1. Molecular structure of **2b**. Cyclohexyl groups are omitted.

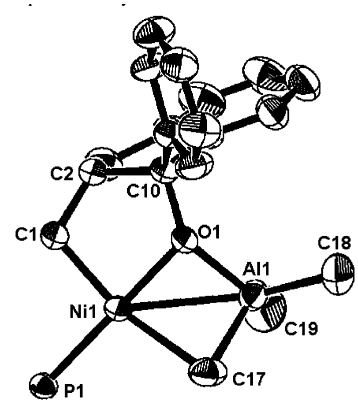
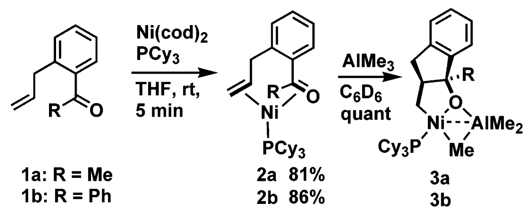


Figure 2. Molecular structure of **3b**. Cyclohexyl groups are omitted.

Scheme 2. $AlMe_3$-Promoted Oxidative Cyclization



since in ^1H NMR spectrum of **3a** the only resonance of $AlMe_3$ was observed at δ −0.89. However, three different broad resonances for $AlMe_3$ appeared (δ −0.15, −0.50, −2.10) at −80 °C in toluene-d_8, which is consistent with the molecular structure in the solid state. Not only is the structural evidence for **3b** relevant for describing the role of $AlMe_3$ in the promotion of the **2** to **3** conversion but also is the nature of **3b** consistent with the role of $ZnMe_2$ proposed by Montgomery and Schlegel in other oxidative cyclization processes. A molecular orbital description for a bridging Zn−C−Ni interaction and a direct Zn−Ni interaction was provided

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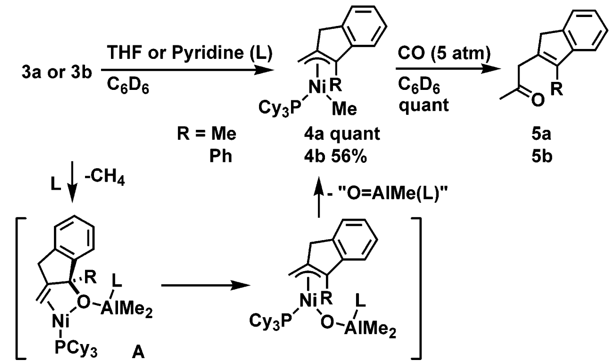
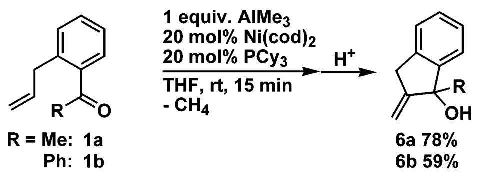
Scheme 3. Formation of η^3-Allylmethylnickel Complex



Scheme 4. Nickel-Catalyzed Cycloisomerization



in that work, and the corresponding structural features involving $AlMe_3$ are now documented in compound **3b**.

Neither **3a** nor **3b** underwent further reaction in benzene, but treatment of these with THF or pyridine resulted in intriguing transformation involving two transmetalation steps. Thus, 6 equiv of THF-d_8 or 1 equiv of pyridine was added to a solution of **3** in C_6D_6 to lead to the generation of an unexpected η^3-allylnickel complex (**4a**, **4b**)[7] concomitant with the evolution of methane gas and insoluble white precipitates (Scheme 3). The complex **4** might be generated via transmetalation in **3** and methane elimination to give an intermediate **A**, followed by the oxidative addition of an allyloxyaluminum unit and the second transmetalation. The treatment of **4a** or **4b** with carbon monoxide led to the formation of the corresponding acylated compound **5a** or **5b**, quantitatively.[8]

We conceived that the allyloxyaluminum compound might be released from the intermediate **A** in Scheme 3 prior to the oxidative addition if the starting material (**1a**, **1b**) is present in excess to trap the Ni(0) unit. We then found a catalytic cycloisomerization of 1,5-enone compounds, as shown in Scheme 4. Thus, in THF, in the presence of a catalytic amount of $Ni(cod)_2$ and PCy_3, both **1a** and **1b** reacted with $AlMe_3$ to give allyl alcohols **6a** and **6b**, respectively, by protonation of the reaction mixture.[9] The evolution of CH_4 as a gas was observed during the reaction, and the formation of **4a** was also confirmed by ^{1}H NMR spectra on the reaction mixture. The reaction might have proceeded via **3** and **A**. The Ni(0) complex did not catalyze the reaction of **1a** with $ZnMe_2$, analogous to Scheme 4 under the same condition, but the Ni(0) species was recovered as **2a**, although the addition of $ZnMe_2$ to a solution of **2a** in C_6D_6 at room temperature led to slow reaction to give nickel black precipitates and an organozinc compound which gave quantitative yield of **6a** by the protonation. This zinc compound is estimated as the corresponding allyloxy(methyl)zinc, which might be also formed via Me_2Zn-promoted oxidative cyclization of **2a** and transmetalation.

In conclusion, we demonstrated that $AlMe_3$ promoted the oxidative cyclization of η^2-alkene and η^2-ketone on nickel(0) to give an intriguing nickel−aluminum dinuclear complex. This complex is a nice model as an intermediate in the transmetalation process. Moreover, the cycloisomerization can proceed catalytically in THF, which encourages us to use a simple alkene or ketone as one component in the nickel-catalyzed multicomponent coupling reaction. Further studies are in progress in our group.

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Supporting Information Available: Experimental procedures (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Selected spectral data for **2a**: ^{1}H NMR (C_6D_6) δ 1.93 (d, J = 4.2 Hz, 3H, CH_3C=O), 2.31 (dd, J = 12.4, 6.5 Hz, 1H, −CH$_2$−CH=CH_2), 2.50 (m, 1H, −CH_2−CH=CH$_2$), 2.55 (m, 1H, −CH$_2$−CH=CH_2), 3.36 (m, 1H, −CH$_2$−CH=CH$_2$), 3.69 (dt, J = 17.3, 4.9 Hz, 1H, −CH_2−CH=CH$_2$). ^{31}P NMR (C_6D_6): δ 38.6 (s). ^{13}C NMR (C_6D_6): δ 30.5 (s, −COCH$_3$), 36.5 (s, −CH$_2$CH=CH$_2$), 49.5 (d, J_{CP} = 3.1 Hz, −CH$_2$CH=CH$_2$), 72.9 (d, J_{CP} = 9.1 Hz, −CH$_2$$C$H=CH$_2$), 112.1 (d, J_{CP} = 9.2 Hz, −COCH$_3$). Anal. calcd for $C_{29}H_{45}NiOP$: C, 69.75; H, 9.08. found: C, 69.71; H, 9.15.

(5) Selected spectral data for **3a**: ^{1}H NMR (C_6D_6) δ −0.89 (s, 9H, −Al-(CH_3)$_3$), 0.97−1.83 (m, 39H, Cy, including 2H of −NiCH_2CH− at δ 1.32 and 1.58, 1H of −NiCH$_2$CH− at δ 1.67, and 3H of −C(CH_3)OAl(CH$_3$)$_3$ at δ 1.74, 2.90 (dd, J = 15.2, 7.2 Hz, 1H, −CHCH_2C$_6$H$_4$−), 3.38 (dd, J = 15.4, 6.0 Hz, 1H, −CHCH_2C$_6$H$_4$−). ^{31}P NMR (C_6D_6): δ 31.8 (s). ^{13}C NMR (C_6D_6): δ −13.1 (brs, Al(CH$_3$)$_3$), 18.7 (d, J_{CP} = 28.2 Hz, −NiCH$_2$−), 26.6 (s, −C(CH$_3$)OAl(CH$_3$)$_3$, 38.8 (s, −CH$_2$C$_6$H$_4$−), 59.6 (d, J_{CP} = 3.0 Hz, −NiCH$_2$$C$H−), 91.1 (s, −C$_6H_4$$C$(CH$_3$)−).

(6) Nickel(0) complexes having bridging methyl group: (a) Kaschube, W.; Pörschke, K.-R.; Angermund, K.; Krüger, C.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1921. (b) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206.

(7) Selected spectral data for **4a**: ^{1}H NMR (toluene-d_8) δ −0.70 (d, J_{HP} = 4.3, 3H, Ni−CH_3), 0.87 (m, 3H, −C$_6$H$_4$CCH_3), 1.00−2.09 (m, 34H, including 1H of NiCH_2−), 2.82 (brs, 1H, NiCH_2−), 3.23 (d, J = 20.3, 1H, −CH_2Ar−), 3.46 (d, J = 20.3, 1H, −CH_2Ar−). ^{31}P NMR (toluene-d_8): δ 50.2 (s). ^{13}C NMR (toluene-d_8): δ −2.9 (d, J_{CP} = 16.0, Ni−CH$_3$), 14.7 (s, −C$_6$H$_4$CCH$_3$), 34.9 (s, −C$_6$H$_4$$CCH_3$), 41.5 (s, −CH$_2CCH_2$−), 41.6 (s, −$CH_2CCH_2$−), 88.1 (d, J_{CP} = 19.0 Hz, −CH$_2$$CCH_2$−).

(8) Selected spectral data for **5a**: ^{1}H NMR (CDCl$_3$) δ 2.01 (t, J = 2.4 Hz, 3H, −C=C(Ar)CH_3), 2.07 (s, 3H, −COCH_3), 3.25 (m, 2H, ArCH_2−), 3.46 (s, 2H, −C=CCH_2CO−), 7.05−7.14 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$): δ 10.8 (s, −C=C(Ar)CH$_3$), 29.7 (s, −COCH$_3$), 41.3 (s, ArCH$_2$−), 44.5 (s, −C=CCH$_2$CO−), 119.0, 123.5, 124.8, 126.5, 134.0 (s, vinyl), 136.5 (s, vinyl), 142.9, 146.7, 206.5 (−CO−). HRMS calcd for $C_{13}H_{14}O$ 186.1045, found m/z 186.1045.

(9) Selected spectral data for **6a**: ^{1}H NMR (C_6D_6) δ 1.50 (s, 3H, −C$_6$H$_4$-CCH_3), 3.35 (s, 2H, −C$_6$H$_4$CH_2−), 4.95 (s, 1H, H_2C=C−), 5.38 (s, 1H, H_2C=C−), 6.99 (m, 1H, Ar), 7.08 (m, 2H, Ar), 7.35 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ 29.5 (−CH$_3$), 36.3 (benzyl), 80.1 (H$_2$C=C−), 107.6 (H$_2$$C$=C−), 123.7, 124.7, 127.5, 128.4, 139.4 (−CH$_2$$C$−), 149.1 (−$C$C-(CH$_3$)OH), 158.0 (−$C$(CH$_3$)OH). HRMS calcd for $C_{11}H_{12}O_1$ 160.0888, found m/z 160.0874.

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