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Formation of Six-membered Aza-nickelacycles by Oxidative Addition of Cyclopropyl Imines to Nickel(0)

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Cyclopropyl imines reacted with nickel(0) in the presence of IPr to give the expected six-membered aza-nickelacycles confirmed by X-ray crystallography. The molecular structure of aza-nickelacyles shows monomeric η^1-aza-nickelenolate structures. The reaction of aza-nickelacycle with an enone occurred to generate an η^3-oxa-allylnickel complex.

Numerous unique transformations of organic molecules have been achieved by using transition-metal catalysts.[1] Among metal catalysts, nickel is known for its high reactivity and inexpensiveness. We have focused on mechanisms of nickel-catalyzed reactions and their reaction intermediates.[2] In our previous work, six-membered oxa-nickelacycles,[3] which were proposed as a key intermediate of [3 + 2] cycloaddition reaction of cyclopropyl ketones with enones,[4] were generated by oxidative addition of cyclopropyl ketones to Ni(0).[5] In addition, nickel-catalyzed crossed reactions of cyclopropyl imines with enones using *N*-heterocyclic carbene ligands have also been reported by Montgomery.[6] In these reactions, a six-membered aza-nickelacycle was assumed as a key intermediate, however, it has not been isolated and determined.[7] In this paper, we report the synthesis and the structure of six-membered aza-nickelacycles generated by oxidative addition of cyclopropyl imines to Ni(0) in the presence of IPr.[8] This aza-nickelacycle reacted with an enone to give an η^3-oxa-allylnickel complex.

In the presence of IPr, both *N*-phenyl cyclopropyl imine **1a** and *N*-benzyl cyclopropyl imine **1b** rapidly reacted with nickel(0) to generate the expected six-membered aza-nickelacycles **2a** and **2b** quantitatively at room temperature (eq 1). The treatment of **2a** and **2b** with carbon monoxide (5 atm) gave the expected lactams, **3a** and **3b**, respectively.[9,10] A single crystal of **2a** was obtained by recrystallization from toluene/hexane solution at −20 °C. The molecular structure of **2a** was confirmed by X-ray crystallography (Figure 1).[11] The sum of the bond angles around nickel along the C1, N1, and C5 is 359.15°. Thus, Ni1, C1, N1, and C5 are on the same plane and **2a** is an unusual T-shaped square-planar nickel(II) 14-electron complex. Bond lengths of C3–C4 (1.334(2) Å) and C4–N1 (1.389(2) Å) are also in the range of a normal carbon–carbon double bond and an sp^2 carbon–nitrogen single bond, respectively. A space-filling model of **2a** clearly indicated that such geometry is mostly due to the bulkiness caused by the phenyl ring on the N1 atom, together with the bulky IPr ligand, that prevents other donor molecules from approaching the fourth-coordination site of the square plane (see Supporting Information[16]). The ^1H and ^{13}C NMR spectra of **2b** are very close to those of **2a**, which indicates that **2b** might have the same structure.[12] The complexes **2a** and **2b** degraded in C_6D_6 at room temperature to yield a complicated mixture.[13]

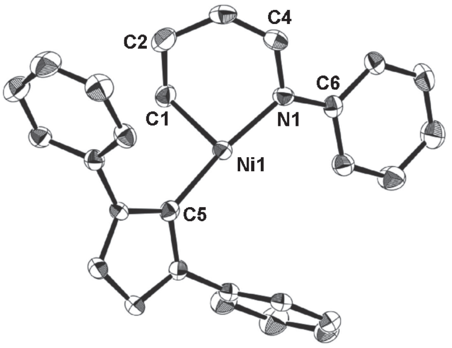


Figure 1. Molecular structure of **2a**. Hydrogen atoms and *i*-Pr groups are omitted for clarity.

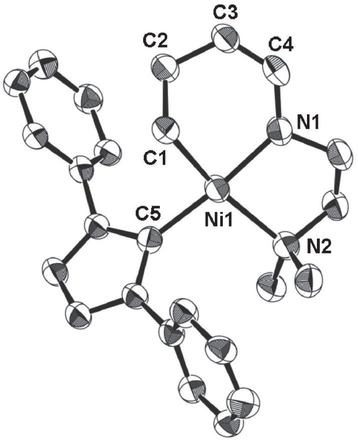
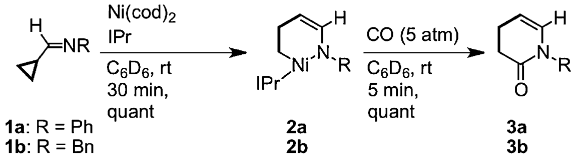
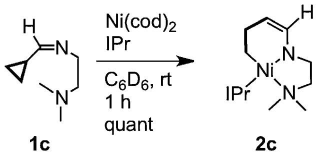


Figure 2. Molecular structure of **2c**. Hydrogen atoms and *i*-Pr groups are omitted for clarity.



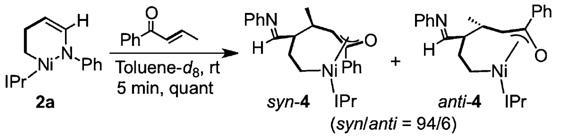
(1)

Cyclopropyl imine **1c** also reacted with nickel(0) to generate the expected six-membered aza-nickelacycle **2c** quantitatively at room temperature (eq 2). A single crystal of **2c** was obtained by recrystallization from THF/hexane solution at −20 °C. The molecular structure of **2c** was also confirmed by X-ray crystallography (Figure 2).[14] The sum of the bond angles around nickel along the C1, N1, N2, and C5 is 360.78°. Thus, Ni1, C1, N1, N2, and C5 are on the same plane and **2c** is a typical square-planar nickel(II) 16-electron complex. Bond lengths of C3–C4 (1.344(6) Å) and C4–N1 (1.360(6) Å) are in the range of a normal carbon–carbon double bond and an sp^2 carbon–nitrogen single bond, respectively. The ^{1}H and ^{13}C NMR spectra of **2c** at room temperature are consistent with **2a** and **2b**, therefore **2c** might have the same structure in solution. Moreover, **2c** was stable in C_6D_6 at room temperature, unlike the analogs **2a** and **2b**. In the use of PCy_3 instead of IPr, oxidative addition of **1a**–**1c** did not occur under the same reaction conditions. It clearly shows the difference between PCy_3 and IPr; a stronger donation seems to be effective to give six-membered structure.

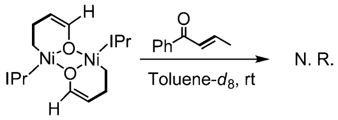


(2)

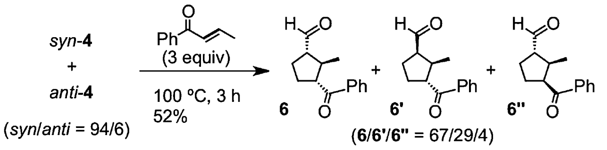
Cyclopropyl imines underwent [3 + 2] cycloaddition with enones in the presence of a catalytic amount of Ni(0).[6] Thus, aza-nickelacycles might also react with enones. In fact, **2a** reacted with (*E*)-1-phenylbut-2-en-1-one to give the corresponding η^3-oxa-allylnickel complex **4** (*syn*/*anti* = 94/6) (eq 3). The stereochemistry of **4** was confirmed by NOESY measurement. In major product *syn*-**4**, the diastereoselectivity of the insertion of enone is consistent with that in the nickel-catalyzed [3 + 2] cycloaddition of cyclopropyl imines with enones.[6] The monomeric structure of **2a** would be crucial for the occurrence of the catalytic reaction, since the corresponding cyclic nickelenolate dimer **5**, prepared by the reaction of cyclopropanecarbaldehyde with $Ni(cod)_2$ and IPr,[3] did not react with (*E*)-1-phenylbut-2-en-1-one at all under the same reaction conditions (eq 4). In the presence of 3 equiv of (*E*)-1-phenylbut-2-en-1-one, heating a solution of **4** (*syn*/*anti* = 94/6) at 100 °C induced reductive elimination to give a mixture of the corresponding cyclopentane derivatives **6** (eq 5).[15] In contrast, neither **5** nor **2c** reacted with (*E*)-1-phenylbut-2-en-1-one under the same reaction conditions.



(3)



(4)



(5)

We demonstrated for the first time the formation of six-membered aza-nickelacycles by oxidative addition of cyclopropyl imines to nickel(0) complexes. The molecular structure of aza-nickelacycles shows η^1-aza-nickelenolate structure. The coordination geometry of the nickel(II) 14-electron center is regarded as an unusual T-shaped planar. Although the 14-electron complex is unstable in solution, the use of a substrate with a coordinative tether group capped the vacant site to generate a more stable 16-electron complex. The insertion of enones into a monomeric η^1-aza-nickelenolate complex took place to generate η^3-oxa-allylnickel complexes.

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10 The treatment of nickel compounds with carbon monoxide can yield $Ni(CO)_4$ (extremely toxic) due to the addition of insufficient amounts of PR_3 or IPr, careless handling or an accident. The reaction mixture must be handled in a well-ventilated fume hood.

11 Crystal data for **2a**: $M_r = 592.50$, green, monoclinic, $P2_1/n$ (No. 14), $a = 11.9351(9)$ Å, $b = 19.1441(14)$ Å, $c = 15.2179(12)$ Å, $\beta = 107.353(3)°$, $V = 3318.8(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.186$ g cm^{-3}, $T = -150.0$ °C, $R_1 = 0.0331$ [$I > 2\sigma(I)$], $wR_2 = 0.0761$ (all data), Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication CCDC#: 805799. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

12 Montgomery briefly mentioned that the reactivity of *N*-phenyl imines to enones is comparable to that of *N*-benzyl imines (ref. 6).

13 After decomposition of six-membered aza-nickelacycle, the corresponding conjugated imine was not observed by the method of ^{1}H NMR and GC-MS analysis (as mentioned ref. 6).

14 Crystal data for **2c**: $M_r = 587.52$, red, tetragonal, $P4_2/n$ (No. 86), $a = 24.7959(10)$ Å, $c = 10.5231(5)$ Å, $V = 6470.0(5)$ Å^3, $Z = 8$, $D_{calcd} = 1.206$ g cm^{-3}, $T = -150.0$ °C, $R_1 = 0.0825$ [$I > 2\sigma(I)$], $wR_2 = 0.2678$ (all data). CCDC#: 805800.

15 The respective yields of products were determined by GC analysis.

16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.