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Reactions of Zirconacyclopentadienes with CO and Isonitriles

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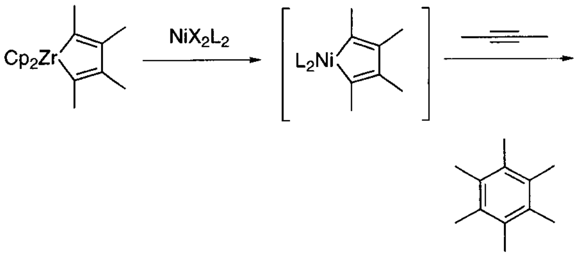
Summary: Treatment of zirconacyclopentadienes with CO in the presence of $NiCl_2(PPh_3)_2$ afforded cyclopentadienones. Isonitriles reacted with zirconacyclopentadienes in the absence or in the presence of $NiCl_2(PPh_3)_2$, and successive treatment of the mixture with CuCl in air gave iminocyclopentadienes.

Introduction

One direct and attractive preparative method of cyclopentadienones is the [2 + 2 + 1] cycloaddition of two alkynes and CO via metallacyclopentadienes. Several examples of the [2 + 2 + 1] coupling for the synthesis of cyclopentadienones have been reported for Co,[1] Fe,[2] Ni,[3] Rh,[4] Ru,[5] and Cr[6] complexes. It is well-known that zirconacyclopentadienes do not react with CO directly, although zirconacyclopentadienes can be conveniently prepared.[7] Transmetalation of zirconacyclopentadienes to Li is an alternative method for the reaction of zirconacyclopentadienes with CO. However, this method gives cyclopentenones but not cyclopentadienones.[8,9] On the other hand, reactions of zirconacyclopentadienes with isonitriles, which are considered as isoelectronic compounds of CO, have not been reported.[10] In this paper we report the reaction of zirconacyclopentadienes with CO in the presence of $NiX_2(PPh_3)_2$ (X = Cl, Br) and the reaction of zirconacyclopentadienes with isonitriles in the absence or in the presence of $NiX_2(PPh_3)_2$.

Recently, we found that transmetalation of the Zr−C bonds of zirconacyclopentadienes to Ni(II) complexes proceeded smoothly under mild reaction conditions, and successive insertion of alkynes into the nickelacyclopentadienes afforded benzene derivatives (eq 1).[11] These results prompted us to examine the insertion of CO or isonitriles into these complexes.



(1)

Results and Discussion

Reaction of Zirconacyclopentadienes with CO. On treatment of the tetrabutylzirconacyclopentadiene **1a** with a stoichiometric amount of $NiCl_2(PPh_3)_2$ under bubbling CO at room temperature, tetrabutylcyclopentadienone (**2a**) was formed in 73% yield. Iodination or hydrolysis was not required to obtain **2a**. This is in contrast to the CO insertion reaction of zirconacyclopentenes or zirconacyclopentanes, which requires treat-

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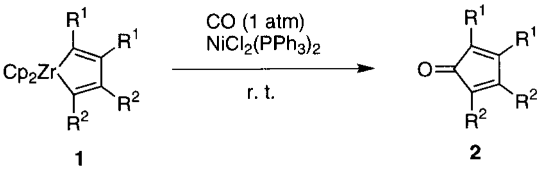


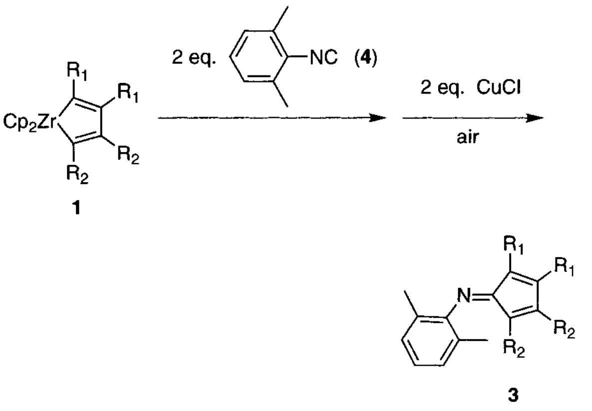
(2)

ment with iodine or aqueous HCl.[7b,12] The reason is that the C=O bond of cyclopentadienones does not strongly coordinate to Ni complexes, as compared with the situation for Zr. After isolation, **2a** became colorless upon standing at room temperature for several days due to dimerization. Some results are shown in Table 1.

When the unsymmetrical zirconacyclopentadiene **1b** was used, **2b** was formed in 54% yield. In the case of the bicyclic zirconacyclopentadiene **1c**, the corresponding product **2c** was formed in 74% yield under similar conditions. When **1d**[13] was used for the reaction with CO in the presence of $NiCl_2(PPh_3)_2$, indenone **2d** was obtained in good yield.[14]

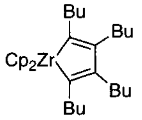
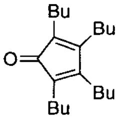
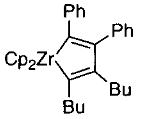
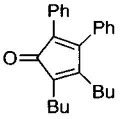
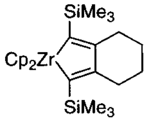
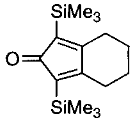
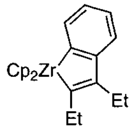
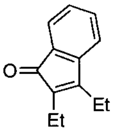
It is interesting to note that the yields of cyclopentadienones depended on the preparative method of **1**. For example, when **1a** was prepared from Cp_2ZrCl_2, 2 equiv of EtMgBr, and 2 equiv of decyne,[7c] the yield of **2a** was only 34% under the same conditions (entry 1). A similar phenomenon was observed in the case of **1b**. When **1b** was prepared from EtMgBr, the desired product **2b** was obtained only in 23% yield. On replacement of EtMgBr with *n*-BuLi and ethylene gas to prepare **1b**,[7c] the following reaction with CO in the presence of $NiCl_2(PPh_3)_2$ proceeded smoothly as described above. This result strongly suggests that the effect of the salts is remarkable. Ate complexation of nickel complexes might play an important role.

Formation of Iminocyclopentadienes. Table 2 shows the results of the formation of iminocyclopentadienes, and the general reaction equation is presented in eq 3. The tetrapropylzirconacyclopentadiene **1e** reacted with 2 equiv of 2,6-dimethylphenyl isocyanide (**4**) at room temperature, and **1e** was completely consumed. However, even after hydrolysis, the desired product **3a** was obtained in only 11% yield. It is interesting to note that the treatment of the mixture with air in the presence of CuCl gave the iminocyclopentadiene **3a** in 63% yield (entry 1). CuCl plays an important role in the reaction. The use of $NiCl_2(PPh_3)_2$ in this reaction instead of CuCl afforded **3a** in very low yield. In the case of two different alkynes, **3b** was selectively formed in 42%



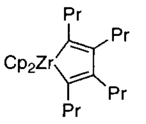
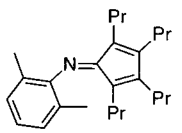
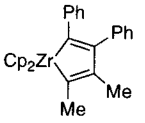
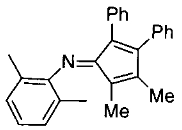
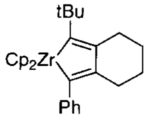
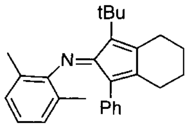
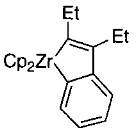
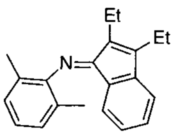
(3)

Table 1. Formation of Cyclopentadienones and Indenone

Entry	Zirconacyclopentadiene		Time (h)	Cyclopentadienone		Yield (%)[a]
1		**1a**	6		**2a**	73 (68)[b]
2		**1b**	9		**2b**	54 (41)
3		**1c**	3		**2c**	74 (51)
4		**1d**	6		**2d**	75 (67)

[a] GC yields. Isolated yields are given in parentheses. [b] When **1a** was prepared from Cp_2ZrCl_2, 2 equiv of EtMgBr, and 5-decyne, the GC yield was 34%.

Table 2. Formation of Iminocyclopentadienes

Entry	Zirconacyclopentadiene		Iminocyclopentadiene		Yield (%)[a]
1		**1e**		**3a**	63 (54)
2		**1f**		**3b**	-- (42)
3[b, c]		**1g**		**3c**	78 (62)
4[c]		**1d**		**3d**	54 (51)

[a] GC yields. Isolated yields are given in parentheses. [b] Addition of 1 equiv of $NiCl_2(PPh_3)_2$ is required. [c] Reaction was carried out at 50 °C.

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(14) Indenones have been prepared by Ni-mediated or Pd-catalyzed reactions. Ni: (a) Liebeskind, L. S.; South, M. S. *J. Org. Chem.* **1980**, *45*, 5426. Pd: (b) Larock, R. C.; Doty, M. J. *J. Org. Chem.* **1993**, *58*, 4579. (c) Larock, R. C.; Tian, Q.; Pletenv, A. A. *J. Am. Chem. Soc.* **1999**, *121*, 3238.

isolated yield. The structure of **3b** was confirmed by an X-ray study. Direct reaction of zirconacyclopentadiene **1g**, which has a bulky substituent in the *t*-Bu group, with isonitrile **4** did not proceed even at 50 °C. Addition of a stoichiometric amount of $NiCl_2(PPh_3)_2$ to the mixture afforded **3c** in 78% yield under identical conditions (entry 3). Treatment of **1d** with isonitrile **4** at 50 °C resulted in the formation of **3d** in 54% yield (entry 4).

Mechanistic Aspects. A plausible mechanism for the formation of cyclopentadienones involves transmetalation of zirconacyclopentadienes to nickel to give nickelacyclopentadienes along with the formation of zirconocene dichloride, as we reported.[11] And then the insertion of CO into nickelacyclopentadienes leads to the formation of free cyclopentadienones.[3a] As far as the formation of iminocyclopentadienes is concerned, the insertion of isonitrile into one of the Zr−C bonds of zirconacyclopentadienes proceeds without transmetalation. Isonitriles are more reactive for the insertion reaction than CO. This high reactivity could provide the reaction products of **1a** with **4** without Ni complexes. On the other hand, the product formed without transmetalation to Ni strongly coordinates to Zr. Therefore, demetalation using CuCl and air is necessary to obtain free products. For zirconacyclopentadienes containing bulky substituents at the α-positions, insertion of **4** into **1g** is not easy. In such cases, transmetalation of the Zr−C bond to the Ni−C bond was required.

A significant role of Zr in the cyclopentadienone or iminocyclopentadiene formation is the selective coupling of two alkyne moieties. Without Zr, for example, preparation of **2b**, **2d**, **3b**, or **3d** from two different alkynes or benzyne is difficult. This is the advantage of the Zr−Ni system developed here.

Experimental Section

General Information. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. THF was distilled over sodium and benzophenone. Zirconocene dichloride and alkynes were purchased from TCI Co. Ltd. or Aldrich Chemical Co., Inc. Butyllithium (1.6 M solution in hexane) and phenyllithium (0.88 M in cyclohexane−diethyl ether solution) were purchased from Kanto Chemical Co. Ltd. 2,6-Dimethylphenyl isocyanide was purchased from Fluka. $NiCl_2(PPh_3)_2$ was prepared according to a previously published paper.[15]

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ or C_6D_6 (contain 1% TMS) solutions at 25 °C on a Bruker-400 or JEOL JNM-AL300 NMR spectrometer. GC analysis was performed on a Shimadzu GC-14A instrument equipped with a Shimadzu CBP1-M25-O25 fused silica capillary column and Shimadzu C-R6A-Chromatopac integrator.

Typical Experimental Procedure for the Formation of Cyclopentadienones. Into a solution of zirconacyclopentadiene **1a** (1.0 mmol) in 10 mL of THF was slowly bubbled carbon monoxide, and $NiCl_2(PPh_3)_2$ (1.0 mmol) was added at room temperature. The mixture was stirred for 6 h, and then 30 mL of hexane was added to the resulting mixture. Filtration and column chromatography on silica gel (hexane/Et_2O = 29/1) afforded **2a** in 68% yield.

2,3,4,5-Tetrabutylcyclopentadienone (2a). Orange oil. GC yield: 73%. Isolated yield: 68%. ^1H NMR (C_6D_6, Me_4Si): δ 0.86 (t, J = 7.1 Hz, 6H), 0.87 (t, J = 7.3 Hz, 6H), 1.24−1.38 (m, 12H), 1.44−1.54 (m, 4H), 2.13−2.22 (m, 8H). ^{13}C NMR (C_6D_6, Me_4Si): δ 14.05, 14.14, 23.14, 23.22, 23.29, 26.16, 31.66, 32.27, 126.21, 154.56, 203.80. IR (neat): ν_{CO} 1707, 1690 cm^{-1}. HRMS: *m/z* calcd for $C_{21}H_{36}O$, 304.2764; found, 304.2769.

2,3-Dibutyl-4,5-diphenylcyclopentadienone (2b). Deep red viscous oil. GC yield: 54%. Isolated yield: 41%. ^1H NMR (C_6D_6, Me_4Si): δ 0.63 (t, J = 6.8 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H), 1.02−1.06 (m, 4H), 1.32−1.40 (m, 2H), 1.54−1.60 (m, 2H), 2.22 (t, J = 7.2 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 6.93−7.04 (m, 8H), 7.42−7.45 (m, 2H). ^{13}C NMR (C_6D_6, Me_4Si): δ 13.75, 14.17, 22.82, 23.22, 23.26, 26.29, 30.59, 32.32, 125.03, 126.76, 127.28, 128.16, 128.30, 128.46, 128.79, 130.25, 131.64, 135.23, 154.19, 156.29, 202.09. IR (neat): ν_{CO} 1709, 1696 cm^{-1}. HRMS: *m/z* calcd for $C_{25}H_{28}O$, 344.2139; found, 344.2148.

4,5,6,7-Tetrahydro-1,3-bis(trimethylsilyl)-2*H*-inden-2-one (2c).[1a] Yellow oil. GC yield: 74%. Isolated yield: 51%. ^1H NMR, ^{13}C NMR, and IR spectra were consistent with the published data.[1a]

2,3-Diethylindenone (2d).[14a] Yellow oil. GC yield: 75%. Isolated yield: 67%. ^1H NMR, ^{13}C NMR, and IR spectra were consistent with the published data.[14a]

Typical Experimental Procedure for the Formation of Iminocyclopentadiene. Method A. To a solution of zirconacyclopentadiene **1** (1.0 mmol) in 10 mL of THF was added 2,6-dimethylphenyl isocyanide (2.0 mmol) at room temperature. The reaction mixture was stirred for 3 h, and then to the mixture was added CuCl (2.0 mmol); this mixture was stirred under air for additional 12 h. Filtration and column chromatography on silica gel afforded products.

Method B. To a solution of zirconacyclopentadiene **1** (1.0 mmol) in 10 mL of THF were added 2,6-dimethylphenyl isocyanide (2.0 mmol) and $NiCl_2(PPh_3)_2$ (1.0 mmol) at room temperature. The mixture was warmed to 50 °C and stirred for 3 h, and then to the resulting mixture was added CuCl (2.0 mmol): this mixture was stirred under air for an additional 12 h. Filtration and column chromatography on silica gel afforded products.

***N*-(2,6-Dimethylphenyl)-2,3,4,5-tetrapropylcyclopentadienimine (3a).** Method A. GC yield: 63%. Column chromatography on silica gel (Et_2O/hexane = 1/49) afforded the product as a red-orange viscous oil in 54% yield. ^1H NMR (C_6D_6, Me_4Si): δ 0.52 (br t, J = 7.0 Hz, 3H), 0.85 (br t, J = 7.1 Hz, 3H), 0.90 (br t, J = 7.0 Hz, 3H), 1.03 (br, 5H), 1.38 (br m, 2H), 1.43 (br m, 2H), 1.78 (br, 4H), 2.08 (s, 6H), 2.11 (br, 2H), 2.21 (br t, J = 7.4 Hz, 2H), 2.55 (br t, J = 7.2 Hz, 2H), 6.84−6.87 (m, 1H), 6.93−6.95 (m, 2H). ^{13}C NMR (C_6D_6, Me_4Si): δ 14.45, 14.54, 14.65, 18.71, 23.41, 23.93, 24.65, 26.69, 27.69, 28.26, 28.56, 122.97, 124.55, 125.02, 128.00, 132.00, 146.56, 149,57, 152.85, 171.40. HRMS: *m/z* calcd for $C_{25}H_{37}N$, 351.2924; found, 351.2914.

***N*-(2,6-Dimethylphenyl)-2,3-dimethyl-4,5-diphenylcyclopentadienimine (3b).** Method A. Column chromatography on silica gel (Et_2O/hexane = 1/49) afforded the product as a red-orange solid in 42% yield. ^1H NMR (C_6D_6, Me_4Si): δ 1.36 (s, 3H), 1.58 (s, 3H), 2.06 (s, 6H), 6.88−6.91 (m, 1H), 6.96−7.04 (m, 6H), 7.10−7.15 (m, 4H), 7.61−7.63 (m, 2H). ^{13}C NMR (C_6D_6, Me_4Si): δ 11.10, 12.44, 18.56, 120.79, 123.34, 123.99, 126.88, 127.76, 127.85, 128.09, 128.53, 129.57, 131.58, 131.67, 133.83, 135.59, 148.36, 149.22, 150.21, 170.97. HRMS: *m/z* calcd for $C_{27}H_{25}N$, 363.1987; found, 363.1998.

2,6-Dimethyl-*N*-(4,5,6,7-tetrahydro-1-*tert*-butyl-3-phenyl-2*H*-inden-2-ylidene)benzenamine (3c). Method B. GC yield: 78%. Column chromatography on silica gel (hexane) afforded the product as a red-orange solid in 62% yield. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.47 (br, 2H), 1.51 (s, 9H), 1.61−1.64 (m, 2H), 1.98 (s, 6H), 2.26 (t, J = 6.6 Hz, 2H), 2.85 (t, J = 6.6 Hz, 2H), 6.40−6.45 (m, 1H), 6.53−6.56 (m, 2H), 6.70−6.72 (m, 2H), 6.83−6.85 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 18.67, 22.35, 23.74, 25.75, 26.86, 32.21, 35.25, 122.44, 123.80, 124.09,

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125.72, 126.70, 126.85, 128.21, 134.46, 135.83, 140.91, 148.64, 151.55, 169.27. HRMS: *m*/*z* calcd for $C_{27}H_{31}N$, 369.2455; found, 369.2450.

***N*-(2,6-Dimethylphenyl)-2,3-diethylindenimine (3d).** Method A. GC yield: 54%. Column chromatography on silica gel (Et_2O/hexane = 1/39) afforded the product as a red-orange viscous oil in 51% yield. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.24 (t, J = 7.5 Hz, 6H), 2.01 (s, 6H), 2.55−2.64 (m, 4H), 6.20−6.23 (m, 1H), 6.73−6.78 (m, 1H), 6.96−7.15 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.13, 15.13, 17.15, 18.02, 18.89, 118.33, 123.12, 123.52, 124.77, 126.52, 127.95, 129.52, 130.70, 138.24, 145.29, 149.25, 149.35, 166.98. HRMS: *m*/*z* calcd for $C_{21}H_{23}N$, 289.1829; found, 289.1831.

Supporting Information Available: Tables and and a figure giving crystallographic data, the structure, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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