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CO insertion reaction of zirconacyclopentadienes

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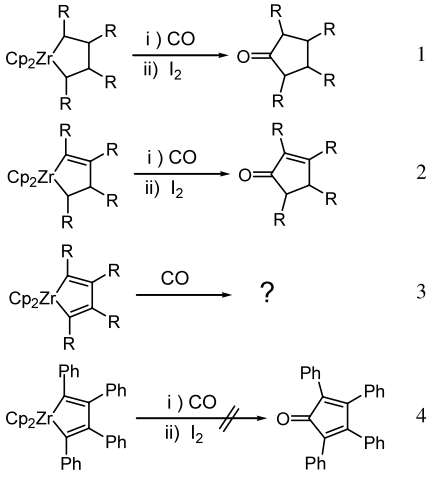
Abstract

Alkyl-substituted zirconacyclopentadienes reacted with CO directly at room temperature to give cyclopentenone derivatives as a mixture of *cis* and *trans* isomers after hydrolysis. Cyclopentadienones were not obtained. In the case of zirconaindene, both of indanones and indenones were obtained after hydrolysis. Treatment of unsymmetrical zirconacyclopentadienes prepared from diphenylacetylene and 4-octyne with CO at room temperature afforded cyclopentenones as a mixture of positional isomers of the double bond.

Keywords: Zirconacyclopentadiene; CO insertion; Cyclopentenone; Zirconaindene; Indanone; Indenone

1. Introduction

CO insertion reaction into metalacyclic compounds is very attractive, since various cyclic ketones can be obtained [1]. It is well known that zirconacycles are very useful intermediate for carbon–carbon bond formation. Concerning reaction with CO, zirconacyclopentanes [2] and zirconacyclopentenes [3] can react with CO directly to give the corresponding cyclopentanones and cyclopentenones, respectively, after treatment with iodine (Eq. (1, 2)).



(1–4)

However, it has been believed for a long time that zirconacyclopentadienes are inert toward the CO insertion (Eq. (3)). In fact, under the same conditions as used for zirconacyclopentanes [2] and zirconacyclopentenes [3], the CO insertion of tetraphenylzirconacyclopentadiene does not proceed (Eq. (4)). It was also reported that the reaction of $Cp_2Zr(CO)_2$ with an excess amount of diphenylacetylene in a sealed vessel at 100 °C provided a cyclopentadienone as a minor product [4]. Therefore, some different approach was required.

Recently, we have reported that zirconacyclopentadienes reacted with CO at −78 °C in the presence of *n*-BuLi and gave cyclopentenone derivatives in high yields [5], and also we have reported that reaction of zirconacyclopentadienes with CO in the presence of nickel complex provided cyclopentadienones [6]. During the course of our reinvestigation of the reaction of zirconacyclopentadienes with CO, we found alkyl-substituted zirconacyclopentadienes could react with CO directly at

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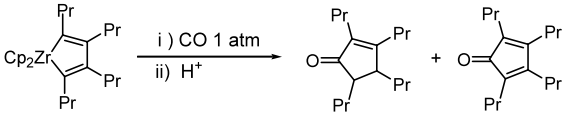
room temperature. And interestingly, cyclopentenone derivatives were obtained after hydrolysis, but not cyclopentadienones. It means one of two double bonds which connected with zirconium was reduced in this reaction. Herein, we report the direct CO insertion reaction of alkyl-substituted zirconacyclopentadienes.

2. Results and discussion

A typical reaction was carried out as follows. CO was introduced to a solution of zirconacyclopentadiene (**1a**), which can be prepared from two equivalents of 4-octyne in situ [3,7], in THF at room temperature. The solution was stirred at the same temperature under slightly positive pressure of CO for 12 h and quenched with 3 N HCl at 0 °C (Eq. (5)). Cyclopentenone (**2a**) was obtained in 82% GC yield (71% isolated yield) as a mixture of *cis* and *trans* isomers in a ratio of 1:3.1. This ratio was determined by NMR. When temperature was raised up to 50 °C, the yield of **2a** became lower (48%), and cyclopentadienone (**3a**) was obtained in 17% yield as a byproduct. And the reaction at 0 °C gave a similar result. The yields of **2a** and **3a** were 38 and 16%, respectively. Thus the formation of cyclopentadienone is significantly dependent on the reaction temperature (Table 1).



(5)

Some results are shown in Table 2. When substituents were alkyl groups, the corresponding cyclopentenones were obtained in good yields (entry 1–3). Bicyclic zirconacyclopentadienes (**1d**) also reacted with CO smoothly, and the expected product was formed (entry 4).

We tried to apply this reaction to zirconaindene (**1e**) (Eq. (6)). Zirconaindene (**1e**) [8] gave indanone (**2e**). And in this case, indenone (**3e**) was also obtained. The result is shown in Table 3. When the reaction was carried out in toluene, indenone (**3e**) was obtained as a major product (entry 4).

Table 1
Reaction conditions for cyclopentenone from zirconacyclopentadiene and CO

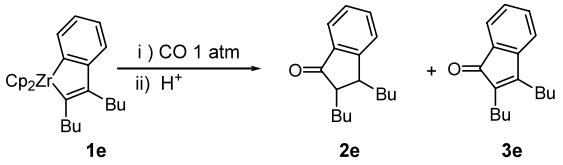
Entry	Temperature (°C)	Time (h)	Yield (%) [a]	
			2a (*cis*:*trans*)	**3a**
1	Room temperature	12	82 (71) (1:3.1)	Trace (< 1)
2	50	12	48 (38) (1:2.7)	17
3	0	24	38 (1:3.3)	16

[a] GC yield. Isolated yields are in parentheses.

Table 2
Formation of cyclopentenones from zirconacyclopentadiene and CO

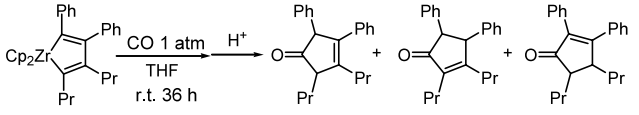
Entry	Zirconacyclopentadienes		Product		Yield (%)[a] (cis:trans)	
1	Cp2Zr, Pr	**1a**	O, Pr	**2a**	82 (71)	(1: 3.1)
2	Cp2Zr, Et	**1b**	O, Et	**2b**	60 (51)	(1:3.0)
3	Cp2Zr, Bu	**1c**	O, Bu	**2c**	69 (53)	(1: 4.4)
4	Cp2Zr, Et	**1d**	O, Et	**2d**	59 (48)	(1: 3.0)

[a] Isolated yields are in parentheses.



(6)

When unsymmetrical zirconacyclopentadiene (**1f**) was used, three products were obtained (Eq. (7)). It is interesting to note that **1f** could react with CO to afford **2f-1**–**3** in 70% combined yield, while tetraphenylzirconacyclopentadiene can not. These results indicate alkyl substituent of zirconacyclopentadiene is necessary for the direct reaction with CO. This can be explained by the nucleophilicity of the carbon attached to zirconium [9].



(7)

The reaction mechanism for the formation of cyclopentenone is not clear yet. It is possible, however, to propose one mechanism shown in Scheme 1. This mechanism is similar to that we proposed for the CO insertion in the presence of BuLi [5]. First, CO insertion of zircnacyclopentadiene (**1**) gives **4**. And the carbon attached to zirconium of **4** attacks the carbonyl carbon to afford **5** as observed for the CO insertion reaction of zirconacyclopentanes [2] or zirconacyclopentenes [3]. In the case of nickelacycle, after transmetalation from Zr to Ni and CO insertion, reductive elimination occurs to give cyclopeantadienone [6]. On the other hand, formation of **6** from **5** is favorable, since the cyclopentadienyl

Table 3
Reaction condition for indanones from zirconaindene and CO

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%) [a]	
				2e (*cis*:*trans*)	**3e**
1	THF	Room temperature	24	51 (42) (1:5.3)	36 (28)
2	THF	50	12	45	13
3 [b]	Toluene:THF = 1:1	Room temperature	24	30	13
4	Toluene	Room temperature	12	22 (21)	53 (36)

[a] GC yield. Isolated yields are in parentheses.
[b] 17% of (*t*-butyl-1-hexenyl)benzene was recovered.

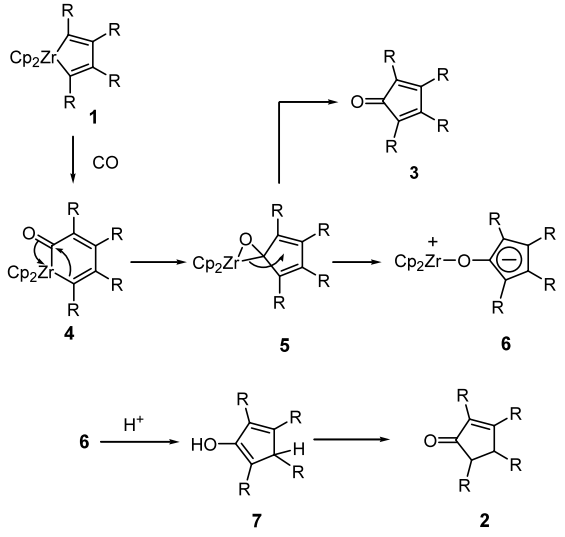
anion in **6** is more stable. This stabilization is a driving force of this reaction. This type of transformation was observed in the case of the reaction with CO in the presence of *n*-BuLi [5]. Hydrolysis of **6** affords **2** via **7** as shown in Scheme 1. Oxidation of Zr of **5** affords cyclopentadienone (**3**) as a byproduct. When this reaction was carried out at 50 °C, we found **3** was formed at the beginning of reaction. It means **5** converted to not only **6** but also **3** at 50 °C. On the other hand, at 0 °C, **3** was formed on the way of reaction. We think conversion of **5** to **6** is slower at 0 °C, then **3** can be formed in the reaction. The ratio of *cis* and *trans* isomers was dependent on the stability of products.

3. Conclusion

We found alkyl-substituted zirconacyclopentadienes could react with CO directly at room temperature.

4. Experimental

All reactions were carried out under dry nitrogen. THF was distilled over sodium and benzophenone.



Scheme 1.

Zirconocene dichloride was purchased from Nichia Co. and alkynes were purchased from TCI Co. Ltd or Aldrich Chemical Co., Inc. Butyllithium (1.6 M in hexane) and phenyllithium (0.96 M in cyclohexane–diethylether solution) were purchased from Kanto Chemical. Co. Ltd.

^{1}H- and ^{13}C-NMR spectra were recorded for $CDCl_3$ (contain 0.3% Me_4Si) solution at 25 °C on a Bruker-400 or JEOL-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. GC yields were determined using dodecane as an internal standard.

4.1. General procedure for the reaction of zirconacyclopentadiene with CO. Formation of 2,3,4,5-tetrapropylcyclopent-2-en-1-one (**2a**)

A 20-ml Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (350 mg, 1.2 mmol) and THF (5 ml). The mixture was cooled to −78 °C (dry ice/acetone bath), and then 1.56 M *n*-BuLi (1.53 ml, 2.4 mmol) was added drop-wise via a syringe. The reaction mixture was stirred at −78 °C for 1 h. 4-Octyne (220 mg, 2.0 mmol) was added, and then the reaction mixture was gradually warmed to room temperature (r.t.) and was stirred for 3 h. Carbon monoxide was slowly introduced in the mixture by bubbling and the mixture was stirred for 12 h at r.t. The reaction mixture was quenched with 3 N HCl aq., and extracted with hexane twice. The extract was then washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo. Column chromatography on silica gel (50/1 hexane/AcOEt) afforded the product as a pale yellow oil. GC yield 82%. Isolated yield 71%. A mixture of *trans* and *cis* isomers with a ratio of 3.1:1. ^{1}H- and ^{13}C-NMR of *trans* isomer were consistent with the published data [5]. ^{1}H-NMR of *cis* isomer was consistent with the published data [5]. *cis* Isomer: ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.01, 14.24, 14.31, 14.42, 20.04, 20.17, 20.77, 21.91, 25.08, 30.44, 34.84, 35.31, 46.41, 50.72, 136.67, 175.52, 211.81.

*4.1.1. 2,3,4,5-Tetraethylcyclopent-2-en-1-one (**2b**)*

Pale yellow oil, GC yield 60%. Isolated yield 51%. A mixture of *trans* and *cis* isomers with a ratio of 3.0:1. ^{1}H- and ^{13}C-NMR were consistent with the published data [5].

*4.1.2. 2,3,4,5-Tetra-n-butylcyclopent-2-en-1-one (**2c**)*

Pale yellow oil, GC yield 69%. Isolated yield 53%. A mixture of *trans* and *cis* isomers with a ratio of 4.4:1. ^{1}H- and ^{13}C-NMR were consistent with the published data [5].

*4.1.3. 2,4-Diethylbicyclo[4,3,0]-1-nonen-3-one (**2d**)*

Pale yellow oil, GC yield 59%. Isolated yield 48%. A mixture of *trans* and *cis* isomers with a ratio of 3.0:1. ^{1}H-NMR was consistent with the published data [10]. *cis* Isomer: ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.62, 13.68, 15.82, 19.14, 25.76, 27.58, 28.75, 30.67, 43.93, 50.09, 137.22, 174.69, 210.67.

*4.1.4. 2,3-Di-n-butylindan-1-one (**2e**)*

Pale yellow oil, GC yield 51%. Isolated yield 42%. A mixture of *trans* and *cis* isomers with a ratio of 5.3:1. *trans* Isomer: IR (neat): ν 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.76–0.89 (m, 6H), 1.16–1.36 (m, 8H), 1.47–1.60 (m, 2H), 1.66–1.80 (m, 2H), 2.26–2.30 (m, 1H), 2.98–3.01 (m, 1H), 7.26–7.31 (m, 1H), 7.39–7.42 (m, 1H), 7.45–7.56 (m, 1H), 7.63–7.67 (m, 1H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.94, 13.96, 22.89, 22.91, 29.23, 29.35, 31.87, 35.86, 44.67, 53.62, 123.63, 126.09, 127.35, 127.39, 134.63, 158.02, 209.30. HRMS: *m*/*z* calc. for $C_{17}H_{24}O$, 244.1827; found, 244.1817.

*4.1.5. 2,3-Di-n-butylinden-1-one (**3e**)*

Light yellow oil, GC yield 36%. Isolated yield 28%. ^{1}H- and ^{13}C-NMR were consistent with the published data [11].

*4.1.6. 2,3-Diphenyl-4,5-dipropylcyclopent-3-en-1-one (**2f-1**)*

Pale yellow oil, isolated yield 41%. *trans* Isomer only: IR (neat): ν 1704 cm^{-1}; ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, $J = 7.2$, 3H), 1.04 (t, $J = 7.2$, 3H), 1.23–1.72 (m, 5H), 1.80–1.92 (m, 1H), 2.01–2.13 (m, 1H), 2.50–2.60 (m, 1H), 3.27 (t, $J = 4.8$, 1H), 4.34 (d, $J = 2.4$, 1H), 7.13–7.25 (m, 10H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.31, 14.42, 18.95, 21.34, 29.14, 30.25, 52.84, 63.15, 127.00, 128.04, 128.12, 128.35, 128.68, 136.17, 136.46, 137.16, 141.47, 216.61. HRMS: *m*/*z* calc. for $C_{23}H_{26}O$, 318.1985; found, 318.1997.

*4.1.7. 2,3-Diphenyl-4,5-dipropylcyclopent-4-en-1-one (**2f-2**)*

Pale yellow oil, isolated yield 15%. A mixture of *trans* and *cis* isomers with a ratio of 2.9:1. *trans* Isomer: IR (neat): ν 1699 cm^{-1}; ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.76 (t, $J = 7.2$, 3H), 1.02 (t, $J = 7.2$, 3H), 1.20–1.62 (m, 7H), 1.93–1.99 (m, 1H), 2.65–2.71 (m, 1H), 3.54–3.59 (m, 1H), 7.16–7.29 (m, 10H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.13, 14.30, 19.34, 21.87, 27.67, 31.28, 43.94, 50.73, 127.43, 128.12, 128.40, 129.02, 129.28, 132.24, 135.51, 138.83, 169.36, 208.06. *cis* Isomer: IR (neat): ν 1714 cm^{-1}; ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.83 (t, $J = 7.2$, 3H), 0.97 (t, $J = 7.2$, 3H), 1.20–1.31 (m, 4H), 1.45–1.66 (m, 3H), 1.76–1.79 (m, 1H), 2.35–2.39 (m, 1H), 3.06–3.09 (m, 1H), 7.14–7.31 (m, 10H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.22, 14.90, 19.98, 20.29, 35.14, 35.75, 47.72, 51.56, 127.54, 128.11, 128.19, 128.44, 129.13, 129.52, 131.96, 135.27, 138.82, 171.71, 209.34. HRMS: *m*/*z* calc. for $C_{23}H_{26}O$, 318.1985; found, 318.1976.

*4.1.8. 2,3-Diphenyl-4,5-dipropylcyclopent-2-en-1-one (**2f-3**)*

Pale orange oil, isolated yield 15%. *trans* Isomer only: IR (neat): ν 1703 cm^{-1}; ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, $J = 7.2$, 3H), 1.03 (t, $J = 7.2$, 3H), 1.40–1.68 (m, 4H), 2.07–2.16 (m, 1H), 2.31–2.42 (m, 2H), 2.50–2.62 (m, 1H), 4.08 (d, $J = 7.2$, 1H), 4.13 (d, $J = 7.5$, 1H), 6.71–6.77 (m, 4H), 6.93–7.02 (m, 6H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.22, 14.28, 20.66, 22.13, 25.43, 31.42, 53.42, 57.76, 125.97, 126.47, 127.54, 127.83, 129.07, 129.93, 136.88, 138.33, 142.22, 172.30. HRMS: *m*/*z* calc. for $C_{23}H_{26}O$, 318.1985; found, 318.1968.

Acknowledgements

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