Double carbonylation of zirconocene–alkyne complexes†

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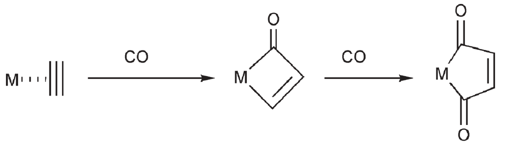
Received (in Cambridge, UK) 2nd February 2005, Accepted 9th March 2005
First published as an Advance Article on the web 1st April 2005
DOI: 10.1039/b501545f

Zirconocene–alkyne complexes prepared from Cp_2ZrBu_2, phosphines and alkynes reacted with CO to give double carbonylation products, 4-hydroxycyclobuten-1-one derivatives after hydrolysis.

The reactions of alkynes with CO in the presence of transition metal complexes have been attractive since Reppe discovered acrylic acid formation using an acetylene, CO and nickel carbonyl complex.[1] Since then, it has been reported that alkynes can react with CO in the presence of various transition metal complexes.[2] However, the carbonylation of metal–alkyne complexes with CO has not been reported. As shown in eqn. (1), formally a metalacyclobutenone is the expected product of the reaction of a metal–alkyne complex and CO. If this four-membered species is reactive towards a second CO molecule, double carbonylation can take place.

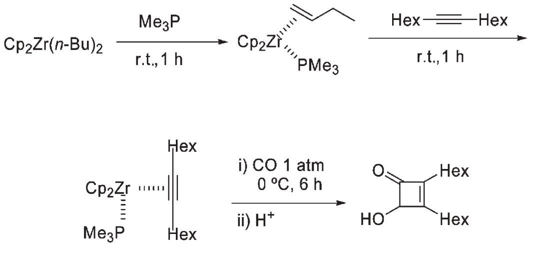


(1)

As for the double carbonylation of an alkyne, only several examples with metal–carbonyl complexes have been reported using nickel[3]and iron[4] complexes.

In this reaction, we selected zirconocene–alkyne complexes as the metal–alkyne complexes, since a zirconocene–alkyne complex can be conveniently prepared from Zr(II) species and an alkyne,[5–7] and they can be stabilized with phosphines. Herein we report that zirconocene–alkyne complexes react with two molecules of CO to afford 4-hydroxycyclobuten-1-one derivatives after hydyrolysis.

The reaction was carried out as follows. $Cp_2Zr(n\text{-}Bu)_2$ (Negishi reagent) was prepared from zirconocene dichloride with 2 equivalents of *n*-BuLi in THF at −78 °C under nitrogen. Me_3P in THF was added, and then the reaction mixture was gradually warmed to room temperature and was stirred for 1 h. The reactive species, a zirconocene–butene complex stabilized with Me_3P, was formed. 7-Tetradecyne was added and the resulting mixture was stirred for 1 h at the same temperature. Zirconocene–alkyne complex **1a** was prepared *in situ*. The ^1H NMR spectrum of **1a** showed doublet peaks at δ 5.09 and 0.81 ppm assigned to Cp and Me_3P, respectively. In the ^{13}C NMR spectrum of **1a**, the Cp signal appeared at δ 102.32 ppm, and the coordinated alkyne carbons appeared at 145.5 and 176.5 ppm as doublet peaks.[5] CO (1 atm) was slowly introduced to the reaction mixture of **1a** by bubbling at 0 °C, and then the solution was stirred under a slightly positive pressure of CO for 6 h and quenched with 3 N HCl. Purification of the extract from ether by column chromatography gave 2,3-dihexyl-4-hydroxycyclobuten-1-one **2a** in 65% yield (48% isolated yield) as shown in eqn. (2). It is clear that the product **2a** was formed from an alkyne and two CO units. One carbonyl group was reduced to a hydroxyl group. Butadiene derivative, 7,9-dihexyl-hexadeca-7,9-diene, was formed as a by-product in only 6% yield by coupling of 7-tetradecyne.

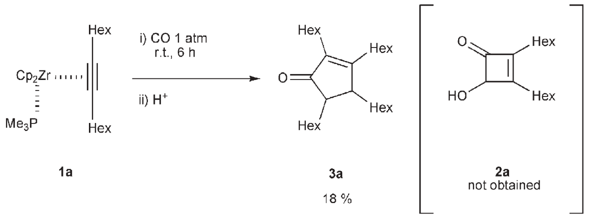


(2)

1a

2a
65 (48)%

When the reaction was carried out at −78 °C or −15 °C, CO insertion did not take place. When the reaction was conducted at room tempraturе, only 18% of tetrahexylcyclopentenone, which was formed from two molecules of alkyne and one CO *via* zirconacyclopentadiene **3a**,[8] was obtained (eqn. (3)). The formation of **2a** was not observed. These results show that the reaction temperature is very important in this double carbonylation.



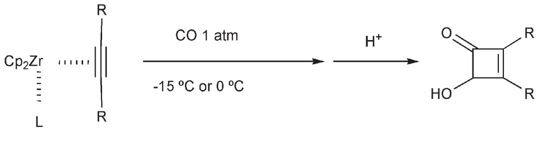
1a

3a
18 %

2a
not obtained

(3)

The use of $MePPh_2$ and $(n\text{-}Bu)_3P$ instead of PMe_3 as a ligand afforded **2a** in 56% and 64% yields, respectively. A nitrogen containing ligand such as 4-dimethylaminopyridine could also be used. In this case, **2a** was obtained in 47% yield. Addition of an excess amount of Me_3P prevented the formation of the desired product **2a**. It indicates that labile phosphine ligands are suitable for this reaction for replacement of phosphine with CO in the reaction.



(4)

1a : R = Hex, L = Me_3P
1b : R = Bu, L = Me_2PPh
1c : R = $C_{10}H_{21}$, L = Me_2PPh

2a : 65 (48) %
2b : 38 (24) %
2c : 26 (13) %

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b5/b501545f/

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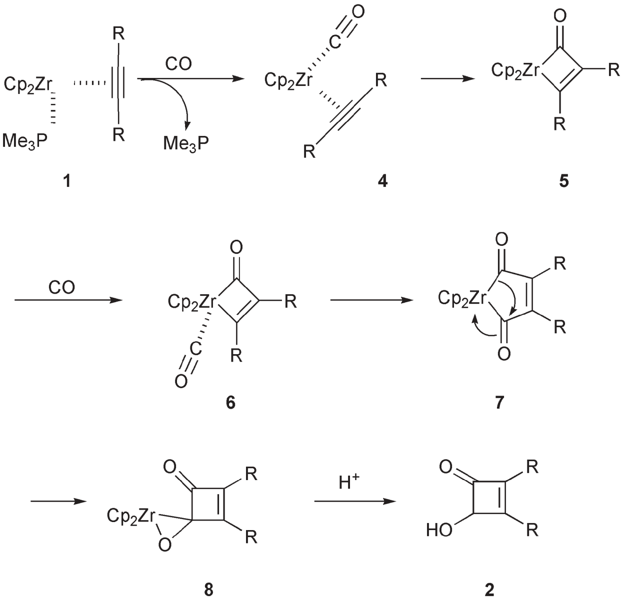
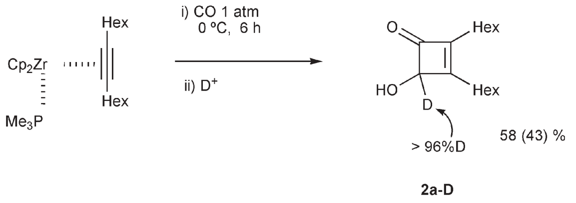


Scheme 1 Possible Mechanism.

When 5-decyne and docos-11-yne, were used instead of tetradecyne for preparing zirconocene–alkyne complexes, the desired products **2b** and **2c** were obtained using Me$_2$PPh in 38% and 26% yields, respectively after hydrolysis (eqn. (4)). In these two cases, the CO insertion reaction was carried out at -15 °C. With a labile phosphine ligand, the reaction proceeded even at lower temperatures.

When a terminal alkyne such as 1-octyne was employed, the reaction gave a complex mixture. In the case of aryl or trimethylsilyl substituted alkynes, such as diphenylacetylene, phenyltrimethylsilylacetylene and 1-phenyl-1-hexyne, the reaction did not proceed. These alkyne carbons on zirconocene are not nucleophilic enough towards CO on zirconocene.[8,9]

Deuterolysis of the resulting mixture instead of hydrolysis afforded deuterated **2a**–D in 43% isolated yield with >96% deuterium incorporation at the 4-position (eqn. (5)). This indicates that zirconium connects to the 4-position carbon before hydrolysis.



(5)

A possible mechanism for the formation of the cyclobutenone derivative is shown in Scheme 1. First, replacement of Me$_3$P with CO to afford **4**. Insertion of CO into the zirconocene–alkyne bond gives a four-membered zirconacycle **5**. This is very reactive towards CO, since the hydrolysis product of the four-membered zirconacycle **5** was not obtained. The second CO insertion is fast and it gives zirconacyclopentadienone (maleoylzirconium complex) **7**. Subsequent skeletal rearrangement of **7** affords **8**, since the oxazirconacyclopropane in **8** is favorable as observed for the CO insertion reaction of zirconacyclopentanes[10] or zirconacyclopentenes.[7] In the case of nickel[3] and iron[4] carbonyl complexes, reductive elimination from maleoylmetal complexes gave cyclobutadione derivatives. On the other hand, zirconium has enough oxophilicity to afford oxazirconacyclopropane. Hydrolysis of **8** produces **2**, in which one carbonyl group is reduced to a hydroxyl group.‡

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Notes and references

‡ *Spectral data for* **2a**: IR (neat): ν 3395 (OH), 1711 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.85–0.92 (m, 6H), 1.26–1.40 (m, 12H), 1.46–1.73 (m, 4H), 2.09–2.15 (m, 2H), 2.58 (t, J = 7.6 Hz, 2H), 3.66 (br, 1H), 5.10 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 13.98, 22.47, 23.30, 26.12, 26.85, 27.50, 28.05, 29.15, 29.40, 31.40, 31.43, 84.00, 151.85, 179.78, 194.18; HRMS calcd for C$_{16}$H$_{28}$O$_2$ 252.2089, found 252.2108.

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