Ruthenium-catalysed Cyclocarbonylation of 1,1′-Bis(silylethynyl)ferrocene involving the 1,2-Migration of a Silyl Group

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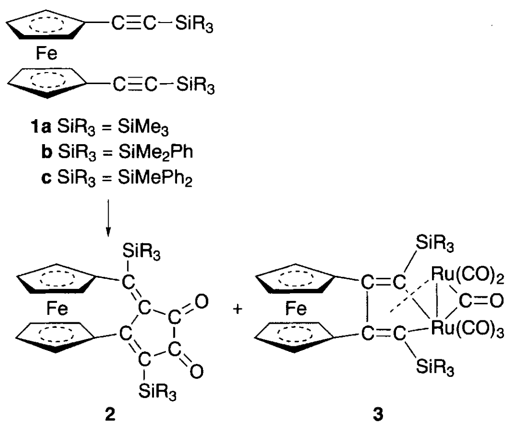
The treatment of 1,1′-bis(trimethylsilylethynyl)ferrocene with a catalytic amount (5 mol%) of [$Ru_3(CO)_{12}$] under 10 kg cm^{-2} of CO at 150 °C causes a novel cyclocarbonylation involving 1,2-silyl migration of a silylethynyl group generating a transition-metal vinylidene intermediate, to give a cyclopent-3-en-1,2-dione derivative.

Despite the extensive studies on cyclocarbonylation of diynes using a stoichiometric amount of transition-metal complexes, their applications to catalytic reactions are still limited.[1] We report herein a new type of catalytic cyclocarbonylation of diynes, where a rare example of 1,2-silyl migration of a silylethynyl group giving a transition-metal vinylidene intermediate is operative.[2]

We are currently interested in the stoichiometric as well as catalytic reactions of 1,1′-dialkynylferrocene derivatives because of their unique reactivity originated from the parallel diyne structures and their potential applications in materials science.[3] In a previous study, we showed the formation of di- and tri-nuclear ruthenacycles including a [2]ferrocenophane skeleton, in the reaction of 1,1′-dialkynylferrocene with [$Ru_3(CO)_{12}$].[4] Under CO pressure this system was found to be extended to a catalytic cyclocarbonylation providing a [3]ferrocenophane bearing a cyclopent-3-ene-1,2-dione structure (Scheme 1).



Scheme 1 *Reagents and conditions*: [$Ru_3(CO)_{12}$] (5 mol%), CO 10 kg cm^{-2}, toluene, 150 °C, 24 h

Treatment of 1,1′-bis(trimethylsilylethynyl)ferrocene **1a**[5] with a catalytic amount of [$Ru_3(CO)_{12}$] (5 mol%) under CO pressure (10 kg cm^{-2}) in toluene at 150 °C for 24 h gave the cyclocarbonylation product **2a** in 36% yield together with a trace amount of a dinuclear ruthenacycle complex **3a**. In this reaction 48% of **1a** was recovered unreacted. The products were isolated by column chromatography (SiO_2, benzene) and characterized by elemental analysis, IR and NMR spectroscopy, and EI mass spectrometry.‡ The mass spectrum of **2a** exhibited a molecular ion peak (*m*/*z* 434) that is consistent with the

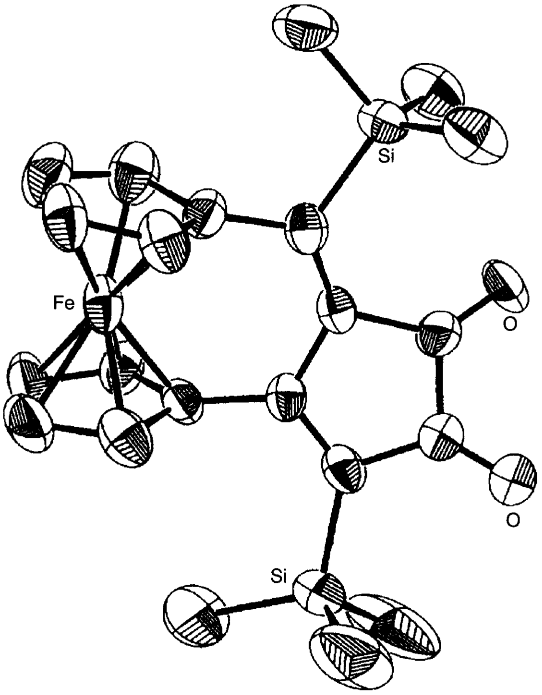


Fig. 1 Molecular structure of **2a**

Table 1 The ruthenium-catalysed cyclocarbonylation of 1,1′-bis(silylethynyl)ferrocene **1**[a]

Run	SiR_3	Ru complex (mol %)	Solvent	P_{CO}[b]/kg cm^{-2}	*T*/°C	*t*/h	Yield[c] (%) 2	Yield[c] (%) 3	Recov. of **1**[c] (%)
1	$SiMe_3$	[$Ru_3(CO)_{12}$] (5)	toluene	10	150	24	36	trace	48
2		[$Ru_3(CO)_{12}$] (10)		10	150	24	38	15	43
3		[$Ru_3(CO)_{12}$] (30)		10	150	24	43	16	16
4		[$Ru_3(CO)_{12}$] (5)		5	150	12	17	0	79
5			THF	5	150	24	18	0	65
6			MeCN	5	170	24	0	0	96
7		$RuCl_3 \cdot nH_2O$ (30)	toluene	10	150	24	0	0	77
8		[$RuCl_2(PPh_3)_3$] (5)		10	150	12	0	0	0
9		[Ru(cod)(cot)] (5)		10	150	12	12	0	83
10	$SiMe_2Ph$	[$Ru_3(CO)_{12}$] (5)		5	160	12	16	0	69
11	$SiMePh_2$			5	160	12	0	0	100

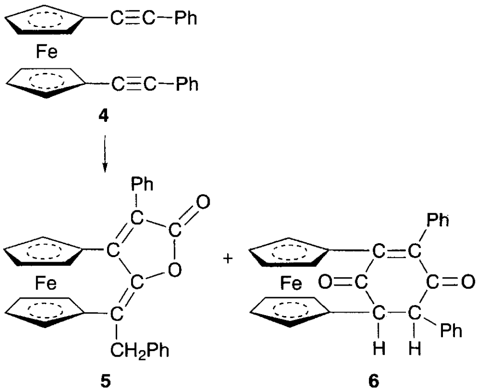
[a] Reaction conditions: [runs 1–9] **1a** (200 mg, 0.528 mmol), solvent (30 ml); [run 10] **1b** (137 mg, 0.273 mmol), toluene (15 ml); [run 11] **1c** (140 mg, 0.223 mmol), toluene (15 ml). [b] Initial pressure at room temperature. [c] Isolated by column chromatography on silica gel.

structure derived from **1a** and two molecules of carbon monoxide. In the IR spectrum, two ν_{CO} absorptions were observed at 1730 and 1690 cm^{-1}, showing the presence of two carbonyl groups in **2a**. The presence of two carbonyl groups were also supported by the appearance of two singlets at δ 193.0 and 191.9 in the ^{13}C NMR spectrum.

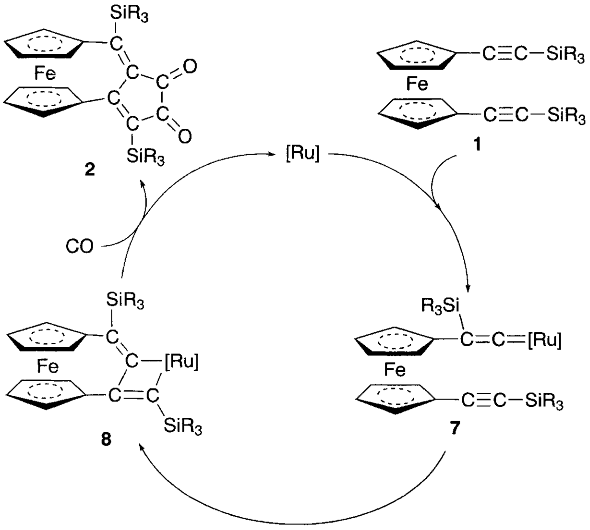
As seen from the X-ray crystal structure of **2a** (Fig. 1),§ the compound has a bicyclic structure comprised of [3]ferrocenophane and cyclopent-3-ene-1,2-dione rings.[6] The most striking feature of the reaction suggested by the structure is the involvement of 1,2-migration of one of the two trimethylsilyl groups originally bonded to the β-acetylenic carbons of **1a**.

Table 1 lists the results obtained under various reaction conditions. Increasing the amount of catalyst gave rise to improvement in the conversion of **1a** and the yield of **2a**, though the amount of **3a** also increased (runs 1–3). Toluene was among the most suitable solvents examined; the reaction proceeded more slowly in THF (run 5) than toluene (run 4), and did not proceed in MeCN (run 6). The complex [Ru(cod)(cot)] (cod = cycloocta-1,5-diene, cot = cyclooctatriene) also showed catalytic activity (run 9), whereas $RuCl_3 \cdot nH_2O$ and $[RuCl_2(PPh_3)_3]$ are inactive (runs 7 and 8).

The catalytic formation of **2** was significantly affected by the nature of the silyl group bound to the β-acetylenic carbons of **1**. Thus, compound **1b** bearing $SiMe_2Ph$ groups also gave the cyclocarbonylation product **2b** (run 10), while **1c** having $SiMePh_2$ groups did not react under similar reaction conditions (run 11). It was further noted that the presence of silyl substituents is of particular importance to obtain the cyclocarbonylation products **2** and 1,1′-diethynylferrocene was too unstable to be handled. Treatment of 1,1′-bis(phenylethynyl)ferrocene **4** with 30 mol% of $[Ru_3(CO)_{12}]$ under CO pressure did not provide any product corresponding to **2** even though small amounts of lactone **5** (4%) and cyclohexenedione **6** (3%) were formed (Scheme 2).



Scheme 2 *Reagents and conditions*: $[Ru_3(CO)_{12}]$ (10 mol%), CO 30 kg cm^{-2}, benzene, 100 °C, 24 h



Scheme 3

Scheme 3 illustrates the most probable catalytic cycle responsible for the formation of **2**. In the first stage, interaction of **1** with a ruthenium species causes the 1,2-migration of a silyl group to produce the vinylidene intermediate **7**. Such a process has recently been documented in stoichiometric systems by Sakurai and Werner and their coworkers.[2] Subsequently, [2 + 2] cycloaddition between the Ru=C bond of the vinylidene moiety and the remaining C≡C bond leads to the formation of ruthenacyclobutene **8**. Successive insertion of two CO molecules into each of the Ru–C bonds in **8** followed by reductive elimination provides the cyclocarbonylation product **2** with concomitant formation of the catalytically active ruthenium(0) species.

The present study exhibits the first catalytic cycle involving a 1,2-silyl migration of silylacetylenes. Further studies focusing on the extention of the scope of present reaction are underway.

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

Received, 2nd August 1995; Com. 5/05140A

Footnotes

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‡ *Spectroscopic data* for **2a**: ^{1}H NMR ($CDCl_3$): δ 4.31–4.30 (m, 2 H, C_5H_4), 4.26–4.25 (m, 2 H, C_5H_4), 4.19–4.18 (m, 2 H, C_5H_4), 3.98–3.97 (m, 2 H, C_5H_4), 0.15 (s, 9 H, CH_3), 0.10 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 193.0, 191.9 (s, CO), 172.0, 154.6, 146.9, 146.6 (s, C=), 94.3, 79.8, 70.7, 70.1, 69.5 (s, C_5H_4), −0.5, −0.7 (s, CH_3). Satisfactory elemental analysis was obtained.

§ *Crystal data* for **2a**: $C_{22}H_{26}FeO_2Si_2$, orthorhombic, space group $Pna2_1$, a = 11.980(3), b = 9.935(2), c = 18.826(3) Å, U = 2218(1) Å^3, Z = 4, D_c = 1.301 g cm^{-3}, μ(Mo-Kα) = 7.97 cm^{-1}. Data were measured on a Rigaku AFC5R diffractometer in the range of $6 < 2\theta < 55.1°$ with ω–2θ scan technique. The structure was solved by Patterson method and refined by full-matrix least-squares method to $R(R_w)$ = 0.054 (0.032) for 243 parameters against 1537 reflections with $I > 1.5\sigma(I)$ out of 2927 unique reflections corrected for absorption using Ψ-scan technique. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No.1.

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