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Preparation, structure, and reaction of the tricarbonyliron complex of tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene, a strongly homo-conjugated nonparallel 1,4-diene

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Abstract

Tricarbonyliron complex **3** is prepared by the reaction of a strongly homo-conjugated nonparallel 1,4-diene, tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (**2**), with $Fe(CO)_5$ or $Fe_2(CO)_9$. Upon complexation, a much larger shielding effect ($\Delta\delta = 111.8$ ppm) of the inner carbons (C3 and C5) than that ($\Delta\delta = 73.5$ ppm) of the outer ones (C2 and C6) is observed in ^{13}C NMR of **3**. The chemical shift value of the carbonyl carbons (216.3 ppm) is intermediate between those of tricarbonyliron complexes of norbornadiene (**1**) and 1,3-cyclohexadiene. An X-ray crystallographic analysis of **3** reveals that the iron atom is located at almost equal distances from the four olefinic carbons and that the geometry of the iron atom retains a square pyramidal coordination. It also shows that the bond lengths of C3–C4 and C4–C5 are relatively short (1.504 and 1.508 Å, respectively) and that the bond angle of C3–C4–C5 is small (95.1°). Furthermore, the olefinic bonds of **3** are markedly distorted. These results suggest a little contribution of the terminal bonding nature **5** to the overall bonding nature of **3**. Reaction of **3** with aluminum trichloride affords the ring expanded dienone **6** by a carbonyl insertion, showing similarity with that of tricarbonyl(1,3-cyclohexadiene)iron.

Introduction

A variety of tricarbonyliron complexes of conjugated dienes have been prepared and their structures and chemical reactivities have been investigated extensively, while relatively fewer tricarbonyliron complexes of nonconjugated dienes have been reported [1]. Among the nonconjugated dienes used, norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, **1**) has attracted much attention because of its unique structure and a strong homo-conjugation between the two double bonds [1b,2,3]. Previously, we reported an extraordinarily strong homo-conjugation of the tricyclic 1,4-diene system, tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (**2**) [4], which is supported by the larger separation between the first and second ionization potentials in **2** (1.15

0022-328X/91/$03.50

1 2

Scheme 1

eV) than that in **1** (0.85 eV) [5a]. This characteristic property of **2** reflects a higher reactivity in the homo-Diels–Adler reaction with TCNE than that of **1** [5]. From a geometrical point of view, it is noteworthy that the two double bonds of **2** are apparently not parallel to each other in contrast with **1** in which the two double bonds are parallel. Two molecular calculations [5a] for **2** suggest that the C3---C5 distance is 2.40 (STO-3G) and 2.32 (MM2) Å and that the C2---C6 distance is 3.54 (STO-3G) and 3.38 (MM2) Å, while the C2---C6 distance of **1** is 2.47 (STO-3G), 2.40 (MM2), and 2.46 (electron diffraction [6]) Å. Thus, it would be interesting to prepare transition metal complexes of **2** and to investigate their structures and reactivities, and comparing them with those of the complexes of **1** and other diene systems. In this article, we report the preparation of tricarbonyl(tricyclo[5.3.1.$0^{4,9}$]-undeca-2,5-diene)iron (**3**), structure determination by X-ray crystallography, and a Lewis acid promoted carbonylation of **3**.

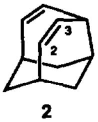
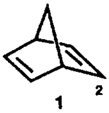
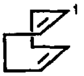
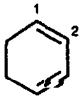
Results and discussion

Tricarbonyliron complex **3** could be readily prepared by two procedures: (a) direct reaction of **2** with a large excess of pentacarbonyliron at the refluxing temperature for 15 h gave **3** as a pale yellow solid in 87% yield; (b) treatment of **2** with 4 eq. of enneacarbonyldiiron in benzene at room temperature followed by heating the reaction mixture at 80 °C for 24 h gave **3** in 76% yield. All of the analytical and spectral data including $^1H-^1H$ and $^1H-^{13}C$ COSY NMR were consistent with the assigned structure. The ^1H NMR spectrum of **3** shows that the signals due to the olefinic protons are shifted to upfield (3.43 and 2.90 ppm for H3, H5 and H2, H6, respectively), indicating the complexation with iron. The large upfield shift of ^{13}C NMR signals due to the olefinic carbons, C2, C6 and C3, C5 of **3** also indicates the coordination of both double bonds. Table 1 summarizes the ^{13}C NMR chemical shifts of olefinic and carbonyl carbons of **3** and tricarbonyliron complexes of other representative dienes as well as those of olefinic carbons of the free dienes.

As is shown in Table 1, the difference ($\Delta\delta = 111.8$ ppm) of the ^{13}C chemical shift of the inner carbons (C3 and C5) between the free diene **2** and the complex **3** is relatively large in comparison with those between other dienes and their complexes. In the norbornadiene system, the difference is 104.7 ppm, while it is only 44.9 ppm in 1,5-cyclooctadiene. It should be noted that the degree of shielding ($\Delta\delta = 111.8$ ppm) of the inner carbons (C3 and C5) in **3** is larger than that ($\Delta\delta = 73.5$ ppm) of the outer carbons (C2 and C6). This is in marked contrast with the fact that, in a conjugated diene system such as 1,3-cyclohexadiene, the

Table 1

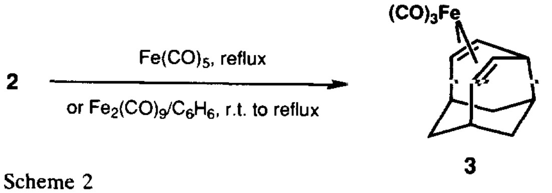
^{13}C NMR chemical shifts of olefinic and/or carbonyl carbons of tricarbonyl(diene)iron complexes and the free dienes

Compound		^{13}C NMR chemical shift [a]		$\Delta\delta$ [b]
		Diene	Complex	
 2	C2	132.7	59.2	73.5
	C3	136.9	25.1	111.8
	CO		216.3	
	C2	143.4 [c]	38.7 [d]	104.7
		145.0 [e]	38.3 [e]	106.7
	CO		218.3 [d]	
			218.2 [e]	
	C1	129.0 [e]	83.7 [e]	45.3
	CO		218.8 [e]	
	C1	126.0 [f]	62.5 [g]	63.5
		126.3 [e]	63.1 [e]	63.2
	C2			
		124.3 [f]	85.4 [g]	38.9
		124.9 [e]	84.3 [e]	40.5
	CO		212.2 [g]	
			213.7 [e]	

[a] Values are shown in ppm from TMS. [b] δ (free ligand) $-\delta$ (complexed ligand). [c] Ref. 7. [d] Ref. 8. [e] Ref. 9. [f] Ref. 10. [g] Ref. 11.

outer carbons (C1 and C4) are more shielded than the inner carbons (C2 and C3) upon complexation.

It has been suggested [9] that, because of the greater back-donation from the metal to the LUMO of conjugated dienes than to those of nonconjugated dienes, the extent of back-donation to the carbonyl groups is smaller in the former than the latter; this rationalizes the fact that the ^{13}C NMR chemical shifts of the carbonyl carbons of the iron complexes of conjugated dienes appear in higher field than those of the nonconjugated ones (201.4–213.7 versus 217.2–218.8 ppm) [9].



Scheme 2

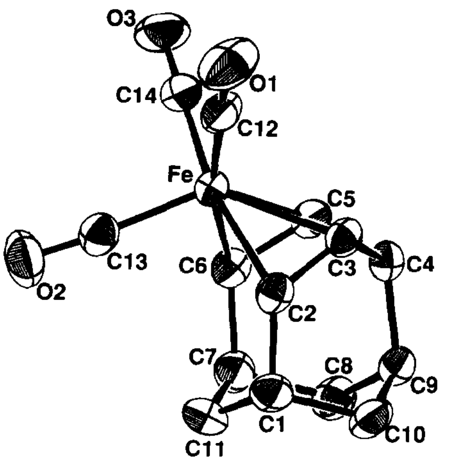


Fig. 1. ORTEP drawing of the crystal structure of 3. Hydrogen atoms are omitted for clarity.

From this point of view, the ^{13}C NMR chemical shift (216.3 ppm) of the carbonyl carbons of **3** is intermediate between those of tricarbonyliron complexes of **1** and 1,3-cyclohexadiene (218.3 and 212.2 ppm, respectively), and the result is consistent with the above mentioned observation that **2** possesses stronger homo-conjugation than **1**.

It is also interesting that the IR spectrum of **3** shows three separated carbonyl absorption bands (2030.7, 1966.1 and 1955.0 cm^{-1}) at room temperature, as is observed for tricarbonyl(1,3-butadiene)iron [12], while one sharp band and one broad band are observed for tricarbonyliron complexes of **1** and 1,5-COD [12]. The C_s symmetry of **2** similar to 1,3-butadiene and the stronger coordination of **2** than **1** and 1,5-COD may be responsible for the appearance of these three separated bands [12].

We have performed a single crystal X-ray structure determination of the tricarbonyliron complex **3** to clarify its precise structure. Recrystallization of **3** from pentane gave yellow triclinic single crystals. Figure 1 shows an ORTEP drawing of the crystal structure of **3** and selected structural data are summarized in Tables 2 and 3.

Several features of the structure of **3** are mentioned here: (1) the geometry of the iron atom retains a square pyramidal coordination in accordance with those of other diene–tricarbonyliron complexes [1c,13] and one of the three carbonyl groups is directed to the wider side (C2---C6) of the 1,4-diene system, showing C_s symmetry of **3**; (2) the iron atom is located at almost equal distance from the four olefinic carbons (C2, C3, C5 and C6), while, in the complexes of conjugated dienes, the distances from the outer carbons are slightly longer than those from the inner ones [1c,13]; (3) the bond lengths (1.392 and 1.384 Å, respectively) of the olefinic carbons (C2–C3 and C5–C6) are intermediate between those of tricarbonyliron complexes of conjugated dienes (1.394–1.434 Å) [1c,13] and that of tricarbonyl(1,5-COD)iron (1.371 Å) [12]; (4) the bond lengths of C3–C4 and C4–C5 are relatively short (1.504 and 1.508 Å, respectively) and in a range of C–C single bonds of cyclopropanes; (5) the bond angle of C3–C4–C5 is small (95.1°) and, therefore,

Table 2

Bond lengths (Å) of non-hydrogen atoms and selected internucleus distances of **3** (esd's in parentheses)

Fe–C(2)	2.157(2)	C(7)–C(8)	1.530(3)
Fe–C(3)	2.162(2)	C(8)–C(9)	1.527(3)
Fe–C(5)	2.157(2)	C(9)–C(10)	1.519(3)
Fe–C(6)	2.150(2)	C(1)–C(10)	1.531(3)
Fe–C(12)	1.777(2)	C(1)–C(11)	1.530(3)
Fe–C(13)	1.789(2)	C(7)–C(11)	1.526(3)
Fe–C(14)	1.772(2)	C(4)–C(9)	1.564(3)
C(1)–C(2)	1.526(3)	C(12)–O(1)	1.139(3)
C(2)–C(3)	1.392(3)	C(13)–O(2)	1.137(3)
C(3)–C(4)	1.504(2)	C(14)–O(3)	1.142(3)
C(4)–C(5)	1.508(3)	C(2)–C(6)	3.021(3)
C(5)–C(6)	1.384(3)	C(3)–C(5)	2.222(3)
C(6)–C(7)	1.527(3)		

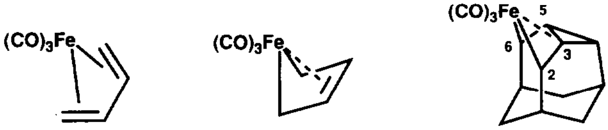
the distance between C3 and C5 is favorably short (2.222 Å) for better homo-conjugation; (6) the dihedral angles of C1–C2–C3–C4 and C4–C5–C6–C7 are relatively large (24.6° and 24.9°, respectively), showing that the double bonds are greatly distorted; the twist of π-orbitals of C3 and C5 to the exo side of the plane of C2–C3–C5–C6 supposedly results in the increase of the overlap between the π-orbitals of the double bonds and the d-orbitals of iron.

There have been many arguments about the bonding nature of transition metal complexes of conjugated dienes [1a,1c,9,11,14]. Two extreme descriptions, **4a** and **4b**, have been considered for tricarbonyliron complexes. The π-donation from the double bonds to the metal makes an important contribution in the canonical form **4a**, while, in **4b**, the σ-bonding at the terminal (outer) carbons and the π-back-donation at the central (inner) carbons make major contributions. Although most

Table 3

Selected bond angles (degrees) of non-hydrogen atoms of **3** (esd's in parentheses)

C(1)–C(2)–C(3)	118.8(2)	Fe–C(3)–C(2)	71.0(1)
C(2)–C(3)–C(4)	118.8(2)	Fe–C(5)–C(6)	71.0(1)
C(3)–C(4)–C(5)	95.1(2)	Fe–C(6)–C(5)	71.5(1)
C(3)–C(4)–C(9)	114.1(2)	C(2)–Fe–C(12)	90.4(1)
C(5)–C(4)–C(9)	114.1(2)	C(2)–Fe–C(13)	92.2(1)
C(4)–C(5)–C(6)	118.8(2)	C(2)–Fe–C(14)	168.8(1)
C(5)–C(6)–C(7)	118.9(2)	C(3)–Fe–C(12)	85.5(1)
C(6)–C(7)–C(8)	106.7(2)	C(3)–Fe–C(13)	129.7(1)
C(6)–C(7)–C(11)	116.0(2)	C(3)–Fe–C(14)	131.2(1)
C(7)–C(8)–C(9)	108.4(2)	C(5)–Fe–C(12)	129.1(1)
C(8)–C(7)–C(11)	109.7(2)	C(5)–Fe–C(13)	130.2(1)
C(4)–C(9)–C(8)	110.4(2)	C(5)–Fe–C(14)	87.1(1)
C(8)–C(9)–C(10)	108.3(2)	C(6)–Fe–C(12)	166.6(1)
C(4)–C(9)–C(10)	110.6(1)	C(6)–Fe–C(13)	92.8(1)
C(9)–C(10)–C(1)	108.8(2)	C(6)–Fe–C(14)	90.8(1)
C(2)–C(1)–C(10)	106.7(2)	Fe–C(12)–O(1)	179.4(3)
C(2)–C(1)–C(11)	116.3(2)	Fe–C(13)–O(2)	175.7(2)
C(1)–C(11)–C(7)	112.2(2)	Fe–C(14)–O(3)	179.2(2)
Fe–C(2)–C(3)	71.4(1)		



4a **4b** **5**

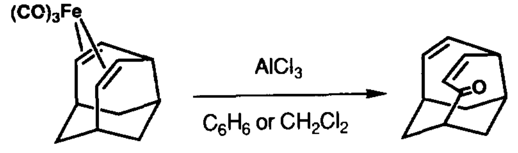
Scheme 3

tricarbonyliron complexes of conjugated dienes are represented by the π-bonding structures such as **4a**, the molecular orbital consideration suggests that there is a smooth transition between the two canonical forms, depending on HOMO and LUMO levels of dienes; the lower the LUMO of the diene, the larger the contribution of **4b** and, therefore, the more stable the complex becomes. In fact, X-ray crystallographic studies [1c,13] have shown that the bond lengths between the inner two carbons (C2–C3) are rather slightly shorter than those between the inner and outer ones (C1–C2 and C3–C4), supporting the important contribution of the terminal bonding structure of **4b**.

On the other hand, it has been suggested [1c,9] that the complexes of the homo- and nonconjugated diene can be considered to contain two separate η^2-coordinations with the metal and can be represented as only π-bonding structure, such as **3**. However, it seems to us that the suggestion might be oversimplified, because contribution of the π-back-donation to the overall bonding nature should be greater in the complex of norbornadiene, having the lower LUMO level through the strong homo-conjugation of the two double bonds, than in the complex of 1,5-COD, where there is little interaction between the two double bonds. In the case of the highly homo-conjugated diene **2**, the LUMO is much lower than that of the isolated π-bonds and, therefore, the extent of the π-back-donation from iron to the LUMO should be much larger. Thus, it is supposed that the high homo-conjugation of **2** leads to the possibility that the terminal bonding nature represented as **5** may contribute to the overall bonding, no matter how little the extent. The several structural features of **3** shown by X-ray crystallography also seem to be in accordance with the supposed contribution of **5**. Furthermore, it seems to us that the any contribution of **5** might be responsible for the larger shielding effect ($\Delta\delta = 111.8$ ppm) of the inner carbons (C3 and C5) than that ($\Delta\delta = 73.5$ ppm) of the outer ones (C2 and C6), though there has been a great deal of controversy in the interpretation of the upfield shifts of signals due to olefinic carbons bonded to transition metals [9,15].

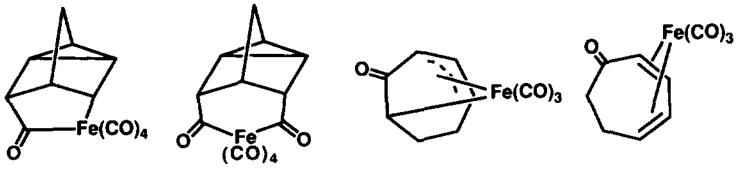
We next focused our attention on the reactivity of the complex **3**, since carbonyl insertion reactions of a few diene–tricarbonyliron complexes promoted by aluminum trichloride have been reported [16]. When **3** was treated with 2–4 eq of aluminum trichloride in benzene or dichloromethane at room temperature for 24–72 h, the carbonyl insertion product **6** was obtained in 24–32% isolation yield. The structure of **6** was assigned to tricyclo[6.3.1.0^{4,10}]dodeca-2,5-dien-7-one by spectroscopic analyses including ^{1}H–^{1}H and ^{1}H–^{13}C COSY NMR spectra. Any other compounds containing iron were not isolated.

It has been reported [16a,b] that the reaction of tricarbonyl(norbornadiene)iron with aluminum trichloride gives cyclic monoacyl- and diacyliron compounds, **7** and



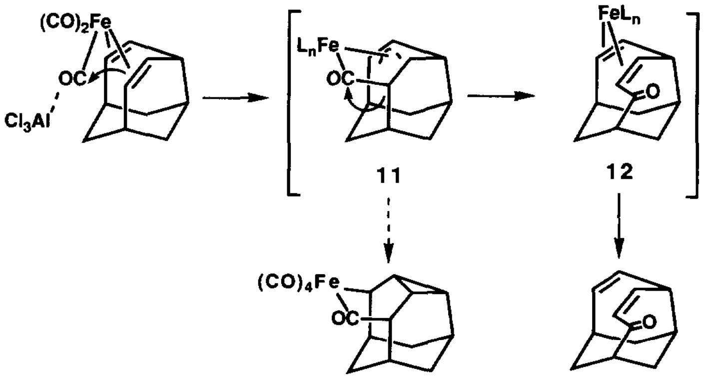
3 **6**

Scheme 4



7 **8** **9** **10**

Scheme 5



11 **12** **13** **6**

Scheme 6

8, in 12% and 16% yield, respectively, while the reaction of tricarbonyl(1,3-cyclohexadiene)iron gives cyclic π-allyliron compound **9** via a carbonyl insertion, which, on heating, affords tricarbonyl(cyclohepta-2,4-dien-1-one)iron (**10**), though the precise mechanisms of these reactions are still unclear.

A plausible pathway of the present reaction is shown in Scheme 6: complexation of aluminum trichloride with one of the carbon monoxides coordinated to iron would induce a carbonyl insertion to give an acyl π-homoallylic iron intermediate **11** [17*], which could collapse to afford **6** via a ring expanded dienone–iron complex **12** followed by decomplexation of the carbonyliron moiety. A pathway to the cyclic acyliron compound **13** might be unfavorable because of a strong homoal-

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* Reference number with asterisk indicates a note in the list of references.

lylic nature of **11** or lability of **13**. Thus, it appears that an intermediacy of the acyl π-homoallylic iron **11** could play an important role in the present reaction, while the mode of the present reaction seems to be similar to that of tricarbonyl(1,3-cyclohexadiene)iron.

Experimental

General methods

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL GX-400 (400 MHz) or a JEOL EX-270 (270 MHz) spectrometer, using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL GX-400 (100 MHz), a JEOL EX-270 (67.5 MHz), or a JEOL FX-90Q (22.5 MHz) spectrometer, using chloroform-*d* (77.00 ppm) as an internal standard. IR spectra were taken on a JASCO IR-810 or a Horiba FT-300 spectrometer. UV-visible spectra were taken on a Shimadzu-UV-260 spectrometer. High resolution mass spectrum was taken on a JEOL JMS D300 instrument equipped with JMA 2000S data analysis system. Analytical thin-layer chromatography (TLC) was performed on a Merck 60 F_{254} silica gel plate (0.25 mm thick). Preparative thin-layer chromatography (PLC) was performed on a Merck 60 F_{254} silica gel plate (1 mm thick). Benzene, dichloromethane, and chloroform (ethanol-free) were freshly distilled over P_2O_5 before use. Pentane, hexane, and carbon tetrachloride were distilled over CaH_2. Aluminum trichloride was freshly sublimed before use. Most reagents were obtained from commercial sources and used without further purification unless otherwise stated. All the reactions requiring exclusion of water and air were run under positive pressure of dry argon deoxygenated with BASF catalyst. All reagents sensitive to water and air were handled under an argon atmosphere with standard Schlenk and syringe techniques. The microanalysis was carried out by Kyoto University Analysis Center.

Preparation of tricarbonyl(tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene)iron (3)

(1) From $Fe(CO)_5$. In an 80 mL-Schlenk tube **2** (292 mg, 2.00 mmol) was dissolved in $Fe(CO)_5$ (10 mL). The solution was heated at reflux for 15 h. The reaction mixture was cooled and excess iron pentacarbonyl was removed under reduced pressure. The products were extracted with hexane (15 mL, four times) and the combined hexane solution was filtered through a Celite pad. The filtrate was concentrated *in vacuo* and the residue was chromatographed on silica gel (60 g). Elution with hexane gave the tricarbonyliron complex **3** (499 mg, 87%): m.p. 92.5–93.5 °C dec.; ^1H NMR ($CDCl_3$): δ 3.43 (dd, $J = 7.9/7.3$ Hz, H_3, H_5), 3.30 (dt, $J = 7.3/9.5$ Hz, H_4), 2.90 (dd, $J = 7.3/9.5$ Hz, H_2, H_6), 2.08 (broad m, H_1, H_7, H_9), 1.35 (d, $J = 13.1$ Hz, H_{11}), 1.21 (dt, $J = 3.6/13.2$ Hz, H_{11}), 1.12 (dd, $J = 2.1/11.9$ Hz, H_8, H_{10}), 0.96 (d, $J = 11.9$ Hz, H_8, H_{10}). ^{13}C NMR ($CDCl_3$): δ 216.3 (s, CO), 59.2 (d, $J_{CH} = 158$ Hz, C_2, C_6), 39.1 (t, $J_{CH} = 122$ Hz, C_{11}), 33.6 (t, $J_{CH} = 122$ Hz, C_8, C_{10}), 27.8 (d, $J_{CH} = 140$ Hz, C4), 26.6 (d, $J_{CH} = 126$ Hz, C_1, C_7), 25.7 (d, $J_{CH} = 129$ Hz, C9), 25.1 (d, $J_{CH} = 172$ Hz, C3, C5). IR ν_{max} (isooctane): 2030.7, 1966.1, 1955.0 cm^{-1}. Anal. Found: C, 58.77; H, 4.93. $C_{14}H_{14}O_3Fe$ calcd.: C, 59.05; H, 4.93.

(2) From $Fe_2(CO)_9$. In an 80 mL-Schlenk tube **2** (292 mg, 2.00 mmol) was dissolved in benzene (10 mL). To the solution was added $Fe_2(CO)_9$ (2.93 g, 8.00

Table 4

Summary of crystallographic data for **3**

Formula	$C_{14}H_{14}O_3Fe$
Lattice type	Triclinic
Space group	$P\bar{1}$
a (Å)	8.519(1)
b (Å)	11.281(2)
c (Å)	6.492(2)
α (deg)	94.28(3)
β (deg)	101.11(2)
γ (deg)	101.97(1)
V (Å^3)	594.7(2)
Z	2
$d_{\text{calcd.}}$ (g cm^{-3})	1.599
μ (cm^{-1})	12.98
Crystal dimensions (mm)	0.56 × 0.31 × 0.23
Collection temperature (°C)	25
Radiation type	Mo-K_α ($\lambda = 0.71073$)
$2\theta_{\max}$ (deg)	60
No. of reflections	3994
No. of unique reflections	3867
No. of unique reflections observed	2635
R_{int}	0.012
R	0.032
R_w	0.043
Maximum shift/esd	0.005
GOF	2.817
Data/parameters	206
$\Delta\rho_{\max}$ (e Å^{-3})	0.61

mmol). The suspension was stirred for 24 h at room temperature and then heated at reflux for 24 h. The reaction mixture was filtered through a Celite pad and the filtrate was concentrated *in vacuo*. The residue was chromatographed on silica gel (60 g). Elution with hexane gave **3** (433 mg, 76%).

X-ray diffraction measurements

Single crystals of **3** were obtained from saturated pentane solution kept at −20 °C overnight. A pale yellow crystal was mounted in a thin-walled capillary under argon and sealed to protect it from air and moisture. The X-ray crystallographic data were obtained on a RIGAKU AFC-5R four-circle computer-controlled diffractometer. Intensity data were obtained by using graphite-monochromatized Mo-K_α radiation. The details of data collection and the cell dimensions, which were obtained from a least-square refinement of 2θ values of 50 independent reflections in the range of $20° < 2\theta < 60°$, are listed in Table 4. The 2635 unique reflections with $|F_o| > 3\sigma|F_o|$ were corrected for effects of Lorentz and polarization. Three standard reflections measured after every 50 reflections showed no damage in the intensity of reflections during measurement. The positions of all non-hydrogen atoms were determined by the CRYSTAN-85 program system. All hydrogen atoms were located by difference Fourier maps. Full-matrix refinement for non-hydrogen atoms with anisotropic and hydrogen atoms with isotropic

Table 5

Fractional coordinates ($\times 10^4$) of non-hydrogen atoms of **3** (esd's in parentheses)

Atom	x	y	z	B_{eq} [a]
Fe	4638.6(2)	7207.7(2)	8691.8(3)	2.46(1)
C(1)	2117(3)	8972(2)	8940(4)	3.40(5)
C(2)	3516(2)	8489(2)	10178(3)	2.81(4)
C(3)	3143(2)	7381(2)	10987(3)	2.74(4)
C(4)	1580(2)	6472(2)	9948(3)	2.75(4)
C(5)	2291(2)	5941(2)	8235(3)	2.76(4)
C(6)	2355(2)	6526(2)	6443(3)	2.87(4)
C(7)	1138(3)	7323(2)	5806(3)	3.40(5)
C(8)	−375(3)	6828(2)	6694(4)	3.57(5)
C(9)	110(2)	7063(2)	9104(3)	3.07(4)
C(10)	577(3)	8434(2)	9745(4)	3.54(5)
C(11)	1762(3)	8687(2)	6532(4)	3.97(6)
C(12)	6318(3)	7514(2)	10904(4)	3.59(5)
C(13)	5402(3)	8287(2)	7034(3)	3.18(4)
C(14)	5414(2)	5963(2)	7819(3)	3.19(4)
O(1)	7396(2)	7701(2)	12320(3)	5.90(6)
O(2)	5971(3)	8942(2)	5992(3)	5.25(5)
O(3)	5929(2)	5164(2)	7275(3)	4.90(5)

[a] Thermal parameters are given by equivalent temperature factors (Å^2).

temperature parameters converged at $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.032$ and $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2} = 0.043$. A weighting scheme, $1/w = \sigma_c^2 + (0.02 | F_o |)^2$, was used. The positional parameters are listed in Tables 5 and 6. Final difference Fourier maps indicated that no significant peak remained.

*Reaction of **3** with $AlCl_3$*

In a 20 mL-Schlenk tube $AlCl_3$ (318 mg, 2.39 mmol) was suspended in CH_2Cl_2 (1 mL). To this was added **3** (239 mg, 0.84 mmol) in CH_2Cl_2 (6 mL) dropwise at

Table 6

Fractional coordinates ($\times 10^3$) of hydrogen atoms of **3** (esd's in parentheses)

Atom	x	y	z	B_{iso} [a]
H(1)	239(4)	981(3)	932(5)	3.2
H(2)	436(4)	906(3)	1088(5)	2.7
H(3)	370(4)	725(2)	1242(5)	2.6
H(4)	133(3)	588(3)	1086(5)	2.6
H(5)	249(4)	518(3)	826(5)	2.7
H(6)	252(4)	611(3)	539(5)	2.8
H(7)	83(4)	725(3)	422(5)	3.3
H(8a)	−75(3)	598(3)	629(5)	2.3
H(8b)	−126(4)	723(2)	613(4)	2.3
H(9)	−81(4)	666(3)	970(5)	2.9
H(10a)	80(4)	864(3)	1125(5)	3.4
H(10b)	−31(4)	881(3)	915(5)	3.4
H(11a)	83(4)	910(3)	591(5)	3.7
H(11b)	275(4)	902(3)	598(5)	3.7

[a] Thermal parameters are given by equivalent temperature factors (Å^2).

room temperature. The resulting mixture was stirred for 48 h at room temperature, and then poured into ice cooled 3% HCl (20 mL). The products were extracted with dichloromethane (25 mL, three times). The combined organic layer was dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by PLC. Elution with CH_2Cl_2 gave tricyclo[6.3.1.0^{4,10}]dodeca-2,5-dien-7-one (**6**) (34 mg, 24%): UV λ_{max} (EtOH): 232 nm ($\epsilon = 1.09 \times 10^4$). IR ν_{max} (CCl_4): 1680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.64 (dd, $J = 9.2/11.0$ Hz, H_5), 5.89 (dd, $J = 1.2/11.0$ Hz, H_6), 5.65 (dd, $J = 9.5/6.7$ Hz, H_2), 5.51 (dd, $J = 9.5/3.7$ Hz, H_3), 3.26 (m, H_4) 2.26–2.35 (m, H_1, H_8, H_{10}, and one of H_9, H_{11}, or H_{12}), 2.06 (d, $J = 13.7$ Hz, H_9, H_{11}, or H_{12}), 1.84 (ddd, $J = 4.6/6.4/13.7$ Hz, H_9, H_{11}, or H_{12}), 1.67–1.75 (m, H_9, H_{11}, or H_{12}). ^{13}C NMR ($CDCl_3$): δ 211.4 (s, CO), 142.8 (d, C_5), 133.7 (d, C3), 132.6 (d, C_6), 128.1 (d, C_2), 41.9 (d, C_1, C_8, or C_{10}), 38.7 (d, C_4), 32.8 (t, C_9, C_{11}, or C_{12}), 32.7 (t, C_9, C_{11}, or C_{12}), 29.7 (t, C_9, C_{11}, or C_{12}), 28.0 (d, C_1, C_8, or C_{10}), 26.5 (d, C_1, C_8, or C_{10}). High resolution mass spectrum: Found: 174.1045. $C_{12}H_{14}O$ calcd.: 174.1045.

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