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Structures of [^{t}BucpFe(CO)$_2$]$_2$ and [^{t}Bu$_2$cpFe(CO)$_2$]$_2$ *

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Abstract

The molecular structures of [^{t}BucpFe(CO)$_2$]$_2$ (**1**) and [^{t}Bu$_2$cpFe(CO)$_2$]$_2$ (**2**) have been determined by single-crystal X-ray diffraction studies. In the solid state, **1** exists solely as the *trans*-carbonyl bridged isomer, whereas **2**, containing the bulkier ^{t}Bu$_2$cp ligand, is unexpectedly found to adopt the *cis* configuration. The Fe–Fe bonds are approximately equal (2.551(1) Å for **1** and 2.5544(7) Å for **2**).

1. Introduction

In our research programme we are exploring the role of steric and electronic effects exerted by bulky cyclopentadienyl ligands on both the structure and reactivity of the corresponding transition metal complexes. We have now carried out a study of iron compounds of t-butyl substituted cyclopentadienyls, namely well-known dinuclear complexes of the type [cp′Fe(CO)$_2$]$_2$, which offer the possibility of examining the substituent influence on the *cis/trans* equilibria for these compounds, and the results of X-ray structural analyses of [^{t}BucpFe(CO)$_2$]$_2$ (**1**) and [^{t}Bu$_2$cpFe(CO)$_2$]$_2$ (**2**) are presented below.

2. Results and discussion

The dimeric iron species are commonly synthesized by thermal reaction of an iron carbonyl together with the corresponding cyclopentadiene [1,2]. In order to attain higher reaction temperatures and so higher yields, the t-butyl substituted cyclopentadienes were treated with Fe(CO)$_5$ in an autoclave. After purification and recrystallization from hexane, single crystals suitable for X-ray analysis were obtained for both title compounds. Atomic coordinates and selected bond lengths and angles are listed in Table 1–4.

In the solid state, **1** adopts the *trans*-carbonyl bridged configuration in which the two bulky t-butyl substituents point away from each other (Fig. 1). The two connected iron atoms are related across a crystallographic centre of symmetry [Fe–Fe, 2.551(1) Å; $-x$, $1-y$, $-z$]. The bridging carbonyl groups and iron atoms are coplanar, as in the parent compound, *trans*-

TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **1** (U_{eq} is defined as one-third of the orthogonalized U_{ij} tensor)

Atom	x	y	z	U_{eq}
Fe(1)	1.03616(4)	0.47807(2)	0.11890(2)	0.0287(1)
O(6)	0.7894(3)	0.3185(1)	0.0821(2)	0.0521(6)
O(7)	1.3413(3)	0.4135(1)	−0.0400(2)	0.0485(5)
C(1)	1.2128(3)	0.4421(1)	0.3030(2)	0.0321(5)
C(2)	1.0306(4)	0.4948(2)	0.3185(2)	0.0413(7)
C(3)	1.0550(5)	0.5765(2)	0.2636(2)	0.0556(8)
C(4)	1.2451(5)	0.5758(2)	0.2113(2)	0.0549(9)
C(5)	1.3439(4)	0.4939(2)	0.2363(2)	0.0437(7)
C(6)	0.8846(3)	0.3818(1)	0.0955(2)	0.0349(6)
C(7)	1.1892(3)	0.4527(1)	−0.0219(2)	0.0335(6)
C(11)	1.2709(3)	0.3542(1)	0.3634(2)	0.0379(6)
C(12)	1.0777(5)	0.3097(2)	0.4059(3)	0.0528(8)
C(13)	1.4378(6)	0.3711(2)	0.4857(3)	0.061(1)
C(14)	1.3649(6)	0.2945(2)	0.2718(3)	0.062(1)

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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TABLE 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **2** (U_{eq} is defined as one-third of the orthogonalized U_{ij} tensor)

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	0.32830(3)	0.70587(3)	0.32026(3)	0.0362(2)
O(6)	0.3713(2)	0.6910(2)	0.1327(2)	0.090(2)
O(7)	0.1621(2)	0.5932(2)	0.2844(2)	0.072(1)
C(1)	0.3841(2)	0.5793(2)	0.3783(2)	0.037(1)
C(2)	0.4568(2)	0.6405(2)	0.3488(2)	0.039(1)
C(3)	0.4545(2)	0.7266(2)	0.3969(2)	0.041(1)
C(4)	0.3756(2)	0.7201(2)	0.4543(2)	0.040(1)
C(5)	0.3331(2)	0.6299(2)	0.4435(2)	0.038(1)
C(6)	0.3512(3)	0.6970(3)	0.2064(3)	0.057(1)
C(7)	0.2002(3)	0.6640(3)	0.3007(2)	0.048(1)
C(11)	0.3745(3)	0.4764(2)	0.3531(3)	0.051(1)
C(12)	0.3691(3)	0.4634(3)	0.2524(3)	0.076(2)
C(13)	0.2880(3)	0.4330(3)	0.3971(3)	0.073(2)
C(14)	0.4635(3)	0.4255(3)	0.3882(3)	0.061(2)
C(31)	0.5303(3)	0.8015(3)	0.3951(3)	0.060(1)
C(32)	0.6169(3)	0.7598(3)	0.4419(4)	0.106(2)
C(33)	0.4993(3)	0.8907(3)	0.4441(3)	0.086(2)
C(34)	0.5570(3)	0.8261(3)	0.2998(3)	0.078(2)

TABLE 3. Selected bond lengths (Å) for **1** and **2**

Bond	**1**	**2**
Fe(1)–Fe(1a) [a]	2.551(1)	2.5544(7)
Fe(1)–C(1)	2.139(2)	2.150(3)
Fe(1)–C(2)	2.113(2)	2.093(3)
Fe(1)–C(3)	2.134(2)	2.151(3)
Fe(1)–C(4)	2.127(3)	2.131(3)
Fe(1)–C(5)	2.137(3)	2.143(3)
Fe(1)–C(6)	1.759(2)	1.745(5)
Fe(1)–C(7)	1.929(2)	1.937(4)
Fe(1)–C(7a) [a]	1.930(2)	1.916(4)
C(6)–O(6)	1.142(3)	1.146(5)
C(7)–O(7)	1.175(3)	1.169(5)
C(1)–C(2)	1.438(3)	1.421(4)
C(1)–C(5)	1.413(3)	1.414(4)
C(2)–C(3)	1.403(3)	1.421(4)
C(3)–C(4)	1.397(4)	1.417(4)
C(4)–C(5)	1.412(4)	1.426(4)

[a] For **1**: $-x$, $1-y$, $-z$; for **2**: $1/2-x$, $3/2-y$, z.

$[\mathrm{cpFe(CO)_2}]_2$ [3]. The bridging groups are essentially symmetrical. The distance Fe to ring centroid is 1.769(3) Å, similar to the distance 1.764(1) Å found for $[\mathrm{Me_5cp\text{-}Fe(CO)_2}]_2$ [4].

Surprisingly, **2** (the complex with the bulkier ${}^t\mathrm{Bu_2cp}$ ligand) exists in the solid state in an eclipsed *cis* form (Fig. 2). The $\mathrm{Fe_2C_2}$ core ring is non-planar; the out-of-plane dihedral angle about the Fe–Fe axis of 23.54(6)° is significantly larger than 16°, as observed for *cis*-$[\mathrm{cpFe(CO)_2}]_2$ [5]. The Fe–Fe bond length is

TABLE 4. Selected bond angles (°) for **1** and **2**

Angle	**1**	**2**
C(6)–Fe(1)–C(7)	92.89(9)	90.3(3)
C(6)–Fe(1)–Fe(1a)	94.57(7)	101.4(1)
C(7)–Fe(1)–Fe(1a)	48.64(6)	48.1(1)
C(6)–Fe(1)–C(7a)	93.15(9)	87.7(2)
C(7)–Fe(1)–C(7a)	97.26(8)	94.3(2)
Fe(1a)–Fe(1)–C(7a)	48.62(6)	48.8(1)
Fe(1)–C(6)–O(6)	178.6(2)	176.3(4)
Fe(1)–C(7)–O(7)	138.6(2)	137.0(3)
C(6)–Fe(1)–Fe(1a)	94.57(7)	101.4(1)
O(7)–C(7)–Fe(1a)	138.6(2)	139.9(3)

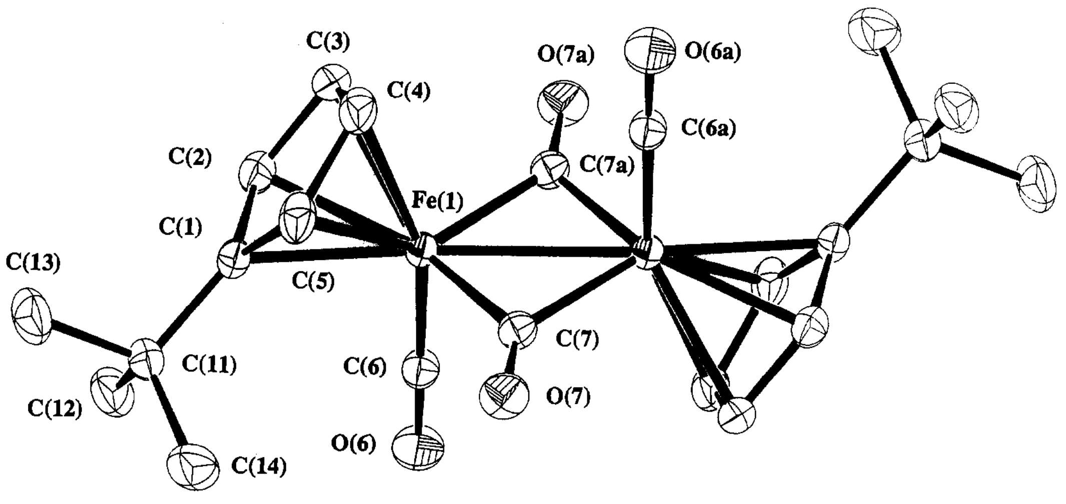

Fig. 1. ORTEP (30% probability) plot of $[{}^t\mathrm{BucpFe(CO)_2}]_2$ (**1**).

TABLE 5. Fe–Fe and Fe–ligand bond lengths (Å) in [cp'Fe(CO)$_2$]$_2$ complexes

cp' =	cp		Me$_5$cp	^{t}Bucp	^{t}Bu$_2$cp
	trans	*cis*	*trans*	*trans*	cis
Fe–Fe	2.534(2)	2.531(2)	2.560(1)	2.551(1)	2.5544(7)
Fe–centroid	1.754(6)	1.742(5)	1.764(1)	1.769(3)	1.783(3)
M–CO (terminal)	1.748(6)	1.730(7)	1.753(3)	1.759(2)	1.745(5)
Fe–CO (bridging)	1.910(5)	1.918(7)	1.922(2)	1.929(2)	1.937(4)

2.5544(7) Å and the distance Fe to ring centroid is 1.783(3) Å. The angle between the two cyclopentadienyl planes, 89.8(2)°, is almost perpendicular. The two ends of the molecule are related by a crystallographic two-fold rotation.

Table 5 gives a comparison of important bond distances for the two title compounds with the unsubstituted and pentamethyl-substituted representatives.

Solution IR studies in the CO stretch region indicate that for **1** in hexane, the *trans* form dominates, whereas in DMSO, the *cis* species is favoured [6]. Attempts to crystallize the *cis* isomer from polar solvents at low temperature were unsuccessful; all the examined crystals were *trans*. Independent of solvent polarity, the *cis* form in **2** was unexpectedly predominant in contrast with earlier findings [2].

3. Experimental part

Mono- and di-t-butyl cyclopentadienes were prepared as previously described [7,8]. All procedures were carried out under an inert gas. The hexane used for the recrystallizations was dried over Na/K alloy and distilled under nitrogen prior to use.

The NMR spectra were recorded on a Bruker AC 200 and a Jeol GX 400 NMR spectrometer and internally referenced to TMS or to residual solvent resonances.

X-Ray diffraction data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer by use of crystal monochromatized Mo Kα X-radiation (λ = 0.71073 Å) at a temperature of 25°C. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied in each case. All structures were solved by Patterson methods (SHELXS-86 [9]). Full-matrix least-squares refinement (SHELX-76 [10]) with anisotropic thermal parameters was carried out for all non-hydrogen atoms. Hydrogens were located by difference methods and both positional and thermal parameters were refined.

3.1. *Synthesis of 1 and 2 (general procedure)*

Two millilitres (3.0 g, 15 mmol) of Fe(CO)$_5$ (Aldrich) and 10 mmol of the cyclopentadiene were mixed in an autoclave, which was filled with argon and heated

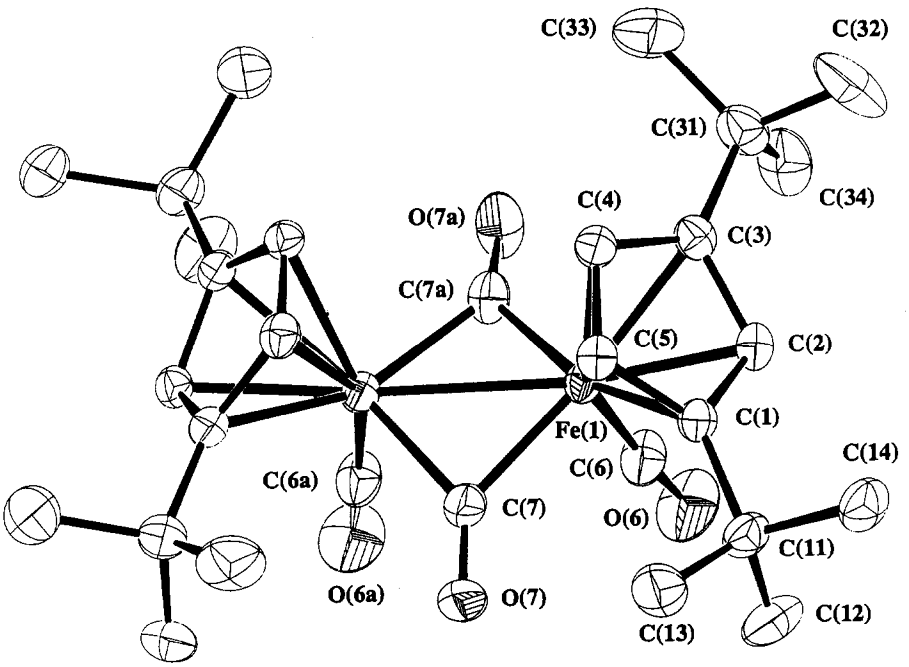

Fig. 2. ORTEP (30% probability) plot of [^{t}Bu$_2$cpFe(CO)$_2$]$_2$ (**2**).

to 170°C for 12 h. After being cooled to room temperature, the red solution was transferred to a Schlenk tube and the excess of iron carbonyl was removed under oil-pump vacuum. The raw product was dissolved in hexane, filtered through a porcelain filter and slowly cooled to -20°C to induce crystallization.

All analytical data (^{1}H NMR, IR, CH analysis) match those given in ref. 2. The ^{13}C NMR shifts are included as additional information.

[^{t}BucpFe(CO)$_2$]$_2$ (1). Yield 55%. $C_{22}H_{26}Fe_2O_4$ (466.14); monoclinic, space group $P2_1/c$, $a = 6.308(2)$, $b = 15.399(3)$, $c = 10.479(4)$ Å, $\beta = 99.31(2)°$, $V = 1004.5(5)$ Å^3; $D_{calc.} = 1.541$ g cm^{-3}, $Z = 2$; μ(Mo Kα) = 14.7 mm^{-1}; $F(000) = 484$, crystal size $0.08 \times 0.16 \times 0.24$ mm^3; 2925 unique reflections, 1882 observed with $I > 2.5\sigma(I)$; $2\theta_{max} = 50°$; 179 refined parameters, $R^* = 0.025$; $R_w = 0.027$, $w^{-1} = \sigma(F) + 5.01 \times 10^{-4}F^2$; GOF = 1.01, maximum/minimum residual electron density: $+0.30/-0.20$ e Å^{-3}.

^{13}C NMR (CDCl$_3$, 50 MHz, 25°C); σ 118.6 (s, 1-*C*-cp); 88.6, 86.0 (S, 2,5-*C*-cp, 3,4-*C*-cp); 31.4 (s, C(CH$_3$)$_3$); 31.2 (s, C(CH$_3$)$_3$) ppm.

[^{t}Bu$_2$cpFe(CO)$_2$]$_2$ (2). Yield 55%. $C_{30}H_{42}Fe_2O_4$ (578.35); tetragonal, space group $P4_2/n$, $a = b = 14.210(1)$, $c = 15.012(2)$ Å, $V = 3031.3(5)$ Å^3; $D_{calc.} = 1.267$ g cm^{-3}, $Z = 4$; μ(Mo Kα) = 9.9 mm^{-1}; $F(000) = 1224$, crystal size $0.05 \times 0.14 \times 0.26$ mm^3; 2665 unique reflections, 1649 observed reflections with $I > 2.5\sigma(I)$; $2\theta_{max} = 50°$; 163 refined parameters, $R^* = 0.031$; $R_w = 0.034$, $w^{-1} = \sigma(F) + 2.71 \times 10^{-4}F^2$; GOF = 1.59, maximum/minimum residual electron density: $+0.20/-0.26$ e Å^{-3}.

^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): δ 117.0 (s, 1,3-*C*-cp); 88.6, 86.0 (s, 2,5-*C*-cp, 3,4-*C*-cp); 31.3 (s, C(CH$_3$)$_3$); 31.1 (s, C(CH$_3$)$_3$) ppm.

Supplementary material available. Lists of complete bond lengths and bond angles, hydrogen atom coordinates, thermal parameters and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$.