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Reactivity of $Fe_3(CO)_9(\mu_3\text{-}C_2Et_2)$. Synthesis and structures of $Fe_2(CO)_6\{C_2Et_2C[CH_2N(Me)CH_2Ph]CH\}$ and $Fe_3(CO)_8\{C_2Et_2C(H)C[CH_2N(Me)CH_2Ph]\}$

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Abstract

The compounds $Fe_2(CO)_6\{C_2Et_2C[CH_2N(Me)CH_2Ph]CH\}$ (**3**) and $Fe_3(CO)_8\{C_2Et_2C(H)C\text{–}[CH_2N(Me)CH_2Ph]\}$ (**4**) resulted from the reaction of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$ (**1**) with the substituted propargylamine *N*-benzyl-*N*-methylpropargylamine. Complexes **3** and **4** were characterized by X-ray structural determinations. Complexes **3** and **4** represent two orientations of insertion of the propargylamine betwccn iron and the alkyne ligand of **1**. The characteristic feature in both structures is the presence of a ferracyclopentadiene ring. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Propargylamine; Ligand; Ferracyclopentadiene ring

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1. Introduction

Reactions between the iron carbonyls and alkynes were among the first to produce organic derivatives of transition metal clusters [1–3], and they initiated the very fruitful chemistry of alkyne-substituted metal carbonyls [4,5]. Almost all of the compounds obtained obey the 18 electron rule. A notable exception is the cluster type $Fe_3(CO)_9(\mu_3\text{-}C_2R_2)$ [2,6,7] which is two electrons short of a noble gas configuration but conforms to Wade's rules if considered a Fe_3C_2 trigonal bipyramid. Being unsaturated. this cluster type should promise a rich derivative chemistry. The exploitation of this has been hampered, however, by its accessibility in only very low yields.

Reactions reported of the cluster type $Fe_3(CO)_9(\mu_3\text{-}C_2R_2)$ include its reduction to the dianion and some investigations thereof [8] as well as cluster expansion with CpNi fragments [9] and degradation with CO under pressure [10]. We have contributed its cluster expansion to $Fe_4(CO)_{12}(\mu_4\text{-}C_2R_2)$ [11]. We, like others, observed that the formally unsaturated compound is unusually unreactive towards donor ligands and does not add 2-electron reagents, but instead undergoes CO substitution [12,13]. We then turned to reagents which should find a point of attack, i.e. reactivity based on unsaturation, at the alkyne ligand. Again several species which are unsaturated themselves, e.g. nitriles, isonitriles, cationic species or carbene sources, did not react spontaneously with compound **1**. We found that alkynes in the form of propargylamines do react. Among them *N*-benzyl-*N*-methylpropargylamine (**2**) yielded products which could be purified with a reasonable effort. This paper describes the two polynuclear species obtained from the reaction between **1** and **2**. The reactions of propargylamines with cobalt, [14]

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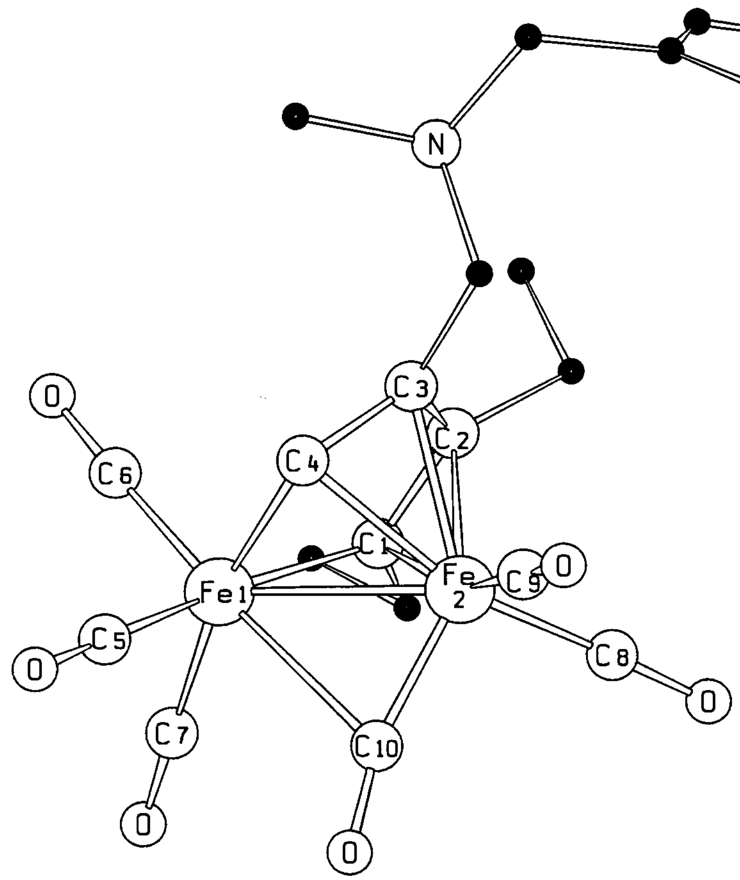
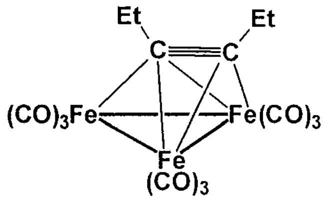


Fig. 1. Molecular structure of compound **3**.

ruthenium [15] and iron carbonyls [16] have been described, their products being derived from cluster fragmentation as well as alkyne coupling.

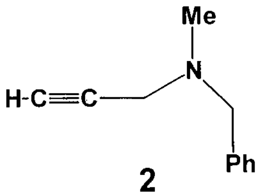


1

2. Results and discussion

Although cluster **1** has been mentioned in several papers [6–8] its synthesis has never been described in detail. In order to make a preparative chemistry of cluster **1** possible, its yield had to be improved. We found that addition of trimethylamine oxide to the reaction mixture of $Fe_3(CO)_{12}$ and 3-hexyne makes it possible to obtain **1** in up to 50% yield. This works, however, on a sub-millimolar scale only and requires careful control of the reaction conditions. Thus the total amounts of **1** available are still small.

The reaction of **1** with the propargylamine **2** in equimolar quantities resulted in the formation of dinuclear **3** and trinuclear **4**. **3** and **4** were separated from a multicomponent product mixture by preparative TLC. After chromatographic workup orange **3** and dark-green **4** were separated by fractional crystallization. The IR spectra of **3** and **4** show the presence of terminal and bridging carbonyl ligands. The proton chemical shifts for the complexes **3** and **4** are in accordance with their structures. The ^{13}CNMR spectrum of **3** afforded further evidence for its identification (see Section 3). In the mass spectrum of **3** the molecular ion is detected at 521 *m*/*z*, as well as the successive loss of six carbonal ligands. The mass spectrum of **4** shows a signal at 605 *m*/*z*, which corresponds to the fragment $[M-CO^+]$.



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The X-ray structural analysis of **3** revealed the structure shown in Fig. 1. The binuclear complex **3** can be classified as a half-sandwich complex and is a member in the family of ferrole complexes [17]. The formation of the ferracyclopentadiene ring in **3** can be explained

Table 1
Important bond lengths (Å) for compound 3

Fe(1)–Fe(2)	2.488(1)	Fe(1)–C(1)	1.989(4)
Fe(1)–C(5)	1.804(5)	Fe(1)–C(4)	1.943(4)
Fe(1)–C(6)	1.765(5)	C(1)–C(2)	1.408(5)
Fe(1)–C(7)	1.813(5)	C(2)–C(3)	1.436(5)
Fe(1)–C(10)	2.406(5)	C(3)–C(4)	1.409(5)
Fe(2)–C(8)	1.781(5)	Fe(2)–C(1)	2.098(4)
Fe(2)–C(9)	1.780(5)	Fe(2)–C(2)	2.153(3)
Fe(2)–C(10)	1.790(5)	Fe(2)–C(3)	2.130(4)
		Fe(2)–C(4)	2.065(4)

as resulting from tail-to-tail coupling of the alkyne entities. The molecule **3** has C_1 symmetry. One of the CO ligands is located between the Fe atoms in a semibridging position, the CO ligand and the two Fe atoms being situated on a pseudo-mirror plane, perpendicular to the butadiene moiety. Bond distances of **3** are listed in Table 1.

The unsymmetrically substituted ferracyclopentadienyl ring in **3** has C–C bond lengths which are typically intermediate between single and double bonds. However, the bond length equalization is not as pronounced as in some other ferroles [17]. This bond length equalization within the butadiene chain has been explained by two different charge redistribution mechanisms, namely π delocalization and metal-induced σ, π rehybridization for ferrole derivatives having various substituents at the butadiene ligand [18,19]. The mechanism of metal-induced σ, π rehybridization predicts a high electron occupancy in the HOMO of the ferrole complexes $Fe_2(CO)_6(C_4R_4)$, mainly constituted by a π_3^* antibonding orbital of the butadiene moiety. This high electron density of the HOMO is caused by the electron donation of both Fe atoms to the butadiene entity. The presence of π acceptors or electronegative substituents on the butadiene moiety should compensate the high electron occupation of the HOMO partially restoring the single and double bonds. In this way, the electronegativity of the amine group reduces the π delocalization within the ferracyclopentadiene ring. The Fe(1)–C(1) and Fe(1)–C(4) bond lengths in **3** are shorter than typical Fe–C single bonds (ca. 2.05 Å)

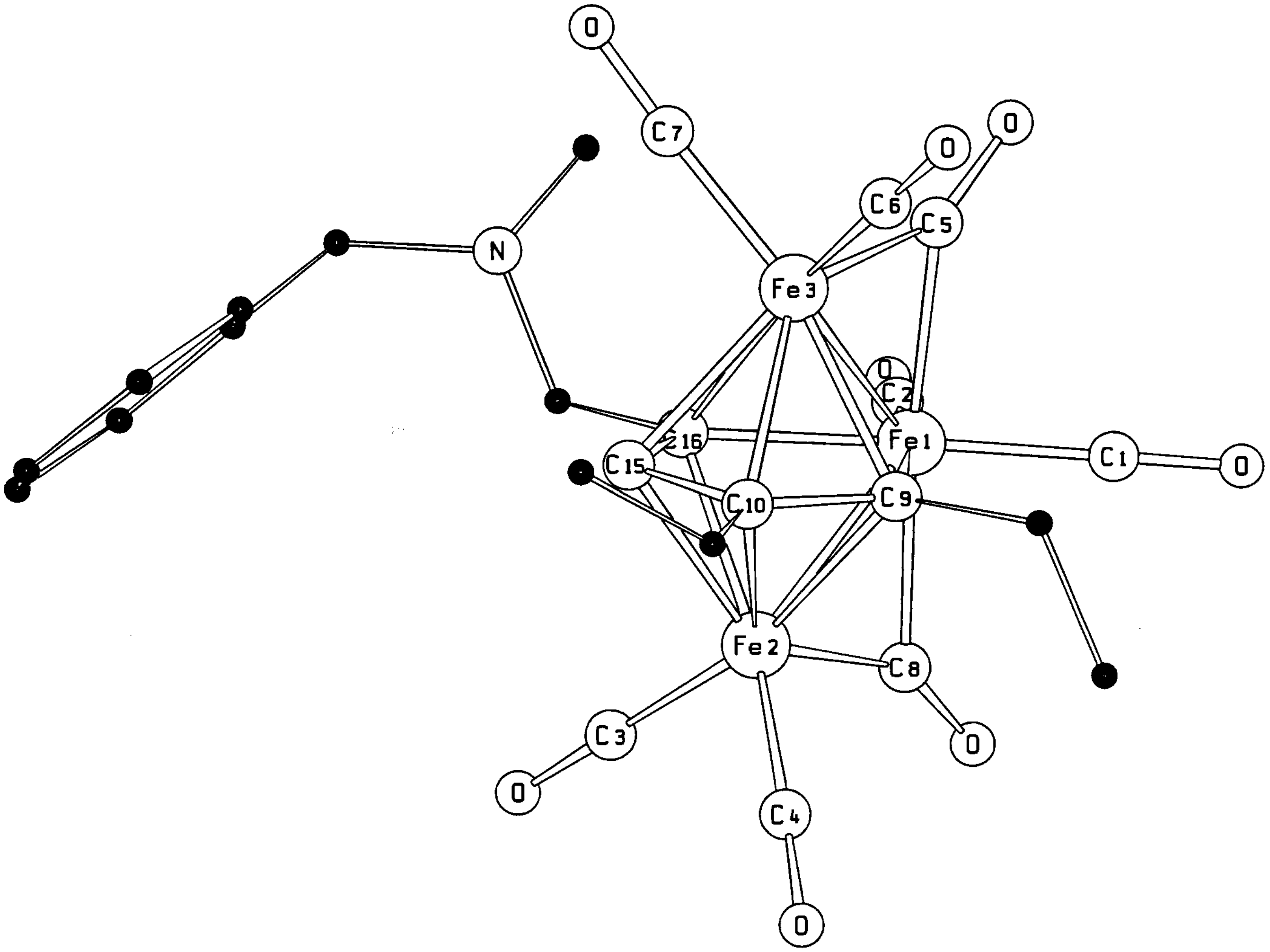

Fig. 2. Molecular structure of compound **4**.

Table 2
Important bond lengths (Å) for compound 4

Fe(1)–Fe(2)	2.431(1)	Fe(1)–C(9)	2.058(3)
Fe(1)–Fe(3)	2.440(1)	Fe(1)–C(16)	2.036(3)
Fe(1)–C(1)	1.787(4)	C(9)–C(10)	1.442(4)
Fe(1)–C(2)	1.783(4)	C(10)–C(15)	1.444(4)
Fe(1)–C(5)	2.046(4)	C(15)–C(16)	1.433(4)
Fe(1)–C(8)	2.086(4)	Fe(2)–C(9)	2.156(3)
Fe(2)–C(3)	1.762(5)	Fe(2)–C(10)	2.176(3)
Fe(2)–C(4)	1.765(4)	Fe(2)–C(15)	2.135(3)
Fe(2)–C(8)	1.845(4)	Fe(2)–C(16)	2.092(3)
Fe(3)–C(6)	1.764(4)	Fe(3)–C(9)	2.109(3)
Fe(3)–C(7)	1.784(4)	Fe(3)–C(10)	2.183(3)
Fe(3)–C(5)	1.860(4)	Fe(3)–C(15)	2.153(3)
		Fe(3)–C(16)	2.136(3)

[20]. Like in other ferrole complexes, the four Fe(2)–C(π) bond lengths show differences; the Fe(2)–C(1) and Fe(2)–C(4) bonds are shorter than the Fe(2)–C(2) and Fe(2)–C(3) bonds.

The molecular structure of **4** is shown in Fig. 2. Bond lengths are given in Table 2. The trinuclear complex **4** is a tripledecker sandwich of the type that was first observed for $Fe_3(CO)_8(C_4Ph_4)$ [21]. It can also be considered as a member of the closo pentagonal-bipyramidal family with two $Fe(CO)_3$ groups at the apexes [22]. Like **3**, complex **4** has a bridging carbonyl ligand over each of its Fe–Fe bonds, which lies in the Fe_3 plane which is also a pseudo-mirror plane for the whole molecule. Contrary to **3**, the formation of the ferracyclopentadiene ring in **4** results from a head-to-tail coupling between the alkyne ligand and the propargylamine. The C–C bond order equalization in the ferracyclopentadiene ring of **4** is almost perfect. the maximum difference in length being 0.01 Å. In contrast, the Fe–C bond lengths of the ring in **4** are. on the average 0.08 Å larger than those in **3**.

While **3** and **4** are both members of a well-established family of ferrole complexes, their propargylamine content and their structural difference based thereon are worth mentioning. If one assumes similar initial reaction steps in their formation, the head-to-head versus head-to-tail coupling of the alkynes must account for the specific appearance of only one of the two possible isomers of the resulting ferracyclopendadiene rings (i.e. head-to-head in **3** and head-to-tail in **4**). We consider two alternative reaction pathways to be most likely, which both involve cluster fragmentation. The first alternative starts with cluster fragmentation giving $Fe_2(CO)_6(\mu\text{-}C_2Et_2)$ as a highly reactive intermediate. This can insert the propargylamine in both possible orientations. Of the two products, **3** is stable as such while the other one is able to add a $Fe(CO)_3$ fragment resulting in **4**. The other alternative starts with alkyne insertion, again in both orientations. This time of the two products **4** is stable as such while the other loses a $Fe(CO)_3$ fragment resulting in **3**. In both alternatives a subtle electronic effect decides upon the reaction course which has not been observed before in reactions between metal carbonyls and propargylamines.

The ferrole-containing cluster products **3** and **4** and the proposed pathways leading to them are realizations of mechanistic speculations which were already made up to 40 years ago [1–4,6,9] in order to understand the multitude of products resulting from reaction of the iron carbonyls with alkynes. But to our knowledge **3** and **4** are actually the first products that have been obtained by alkyne–alkyne coupling starting from a pure $Fe_3(CO)_9(\mu_3\text{-}R_2C_2)$ complex.

3. Experimental

The general experimental techniques and the measuring instruments were as described before [23]. All reagents were obtained commercially. Trimethylamine oxide was dehydrated by repeated sublimation.

Preparation of $Fe_3(CO)_9(\mu_3\text{-}C_2Et_2)$ (**1**): A 500 ml Schlenk flask was charged with 252 mg (0.50 mmol) of $Fe_3(CO)_{12}$, 123 mg (1.50 mmol) of 3-hexyne and 300 ml of pentane. This solution was cooled to −78°C and a solution of 113 mg (1.50 mmol) of dehydrated trimethylamine-*N*-oxide in 30 ml of CH_2Cl_2 was added. Nitrogen was gently bubbled through the solution until it achieved room temperature. Then it was heated to 40°C under reflux during 48 h with constant stirring. The progress of the reaction was followed by IR-spectroscopy and TLC chromatography until the green fraction of $Fe_3(CO)_{12}$ on the TLC plates was considerably smaller than the brown fraction of product **1**. The solvent was removed in vacuo. The solid residue was dissolved in 5 ml of CH_2Cl_2 and chromatographed over a 3 × 50 cm silica gel column. Elution with hexane yielded a dark brown band which gave 100 mg (0.22 mmol, 44%) **1** in the form of dark brown crystals, m.p. 109–110°C after recrystallisation from hexane. Anal. Found: C, 35.42; H, 1.97. $C_{15}H_{10}Fe_3O_9$ (501.78) Calc.: C, 35.91; H, 2.01. The spectroscopic data are in accordance with the data described for this compound [6,7].

Preparation of complexes **3** and **4**: In a 100 ml Schlenk flask, 210 mg (0.42 mmol) of **1** were dissolved in 30 ml of hexane. A solution of 80 mg (0.50 mmol) of **2** in 15 ml of hexane was slowly added. The reaction mixture was heated to 50°C for 1 h. The progress of the reaction was followed by TLC. When **1** was almost completely used up the solvent was removed in vacuo. The solid residue was picked up in 5 ml of CH_2Cl_2 and purified on preparative TLC plates (Merck silica gel 60 F_{254}, 0.2 mm). Elution with hexane yielded a dark green band containing a mixture of **3** and **4**. Recrystallysation from hexane at −20°C gave 125 mg (50%) of **3** in the

Table 3
Crystallographic data of compounds **3** and **4**

Complex	**3**	**4**
Formula	$C_{23}H_{23}Fe_2NO_6$	$C_{25}H_{23}Fe_3NO_8$
Molecular weight	521.13	633.00
Crystal size [mm]	0.60 × 0.50 × 0.40	1.00 × 0.80 × 0.70
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)	Pbca
Z	2	8
Unit cell dimension		
a (Å)	8.3090(5)	16.273(1)
b (Å)	13.313(1)	17.561(1)
c (Å)	10.934(1)	18.565(1)
α (°)	90	90
β (°)	98.090(5)	90
γ (°)	90	90
Volume (Å^3)	1202.9(1)	5307.0(5)
d(calcd.) (g cm^{-3})	1.44	1.59
d(exptl.) (g cm^{-3})	1.38	1.62
μ(MoK$_\alpha$) (mm^{-1})	1.24	1.67
θ-range (°)	3 to 26	3 to 26
hkl-range	$-10 \leq h \leq 0$	$0 \leq h \leq 20$
	$-16 \leq k \leq 16$	$0 \leq k \leq 21$
	$-13 \leq l \leq 13$	$0 \leq i \leq 22$
Reflections collected	5050	5185
Indendent reflections	4721	5185
	(R(int) = 0.052)	(R(int) = 0.032)
Reflections observed	4282($I > 2\sigma$)	3903($1 > 2\sigma$)
Parameters	289	334
R_1 (obs. refl.)[a]	0.0354	0.0382
wR^2 (all refl.)[a]	0 1042	0.1064
Res. el. Densities	+0.3	+0.4
[10^{-6} e·pm^{-3}]	−0.2	−0.3

[a] $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

form of orange crystals, m.p. 165–166°C. Anal. Found: C, 48.96. H. 3.92; N. 2.47. $C_{23}H_{23}Fe_2NO_6$ (521.13) Calc.: C, 53.01; H, 4.45; N. 2.69. IR (pentane): 2066m, 2029vs, 2013w, 1993vs, 1985s, 1948w, 1870vw, 1859vw cm^{-1}. ^{1}H-NMR(CD_2Cl_2): $\delta = 1.18$–1.35 (m, 10H, Et), 2.25 (s, 3H, N–CH_3), 3.18 (s, 2H, C–CH_2–N), 3.60–3.72 (m, 2H, N–CH_2–Ph), 6.62 (s, 1H, Fe–CH), 7.28–7.34 (m, 5H, C_6H_5). ^{13}C-NMR(CD_2Cl_2): $\delta = 16.11$, 18.58, 22.17, 35.72, 42.19, 60.80, 63.14, 127.48, 128.53, 129.49, 131.57, 132.31, 139.10, 153.40, 182.12, 207.43, 211.06, 213.58. EI-MS: $m/z = 521$ (M^+). After crystallysation of **3** the mother liquor was again cooled to −20°C.

Dark green crystals separated from the solution giving 106 mg, (40%) of **4**, m.p. 197–198°C. Anal. Found: C, 46.82: H, 4.13: N, 2.22. $C_{25}H_{23}Fe_3NO_8$ (633.00) Calc.: C, 47.44: H, 3.66; N, 2.21. IR(hexane): 2061s, 2042vw, 2029w, 2017vs, 1993s, 1975w, 1956s, 1870w, 1859w, 1734s, brcm^{-1}. ^{1}H-NMR($CDCl_3$): $\delta = 0.50$ (t, $J = 6.5$ Hz, 3H, CH_3), 1.29 (q, $J = 6.5$ Hz, 2H, CH_2), 1.88 (t, $J = 7.1$ Hz, 3H, CH_3), 2.00 (s, 2H, C–CH_2–N), 2.05 (s, 3H, N–CH_3), 3.04 (q, $J = 7.1$ Hz, 2H, CH_2), 3.32 (s, 2H, N–CH_2–Ph), 7.04 (s, 1H, CH), 7.27–7.44 (m, 5H, C_6H_5). EI-MS: $m/z = 605$ (M^+–CO).

Structure determinations: [24] Crystals of **3** and **4** were obtained by slow evaporation from solutions in hexane. Diffraction data were taken by the $\omega/2\theta$ technique on a Nonius CAD4 diffractometer using graphite-filtered Mo–K$_\alpha$ radiation. They were treated without an absorption correction. The structures were solved with direct methods and refined anisotropically with the SHELX program suite [25]. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. Drawings were produced with SCHAKAL [26]. Table 3 lists the crystallographic data.

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