Buta-1,3-dienylidene versus Cyclopentylidene Bridging Ligands in the Reaction of Tetracyanoethylene with Substituted-Alkenylidene-Bridged Diiron Complexes. X-ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}\overline{CCH_2C(CH_3)_2C(CN)_2C}(CN)_2]$

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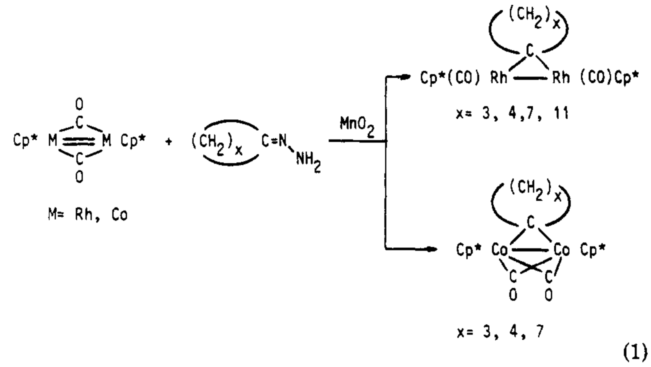
Substituted-alkenylidene-bridged diiron complexes $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)$ (R = CH_3 (2), $CH(CH_3)_2$ (4)) react with tetracyanoethylene to give different types of products depending on R. When R = CH_3 (2), the tricyanovinylation of the alkenylidene ligand affords the μ-3,4,4-tricyanobuta-1,3-dienylidene complex $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CCH_3C(CN){=}C(CN)_2]$ (3). The IR and NMR data indicate that the bridging ligand is a powerful π-acceptor. When R = $CH(CH_3)_2$ (4), a formal [3 + 2] cycloaddition accompanied by a 1,2-hydrogen shift occurs, leading to the novel tetracyano-substituted μ-cyclopentylidene complex $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}\overline{CCH_2C(CH_3)_2C(CN)_2C}(CN)_2]$ (5), characterized by an X-ray analysis. Crystals of 5 are monoclinic, space group $P2_1/n$, with a = 8.880 (3) Å, b = 17.112 (4) Å, c = 14.882 (4) Å, β = 105.33 (3)°, and Z = 4. The structure was refined to R = 0.041 and R_w = 0.035 for 2505 reflections with $I > \sigma(I)$. An elongated Fe–Fe bond (2.538 (3) Å) and Fe–(μ-C) bonds (Fe1–C14 = 2.024 (3) Å; Fe2–C14 = 2.030 (3) Å) associated with an Fe–(μ-C)–Fe angle of 77.5 (1)° reveal a relatively weak bonding between the μ-cyclopentylidene ligand and the bimetallic moiety, largely attributed to steric interactions and cycle strain within the bridging five-membered ring. The availability of a tertiary allylic hydrogen in 4, and not in 2, together with steric demands due to the bulkiness of the isopropyl group in 4 may explain the different reactivities of these complexes.

Introduction

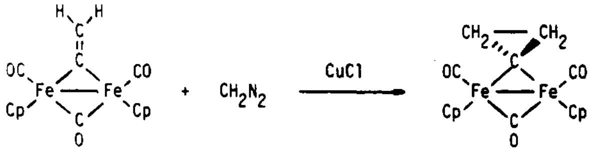
The synthesis and reactivity of μ-alkylidene bimetallic complexes have given rise to a plethora of papers and studies during the last 15 years. Excellent reviews emphasizing the structural and chemical aspects of their properties as well as their implication in catalysis are now available.[1] From all this literature, it appears that complexes containing a cyclic alkylidene bridging ligand, i.e. in which the bridging carbon atom can be described as a spiro carbon, are not very common. If we ignore those containing an heteroatom within the ring skeleton or those with unsaturated cyclic bridges, true μ-cycloalkylidene complexes remain an exceedingly small class of compounds. As far as we are aware, there are only two kinds of reactions that lead to that type of complex.

Herrmann and co-workers have extended the use of the diazoalkane route to the hydrazone route[2] (eq 1) for the synthesis of a whole family of Co and Rh μ-cycloalkylidene complexes, the carbon ring size of which varies from 4 (μ-C_4) to 12 (μ-C_{12}).



(1)

More recently, an interesting reaction involving the modification of a coordinated ligand has been discovered by Hoel and co-workers.[3] The reaction of diazomethane with the (μ-ethenylidene)diiron complex $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (1) leads to carbon–carbon coupling, a μ-cyclopropylidene (μ-C_3) diiron complex being isolated (eq 2).



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(2)

This reaction has been applied to substituted diazoalkanes[4a] and substituted alkenylidene ligands.[4b] When conducted under photochemical activation, it gives μ-allene complexes.[4a,5] These reactions are good indications that

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[1] (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (d) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81. (e) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339. (f) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[2] Herrmann, W. A.; Weber, C.; Ziegler, M. L.; Pahl, C. *Chem. Ber.* **1984**, *117*, 875.

[3] Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633.

[4] (a) Casey, C. P.; Austin, E. A. *Organometallics* **1986**, *5*, 584. (b) Hoel, E. L. *Ibid.* **1986**, *5*, 587.

[5] (a) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1986**, *5*, 585. (b) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106.

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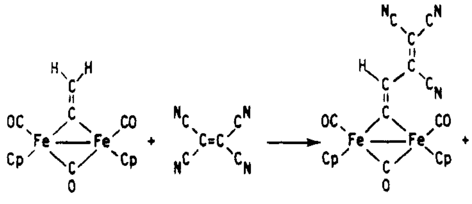
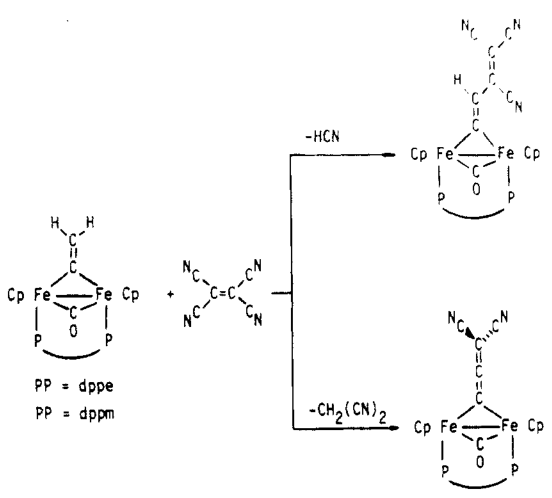
(μ-alkenylidene)diiron complexes can be viewed as 1,1-dimetalated electron-rich olefins, and this has also been suggested from the results of a theoretical analysis[6] on the μ-ethenylidene complex **1**. Following this idea, we have sought to study the reactivity of such complexes toward the electrophilic tetracyanoethylene (tcne). This unsaturated cyano compound has a rich organic and organometallic chemistry,[7] and particularly interesting are the studies of Huisgen showing[8] that tcne reacts with enol ethers, which are electron-rich olefins, to give cyclobutanes via zwitterionic intermediates ([2 + 2] cycloadditions). When tcne reacts with the μ-ethylidene complex **1** or its diphosphine-bridged congener, no (μ-cyclobutylidene)diiron complex is isolated, but μ-tricyanobuta-1,3-dienylidene[9] and μ-3,3-dicyanoallenylidene[10] complexes have been fully characterized (eqs 3 and 4).



1

(3)

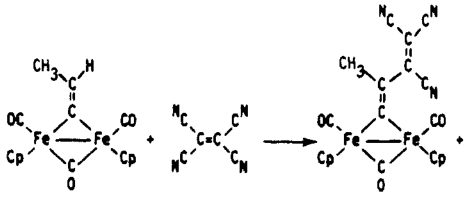


(4)

In the case of a singly substituted alkenylidene ligand, loss of malononitrile is not possible; we report here that the reaction of tcne with μ-alkenylidene complexes of the type [CpFe(CO)]$_2$(μ-CO)(μ-C=CHR) (R ≠ H) is dramatically dependent on the nature of the substituent R. When R = CH$_3$, the μ-buta-1,3-dienylidene derivative is formed, but when R = CH(CH$_3$)$_2$, a formal [3 + 2] cycloaddition leads to a rare (μ-cyclopentylidene)diiron complex.

Results and Discussion

The (μ-prop-1-enylidene)diiron complex[11] [CpFe(CO)]$_2$(μ-CO)(μ-C=CHCH$_3$) (**2**) and tcne in stoichiometric amounts react overnight in toluene to give a bright orange-red solution, from which crystals of the methyl-substituted μ-3,4,4-tricyanobuta-1,3-dienylidene complex [CpFe(CO)]$_2$(μ-CO)[μ-C=C(CH$_3$)C(CN)=C(CN)$_2$] (**3**) can be isolated in ca. 60% yield (eq 5). Full characterization of **3** includes analytical and spectroscopic data that compare well with those of the previously X-ray-characterized[9] (μ-tricyanobuta-1,3-dienylidene)diiron complex [CpFe(CO)]$_2$(μ-CO)[μ-C=CHC(CN)=C(CN)$_2$].



2 3

(5)

In the infrared spectrum of **3** (CH$_2$Cl$_2$ solution), two terminal carbonyl stretches appear at 2012 (vs) and 1980 (m) cm^{-1}, suggesting a cis arrangement of these groups.[11,12] It is interesting to note a pronounced hypsochromic shift, ca. 15 cm^{-1}, compared to the wavenumbers in the starting complex **2**. The substantially shifted bridging carbonyl band is observed at 1812 (m br) cm^{-1} for **3**, consistent with the μ-3,4,4-tricyano-2-methylbuta-1,3-dienylidene ligand being a very strong π-acceptor, stronger than simple alkenylidene ligands.[13] The nitrile stretch is observed at 2210 cm^{-1} as a medium-intensity band due to conjugation.

In the ^{1}H NMR spectrum of **3**, the methyl group (δ 3.12) is somewhat deshielded compared to that in **2**. ^{13}C NMR spectroscopy has proved to be a powerful tool for the identification of the four-carbon chain of buta-1,3-dienylidene bridging ligands.[9,10,14,15] The bridgehead carbon C$_\alpha$ resonance appears at δ 335.7, far downfield. Moving away stepwise from the bridgehead, we find signals at δ 143.3 and 138.0, respectively, for C$_\beta$ and C$_\gamma$. Highly shielded, C$_\delta$ gives rise to a resonance at δ 77.8. These features again demonstrate the great electron-withdrawing abilities of the 3,4,4-tricyanobuta-1,3-dienylidene ligand.

The observed reaction is thus a tricyanovinylation of the alkenylidene ligand. This type of reaction occurs between tcne and aromatic amines,[7] and interestingly, it has been shown to compete with [2 + 2] cycloadditions in the reactions of certain exocyclic olefins and tcne.[7,16] Up to now, we have not characterized a hypothetical μ-cyclobutylidene complex of the type [CpFe(CO)]$_2$(μ-CO)[μ-CCHRC(CN)$_2$C(CN)$_2$].

When we turned to the reaction between the isopropyl-substituted (μ-alkenylidene)diiron complex[11] [CpFe(CO)]$_2$(μ-CO)[μ-C=CHCH(CH$_3$)$_2$] (**4**) and tcne, we found to our surprise that the tricyanovinylation did not occur (^{1}H NMR). Crystals of the new μ-cyclopentylidene complex [CpFe(CO)]$_2$(μ-CO)[μ-CCH$_2$C(CH$_3$)$_2$C(CN)$_2$C(CN)$_2$] (**5**) could be obtained from a filtered toluene reaction mixture containing **4** and tcne in stoichiometric amounts (eq 6).

Elemental analysis clearly showed the presence of four nitrogen atoms in the molecule. Spectroscopic data, fully interpreted after an X-ray diffraction analysis (see below),

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(6) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 8241.

(7) Recent reviews on tcne chemistry: Fatiadi, A. J. *Synthesis* **1986**, 249; **1987**, 749, 959.

(8) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117, 199.

(9) Etienne, M.; Toupet, L. *J. Organomet. Chem.* **1988**, *344*, C19.

(10) Etienne, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1989**, 1110.

(11) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043.

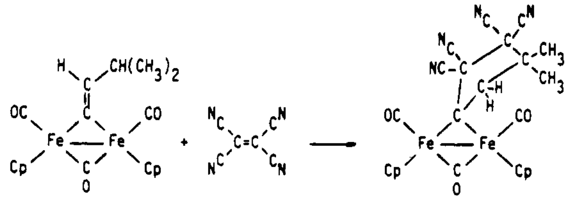
(12) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499.

(13) Basic review on alkenylidene and allenylidene metal complexes: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(14) (a) Etienne, M.; Guerchais, J. E. *J. Organomet. Chem.* **1986**, *314*, C81. (b) Etienne, M.; Guerchais, J. E. *J. Chem. Soc., Dalton Trans.* **1989**, 2187.

(15) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411.

(16) It is also interesting to note that stable cyclobutanes are obtained in the reaction of tcne with enol ethers,[8] whereas tricyanobutadienes are produced when enamines react with tcne; see: Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312.



4 5 (6)

indicated the rearrangement of both the isopropyl group and the alkenylidene function. In the infrared spectrum of **5**, no characteristic hypsochromic shift (see above) is observed for the carbonyl absorptions (1990 (vs), 1960 (m), and 1800 (m br) cm^{-1} in CH_2Cl_2); neither is a band due to any conjugated nitrile group detected. Only in a solid-state spectrum (Nujol mull) are very weak bands present at higher energy at 2240 and 2220 cm^{-1}. Such a behavior, distinguishing conjugated from nonconjugated nitriles, has been observed by others[17] in cyano-substituted hydrocarbyl complexes. In the ^1H NMR spectrum, the methylene, methyl, and cyclopentadienyl resonances appear as singlets at, respectively, δ 4.02, 1.89, and 5.18. Although the hydrogens of the methylene group are diastereotopic, no splitting of their signal due to an AB type spectrum, but simply broadening, was observed by cooling an acetone-d_6 solution of **5** down to −90 °C. This suggests that the inversion motion of the five-membered ring is just becoming slower at this temperature but is not frozen out. Indicative of a bridging alkylidene carbon[1,18] is the observation, in the ^{13}C NMR spectrum of **5**, of a non-hydrogen-coupled resonance at δ 166.6. The methylene carbon resonance appears at δ 72.1 (t, $^1J_{CH}$ = 133 Hz).

Crystal Structure of $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}CCH_2C(CH_3)_2C(CN)_2C(CN)_2]$ (5). Crystals of **5** suitable for X-ray diffraction analysis were obtained from a filtered and concentrated reaction mixture. A summary of crystallographic data and experimental conditions is given in Table I. Positional parameters and bond lengths and angles are provided in Tables II and III, and a perspective view of the molecule is depicted in Figure 1.

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Analysis of 5

formula	$Fe_2O_3N_4C_{24}H_{18}$
mol wt	570.2
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.880 (3)
b, Å	17.112 (4)
c, Å	14.882 (4)
β, deg	105.33 (3)
V, Å^3	2180.8 (6)
Z	4
cryst dimens, mm	0.10 × 0.12 × 0.20
D(calcd), Mg m^{-3}	1.74
F(000)	1040
radiatn	Mo Kα (0.71073 Å)
abs coeff, cm^{-1}	12.3
scan type	$\omega/2\theta = 1$
$2\theta_{max}$, deg	50
data collected	$0 \leq h \leq 10$, $0 \leq k \leq 20$, $-17 \leq l \leq +17$
no of reflns measd	4194
no. of reflns with $I > \sigma(I)$	2505
no. of variables	353
R	0.041
R_w	0.035
S_w, goodness of fit	1.42
Δe, final electron density, eÅ^{-3}	0.28

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Fe1	0.85066 (6)	0.05974 (3)	0.17281 (3)	2.54 (1)
Fe2	0.92772 (6)	0.11900 (3)	0.33488 (3)	3.03 (1)
O1	1.4044 (3)	0.4512 (2)	0.3376 (2)	5.52 (8)
O2	1.2172 (4)	0.0500 (2)	0.4401 (2)	6.83 (9)
O3	1.1584 (4)	0.0457 (2)	0.6762 (2)	5.17 (8)
N1	1.4447 (4)	0.2830 (2)	0.1744 (3)	4.91 (9)
N2	1.3036 (4)	0.2477 (2)	0.4140 (2)	4.82 (9)
N3	1.3605 (4)	0.0631 (2)	0.2805 (3)	4.59 (9)
N4	1.1300 (4)	0.1477 (2)	0.0236 (2)	4.84 (9)
C1	0.6763 (5)	−0.0150 (2)	0.0935 (3)	4.2 (1)
C2	0.6055 (4)	0.0389 (3)	0.1389 (3)	4.0 (1)
C3	0.6335 (5)	0.1141 (2)	0.1077 (3)	4.0 (1)
C4	0.7194 (5)	0.1050 (2)	0.0423 (3)	3.91 (9)
C5	0.7477 (5)	0.0255 (3)	0.0345 (3)	4.1 (1)
C6	0.8185 (6)	0.2246 (3)	0.3640 (3)	7.0 (1)
C7	0.7082 (6)	0.1679 (3)	0.3424 (3)	5.8 (1)
C8	0.7476 (5)	0.1078 (3)	0.4047 (3)	4.9 (1)
C9	0.8859 (6)	0.1252 (3)	0.4671 (3)	6.1 (1)
C10	0.9347 (6)	0.1994 (3)	0.4414 (3)	7.6 (1)
C11	1.1095 (5)	0.0785 (3)	0.3916 (3)	4.3 (1)
C12	1.0068 (4)	−0.0022 (2)	0.1694 (3)	3.49 (9)
C13	0.8629 (4)	0.0149 (2)	0.2917 (3)	3.40 (9)
C14	0.9751 (4)	0.1581 (2)	0.2165 (2)	2.37 (7)
C15	0.9147 (4)	0.2380 (2)	0.1739 (2)	2.97 (8)
C16	1.0496 (5)	0.2999 (2)	0.1949 (3)	3.43 (9)
C17	1.2013 (4)	0.2476 (2)	0.2331 (2)	2.90 (8)
C18	1.1423 (4)	0.1620 (2)	0.2011 (2)	2.67 (8)
C19	1.3363 (4)	0.2694 (2)	0.1990 (3)	3.41 (9)
C20	1.2551 (4)	0.2474 (2)	0.3354 (2)	3.11 (8)
C21	1.2613 (4)	0.1048 (2)	0.2487 (3)	2.97 (8)
C22	1.1344 (4)	0.1547 (2)	0.0999 (3)	3.16 (8)
C23	1.0576 (5)	0.3432 (3)	0.1068 (3)	4.7 (1)
C24	1.0321 (5)	0.3602 (2)	0.2681 (3)	4.6 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Complex **5** consists of two (η^5-C_5H_5)Fe(CO) units in a cis arrangement, bridged by a carbonyl group and a 2,2,3,3-tetracyano-4,4-dimethylcyclopentylidene group. The overall geometry is that observed[1] for any complex of the type *cis*-$[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}L)$. The cyclopentylidene unit is oriented in such a manner that the methylene group, in the β-position with respect to the bridging carbon, is syn to the cyclopentadienyl groups. It seems safe to propose that this arises from minimization of steric interactions.[19] The sp^3-type hybridization of the bridging carbon is evidenced by an 86.9 (2)° angle between the planes Fe1–C14–Fe2 and C15–C14–C18. The iron atoms are at a single-bond distance of 2.538 (3) Å. This bond length is longer than that of the μ-ethylidene congener *cis*-$[CpFe(CO)]_2(\mu\text{-}CHCH_3)$ (2.520 (2) Å) and seems to be the longest in that type of compound.[3] In complex **5**, the iron–bridging-carbon bond lengths (Fe1–C14 = 2.024 (3) Å and Fe2–C14 = 2.030 (3) Å) are markedly longer than those in the μ-ethylidene complex (1.987 (1) Å). In the same way, the internal angle (Fe1–C14–Fe2 = 77.5 (1)°) is smaller than that of the μ-ethylidene complex (78.9 (1)°). Taken altogether, these observations indicate a weaker bonding between the bridging ligand and the $[CpFe(CO)]_2(\mu\text{-}CO)$ moiety compared to that in its μ-ethylidene congener. This can be most probably attributed to a more important steric congestion in **5** due to the substituents within the five-membered ring, which will overcome small

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(17) See for example: Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494, 501.

(18) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

(19) (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441. (b) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1427. (c) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024.

Table III. Bond Lengths (Å) and Angles (deg) with Esd's for 5

Bond Lengths					
Fe1-Fe2	2.538 (3)	N3-C21	1.134 (4)	C14-C15	1.543 (4)
Fe1-C12	1.756 (4)	N4-C22	1.132 (4)	C14-C18	1.562 (4)
Fe1-C13	1.906 (3)	C1-C2	1.389 (5)	C15-C16	1.567 (5)
Fe1-C14	2.024 (3)	C1-C5	1.394 (5)	C16-C17	1.591 (5)
Fe2-C11	1.754 (4)	C2-C3	1.412 (5)	C16-C23	1.524 (5)
Fe2-C13	1.929 (4)	C3-C4	1.395 (6)	C16-C24	1.539 (5)
Fe2-C14	2.030 (3)	C4-C5	1.394 (6)	C17-C18	1.586 (4)
O1-C12	1.145 (4)	C6-C7	1.355 (8)	C17-C19	1.468 (5)
O2-C11	1.144 (4)	C6-C10	1.396 (8)	C17-C20	1.469 (4)
O3-C13	1.177 (3)	C7-C8	1.368 (6)	C18-C21	1.477 (4)
N1-C19	1.141 (4)	C8-C9	1.362 (7)	C18-C22	1.495 (4)
N2-C20	1.135 (4)	C9-C10	1.427 (8)	Fe1-Ct′	1.757 (5)
				Fe2-Ct″	1.770 (5)
Bond Angles					
Fe2-Fe1-C12	104.6 (2)	C7-C8-C9	108.7 (5)	C17-C16-C24	111.0 (3)
Fe2-Fe1-C13	49.0 (2)	C8-C9-C10	107.1 (5)	C23-C16-C24	108.6 (3)
Fe2-Fe1-C14	51.36 (8)	C6-C10-C9	106.6 (5)	C16-C17-C18	103.3 (2)
Fe1-Fe2-C11	106.4 (1)	Fe1-C12-O1	172.4 (3)	C16-C17-C19	115.1 (3)
Fe1-Fe2-C13	48.2 (2)	Fe1-C13-O3	139.1 (3)	C16-C17-C20	112.7 (3)
Fe1-Fe2-C14	51.13 (8)	Fe2-C11-O2	169.0 (3)	C18-C17-C19	111.4 (3)
C12-Fe1-C13	86.1 (2)	Fe2-C13-O3	138.1 (3)	C18-C17-C20	107.5 (3)
C12-Fe1-C14	98.2 (1)	Fe1-C13-Fe2	82.9 (1)	C19-C17-C20	106.7 (3)
C13-Fe1-C14	98.3 (1)	Fe1-C14-Fe2	77.5 (1)	C14-C18-C17	104.3 (2)
C11-Fe2-C13	87.2 (2)	Fe1-C14-C15	120.3 (2)	C14-C18-C21	119.2 (3)
C11-Fe2-C14	99.9 (1)	Fe1-C14—C18	116.6 (2)	C14-C18-C22	110.5 (3)
C13-Fe2-C14	97.3 (1)	Fe2-C14-C15	121.3 (2)	C17-C18-C21	109.3 (3)
C2-C1-C5	108.4 (4)	Fe2-C14-C18	124.4 (2)	C17-C18-C22	107.7 (3)
C1-C2-C3	107.7 (4)	C15-C14-C18	98.2 (3)	C21-C18-C22	105.3 (3)
C2-C3-C4	107.7 (4)	C14-C15-C16	110.6 (3)	N1-C19-C17	176.6 (4)
C3-C4-C5	108.1 (4)	C15-C16-C17	102.9 (3)	N2-C20-C17	176.8 (4)
C1-C5-C4	108.1 (4)	C15-C16-C23	111.4 (3)	N3-C21-C10	174.1 (4)
C7-C6-C10	107.7 (5)	C15-C16-C24	112.3 (3)	N4-C22-C18	178.6 (4)
C6-C7-C8	109.8 (5)	C17-C16-C23	110.7 (3)	Fe1-Fe2-Ct′	132.7 (4)
				Fe2-Fe1-Ct″	134.9 (4)

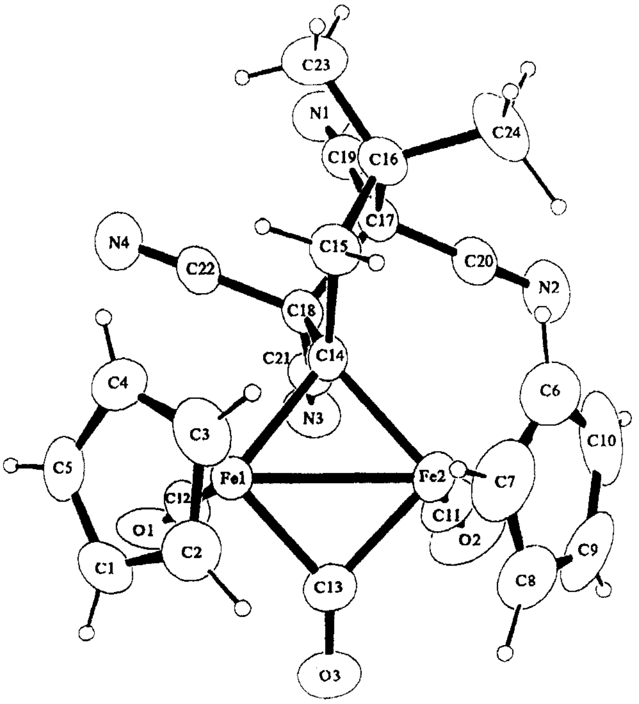

Figure 1. ORTEP plot of $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}\overline{CCH_2C(CH_3)_2C(CN)_2C}(CN)_2]$ (5).

differences in π-accepting properties of the two ligands. A certain ring strain, especially obvious if one considers the bonding angles around the bridging spiro carbon, may also participate in the weakening of the bonding. Although these angles roughly remain in the known ranges,[1] the external angle (C15–C14–C18 = 98.2 (3)°) is notably acute. It must be compared to other external angles in rare μ-cycloalkylidene complexes for which structures are available. The only compounds of which we are aware have been described in the Introduction. These are (i) $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(\mu\text{-}\overline{C(CH_2)_2CH_2})$ (A), a μ-cyclobutylidene complex[2] with no additional carbonyl bridge, and (ii) the (μ-cyclopropylidene)diiron complex[3] $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}\overline{CCH_2CH_2}]$ (B).

A marked decrease of the external angle is obvious as the ring size decreases (for A 89.7 (4)°, for B 59.4 (9)°); i.e., the larger the ring size, the less distorted the bonding around the bridging carbon. This can be attributed to a decrease in the cycle strain, which is reduced for larger rings. (In B, electronic factors certainly actively participate because of the similarity between cyclopropyl groups and double bonds[3].) The internal angles show more subtle differences that have already been discussed.[1a]

Apart from the bridging carbon, which is unique to 5, the bond angles and distances within the five-membered ring compare well with those of σ-metalated tetracyano-substituted cyclopentyl derivatives,[20-22] with small variations of the torsional angles.[21] An important feature is that the angle around the methylene group (C14–C15–C16 = 110.6 (3)°) is rather large compared to the other angles within the ring, and this can again be attributed to cycle and bridging bonding strains, which are here alleviated at the less congested site.

Of particular interest with respect to the mechanism of the reaction that leads to this μ-cyclopentylidene complex is the topology of the ligand: tcne is bonded to the bridging carbon and to the carbon bearing the methyl groups, i.e.,

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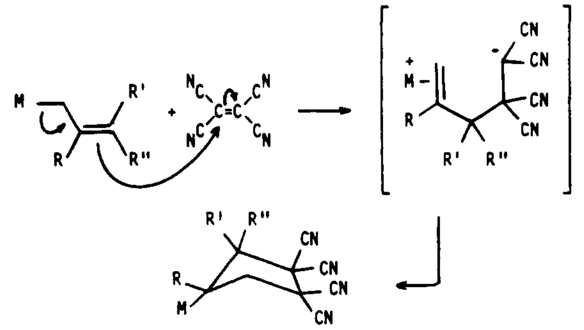
Scheme I



to the carbon that was the tertiary allylic carbon of the isopropyl group in 4. This apparent [3 + 2] cycloaddition is thus accompanied by a formal 1,2-hydrogen shift from the isopropyl allylic position to the β-carbon of the μ-alkenylidene complex 4. The substituent arrangement is thus completely different from that observed in the above-quoted cyclopentyl derivatives resulting from [3 + 2] cycloadditions of tcne with σ-allyl complexes: in these cases, an ionic mechanism[23,24] is responsible for a 1,2-*metal shift* that places the cyano groups on the remote carbons with respect to the metal (Scheme I).

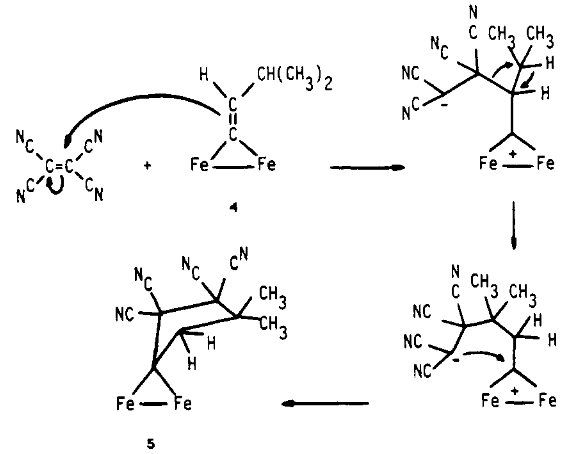
In the case of the reaction we describe, it is a hydrogen that apparently undergoes a 1,2-shift; the bimetallic moiety remains bonded to the same carbon atom.

Reaction 6 has been studied by ^{1}H NMR spectroscopy, but efforts to gain insights into a possible mechanism have been frustrated by an important loss of resolution of the spectra so obtained, precluding any interpretation. Nevertheless, there is some evidence that the γ-hydrogen in 4 is undoubtedly highly reactive. First, it is allylic, and second, it is bonded to a tertiary carbon, a distinguishing feature between complexes 2 and 4. It has been shown[15,25] that this hydrogen can be easily abstracted as an hydride to give a stable cationic μ-vinylcarbyne complex. Moreover, due to steric demand around the bulky isopropyl group, conformational effects that would place this hydrogen in a favored position may play an important role. A first step of a possible mechanism (Scheme II) would involve electrophilic attack of tcne at the β-carbon of 4, generating a 1,4-dipole, followed by an extension occurring with the migration of the allylic hydrogen and then ring closure. The rearrangement might also take place because of the subsequent formation of a five-membered ring, more stable than a hypothetical, strained, substituted-cyclobutylidene bridging ligand.

Experimental Section

All reactions were performed under a nitrogen atmosphere with use of standard Schlenk techniques. Toluene was obtained from purple sodium–benzophenone solutions. CH_2Cl_2 and hexane were dried by refluxing over CaH_2. Solvents were degassed before use. Deuterated solvents for NMR studies were dried over molecular sieves and degassed before use. IR spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. NMR spectra were recorded on a JEOL FX 100 spectrometer operating at 99.60 MHz for ^{1}H and 25.05 MHz for ^{13}C. Analytical data[26] were collected by the Service Central d'Analyse du CNRS, Villeurbanne, France.

Scheme II



The complex $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$ (2) was synthesized according to a published procedure.[11] The synthesis of $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHCH(CH_3)_2]$ (4) was derived from a published procedure[28] for related complexes and involved treatment of $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C\text{-}CH{=}C(CH_3)_2]^+BF_4^-$ with $LiBEt_3H$ followed by salt elimination on a short column of alumina. Tcne was sublimated before use.

$[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CCH_3C(CN){=}C(CN)_2]$ (3). Tcne (0.070 g, 0.55 mmol) and complex 2 (0.203 g, 0.55 mmol) dissolved in toluene (40 mL) were stirred for 18 h in the dark. During this time a precipitate formed and the solution turned bright orange-red. The solution was filtered, concentrated (ca. 15 mL), and set aside to deposit crystals of 3. The precipitate formed during the reaction could be extracted with CH_2Cl_2 and recrystallized from a CH_2Cl_2/hexane mixture to give additional 3, which was washed with pentane and dried under vacuum. Repeated column chromatography and/or recrystallization failed to give perfect carbon analysis; typical combined yield 0.165 g, 0.35 mmol, 64%. Anal. Calcd for $C_{21}H_{13}Fe_2N_3O_3$: C, 54.0; H, 2.8; N, 9.0. Found: C, 53.1; H, 2.8; N, 8.9. MS (70 eV, EI): *m/z* 467 (M^+), 439 ($[M - CO]^+$), 411 ($[M - 2CO]^+$), 383 ($[M - 3CO]^+$). IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2210 (m); ν_{CO} 2012 (vs), 1980 (m), 1812 (s br); $\nu_{C=C}$ 1460 (m). ^{1}H NMR (acetone-d_6): δ 5.33 (s, 10 H, C_5H_5), 3.12 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.075 M $Cr(acac)_3$): δ 335.7 (μ-*C*), 261.1 (μ-*C*O), 207.5 (Fe–*C*O), 143.3 (μ-C=*C*), 138.0 (μ-C=C(CH_3)*C*(CN)=C(CN)$_2$), 115.9, 114.2, 113.7 (*C*N), 89.3 (C_5H_5), 77.5 (μ-C=C(CH_3)C(CN)=*C*(CN)$_2$, obscured by solvent; value obtained in acetone-d_6), 29.8 (*C*H_3).

$[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}\overline{CCH_2C(CH_3)_2C(CN)_2C}(CN)_2]$ (5). Tcne (0.063 g, 0.5 mmol) and complex 4 (0.197 g, 0.5 mmol) were mixed as for the reaction between 3 and tcne, and similar workup led to crystalline 5 (0.158 g, 0.3 mmol, 60%). complex 5 was found to be not very stable in solution, and obtention of a reliable ^{13}C NMR spectrum proved difficult. Anal. Calcd for $C_{24}H_{18}Fe_2N_4O_3$: C, 55.2; H, 3.45; N, 10.7. Found: C, 54.6; H, 3.43; N, 10.8. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1990 (s), 1960 (m), 1800 (m br). IR (Nujol, cm^{-1}): ν_{CN} 2240, 2220 (vw). ^{1}H NMR (acetone-d_6): δ 5.18 (10 H, C_5H_5), 4.02 (s, 2 H, CH_2), 1.89 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 263.9 (μ-*C*O), 212.6 (Fe–*C*O), 166.6 (μ-*C*), 116.0, 113.5 (*C*N), 91.9 (C_5H_5), 72.1 (t, $^1J_{CH}$ = 133 Hz, from coupled spectrum, *C*H_2), 48.6 (*C*(CH_3)$_2$), 31.4 (*C*H_3, obscured by solvent, value obtained in CD_2Cl_2). Other carbon resonances (*C*(CN)$_2$) were not observed.

X-ray Analysis of 5. Crystals of 5 suitable for X-ray work were obtained from a filtered, concentrated toluene reaction mixture. Intensity data were obtained on an Enraf-Nonius CAD-4 automatic diffractometer. Cell dimensions were obtained and refined from a set of 25 high-θ reflections. The scattering factors were taken from ref 29. The structure was solved by a combi-

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(26) We have observed systematic low carbon analyses for the compounds reported herein. Others have had similar problems with related diiron complexes.[27]

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Organometallics **1990**, *9*, 2028–2033

nation of Patterson function and Fourier differences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were defined between 0.58 and 0.33 e Å^{-3} and refined isotropically. The weighting scheme used was $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{1/2}$. The best full-matrix least-squares refinement of the structure[30] (x, y, z, β_{ij} for non-hydrogen atoms and x, y, z for hydrogen atoms) gave $R_w = 0.035$ (goodness of fit $S_w = 1.42$). See Table I for full details of the analysis. Positional parameters are given in Table II, and bond lengths and angles are provided in Table III.

Supplementary Material Available: Tables of general temperature factor expressions, torsional angles, hydrogen positional parameters, and C–H bond distances (5 pages); a table of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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[30] All calculations were performed by using the SDP package provided by Enraf-Nonius.

Synthesis, Characterization, and X-ray Studies of Nonplanar Mesogens: Carboxylato-Bridged Orthopalladated Azine Complexes

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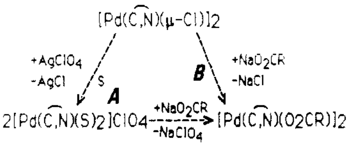
The family of book-shaped orthopalladated dimers $[Pd(H_{21}C_{10}OC_6H_3CH{=}NN{=}CHC_6H_4OC_{10}H_{21})(\mu\text{-}O_2CC_nH_{2n+1})]_2$ (n = 0–11, 13, 15, 17), which show mesogenic behavior influenced by the length of the bridging carboxylate, have been prepared. The shortest (n = 1–3) and longest ($n \geq 10$) carboxylates give rise to more ordered mesophases and wider ranges of mesogenic behavior than the carboxylates of medium length. This is interpreted as a consequence of the molecular packing being disturbed on changing from short to medium chains and facilitated again when the carboxylate chains are long enough to situate themselves parallel to the azine chains. X-ray diffraction studies on monodomains give evidence of a peculiar molecular packing in these mesophases: some palladium–palladium correlations are found, which indicate the tendency to both a lateral association and a longitudinal shifting between neighboring molecules.

Introduction

Rodlike molecules containing rigid cores have traditionally been regarded as having the most suitable geometry to give rise to mesogenic behavior[1,2] In 1977, a new type of thermotropic compound, based on disklike molecules, was discovered[3] and since then other molecular shapes described as cone-shaped,[4] lamellar,[5,6] phasmids,[7] and sandwich-shaped[8] have been reported to give mesogens.

The synthesis of liquid crystals based on organometallic or coordination compounds opens new perspectives in the design of mesogenic molecules. In this respect we have recently reported the unexpected finding of mesogenic behavior in the book-shaped orthopalladated dimers $[Pd(R'OC_6H_3CH{=}NN{=}CHC_6H_4OR')(\mu\text{-}O_2C\text{-}CH_3)]_2$ (R' = n-C_nH_{2n+1}; n = 6–10, 12, 14).[9]

Scheme I



$\widehat{C,N}$ = $H_{21}C_{10}OC_6H_3$-CH=N-N=CH-C_6H_4-$OC_{10}H_{21}$
R = C_nH_{2n+1}, n=0-11,13,15,17
S = acetone

The presence of a metal atom, in addition, makes it possible to synthesize related derivatives by means of very simple coordination chemistry, which can be advantageous in comparison with the usually more tedious procedures when a series of related molecules is needed. Thus, we have shown how optical activity can easily be introduced in the above-mentioned complexes simply by replacing the bridging acetate with (R)-2-chloropropionate.[10]

We were intrigued by the possibility of using the bridging system in our open-book-shaped molecules as a tuner of their thermotropic properties. Changing the

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