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Reaction of Diphenylacetylene and Diphenyldiazomethane on the Carbene Bond of $[Fe_2(CO)_7\{\mu,\eta^2\text{-}C(Me)CN(C_2H_5)_2\}]$ Leading to $[Fe_2(CO)_6\{C(Me)C(NEt_2)C(Ph)C(Ph)\}]$ and to $[Fe_2(CO)_6\{C(Me)C(NEt_2)NN(CPh_2)\}]$

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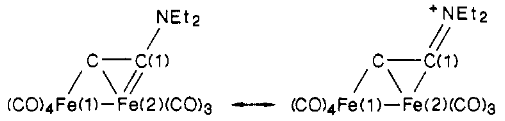
Syntheses and single-crystal X-ray diffraction studies have been completed on two compounds prepared by reacting the dinuclear complex $[Fe_2(CO)_7\{\mu,\eta^2\text{-}C(Me)C(NEt_2)\}]$ (compound 1) with diphenylacetylene giving compound 2 and with diphenyldiazomethane giving compound 3. The reaction involves the aminocarbene of 1. Crystal data for compound 2 $[Fe_2(CO)_6\{C(Me)C(NEt_2)C(Ph)C(Ph)\}]$: monoclinic, $P2_1/c$, a = 8.687 (1), Å, b = 32.006 (4) Å, c = 9.728 (2) Å, β = 103.96 (1)°, R_w = 0.0304 for 2549 reflections. It is another example of ferracyclopentadiene complexes that may result from the cycloaddition of diphenylacetylene on the Fe=C carbene bond followed by a rearrangement. Crystal data for compound 3 $[Fe_2(CO)_6\{\mu,\eta^3\text{-}C(Me)C(NEt_2)NN(CPh_2)\}]$: orthorhombic, $P2_12_12_1$, a = 10.065 (3) Å, b = 13.609 (3) Å, c = 19.332 (3) Å, R_w = 0.0419 for 2143 reflections. It contains a five-membered heterocycle that is bonded to the first iron atom by a μ,η^3-azaallyl group and by a dative bond from the other nitrogen to the second iron atom; this may result from the nucleophilic attack of the α-nitrogen atom of the diazo group on the electrophilic aminocarbene carbon atom.

In a preceding paper we described the synthesis and the structure of an iron dinuclear complex 1 $[Fe_2(CO)_7\{\mu,\eta^2\text{-}C(Me)CNEt_2\}]$[1] containing one aminoalkyne molecule attached to the iron atoms by a bridging carbene and a terminal carbene.



Such a particular bonding mode of the triple bond onto two metal centers is attributed to an electron delocalization on the C–C bond, on the Fe(2)–C bond, and on the C–N bond with the participation of the nitrogen lone pair. Indeed the X-ray structure of 1 shows short bond lengths for Fe–C = 1.878 Å and C–N = 1.327 Å. It suggests an electron-deficient C(1) carbon atom which then should present some electrophilic behavior; as a matter of fact it can be considred as an aminocarbene which is known to behave this way.[2] We undertook the study of the reactions of 1 toward various reagents. First of all, we showed that this compound may add one more molecule of aminoalkyne to yield a mixture of cycloferrapentadiene and diferracycloheptadiene in the ratio 70/30.[1]

In a search for carbon–carbon bond-forming reactions starting from this diiron complex, we explored its reactivity toward unsaturated ligand molecules such as alkynes, diazoalkanes, isocyanates, and heterocumulenes. We describe herein some reactions in which diphenylacetylene and diphenyldiazomethane are added to complex 1. It is assumed that the first step of this addition reaction is a cycloaddition on the Fe=C bond in the case of diphenylacetylene leading to $[Fe_2(CO)_6\{CMeCNEtCPhCPh\}]$ (2) or a nucleophilic attack of the α-nitrogen of the diazoalkane molecule on the carbene carbon atom, then yielding a product of formula $[Fe_2(CO)_6\{CMeCNEt_2NN(CPh_2)\}]$ (3). Their structures have been determined by X-ray diffraction.

Results and Discussion

Compound 2. The reaction of diphenylacetylene in excess with 1 occurs under reflux in hexane within 3 h leading to complex 2 which is formed in 70% yield. The reaction mixture was separated by chromatography. A green unstable compound was observed but not isolated. Complex 2 can also be formed in quantitative yield under CO pressure in hexane at 50 °C. Compound 2 is not airsensitive as a pure solid and is soluble in nonpolar solvents. Yellow crystals are obtained from an hexane solution.

The reason why CO pressure enhances the formation of 2 is not clear. However, the following mechanism might be assumed: CO pressure prevents the loss of CO and the first step would be a cycloaddition of the incoming alkyne triple bond to the Fe=C bond to form a ferracyclobutene as suggested by Semmelhack and Park to explain the reaction of (aminocarbene)iron complexes $[(CO)_4Fe{=}C(Ph)(NMe_2)]$ with alkynes.[3] This intermediate could then rearrange to form the more stable cycloferrapentadiene ring (Scheme I, a). Under normal pressure the side-on coordination of the alkyne triple bond on a vacant site created by the loss of a CO group might compete with the attack onto the Fe=C bond, resulting in the formation of different products as, for example, the above-mentioned green product.

The molecular structure of 2 is shown in Figure 1 which specifies the atom-labeling scheme. Intramolecular distances and angles are indicated in Table I. The molecule can be described as another example of well-known metallacyclopentadiene complexes.[4] Two $Fe(CO)_3$ moieties are linked by a Fe–Fe bond, 2.4975 (8) Å; Fe(1) forms two σ-bonds with the terminal carbon atoms of a butadiene group that is π-bonded to Fe(2). However, in the present case, this alkyne addition leads to an asymmetrical ferracyclopentadiene fragment. Only a few examples are known

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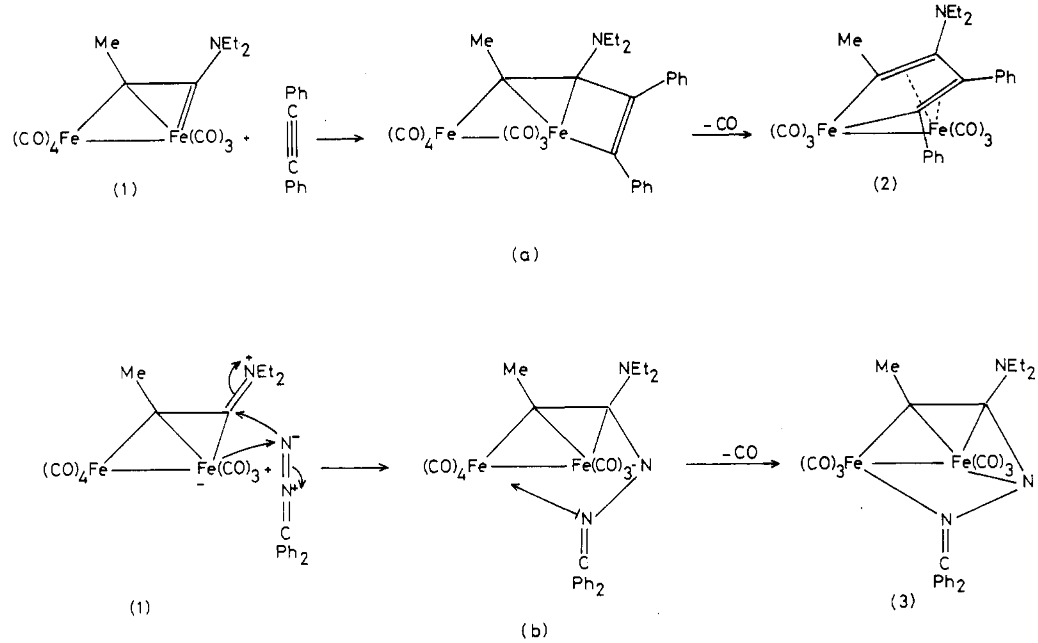
Scheme I



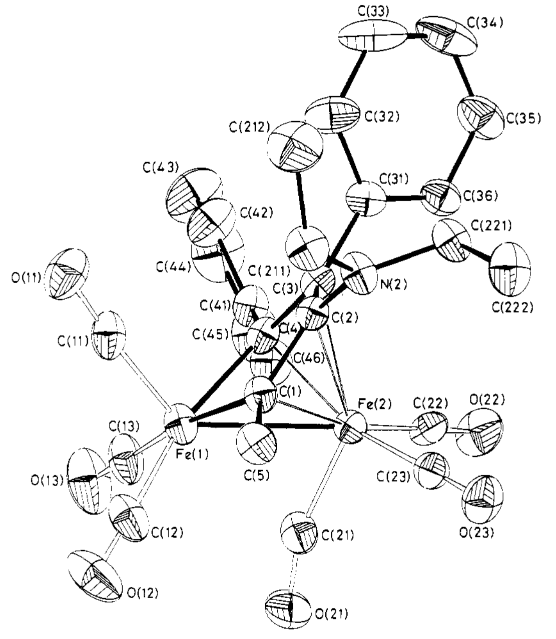


Figure 1. ORTEP view of compound 2 with the atom-labeling scheme. Ellipsoids represent 30% probability.

that were prepared by different routes.[5] As observed in previous structures, the Fe(1)–C(1)–C(2)–C(3)–C(4) ring is folded around C(1)–C(4) with Fe(1) located 0.38 Å above the butadiene plane; the two Fe(1)–C(1) and Fe(1)–C(4) distances (2.071 (3) and 2.050 (4) Å) are much shorter than the two Fe(2)–C(2) and Fe(2)–C(3) bonds (2.230 (3) and 2.172 (4) Å). These last distances are significantly different because of the different electron-donating abilities of $N(C_2H_5)_2$ and C_6H_5, respectively, fixed on C(2) and C(3). Indeed in $[Fe_2(CO)_6\{C_4(Me)_2(NEt_2)_2\}]$, 2.24 Å was observed for $Fe–CN(C_2H_5)_2$[6] whereas 2.14 Å was observed for $Fe–C(C_6H_5)$ in $[Fe_2(CO)_6(C_4Ph_4)]$.[7]

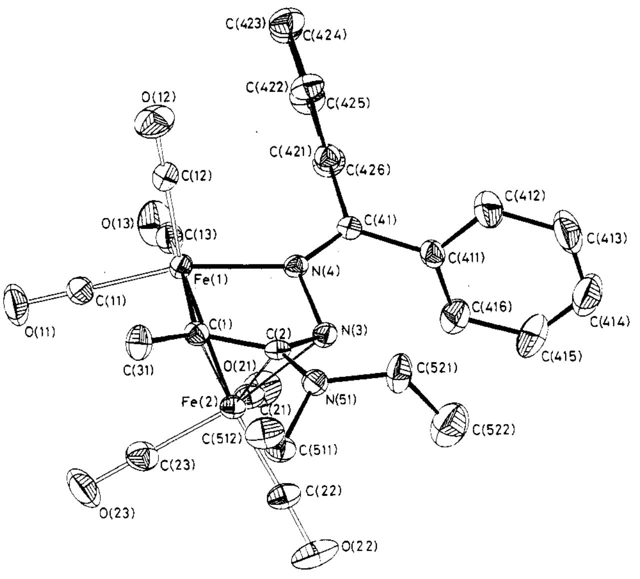


Figure 2. ORTEP view of compound 3 with the atom-labeling scheme. Ellipsoids represent 30% probability.

Compound 3. Complex 1 rapidly adds nearly quantitatively one molecule of diphenyldiazomethane, $(C_6H_5)_2CN_2$, at 40 °C in CH_2Cl_2 solution. The structure was confirmed by X-ray diffraction (vide infra). Dark red crystals were obtained by cooling a CH_2Cl_2 solution. The crystals are not air-sensitive and are also soluble in THF and sparingly soluble in hexane or cyclohexane. The formation of complex 3 can be explained as follows. Let us consider the canonical form $Ph_2C{=}N^+{=}N^-$. A nucleophilic attack of the α-nitrogen at the terminal carbene centre is considered to be the first step resulting in an azaallyl group attached on Fe(2). Then the second nitrogen gives its lone pair to Fe(1) forming the five-membered ring (Scheme Ib).

Contrary to our expectation, the phenyldiazomethane did not behave as a one-carbon fragment precursor for carbon–carbon bond synthesis, but an intact diazoalkane molecule has been added to 1. Although in a few instances stable transition-metal complexes of diazoalkanes have been structurally characterized, they prefer mainly ter-

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Table I. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 2

Bond Distances			
Fe(1)–Fe(2)	2.4975 (8)	N(2)–C(221)	1.456 (5)
Fe(1)–C(1)	1.972 (4)	C(211)–C(212)	1.507 (7)
Fe(1)–C(4)	1.979 (4)	C(221)–C(222)	1.511 (6)
Fe(1)–C(11)	1.749 (5)	C(31)–C(32)	1.385 (6)
Fe(1)–C(12)	1.807 (5)	C(31)–C(36)	1.385 (5)
Fe(1)–C(13)	1.818 (4)	C(32)–C(33)	1.370 (7)
Fe(1)–C(21)	2.398 (4)	C(33)–C(34)	1.364 (8)
Fe(2)–C(1)	2.071 (3)	C(34)–C(35)	1.359 (7)
Fe(2)–C(2)	2.230 (3)	C(35)–C(36)	1.370 (6)
Fe(2)–C(3)	2.172 (4)	C(41)–C(42)	1.380 (6)
Fe(2)–C(4)	2.050 (4)	C(41)–C(46)	1.392 (5)
Fe(2)–C(21)	1.780 (4)	C(42)–C(43)	1.392 (6)
Fe(2)–C(22)	1.781 (4)	C(43)–C(44)	1.366 (8)
Fe(2)–C(23)	1.784 (4)	C(44)–C(45)	1.346 (8)
C(1)–C(2)	1.431 (5)	C(45)–C(46)	1.385 (6)
C(1)–C(5)	1.506 (5)	C(11)–O(11)	1.151 (5)
C(2)–C(3)	1.443 (5)	C(12)–O(12)	1.137 (5)
C(2)–N(2)	1.385 (4)	C(13)–O(13)	1.129 (5)
C(3)–C(4)	1.422 (5)	C(21)–O(21)	1.163 (5)
C(3)–C(31)	1.479 (5)	C(22)–O(22)	1.140 (4)
C(4)–C(41)	1.498 (5)	C(23)–O(23)	1.142 (5)
N(2)–C(211)	1.472 (5)		

Bond Angles			
C(4)–Fe(1)–C(1)	80.3 (1)	C(31)–C(3)–C(2)	122.9 (3)
C(11)–Fe(1)–C(1)	89.1 (2)	C(31)–C(3)–C(4)	124.3 (3)
C(11)–Fe(1)–C(4)	90.1 (2)	C(3)–C(4)–Fe(1)	115.9 (3)
C(12)–Fe(1)–C(1)	92.3 (2)	C(41)–C(4)–Fe(1)	122.1 (3)
C(12)–Fe(1)–C(4)	167.3 (2)	C(41)–C(4)–C(3)	119.6 (3)
C(12)–Fe(1)–C(11)	100.1 (2)	C(211)–N(2)–C(2)	118.4 (3)
C(13)–Fe(1)–C(1)	169.4 (2)	C(221)–N(2)–C(2)	122.9 (3)
C(13)–Fe(1)–C(4)	94.7 (2)	C(221)–N(2)–C(211)	117.8 (3)
C(13)–Fe(1)–C(11)	100.3 (2)	C(212)–C(211)–N(2)	113.1 (4)
C(13)–Fe(1)–C(12)	90.9 (2)	C(222)–C(221)–N(2)	111.9 (4)
C(22)–Fe(2)–C(21)	95.1 (2)	C(32)–C(31)–C(3)	118.8 (4)
C(23)–Fe(2)–C(21)	96.8 (2)	C(36)–C(31)–C(3)	123.9 (4)
C(23)–Fe(2)–C(22)	93.0 (2)	C(36)–C(31)–C(32)	117.2 (4)
O(11)–C(11)–Fe(1)	175.1 (4)	C(33)–C(32)–C(31)	120.5 (5)
O(12)–C(12)–Fe(1)	179.0 (5)	C(34)–C(33)–C(32)	121.0 (5)
O(13)–C(13)–Fe(1)	177.3 (4)	C(35)–C(34)–C(33)	119.7 (5)
O(21)–C(21)–Fe(2)	162.7 (4)	C(36)–C(35)–C(34)	119.7 (5)
O(22)–C(22)–Fe(2)	178.2 (4)	C(35)–C(36)–C(31)	121.9 (4)
O(23)–C(23)–Fe(2)	179.0 (4)	C(42)–C(41)–C(4)	119.5 (4)
Fe(2)–C(1)–Fe(1)	76.2 (1)	C(46)–C(41)–C(4)	122.1 (4)
C(2)–C(1)–Fe(1)	114.8 (3)	C(46)–C(41)–C(42)	118.3 (4)
C(5)–C(1)–Fe(1)	123.6 (3)	C(43)–C(42)–C(41)	120.5 (5)
C(5)–C(1)–C(2)	120.7 (3)	C(44)–C(43)–C(42)	119.9 (5)
C(3)–C(2)–C(1)	113.0 (3)	C(45)–C(44)–C(43)	120.3 (5)
N(2)–C(2)–C(1)	122.5 (3)	C(46)–C(45)–C(44)	120.9 (5)
N(2)–C(2)–C(3)	124.2 (3)	C(45)–C(46)–C(41)	120.1 (5)
C(4)–C(3)–C(2)	112.4 (3)		

Table II. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound 3

Bond Distances			
Fe(1)–Fe(2)	2.551 (1)	C(2)–N(51)	1.380 (6)
Fe(1)–C(11)	1.778 (6)	N(3)–N(4)	1.439 (5)
Fe(1)–C(12)	1.796 (6)	N(4)–C(41)	1.295 (6)
Fe(1)–C(13)	1.819 (6)	N(51)–C(511)	1.472 (7)
Fe(1)–C(1)	1.978 (5)	N(51)–C(521)	1.458 (7)
Fe(1)–N(4)	1.970 (4)	C(511)–C(512)	1.499 (8)
Fe(2)–C(21)	1.801 (5)	C(521)–C(522)	1.46 (1)
Fe(2)–C(22)	1.782 (6)	C(41)–C(411)	1.490 (7)
Fe(2)–C(23)	1.768 (6)	C(41)–C(421)	1.485 (7)
Fe(2)–C(1)	2.056 (5)	C(411)–C(412)	1.379 (9)
Fe(2)–C(2)	2.109 (5)	C(411)–C(416)	1.349 (9)
Fe(2)–N(3)	2.085 (4)	C(412)–C(413)	1.42 (1)
Fe(2)–N(4)	2.634 (4)	C(413)–C(414)	1.35 (1)
C(11)–O(11)	1.137 (7)	C(414)–C(415)	1.33 (1)
C(12)–O(12)	1.134 (7)	C(415)–C(416)	1.37 (1)
C(13)–O(13)	1.139 (7)	C(421)–C(422)	1.387 (8)
C(21)–O(21)	1.138 (6)	C(421)–C(426)	1.396 (8)
C(22)–O(22)	1.140 (7)	C(422)–C(423)	1.379 (8)
C(23)–O(23)	1.146 (7)	C(423)–C(424)	1.37 (1)
C(1)–C(2)	1.429 (7)	C(424)–C(425)	1.378 (9)
C(1)–C(31)	1.506 (7)	C(425)–C(426)	1.373 (8)
C(2)–N(3)	1.390 (6)		

Bond Angles			
C(12)–Fe(1)–C(11)	92.9 (3)	N(3)–N(4)–Fe(1)	109.7 (3)
C(13)–Fe(1)–C(11)	87.4 (3)	C(41)–N(4)–Fe(1)	135.3 (3)
C(13)–Fe(1)–C(12)	103.3 (3)	C(41)–N(4)–N(3)	113.6 (4)
C(1)–Fe(1)–C(11)	90.0 (2)	C(511)–N(51)–C(2)	120.8 (4)
C(1)–Fe(1)–C(12)	96.5 (2)	C(521)–N(51)–C(2)	118.3 (4)
C(1)–Fe(1)–C(13)	160.1 (2)	C(521)–N(51)–C(511)	116.4 (4)
N(4)–Fe(1)–C(11)	166.9 (2)	C(512)–C(511)–N(51)	113.9 (5)
N(4)–Fe(1)–C(12)	98.4 (2)	C(522)–C(521)–N(51)	118.8 (7)
N(4)–Fe(1)–C(13)	96.2 (2)	C(411)–C(41)–N(4)	123.2 (4)
N(4)–Fe(1)–C(1)	82.3 (2)	C(421)–C(41)–N(4)	119.4 (4)
C(22)–Fe(2)–C(21)	100.1 (3)	C(421)–C(41)–C(411)	117.2 (4)
C(23)–Fe(2)–C(21)	100.0 (3)	C(412)–C(411)–C(41)	118.8 (6)
C(23)–Fe(2)–C(22)	91.6 (3)	C(416)–C(411)–C(41)	121.8 (6)
O(11)–C(11)–Fe(1)	178.9 (5)	C(416)–C(411)–C(412)	119.2 (6)
O(12)–C(12)–Fe(1)	177.1 (6)	C(413)–C(412)–C(411)	118.1 (8)
O(13)–C(13)–Fe(1)	172.9 (5)	C(414)–C(413)–C(412)	120.6 (8)
O(21)–C(21)–Fe(2)	177.9 (6)	C(415)–C(414)–C(413)	119.8 (7)
O(22)–C(22)–Fe(2)	177.9 (6)	C(416)–C(415)–C(414)	121.1 (9)
O(23)–C(23)–Fe(2)	177.7 (6)	C(415)–C(416)–C(411)	121.2 (8)
Fe(2)–C(1)–Fe(1)	78.5 (2)	C(422)–C(421)–C(41)	119.3 (5)
C(2)–C(1)–Fe(1)	110.5 (3)	C(426)–C(421)–C(41)	121.4 (5)
C(31)–C(1)–Fe(1)	124.8 (4)	C(426)–C(421)–C(422)	119.3 (5)
C(31)–C(1)–C(2)	121.3 (5)	C(423)–C(422)–C(421)	119.4 (6)
N(3)–C(2)–C(1)	114.8 (4)	C(424)–C(423)–C(422)	120.9 (6)
N(51)–C(2)–C(1)	129.2 (4)	C(425)–C(424)–C(423)	119.9 (5)
N(51)–C(2)–N(3)	115.9 (4)	C(426)–C(425)–C(424)	120.0 (6)
N(4)–N(3)–C(2)	109.1 (4)	C(425)–C(426)–C(421)	120.4 (6)

minal η- and μ-bonding modes resulting from the attack of the α-nitrogen on one or two metal atoms.[8-12] The structurally characterized title complex 3, resulting from this nucleophilic attack of the α-nitrogen on a carbene carbon atom, seems to be unprecedented. The atomic numbering scheme is shown in Figure 2. Selected bond lengths and bond angles are shown in Table II. Two important features may be emphasized. The first one is the formation of the five-membered ring Fe(1)–C(1)–C(2)–N(3)–N(4). The second one is its bonding. The C(1)–C(2)–N(3) angle appears like an azaallyl group which is σ-bound to Fe(1) and π-bound to Fe(2). The Fe(1)–C(1) = 1.972 (4) bond is significantly shorter than the π-bonds, Fe(2)–C(1) = 2.055 (5), Fe(2)–C(2) = 2.109, and Fe(2)–N(3) = 2.085 Å. The C(1)–C(2) = 1.431 (5) and C(2)–N(3) = 1.385 (4) Å lengths indicate a substantial double-bond character, and the angles around C(1) and C(2) fall within the expected range for an allyl system. The geometry of the Fe(1)–C(1)–Fe(2) triangle correlates closely with the framework of the $[\mu\text{-CRR}']Fe_2$ moiety of other reported bridged diiron complexes shown in Table III.

The 18-electron rule requires (N4) to donate a lone pair to Fe(1). The Fe(1)–N(4) distance of 1.970 (4) Å is consistent with a coordinative bond although it is somewhat shorter than values observed in other N→Fe containing complexes; examples are $[Fe_2(CO)_6\{\mu\text{-}C(OEt)C_6H_4NMe_2\}]$[13] with Fe–N = 2.087 (3) Å or $[Fe_2(CO)_8\{\mu\text{-}CHCH_2CH_2CH_2CH_2NEt\}]$[14] with Fe–N = 2.100 (2) Å. The

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Table III. Distances (Å) and Angles (deg) in the Triangular Framework Fe–C–Fe for Relevant Complexes

complexes	Fe(1)–Fe(2)	Fe(1)–C(1)	Fe(2)–C(1)	Fe(1)–C(1)–Fe(2)	ref
[$Fe_2(CO)_6\{CMeC(NEt_2)N_2CPh_2)\}$]	2.551 (2)	1.978 (5)	2.056 (5)	78.5 (2)	
[$Fe_2(CO)_6\{C(OEt)C_6H_4NMe_2\}$]	2.552 (2)	1.965 (3)	2.120 (3)	77.9 (1)	8
[$Fe_2(CO)_6\{C(OMe)C(OOMe)CHC(OOMe)\}$]	2.638 (1)	1.957 (4)	2.140 (3)	80.0 (1)	23
[$Fe_2(CO)_6\{C(OEt)CHC(OEt)Me\}$]	2.550 (4)	1.93 (2)	2.15 (2)	77.2 (7)	24
[$Fe_2(Cp)_2(CO)_2(CHCMeCMeCO)$]($PF_6$)	2.597 (2)	1.945 (12)	2.022 (12)	81.8 (5)	25
[$Fe_2(Cp)_2(CO)_2\{C(COOMe)C(COOMe)CHMe\}$]	2.540 (2)	1.968 (12)	1.969 (12)	80.4 (1)	26
[$Fe_2(CO)_6\{C(OMe)CHCHC(OMe)N(SO_2C_6H_4Me)\}$]	2.636 (2)	1.909 (10)	2.138 (8)	81.1 (3)	27
[$Fe_2(CO)_6(CPhCPhCHPh)$]	2.602 (2)	1.997 (3)	2.080 (3)	79.3 (1)	28
[$Fe_2(CO)_6\{CMeCHCHCHCH(COMe)\}$]	2.642 (1)	2.002 (2)	2.088 (2)	80.5 (1)	29
[$Fe_2(CO)_6\{CPhCPhC(CF_3)CHC(OEt)_2\}$]	2.599 (2)	2.017 (9)	2.098 (9)	78.3 (3)	30
[$Fe_2(CO)_6\{CPhCPhC(CF_3)C(CF_3)H)\}$]($PPh_4$)	2.589 (2)	1.99 (1)	2.07 (1)	79.2 (4)	31
[$Fe_2(CO)_6\{C(CF_3)C(CF_3)CHCHCH(NEt_2)\}$]	2.617 (1)	2.02 (1)	2.01 (1)	81.0 (4)	32
[$Fe_2(CO)_6\{C(OEt)CPhCPhH\}$]	2.635 (1)	1.970 (7)	2.129 (7)	79.9 (2)	33

N(3)–N(4) bond length, 1.439 (5) Å, indicates that a decrease of its bond order has occurred on coordination; this value is close to the N–N distance in N_2H_4.[15] The C(41)—N(4) = 1.295 (6) Å distance is similar to C═N bond found in some other organometallic complexes such as [$Ru_5(CO)_{12}(\mu$-$C{\equiv}CPh)(\mu_4$-$N_2CPh_2)$][8] with C═N = 1.304 Å or [$Cp_2Mo_2(CO)(NAr)(\mu$-$N_3(Ar)CO)$][16] with C═N = 1.303 Å. Another striking feature of the crystal structure of **3** is found in the position of the N(4) atom. It is displaced from the azaallyl plane by 0.49 Å. This displacement of the nitrogen atom results in a torsion angle for C(1)–C(2)–N(3)–N(4) of 36.7°. A similar distortion was observed in the related compound [$Fe_2(CO)_6\{C(OEt)C_6H_4NMe_2\}$][13] with the nitrogen located 0.82 Å above the allyl plane.

Experimental Section

All reactions were carried out under dry nitrogen by using standard Schlenk or high-vacuum line techniques. Chromatography was carried out on a 50 × 3 cm deactivated silica gel column. Infrared absorption spectra were measured with a Perkin-Elmer 597 spectrometer. A Nermag R10.10 spectrometer was used for molecular mass determination. NMR spectra were obtained on either a Bruker WP 80 or WM 250 spectrometer. All spectra were recorded by using tetramethylsilane as reference.

Hexane and dichloromethane were purified by standard procedures and stored over molecular sieves. Trimethylamine *N*-oxide was dehydrated by benzene azeotropic distillation.

Literature procedures were used to prepare $CH_3C{\equiv}CN(C_2H_5)_2$[17] and $(C_6H_5)_2CN_2$.[18]

Synthesis of Complex 1. The synthesis has been described in a preceding paper, but the yield was poor (10–20%). Improvement is obtained when trimethylamine *N*-oxide is added to the reaction mixture cooled to 0 °C. Excess of (diethylamino)propyne (0.8 g, 8.25 mmol) was added to a suspension of [$Fe_2(CO)_9$] (1 g, 2.75 mmol) in 100 mL of *n*-hexane, and then 0.5 g (6.67 mmol) of Me_3NO was added dropwise. The color rapidly changed from yellow to dark orange. After 2 h the reaction mixture was evaporated. The residue was chromatographed, giving a red band with *n*-hexane as eluant. Red crystals were obtained from the *n*-hexane solution (yield 60–70%). Complex 1 was characterized by its infrared spectrum in the ν_{CO} region[1] and its ^1H NMR spectrum (80 MHz, $CDCl_3$): δ 3.9–3.6 (m, 4 H, NCH_2), 2.4 (s, 3 H, CH_3 bridge), 1.5–1.2 (m, 6 H, CH_2CH_3).

Synthesis of Complex 2. [($Fe_2(CO)_6\{C(CH_3)C(NEt_2)C(Ph)C(Ph)\}$]. Complex 1 (20 mg, 0.048 mmol) was dissolved in dry hexane (10 mL), and 8 mg (0.048 mmol) of diphenylacetylene was added. This mixture was heated at 50 °C under CO pressure (40 atm) for 2 h. Thin-layer chromatography showed only one product. Evaporation of the solution gave a yellow crystalline powder of complex **2** (25 mg, 92%).

Table IV. Crystal Data for Compounds 2 and 3

	2	**3**
empirical formula	$C_{27}H_{23}NO_6Fe_2$	$C_{26}H_{23}N_3O_6Fe_2$
fw	569.18	585.18
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	8.687 (1)	10.065 (3)
b, Å	32.006 (4)	13.609 (3)
c, Å	9.728 (2)	19.332 (3)
β, deg	103.96 (1)	90.0
V, Å^3	2624	2648
Z	4	4
cryst size, mm	0.3 × 0.4 × 0.3	0.4 × 0.4 × 0.28
μ(Mo Kα), cm^{-1}	11.43	11.38
ρ(calcd), g·cm^{-3}	1.439	1.468
temp, °C	20	20
radiatn	Mo Kα (graphite monochromator)	
scan range, θ, deg	$1.35 + 0.345 \tan\theta$	$1.5 + 0.34 \tan\theta$
2θ range, deg	3–46	3–50
scan type	$\omega/2\theta$	$\omega/1.33\theta$
std reflctns	071;03$\bar{2}$	509;390
reflctns collected	4115	2964
reflctns merged	3642 (R_m = 1.18)	2633 (R_m = 2.72)
reflctns used	2549	2143
criteria	$I > 3\sigma(I)$	$I > 3\sigma(I)$
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0286	0.0354
$R_w = \{\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2\}^{1/2}$	0.0304	0.0419
rms (shift/esd)	0.204	0.054
weighting scheme	1	$w = w'[1 - (\Delta F)/6\sigma(F_o))^2]^2$ [a]

[a] $w' = 1/\sum^n_{r=1} \mathrm{ArTr}(x)$ with three coefficients Ar (3.833, −1.180, 2.533) for the Chebyshev polynomial ArTr(x) where x was F_c/F_c(max).[22]

An excess of diphenylacetylene (50 mg, 0.28 mmol) was added to a solution of complex 1 (50 mg, 0.14 mmol) in dry *n*-hexane. After being refluxed under nitrogen for 3 h, the reaction mixture was evaporated. The residue was separated by chromatography giving two main bands with *n*-hexane as eluant: a yellow one which was collected and a green one which slowly disappeared on the column due to decomposition. Complex **2** was obtained as yellow crystals from the yellow solution (49 mg, 60%): MS, *m/e* 569 (M^+), 541 (M^+ – CO), 513 (M^+ – 2CO), 485 (M^+ – 3CO), 457 (M^+ – 4CO), 429 (M^+ – 5CO), 401 (M^+ – 6CO); IR ν_{CO} 2075 (s), 2035 (s), 2010 (s), 1985 (s), 1970 (s), 1935 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.5–7.28 (m, 10 H, H aromatic), 3.12–3.0 (q, 2 H, NCH_2), 2.9–2.8 (q, 2 H, NCH_2), 2.5 (s, 3 H, CH_3 bridge), 1.2–1.05 (t, 3 H, CH_2CH_3). Anal. Calcd for $C_{27}H_{23}Fe_2O_6N$: C, 56.98; N, 2.46; H, 4.05. Found: C, 56.92; N, 2.51; H, 4.65.

Synthesis of Complex 3. [($Fe_2(CO)_6\{C(CH_3)C(NEt_2)N_2C(Ph_2)\}$]. $(C_6H_5)_2CN_2$ (13.8 mg, 0.071 mmol), complex 1 (30 mg, 0.0715 mmol), and hexane (20 mL) were mixed in a round-bottom flask. The reaction mixture was refluxed under nitrogen for 3 h. Thin-layer chromatography showed only one reaction product. The solution was then concentrated to ca. 10 mL and left at −20 °C; purple-red crystals were obtained (31 mg, 74%): MS, *m/e* 585 (M^+), 557 (M^+ – CO), 529 (M^+ – 2CO), 501 (M^+ – 3CO), 473

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Table V. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameter [U(eq)] for Compound 2[a]

atom	*x*/*a*	y/b	z/c	*U*(eq), Å^2
Fe(1)	0.17619 (6)	0.09251 (2)	0.17097 (6)	0.0460
Fe(2)	0.43951 (6)	0.06822 (2)	0.14163 (5)	0.0393
C(1)	0.3648 (4)	0.0802 (1)	0.3244 (4)	0.0416
C(2)	0.4942 (4)	0.1086 (1)	0.3340 (4)	0.0391
C(3)	0.4817 (4)	0.1329 (1)	0.2069 (3)	0.0386
C(4)	0.3361 (4)	0.1260 (1)	0.1055 (4)	0.0399
C(5)	0.3664 (5)	0.0487 (1)	0.4398 (4)	0.0540
N(2)	0.6234 (4)	0.1096 (1)	0.4496 (3)	0.0454
C(211)	0.5946 (5)	0.1164 (2)	0.5909 (4)	0.0567
C(212)	0.6455 (7)	0.1591 (2)	0.6503 (5)	0.0874
C(221)	0.7865 (5)	0.1118 (1)	0.4360 (4)	0.0527
C(222)	0.8929 (5)	0.0813 (2)	0.5334 (5)	0.0692
C(31)	0.5995 (5)	0.1650 (1)	0.1928 (4)	0.0440
C(32)	0.6131 (6)	0.2007 (1)	0.2755 (5)	0.0668
C(33)	0.7161 (8)	0.2318 (2)	0.2613 (6)	0.0795
C(34)	0.8062 (7)	0.2287 (2)	0.1647 (6)	0.0778
C(35)	0.7951 (6)	0.1941 (2)	0.0821 (5)	0.0685
C(36)	0.6920 (5)	0.1628 (1)	0.0953 (4)	0.0529
C(41)	0.2933 (5)	0.1528 (1)	−0.0244 (4)	0.0471
C(42)	0.2781 (6)	0.1954 (2)	−0.0103 (5)	0.0687
C(43)	0.2305 (8)	0.2207 (2)	−0.1294 (6)	0.0911
C(44)	0.2004 (7)	0.2033 (2)	−0.2616 (6)	0.0829
C(45)	0.2131 (6)	0.1618 (2)	−0.2771 (5)	0.0722
C(46)	0.2575 (5)	0.1359 (2)	−0.1602 (4)	0.0575
C(11)	0.1354 (5)	0.1351 (2)	0.2688 (4)	0.0545
O(11)	0.1201 (4)	0.1634 (1)	0.3375 (3)	0.0772
C(12)	0.0607 (5)	0.0525 (2)	0.2309 (4)	0.0608
O(12)	−0.0128 (4)	0.0278 (1)	0.2696 (4)	0.0887
C(13)	0.0226 (5)	0.0992 (2)	0.0086 (4)	0.0604
O(13)	−0.0769 (4)	0.1033 (1)	−0.0893 (3)	0.0812
C(21)	0.2789 (5)	0.0345 (1)	0.0649 (4)	0.0565
O(21)	0.2048 (4)	0.0066 (1)	0.0075 (4)	0.0780
C(22)	0.5212 (5)	0.0688 (1)	−0.0095 (4)	0.0503
O(22)	0.5728 (4)	0.0681 (1)	−0.1066 (3)	0.0694
C(23)	0.5725 (5)	0.0285 (1)	0.2274 (4)	0.0499
O(23)	0.6560 (4)	0.0029 (1)	0.2835 (3)	0.0690

[a] $U(\text{eq}) = [U(11)U(22)U(33)]^{1/3}$.

Table VI. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameter [*U*(eq)] for Compound 3[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Fe(1)	−0.08934 (7)	0.07394 (5)	0.12460 (3)	0.0301
Fe(2)	0.09257 (8)	0.12414 (5)	0.03969 (3)	0.0305
C(11)	−0.2270 (6)	0.1025 (4)	0.0706 (3)	0.0404
O(11)	−0.3158 (5)	0.1196 (4)	0.0363 (3)	0.0626
C(12)	−0.1758 (6)	−0.0252 (5)	0.1663 (3)	0.0399
O(12)	−0.2304 (5)	−0.0898 (3)	0.1901 (3)	0.0620
C(13)	−0.1345 (6)	0.1803 (5)	0.1764 (3)	0.0448
O(13)	−0.1718 (5)	0.2493 (4)	0.2036 (3)	0.0612
C(21)	0.1031 (6)	0.2361 (4)	0.0889 (3)	0.0392
O(21)	0.1131 (5)	0.3059 (3)	0.1211 (2)	0.0563
C(22)	0.2372 (6)	0.1362 (4)	−0.0128 (3)	0.0426
O(22)	0.3279 (5)	0.1462 (4)	−0.0474 (3)	0.0663
C(23)	−0.0109 (6)	0.1636 (4)	−0.0287 (3)	0.0475
O(23)	−0.0777 (6)	0.1863 (4)	−0.0740 (2)	0.0692
C(1)	−0.0107 (5)	−0.0055 (3)	0.0494 (3)	0.0305
C(2)	0.1261 (5)	−0.0252 (3)	0.0632 (2)	0.0273
N(3)	0.1834 (4)	0.0346 (3)	0.1134 (2)	0.0314
N(4)	0.0869 (4)	0.0538 (3)	0.1666 (2)	0.0280
C(31)	−0.0889 (6)	−0.0672 (4)	−0.0008 (3)	0.0443
N(51)	0.2109 (4)	−0.0904 (3)	0.0310 (2)	0.0340
C(511)	0.2088 (6)	−0.1025 (4)	−0.0446 (3)	0.0409
C(512)	0.1789 (8)	−0.2051 (5)	−0.0680 (3)	0.0540
C(521)	0.3342 (6)	−0.1167 (5)	0.0659 (3)	0.0499
C(522)	0.4461 (8)	−0.0493 (8)	0.0622 (5)	0.0853
C(41)	0.1391 (5)	0.0701 (4)	0.2267 (2)	0.0312
C(411)	0.2851 (5)	0.0718 (4)	0.2391 (2)	0.0353
C(412)	0.3415 (7)	−0.0010 (6)	0.2790 (4)	0.0639
C(413)	0.4792 (9)	0.0052 (8)	0.2943 (4)	0.0724
C(414)	0.5523 (7)	0.0814 (9)	0.2704 (4)	0.0737
C(415)	0.4950 (8)	0.1512 (8)	0.2331 (5)	0.0767
C(416)	0.3625 (7)	0.1460 (6)	0.2165 (4)	0.0604
C(421)	0.0516 (5)	0.0955 (4)	0.2859 (3)	0.0362
C(422)	0.0520 (6)	0.1907 (4)	0.3114 (3)	0.0433
C(423)	−0.0311 (7)	0.2149 (5)	0.3655 (3)	0.0516
C(424)	−0.1110 (7)	0.1454 (5)	0.3957 (3)	0.0517
C(425)	−0.1095 (7)	0.0502 (5)	0.3719 (3)	0.0536
C(426)	−0.0285 (6)	0.0249 (5)	0.3176 (3)	0.0432

[a] $U(\text{eq}) = [U(11)U(22)U(33)]^{1/3}$.

(M^+ − 4CO), 445 (M^+ − 5CO), 417 (M^+ − 6CO); IR ν_{CO} 2065 (s), 2025 (s), 2000 (s), 1975 (vs), 1960 (s), 1945 (s), 1920 (sh), 1915 (sh) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.8–7.4 (m, 10 H, H aromatic), 3.68–3.58 (q, 2 H, NCH_2), 3.28–3.12 (q, 2 H, NCH_2), 3.2 (s, 3 H, CH_3 bridge), 1.2–1.1 (t, 3 H, CH_2CH_3). Anal. Calcd for $C_{26}H_{23}Fe_2O_6N_3$: C, 53.36; N, 7.18; H, 3.93. Found: C, 53.27; N, 7.3; H, 4.33.

Crystal Data for Complexes 2 and 3. For both compounds, preliminary unit-cell dimensions and symmetry informations were derived from precession photographs; the selected crystals were set up on a Nonius CAD4 automatic diffractometer. Cell dimensions and orientation matrices were obtained from least-squares refinements of the setting angles of 25 reflections (28 < 2θ < 30°).

Crystal data and data collection parameters are listed in Table IV. Intensities of two standard reflections were monitored every hour; they showed no change during data collections. Corrections were made for Lorentz and polarization effects. Absorption corrections were applied via an empirical absorption correction technique.[19]

Computations were performed by using CRYSTALS[20] adaped on a VAX 11/725. Atomic form factors for neutral Fe, C, N, O, and H were taken from ref 21; anomalous dispersion was taken into account in both cases. In the two compounds Fe atom positions were determined by Harker vector analysis of three-dimensional Patterson maps. All remaining non-hydrogen atoms were found by successive electron density map calculations. All non-hydrogen atoms were refined anisotropically. For both compounds, hydrogen atoms were located on difference electron density maps; in complex 2, hydrogen atomic coordinates were refined with an overall isotropic thermal parameter. In complex 3, hydrogen atoms were given calculated positions (C–H = 0.96 Å) with a fixed overall isotropic thermal parameter (*U* = 0.08); coordinates of these atoms were not refined but were recalculated after each cycle. The two structures were refined by least squares with approximation (in four blocks) to the normal matrix. The criteria for a satisfactory complete analysis were the ratios of the

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parameter shifts to standard deviations being all less than 0.1 and no significant features in the final difference maps. Main features of the refinements appear in Table IV. Atomic coordinates are given in Table V and VI.

Registry No. **1**, 115590-65-3; **2**, 115590-66-4; **3**, 115590-67-5; $Fe_2(CO)_9$, 15321-51-4; $CH_3(\equiv CN(C_2H_5)_2$, 4231-35-0; Me_3NO, 1184-78-7; $(C_6H_5)_2CN_2$, 883-40-9; diphenylacetylene, 501-65-5.

Supplementary Material Available: Tables of anisotropic temperature factors, important least-squares planes, and hydrogen coordinates (6 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Photolysis of Cyclotrigermane. Synthesis and Chemistry of Digermiranes and Digermetanes Containing Sulfur and Selenium

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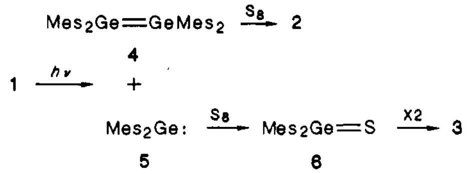
Photolysis of hexamesitylcyclotrigermane (**1**) produces tetramesityldigermene (**4**) and dimesitylgermylene (**5**) which react with elemental sulfur to give 2,2,3,3-tetramesitylthiadigermirane (**2**) and 2,2,4,4-tetramesityl-1,3,2,4-dithiadigermetane (**3**). Selenium also reacts with digermene **4** to afford 2,2,3,3-tetramesitylselenadigermirane (**7**). Photolysis of **2** with 2,3-dimethyl-1,3-butadiene produces only products from dimesitylgermylene (**5**) and dimesitylgermanethione (**6**). The reactions of **2** with pyridine *N*-oxide, sulfur, and selenium yield digermetanes containing O, S, and Se.

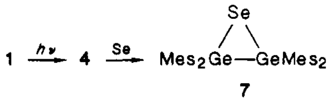
Introduction

In recent years interest in the chemistry of small-ring compounds has remarkably increased because of their unique properties resulting from strain energy. In contrast to rather extensive studies of the chemistry of small-ring silanes,[2] very little is known about germanium analogues.[3-8] Few small-ring compounds containing Ge–Ge bonds[3c,d,4-8] have been studied, and direct reaction of a digermene with sulfur and selenium appears to be the most suitable method for the synthesis of thia- and selenadigermiranes. We report here a convenient synthesis and some chemistry of thia- and selenadigermiranes, which cleanly reacted with pyridine *N*-oxide, sulfur, and selenium to afford heteroatom-containing digermetanes.

Scheme I

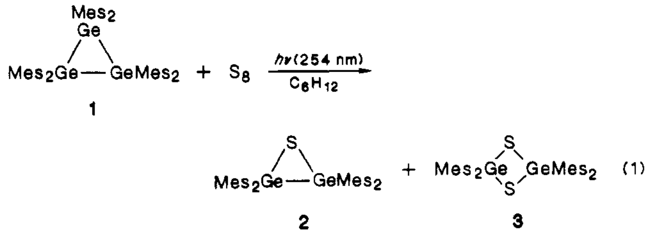


Scheme II



Results and Discussion

Synthesis of Thiadigermirane and Selenadigermirane.[4] Irradiation of a cyclohexane solution of hexamesitylcyclotrigermane (**1**, 0.1 mmol) and elemental sulfur (0.8 mmol) in a quartz tube at room temperature with a low-pressure mercury lamp produced a colorless crystalline product, 2,2,3,3-tetramesitylthiadigermirane (**2**), in 26% yield. Also formed was 2,2,4,4-tetramesityl-1,3,2,4-dithiadigermetane (**3**) in 24% yield (eq 1). Thiadigermirane **2** was readily separated from **3** by flash column chromatography, and its structure was confirmed by ^1H NMR and mass spectroscopic analyses and also by an X-ray diffraction study. Thiadigermirane **2** thus obtained is stable



Mes = 2,4,6-trimethylphenyl

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