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Organonitrogen derivatives of metal carbonyls

XIII *. Reactions of dialkylaminotrimethylsilylacetylenes with metal carbonyls **

R.B. King[★], **R.M. Murray**,

Department of Chemistry, University of Georgia, Athens, Georgia 30602 (U.S.A.)

R.E. Davis[★] **and P.K. Ross** ***

Department of Chemistry, University of Texas, Austin, Texas 78712 (U.S.A.)

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Abstract

Reactions of the dialkylaminotrimethylsilylacetylenes, $(CH_3)_3SiC{\equiv}CNR_2$, with $Fe(CO)_5$ in boiling heptane (R = methyl or ethyl or R_2N = piperidino) or decalin (R = isopropyl) give the yellow air-stable solid cyclobutadiene derivatives $[(CH_3)_3Si]_2(R_2N)_2C_4Fe(CO)_3$ as the major organometallic product; in some cases (R = ethyl or R_2N = piperidino) the dark red tricarbonylferrole-iron tricarbonyl derivatives $[(CH_3)_3Si]_2(R_2N)_2C_4Fe_2(CO)_6$ are also obtained in low yield. The cyclobutadiene complex $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$ crystallizes in the triclinic space group $P\bar{1}$ with cell constants a 10.602(2), b 14.877(2), c 9.955(2) Å, α 96.61(1), β 111.98(1), γ 109.66(1)°, and $Z = 2$. Solution of the structure using the heavy-atom positions derived from a Patterson map, followed by full-matrix least-squares refinement of the 4924 observed reflections to a final R value of 0.032, indicates the position of the substituents to be $1{,}3\text{-}[(CH_3)_3Si]_2\text{-}2{,}4\text{-}(C_5H_{10}N)_2\text{-}C_4Fe(CO)_3$ in accord with head-to-tail dimerization of the acetylene. Reactions of $(CH_3)_3SiC{\equiv}CNR_2$ with $Fe_2(CO)_9$ in diethyl ether at room temperature give orange-red $(CH_3)_3SiC_2NR_2Fe_2(CO)_6$ suggested by their NMR spectra to have the nitrogen atom as well as the two acetylenic carbon atoms involved in the bonding to the diiron unit. Reactions of $(CH_3)_3SiC{\equiv}CNR_2$ with $Co_2(CO)_8$ in diethyl ether at ambient temperature give deep green $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ apparently analo-

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* For part XII see ref. 1 and 2.

** Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

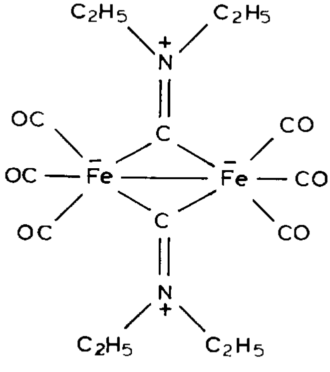
*** Present address: Department of Chemistry, Stanford University, Stanford, California 94305 (U.S.A.)

gous to other (alkyne)$Co_2(CO)_6$ derivatives except for their unusual colors. Reactions of $(CH_3)_3SiC{\equiv}CNR_2$ with $C_5H_5Co(CO)_2$ in boiling n-octane give the black trinuclear $(CH_3)_3SiC_2NR_2Co_3(C_5H_5)_3$ derivatives. Ultraviolet irradiation of $(CH_3)_3SiC{\equiv}CNR_2$ with $Mn_2(CO)_{10}$ in tetrahydrofuran gives low yields of the red-orange $(CH_3)_3SiC_2NR_2Mn_2(CO)_8$.

Introduction

Several years ago an earlier paper of this series [3] reported reactions of various metal carbonyls with the bis(dialkylamino)acetylene, $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$, and with several dialkylaminoacetylenes, namely $C_6H_5C{\equiv}CN(CH_3)_2$, $CH_3C{\equiv}CN(C_2H_5)_2$, and $HC{\equiv}CN(CH_3)_2$. The reactions of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with iron carbonyls were of interest because they gave not only an expected cyclopentadienone complex $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ but also a yellow complex $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$, shown subsequently by X-ray diffraction [4,5] to have the unprecedented structure I in which the carbon–carbon triple bond of the acetylene has undergone complete rupture ("dichotomy"). In addition a number of products were obtained from aminoalkynes and metal carbonyls in which not only the triple bond carbons but also the dialkylamino group appear to be involved in the interaction with the transition metal.

This paper extends our study of the reactions of aminoalkynes with metal carbonyls to aminoalkynes of the type $R_2NC{\equiv}CSi(CH_3)_3$ (R = methyl, ethyl, isopropyl or R_2N = piperidino) [6]. Such alkynes are of interest since one end of the carbon–carbon triple bond is capped by a bulky inert trimethylsilyl group and the other end of the carbon–carbon triple bond bears a potentially coordinating dialkylamino group, the size of which can be varied in a systematic manner. This work has resulted in the discovery of a series of cyclobutadiene-iron tricarbonyl derivatives $[(CH_3)_3Si]_2(R_2N)_2C_4Fe(CO)_3$, a result of interest since neither of the correspondingly symmetrically substituted acetylenes, namely $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ [3] and $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ [7], gives a cyclobutadiene-iron tricarbonyl derivative with iron carbonyls. A structure study by X-ray diffraction of the



(I)

Table 1

Products from the reactions of dialkylaminotrimethylsilylacetylenes with metal carbonyls

Complex [a]	Yield (%)	Color	M.p. (°)	Subl. temp. (°C/ mmHg)	Analyses (Found (calc) (%))		
					C	H	N
Iron complexes							
$(Me_3Si)_2(Me_2N)_2C_4Fe(CO)_3$	12	yellow	116–119		48.3	7.1	6.5
					(48.4)	(7.1)	(6.6)
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe(CO)_3$	23	yellow	159	55/0.1	55.0	7.6	5.6
					(55.0)	(7.6)	(5.6)
$(Me_3Si)_2(Et_2N)_2C_4Fe(CO)_3$	23	yellow	146	60/0.1	52.7	7.9	5.9
					(52.7)	(7.9)	(5.9)
$(Me_3Si)_2(Pr^i_2N)_2C_4Fe(CO)_3$	1	yellow	163	60/0.1	53.0	8.0	5.7
					(56.0)	(8.6)	(5.2)
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe_2(CO)_6$	1	red	94		47.7	4.0	4.2
					(48.5)	(4.3)	(4.3)
$(Me_3Si)_2(Et_2N)_2C_4Fe_2(CO)_6$	<1	red	87(dec.)		46.8	6.4	4.5
					(46.6)	(6.2)	(4.5)
$Me_3SiC_2NMe_2Fe_2(CO)_6$	11	orange-red	76(dec.)		37.2	3.2	3.1
					(37.1)	(3.6)	(3.3)
$Me_3SiC_2NC_5H_{10}Fe_2(CO)_6$	20	orange-red	81(dec.)		43.7	4.0	3.3
					(41.7)	(4.1)	(3.0)
$Me_3SiC_2NEt_2Fe_2(CO)_6$	19	orange-red	85(dec.)		40.1	4.1	3.0
					(40.1)	(4.2)	(3.1)
$Me_3SiC_2NPr^i_2Fe(CO)_6$	31	orange-red	91(dec.)		40.3	5.0	2.9
					(42.8)	(4.8)	(2.9)
Cobalt complexes							
$Me_3SiC_2NMe_2Co_2(CO)_6$	40	dark-green	156(dec.)		36.2	3.3	3.3
					(36.5)	(3.5)	(3.2)
$Me_3SiC_2NC_5H_{10}Co_2(CO)_6$	86	dark-green	160(dec.)	60/0.01	40.9	4.2	2.9
					(41.1)	(4.1)	(3.0)
$Me_3SiC_2NEt_2Co_2(CO)_6$	56	dark-green	160(dec.)	60/0.01	39.0	4.2	3.1
					(39.5)	(4.2)	(3.0)
$Me_3SiC_2NPr^i_2Co_2(CO)_6$	53	dark-green	163(dec.)	60/0.01	42.1	4.9	2.8
					(42.2)	(4.8)	(2.9)
$Me_3SiC_2NC_5H_{10}Co_3Cp_3$	20	black	153		55.1	6.4	2.8
					(54.3)	(6.1)	(2.5)
$Me_3SiC_2NEt_2Co_3Cp_3$	33	black	156		51.7	6.3	2.5
					(53.3)	(6.2)	(2.5)
$Me_3SiC_2NPr^i_2Co_3Cp_3$	8	black	164		55.5	6.9	2.7
					(54.8)	(6.7)	(2.5)
Manganese complexes							
$Me_3SiC_2NC_5H_{10}Mn_2(CO)_8$	0.4	red-orange	62(dec.)		42.4	4.1	2.5
					(41.9)	(3.7)	(2.7)
$Me_3SiC_2NEt_2Mn_2(CO)_8$	3	red-orange	65(dec.)		41.3	4.0	2.6
					(40.9)	(3.8)	(2.8)

[a] Me = methyl, Et = ethyl, Pr^i = isopropyl, Cp = cyclopentadienyl, NC_5H_{10} = piperidino.

piperidino derivative $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$, the details of which are presented in this paper, indicates head-to-tail dimerization of the acetylene to form the cyclobutadiene derivative. In addition, a number of complexes are described in this paper in which the dialkylamino group as well as the triple bond carbon atoms are involved in bonding to a transition metal.

Experimental

Microanalyses (Table 1) were performed by Atlantic Microanalytical Laboratory, Atlanta, Georgia. Melting points (Table 1) were taken in capillaries and are uncorrected. Infrared spectra in the ν(CO) region (Table 2) were obtained in hexane solution on a Perkin–Elmer Model 599B infrared spectrometer with grating optics. Each spectrum was calibrated with the 1601 cm^{-1} band of polystyrene film. ^1H NMR spectra (Table 3) were taken on a continuous wave Varian T-60 spectrometer

Table 2

Infrared ν(CO) spectra of products obtained from reactions of dialkylaminotrimethylsilylacetylenes with metal carbonyls

Complex [a]	ν(CO) (cm^{-1})
$(Me_3Si)_2(Me_2N)_2C_4Fe(CO)_3$	2020s, 1950s, 1946s
$(Me_3Si)_2(Et_2N)_2C_4Fe(CO)_3$	2020s, 1950s, 1948s
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe(CO)_3$	2020s, 1952s, 1944s
$(Me_3Si)_2(Pr^i_2N)_2C_4Fe(CO)_3$	2020s, 1955s, 1940s
$C_4H_4Fe(CO)_3$ [b]	2055s, 1985s
$(Me_3Si)_2(Et_2N)_2C_4Fe_2(CO)_6$	2050s, 1990s, 1975s, 1970s
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe_2(CO)_6$	2035s, 2000s, 1965s, 1950s
$(Me_2N)_2C_4H_2Fe_2(CO)_6$ [c]	2072m, 2027s, 1978s, 1972s, 1939w
$Me_4C_4Fe_2(CO)_6$ [d]	2069m, 2027s, 1981vs, 1937w
$Me_3SiC_2NMe_2Fe_2(CO)_6$	2066s, 2010s, 1990s, 1950s
$Me_3SiC_2NEt_2Fe_2(CO)_6$	2065s, 2010s, 1990s, 1950s
$Me_3SiC_2NC_5H_{10}Fe_2(CO)_6$	2080s, 2020s, 1990s, 1960s
$Me_3SiC_2NPr^i_2Fe_2(CO)_6$	2060s, 2000s, 1985s, 1950s
$PhC_2NMe_2Fe_2(CO)_6$	2091m, 2023s, 1998s, 1986s, 1966m, 1950s
$Me_3SiC_2NMe_2Co_2(CO)_6$	2080s, 2025s, 2010s
$Me_3SiC_2NEt_2Co_2(CO)_6$	2080s, 2020s, 2010s
$Me_3SiC_2NC_5H_{10}Co_2(CO)_6$	2075s, 2030s, 2010s, 1995w
$Me_2SiC_2NPr^i_2Co_2(CO)_6$	2070s, 2030s, 2005s, 1995w
$(Et_2NCH_2)_2C_2Co_2(CO)_6$ [e]	2088s, 2049s, 2027s, 2017s
$Me_2C_2Co_2(CO)_6$ [f]	2086s, 2045vs, 2023vs, 2011vs
$(Me_3Si)_2C_2Co_2(CO)_6$ [g]	2080m, 2043s, 2021s, 2013s
$Me_3SiC_2NEt_2Mn_2(CO)_8$	2050, 2010, 1988, 1955, 1930
$Me_3SiC_2NC_5H_{10}Mn_2(CO)_8$	2051, 2008, 1980, 1956, 1930
$Et_2NC_2NEt_2Mn_2(CO)_8$ [c]	2062m, 1992s, 1965s, 1948s, 1932s, 1917s
$MeC_2NEt_2Mn_2(CO)_8$ [c]	2080w, 2027m, 1980s, 1966m, 1957m, 1944w, 1935m

[a] Me = methyl, Et = ethyl, Pr^i = isopropyl, NC_5H_{10} = piperidino, Ph = phenyl. [b] Data of G.F. Emerson, L. Watts, and R. Pettit, J. Am. Chem. Soc., 87 (1965) 131. [c] Data of R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879. [d] R.B. King and M.N. Ackermann, J. Organomet. Chem., 60 (1973) C57 and further unpublished results. [e] Data of G. Cetini, O. Gambino, R. Rossetti, and E. Sappa, J. Organomet. Chem., 8 (1967) 149; n-heptane solution. [f] Data of R.S. Dickson and P.J. Fraser, Austr. J. Chem., 23 (1970) 2043; cyclohexane solution. [g] Data of K.H. Pannell and G.M. Crawford, J. Coord. Chem., 2 (1973) 251.

Table 3

^1H NMR spectra of products obtained from the reactions of dialkylaminotrimethylsilylacetylenes with metal carbonyls [a]

Complex [b]	$\delta(Me_3Si)$	$\delta(R_2N)$	$\delta(C_5H_5)$
$(Me_3Si)_2(Me_2N)_2C_4Fe(CO)_3$	0.34s	3.10s	
$Me_3SiC_2NMe_2Fe_2(CO)_6$	0.36s	3.42s, 3.05s	
$Me_3SiC_2NMe_2Co_2(CO)_6$	0.38s	3.25s	
$(Me_3Si)_2(Et_2N)_2C_4Fe(CO)_3$	0.28s	2.90q (7), 1.09t (7)	
$(Me_3Si)_2(Et_2N)_2C_4Fe_2(CO)_6$	0.25s	2.77q (7), 1.15t (7)	
$Me_3SiC_2NEt_2Fe_2(CO)_6$	0.28s	3.30q (7), 3.20q (7), 1.10t (7)	
$Me_3SiC_2NEt_2Co_2(CO)_6$	0.30s	3.40br, 1.41br	
$Me_3SiC_2NEt_2Co_3Cp_3$	0.80s	4.83br, 2.10br	4.68s
$Me_3SiC_2NEt_2Mn_2(CO)_8$	0.28s	3.70q (7), 3.60q (7), 1.40t (7), 1.28t (7)	
$(Me_3Si)_2(Pr^i_2N)_2C_4Fe(CO)_3$	0.30s	3.25sp (7), 1.07d (7)	
$Me_3SiC_2NPr^i_2Fe_2(CO)_6$	0.30s	3.35sp (7), 3.25sp (7), 1.08d (7), 0.96d (7)	
$Me_3SiC_2NPr^i_2Co_2(CO)_6$	0.30s	3.4sp (7), 1.00d (7)	
$Me_2SiC_2NPr^i_2Co_3Cp_3$	0.54s	3.5br, 1.95br	4.50s
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe(CO)_3$	0.31s	3.3br, 1.3br	
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe_2(CO)_6$	0.29s	3.3br, 1.35	
$Me_3SiC_2NC_5H_{10}Fe_2(CO)_6$	0.30s	3.5br, 1.36br	
$Me_3SiC_2NC_5H_{10}Co_2(CO)_6$	0.35s	3.6br, 1.5br	
$Me_3SiC_2NC_5H_{10}Co_3Cp_3$	0.41s	3.8br, 1.7br	4.43s
$Me_3SiC_2NC_5H_{10}Mn_2(CO)_8$	0.35s	3.75br, 1.6br	

[a] s = singlet, d = doublet, t = triplet, q = quartet, sp = septet, br = broad; δ in ppm, coupling constants in Hz are given in parentheses. [b] Me = methyl, Et = ethyl, Pr^i = isopropyl, Cp = cyclopentadienyl, NC_5H_{10} = piperidino.

at 60 MHz and ^{13}C NMR spectra (Table 4) were taken on a Fourier transform JEOL FX-90Q spectrometer using $CDCl_3$ solutions in both cases. Chemical shifts are reported in ppm downfield fron internal tetramethylsilane for both ^1H and ^{13}C spectra.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) handling all filtered solutions; (c) filling evacuated vessels containing organometallic compounds; (d) storage of organometallic compounds. When necessary Schlenk ware or a polyethylene glove bag was used to provide the nitrogen atmosphere. Reactions using ultraviolet irradiation were performed with an Englehard-Hanovia medium pressure lamp immersed in a water-cooled quartz well in the reaction flask.

Tetrahydrofuran and diethyl ether were purified by refluxing over sodium benzophenone ketyl and were then distilled immediately before use. Hydrocarbon solvents were refluxed over calcium hydride and then distilled and stored over molecular sieves type 4Å. Dimethylamine was purchased from Matheson Inc., Morrow, Georgia. The metal carbonyls $Fe(CO)_5$, $Co_2(CO)_8$, and $CH_3C_5H_4Mn(CO)_3$ were purchased from GAF Corp., Alfa Products, and Ethyl Corporation, respectively. The remaining metal carbonyls $Fe_2(CO)_9$ [8], $Fe_3(CO)_{12}$ [9], $C_5H_5Co(CO)_2$ [10] and $Mn_2(CO)_{10}$ [11] were prepared by the cited published procedures. The *N,N*-dialkyl-2,2,2-trichloroacetamides were prepared by the reactions of the corresponding dialkylamine with trichloroacetyl chloride [12]. All other chemicals were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin.

Table 4

^{13}C NMR spectra of products obtained from the reactions of dialkylaminotrimethylsilylacetylenes with metal carbonyls [a]

Complex [b]	δ(CO) or δ(Cp)	δ(N-C)	δ(Si-C)	δ(Me_3Si)	δ(NR_2)
$(Me_3Si)_2(Me_2N)_2C_4Fe(CO)_3$	212	121.4	58.7	1.5	47.4(CH_3)
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe(CO)_3$	215	119.9	52.6	1.9	49.8(2CH_2), 25.6(2CH_2), 23.7(1CH_2)
$(Me_3Si)_2(Et_2N)_2C_4Fe(CO)_3$	214.9	122.0	59.8	1.6	46.8(CH_2), 13.0(CH_3)
$(Me_2Si)_2(Pr^i_2N)_2C_4Fe(CO)_3$	215	120.5	55.6	1.9	42.6(CH), 12.7(CH_3)
$(Me_3Si)_2(C_5H_{10}N)_2C_4Fe_2(CO)_6$	209	222, 128	78.4, 66.0	1.9	54.1, 48.5, 25.6, 25.3, 24.9, 23.9
$(Me_3Si)_2(Et_2N)_2C_4Fe_2(CO)_6$	214.2	220, 132	78.6, 69.0	1.7	48.7(CH_2), 45.4(CH_2), 13.2(CH_3), 12.9(CH_3)
$Me_3SiC_2NMe_2Fe_2(CO)_6$	214	226	61.7	2.2	52.4(CH_3), 47.5(CH_3)
$Me_3SiC_2NC_5H_{10}Fe_2(CO)_6$	215	226	81.6	2.4	66.3, 48.9, 22.6, 20.9
$Me_3SiC_2NEt_2Fe_2(CO)_6$	212.5	228.4	82.9	2.3	67.2(CH_2), 52.2(CH_2), 21.4(CH_3), 20.9(CH_3)
$Me_3SiC_2NPr^i_2Fe_2(CO)_6$	212	227.3	77.7	1.8	53.5(CH), 48.6(CH), 12.8(CH_3), 11.8(CH_3)
$PhC_2NMe_2Fe_2(CO)_6$ [c]	211	228.3	102.6(Ph-C)		44.7(CH_3)
$Me_3SiC_2NMe_2Co_2(CO)_6$	*d*	*d*	*d*	2.3	54.2(CH_3)
$Me_3SiC_2NC_5H_{10}Co_2(CO)_6$	199.4	*d*	*d*	2.2	54.2(2CH_2), 24.3(2CH_2), 22.8(1CH_2)
$Me_3SiC_2NEt_2Co_2(CO)_6$	*d*	*d*	*d*	2.4	51.8(CH_2), 19.6(CH_3)
$Me_3SiC_2NPr^i_2Co_2(CO)_6$	*d*	*d*	*d*	2.4	52.5(CH), 19.3(CH_3)
$Me_3SiC_2NC_5H_{10}Co_3Cp_3$	81.5	*d*	*d*	1.8	53.6(2CH_2), 24.5(2CH_2), 23.7(1CH_2)
$Me_3SiC_2NEt_2Co_3Cp_3$	82.4	*d*	*d*	2.3	53.1(CH_2), 22.7(CH_3)
$Me_3SiC_2NPr^i_2Co_3Cp_3$	82.1	*d*	*d*	1.9	52.5(CH), 19.3(CH_3)
$Me_3SiC_2NC_5H_{10}Mn_2(CO)_8$	*d*	231	143	2.2	52.3, 51.5, 25.8
$Me_3SiC_2NEt_2Mn_2(CO)_8$	*d*	234	141	2.1	51.2(CH_2), 50.8(CH_2), 13.4(CH_3), 12.7(CH_3)
$MeC_2NEt_2Mn_2(CO)_8$ [c]	221	232.9	136.8	30.2(Me)	54.0(CH_2), 50.6(CH_2), 14.0(CH_3), 13.2(CH_3)

[a] All resonances were singlets when run with proton decoupling; assignments are given in parentheses when not clear from the table. [b] Me = methyl, Et = ethyl, Pr^i = isopropyl, Cp = cyclopentadienyl, Ph = phenyl, NC_5H_{10} = piperidino. [c] Data of R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879. [d] Not observed, probably owing to direct coupling of the carbon to the directly bonded quadrupolar manganese or cobalt atom.

Preparation of the dialkylaminotrimethylsilylacetylenes

The general method followed the published procedure [6] and is illustrated below for the preparation of $[(CH_3)_2CH]_2NC{\equiv}CSi(CH_3)_3$.

A 250 ml flask containing 49 g (0.2 mol) of *N*,*N*-diisopropyl-2,2,2-trichloroacetamide was treated dropwise at 25 ° C under nitrogen with 40.5 g (0.2 mol) of tri-n-butylphosphine. The reaction temperature rose quickly to 50 ° C. The addition was completed in 1 h by cooling with tap water. After heating for an additional 2 h at 50–55 ° C, the solution was stirred at room temperature for 16 h. Distillation then gave 25.9 g (56% yield) of *N*,*N*-diisopropyl-1,2,2-trichlorovinylamine, b.p. 80–85 ° C/6 mmHg, identified by its mass spectrum.

A solution of the 25.9 g (0.113 mol) of *N*,*N*-diisopropyl-1,2,2-trichlorovinylamine in 100 ml of diethyl ether at 0 ° C was treated dropwise with 177 ml of commercial 1.6 *M* n-butyllithium (0.283 mol). The reaction mixture was then stirred for 8 h at room temperature. After cooling back to 0 ° C a solution of 21.7 g (0.2 mol) of trimethylchlorosilane in 100 ml of diethyl ether was added dropwise. The reaction mixture was stirred for 4 h at room temperature. Distillation of the filtered reaction mixture gave 7.6 g (34% yield) of diisopropylaminotrimethylsilylacetylene, b.p. 80–85 ° C/6 mmHg; $\nu(C{\equiv}C)$ 2130 cm^{-1}, identified by its mass spectrum.

A similar procedure was used to prepare the other dialkylaminotrimethylsilylacetylenes, which were characterized before use by their infrared $\nu(C{\equiv}C)$ frequencies at 2130–2160 cm^{-1} and mass spectra.

Reaction of $(CH_3)_2NC{\equiv}CSi(CH_3)_3$ with $Fe(CO)_5$

A mixture of 1.7 g (12 mmol) of $(CH_3)_2NC{\equiv}CSi(CH_3)_3$, 4.0 g (20 mmol) of $Fe(CO)_5$, and 100 ml of heptane was boiled under reflux for 6 h. Solvent was removed from the filtered reaction mixture at 25 ° C/5 mmHg. A concentrated diethyl ether extract of the brown solid was chromatographed on a 2 × 35 cm alumina column. Elution of the yellow band with hexane followed by evaporation to dryness at 25 ° C/25 mmHg gave 0.1 g (12% yield) of yellow crystalline $[(CH_3)_3Si]_2[(CH_3)_2N]_2C_4Fe(CO)_3$, m.p. 116–119 ° C; mass spectrum: $[(CH_3)_3Si]_2[(CH_3)_2N]_2C_4Fe(CO)_n^+$ ($n = 3, 2, 1, 0$).

Reaction of $C_5H_{10}NC{\equiv}CSi(CH_3)_3$ with $Fe(CO)_5$

A mixture of 2.0 g (11 mmol) of $C_5H_{10}NC{\equiv}CSi(CH_3)_3$, 10.8 g (55 mmol) of $Fe(CO)_5$, and 100 ml of heptane was boiled under reflux for 6 h. Solvent was removed from the filtered reaction mixture in vacuum. A concentrated diethyl ether extract of the brown residue was chromatographed on a 2 × 35 cm alumina column. Elution of the yellow band with hexane followed by evaporation of the eluate at 25 ° C/25 mmHg and sublimation of the residue at 55 ° C/0.1 mmHg gave 0.64 g (23% yield) of yellow crystalline $[(CH_3)_3Si]_2[C_5H_{10}N]_2C_4Fe(CO)_3$, m.p. 159 ° C; mass spectrum: $[(CH_3)_3Si]_2[C_5H_{10}N]_2C_4Fe(CO)_n^+$ ($n = 3, 2, 1, 0$). Elution of the orange-red band with 1/1 diethyl ether/hexane followed by evaporation of the eluate to dryness at 25 ° C/25 mmHg and crystallization of the residue from hexane at −20 ° C gave 0.05 g (1% yield) of dark red $[(CH_3)_3Si]_2[C_5H_{10}N]_2C_4Fe_2(CO)_6$, m.p. 94 ° C (dec.).

Reaction of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$ with $Fe(CO)_5$

A mixture of 2.0 g (12 mmol) of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$, 4.0 g (20 mmol) of $Fe(CO)_5$, and 100 ml of heptane was boiled under reflux for 6 h. Solvent was removed from the filtered dark red reaction mixture at 25 °C/5 mmHg. A concentrated diethyl ether extract of the reddish brown residue was chromatographed on a 2 × 35 cm alumina column. Elution of the yellow band with hexane followed by evaporation of the eluate at 25 °C/25 mmHg and sublimation of the residue at 60 °C/0.1 mmHg gave 0.64 g (23% yield) of yellow crystalline $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$, m.p. 146 °C; mass spectrum: $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_n{}^+$ ($n = 3, 2, 1, 0$). Elution of the red-orange band with 1/1 diethyl ether/hexane followed by evaporation of the eluate to dryness at 25 °C/25 mmHg and crystallization of the residue from hexane at −20 °C gave 0.04 g (~1% yield) of dark red crystalline $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe_2(CO)_6$, m.p. 87 °C (dec.).

Reaction of $[(CH_3)_2CH]_2NC{\equiv}CSi(CH_3)_3$ with $Fe(CO)_5$

A mixture of 2.0 g (10 mmol) of $[(CH_3)_2CH]_2NC{\equiv}CSi(CH_3)_3$, 10.8 g (55 mmol of $Fe(CO)_5$, and 70 ml of decahydronaphthalene (decalin) was boiled under reflux for 6 h. Solvent was removed from the filtered reaction mixture at 50 °C/1.0 mmHg. A concentrated diethyl ether extract of the brown residue was chromatographed on a 2 × 35 cm alumina column. Elution of the yellow band with hexane followed by evaporation of the eluate at 25 °C/25 mmHg and sublimation of the residue at 60 °C/0.1 mmHg gave 0.04 g (~1% yield) of yellow, crystalline $[(CH_3)_2Si]_2\{[(CH_3)_2CH]_2N\}_2C_4Fe(CO)_3$, m.p. 163 °C; mass spectrum: $[(CH_3)_3Si]_2[(C_3H_7)_2N]_2C_4Fe(CO)_n{}^+$ ($n = 3, 2, 1, 0$).

Reactions of dialkylaminotrimethylsilylacetylenes with $Fe_2(CO)_9$

A mixture of 12 mmol of the dialkylaminotrimethylsilylacetylene, 8.6 g (24 mmol) of $Fe_2(CO)_9$, and 100 ml of diethyl ether was stirred at room temperature for 24 h. The filtered and concentrated reaction mixture was chromatographed on a 2 × 35 cm alumina column. Elution of the red band with hexane followed by evaporation of the filtered eluate to dryness at 25 °C/25 mmHg gave the orange-red $(CH_3)_3SiC_2NR_2Fe_2(CO)_6$ derivative (Table 1).

Photolysis of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$ with $Fe(CO)_5$

A mixture of 2.0 g (12 mmol) of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$, 10 g (50 mmol) of $Fe(CO)_5$, and 350 ml of hexane was exposed to ultraviolet irradiation for 36 h at room temperature. Concentration of the filtered reaction mixture at 25 °C/25 mmHg gave 2.1 g (40% yield) of orange-red $(CH_3)_3SiC_2N(C_2H_5)_2Fe_2(CO)_6$ identical to the product obtained from $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$ and $Fe_2(CO)_9$ as described above.

Reaction of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$ with $Fe_3(CO)_{12}$

A mixture of 2.0 g (12 mmol) of $(C_2H_5)_2NC{\equiv}CSi(CH_3)_3$, 3.0 g (8 mmol) of $Fe_3(CO)_{12}$, and 100 ml of hexane was boiled under reflux for 16 h. The filtered and concentrated dark green reaction mixture was chromatographed on a 2 × 35 cm alumina column. Elution of the red band with hexane followed by evaporation of the filtered eluate at 25 °C/25 mmHg gave 0.2 g (4% yield) of orange-red $(CH_3)_3SiC_2N(C_2H_5)_2Fe_2(CO)_6$ identical to the product obtained as described above.

Reactions of dialkylaminotrimethylsilylacetylenes with $Co_2(CO)_8$

Equimolar quantities of the dialkylaminotrimethylsilylacetylene and $Co_2(CO)_8$ were stirred in diethyl ether solution (100 ml for 5 mmol of reactants) at room

Table 5

Crystallographic summary

Crystal data (− 110 °C) [a]	
a, b, c (Å)	10.602(2), 14.877(2), 9.955(2)
α, β, γ (°)	96.61(1), 111.98(1), 109.66(1)
V (Å^3)	1317.8
d_{measd} (g cm^{-3}) at 21 °C [b]	1.237
d_{calc} (g cm^{-3}) at −110 °C	1.273
Empirical formula, FW	$C_{23}H_{38}N_2O_3Si_2Fe$, 504.9
Crystal system, space group, Z	triclinic, $P\bar{1}$, 2
$F(000)$ (electrons)	536
Data collection (− 110 °C) [b]	
Radiation, λ (Å)	Mo-K_α, 0.71069
Mode	ω-scan
Scan range	symmetrically over 1.0 ° about $K_{\alpha_{1,2}}$ maximum
Background	offset 1.0 and −1.0 in ω from $K_{\alpha_{1,2}}$ maximum
Scan rate (° min^{-1})	3.0–6.0
2θ range (°)	4.0–54.0
Total reflections measured	5753
Exposure time (h)	72.5
Stability analysis:	
Computed s, t	−0.0004(3), 0.000013(4)
Correction range (on I)	0.961–1.003
Data crystal faces	(001, {1, −1, 0}, {100}, {010}, fragment { ~ −1, 2, −4}
Data crystal volume (mm^3)	0.0383
Absorption coeff, μ(Mo-K_α) (cm^{-1})	6.92
Transmission factor range	0.786–0.864
Structure refinement [c]	
Ignorance factor, p	0.02
Reflections used, m, with $F \leq 4\ \sigma(F_o)$	4924
No. of variables, n	336
R, wR	0.032, 0.035
R for all data	0.040
Goodness of fit, S	1.54
Max shift/esd (non-H)	0.66
Max shift/esd (H)	0.72
Max, min peaks in diff map (e Å^{-3})	0.33, −0.28

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[a] Unit cell parameters were obtained by least squares refinement of the setting angles of 60 reflections with $22.0° \leq 2\theta \leq 24.9°$. Crystal density was measured by flotation in an aqueous $ZnCl_2$ solution. [b] Syntex P2$_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in P.E. Riley and R.E. Davis, Acta Crystallogr., Sect. B, 32 (1976) 381–386. Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. These data were analyzed as detailed in W.H. Henslee and R.E. Davis, Acta Crystallogr., Sect. B, 31 (1975) 1511–1519. [c] Relevant expressions are as follows, where in this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes. Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$. $R = \Sigma|(F_o - F_c)|/\Sigma F_o$. $wR = [\Sigma w(F_o - F_c)^2/\Sigma w F_o{}^2]^{1/2}$. $S = [\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$.

temperature for 16 h. A rapid reaction occurred with gas evolution and the reaction mixture became dark green. The filtered and concentrated reaction mixture was chromatographed on a 2 × 35 cm alumina column. Elution of the green band with hexane followed by evaporation of the eluate at 25 °C/25 mmHg and sublimation of the residue at 60 °C/0.01 mmHg gave the dark green $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ derivative (Table 1). All four $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ complexes exhibited the complete series of ions $[(CH_3)_3SiC_2NR_2Co_2(CO)_n]^+$ in their mass spectra.

Reactions of dialkylaminotrimethylsilylacetylenes with $C_5H_5Co(CO)_2$

A mixture of 1.0 g of the dialkylaminotrimethylsilylacetylene, 1.0 g of $C_5H_5Co(CO)_2$, and 50 ml of n-octane was boiled under reflux for 24 h. Solvent was

Table 6

Fractional coordinates and isotropic or equivalent isotropic [a] thermal parameters (Å^2) for non-hydrogen atoms

Atom	*x*	*y*	*z*	*U*
Fe	0.31083(3)	0.35216(2)	1.03424(3)	0.01686(12)
Si(1)	0.39684(6)	0.24327(4)	1.34810(6)	0.0189(2)
Si(2)	−0.06038(6)	0.20856(4)	0.76227(6)	0.0192(2)
O(1)	0.6337(2)	0.43165(11)	1.2167(2)	0.0339(7)
O(2)	0.3261(2)	0.34691(12)	0.7455(2)	0.0361(8)
O(3)	0.2757(2)	0.53953(11)	1.0935(2)	0.0367(8)
N(1)	0.2374(2)	0.13030(11)	0.9143(2)	0.0173(7)
N(2)	0.0753(2)	0.31260(11)	1.1829(2)	0.0181(7)
C(1)	0.5075(2)	0.40050(14)	1.1447(2)	0.0224(9)
C(2)	0.3185(2)	0.35066(14)	0.8573(2)	0.0237(9)
C(3)	0.2894(2)	0.46673(15)	1.0737(2)	0.0228(9)
C(4)	0.2711(2)	0.25196(13)	1.1621(2)	0.0168(7)
C(5)	0.2248(2)	0.20728(13)	0.9989(2)	0.0158(7)
C(6)	0.0983(2)	0.23713(13)	0.9507(2)	0.0162(7)
C(7)	0.1416(2)	0.27647(13)	1.1104(2)	0.0164(7)
C(8)	0.5205(2)	0.1841(2)	1.3258(2)	0.0305(10)
C(9)	0.2757(3)	0.1619(2)	1.4212(3)	0.0340(11)
C(10)	0.5236(2)	0.3666(2)	1.4923(2)	0.0312(9)
C(11)	−0.0295(3)	0.1414(2)	0.6154(2)	0.0283(9)
C(12)	−0.2415(2)	0.1239(2)	0.7554(3)	0.0342(10)
C(13)	−0.0759(3)	0.3246(2)	0.7170(2)	0.0285(10)
C(14)	0.3864(2)	0.14427(14)	0.9304(2)	0.0229(8)
C(15)	0.3735(2)	0.06209(15)	0.8122(2)	0.0261(9)
C(16)	0.2928(2)	−0.03962(15)	0.8268(2)	0.0260(9)
C(17)	0.1398(2)	−0.05164(14)	0.8126(2)	0.0267(9)
C(18)	0.1537(2)	0.03295(13)	0.9272(2)	0.0212(8)
C(19)	0.1628(2)	0.3716(2)	1.3408(2)	0.0242(9)
C(20)	0.0631(2)	0.3650(2)	1.4192(2)	0.0278(10)
C(21)	−0.0642(2)	0.3934(2)	1.3338(2)	0.0277(10)
C(22)	−0.1496(2)	0.3311(2)	1.1701(2)	0.0264(9)
C(23)	−0.0443(2)	0.3407(2)	1.0972(2)	0.0238(9)
Cent	0.183965	0.243212	1.053554	

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star A_{ij}$; where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors. Cent represents the position of the cyclobutadiene ring centroid.

Table 7

Bond lengths (Å) and angles (°)

1	2	3	1–2	1–2–3
C(1)	Fe	C(2)	1.779(2)	95.37(11)
C(2)	Fe	C(3)	1.791(2)	100.85(11)
C(3)	Fe	C(1)	1.812(2)	97.44(9)
Cent	Fe	C(1)	1.809(0)	121.96(8)
C(2)	Fe	Cent		119.56(6)
C(3)	Fe	Cent		116.93(8)
C(4)	Fe	C(5)	2.106(2)	43.14(8)
C(5)	Fe	C(6)	1.966(2)	42.70(9)
C(6)	Fe	C(7)	2.091(2)	39.55(7)
C(7)	Fe	C(4)	2.217(2)	39.38(8)
O(1)	C(1)	Fe	1.144(2)	179.49(23)
O(2)	C(2)	Fe	1.143(3)	177.08(23)
O(3)	C(3)	Fe	1.145(3)	177.44(21)
Si(1)	C(4)	Fe	1.883(2)	131.58(9)
C(5)	C(4)	Fe	1.503(3)	63.43(11)
C(5)	C(4)	Si(1)		135.89(17)
C(5)	C(4)	C(7)		86.85(15)
C(7)	C(4)	Si(1)		134.61(17)
N(1)	C(5)	Fe	1.416(3)	132.04(16)
C(6)	C(5)	Fe	1.482(3)	73.17(11)
C(6)	C(5)	N(1)		126.24(13)
C(6)	C(5)	C(4)		91.49(17)
Si(2)	C(6)	Fe	1.872(2)	125.46(11)
C(7)	C(6)	Fe	1.462(3)	74.89(9)
C(7)	C(6)	Si(2)		139.44(18)
C(5)	C(6)	Si(2)		132.01(17)
C(7)	C(6)	C(5)		87.57(15)
N(2)	C(7)	Fe	1.360(3)	131.35(13)
C(4)	C(7)	Fe	1.461(3)	66.21(12)
C(4)	C(7)	N(2)		133.24(17)
C(4)	C(7)	C(6)		94.00(18)
C(8)	Si(1)	C(4)	1.869(3)	111.49(11)
C(9)	Si(1)	C(4)	1.871(3)	107.74(10)
C(10)	Si(1)	C(4)	1.877(2)	113.87(10)
C(8)	Si(1)	C(9)		107.43(13)
C(9)	Si(1)	C(10)		109.84(11)
C(10)	Si(1)	C(8)		106.30(11)
C(11)	Si(2)	C(6)	1.868(3)	108.70(11)
C(12)	Si(2)	C(6)	1.879(2)	110.62(10)
C(13)	Si(2)	C(6)	1.878(3)	111.60(8)
C(11)	Si(2)	C(12)		107.22(11)
C(12)	Si(2)	C(13)		109.25(12)
C(13)	Si(2)	C(11)		109.34(12)
C(14)	N(1)	C(5)	1.465(3)	117.85(13)
C(18)	N(1)	C(5)	1.471(3)	110.97(18)
C(18)	N(1)	C(14)		113.23(16)
C(15)	C(14)	N(1)	1.527(3)	109.73(14)
C(16)	C(15)	C(14)	1.521(3)	110.70(21)
C(17)	C(16)	C(15)	1.521(4)	109.75(21)
C(18)	C(17)	C(16)	1.525(3)	110.56(14)
N(1)	C(18)	C(17)		111.33(20)
C(19)	N(2)	C(6)	1.465(2)	119.70(18)
C(23)	N(2)	C(6)	1.462(3)	119.02(16)

Table 7 (continued)

1	2	3	1–2	1–2–3
C(23)	N(2)	C(19)		113.49(16)
C(20)	C(19)	N(2)	1.517(4)	110.90(15)
C(21)	C(20)	C(19)	1.526(4)	111.20(20)
C(22)	C(21)	C(20)	1.522(3)	110.20(22)
C(23)	C(22)	C(21)	1.522(4)	110.57(16)
N(2)	C(23)	C(22)		110.30(19)

removed from the filtered reaction mixture at 40 °C/1 mmHg. A concentrated diethyl ether solution of the black residue was chromatographed on a 2 × 35 cm alumina column. Elution of the black band with 1/1 diethyl ether/hexane followed by evaporation of the filtered eluate at 25 °C/25 mmHg gave the black $(CH_3)_3SiC_2NR_2Co_3(C_5H_5)_3$ derivative (Table 1).

Photolyses of dialkylaminotrimethylsilylacetylenes with $Mn_2(CO)_{10}$

A solution of approximately equimolar quantities of the dialkylaminotrimethylsilylacetylene and $Mn_2(CO)_{10}$ (~ 5 mmol each) in 300 ml of tetrahydrofuran was exposed to ultraviolet irradiation for 36 h. The filtered and concentrated orange reaction mixture was chromatographed on a 2 × 35 cm alumina column. Elution of the red to orange band with hexane followed by evaporation of the filtered eluate to dryness gave a very low yield of the red-orange $(CH_3)_3SiC_2NR_2Mn_2(CO)_8$ derivative (Table 1).

Structure determination of $[(CH_3)_3Si]_2[C_5H_{10}N]_2C_4Fe(CO)_3$

A single crystal of $[(CH_3)_3Si]_2[C_5H_{10}N]_2C_4Fe(CO)_3$ was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex $P2_1$ autodiffracto-

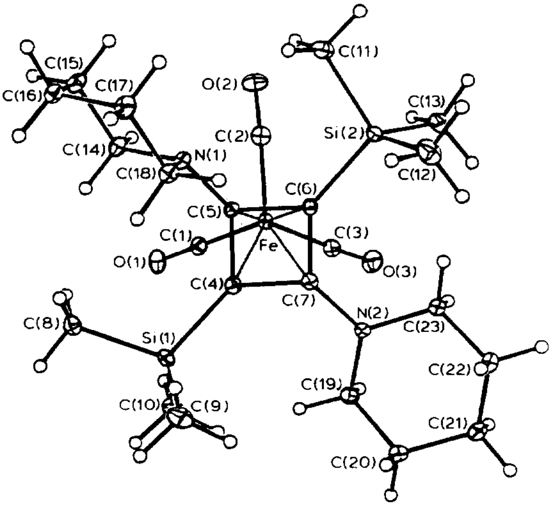


Fig. 1. Structure of $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$ showing the atom numbering and the relationship of the $Fe(CO)_3$ group to the cyclobutadiene ring.

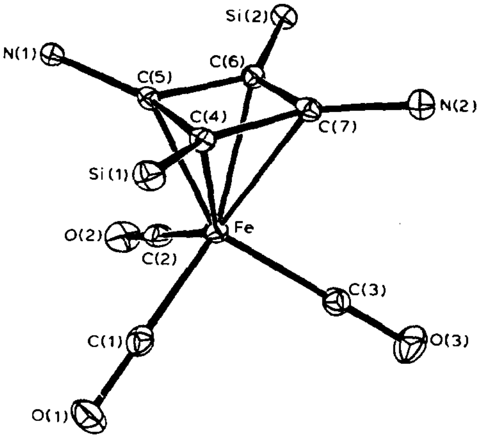


Fig. 2. View of $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$ showing the FeC_4 square pyramid; the trimethylsilyl methyl groups and the piperidino methylene groups are omitted for clarity.

meter, where it was maintained in a cold (−110 °C) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystal for intensity data collection. A summary of the pertinent crystal data and details of the X-ray diffraction data and processing is presented in Table 5. The measured intensities were reduced and assigned standard deviations as described elsewhere [13], including corrections for absorption based on measured crystal shape.

The structure was solved [14] by the heavy-atom method using heavy-atom positions determined from a sharpened Patterson map. The structure was refined by the full-matrix least-squares method, using the program SHELX-76. Neutral atom scattering factors [15] for H, C, N, O, Si, and Fe were used, including real and imaginary corrections for anomalous dispersion. Figures 1 and 2 provide views of the molecule and indicate the atom-numbering scheme used in this paper. Coordinates for non-hydrogen atoms are given in Table 6, and Table 7 presents bond lengths and angles. Tables of observed and calculated structure amplitudes, anisotropic thermal parameters, and hydrogen positions and thermal parameters are available from one of the authors (R.E.D.).

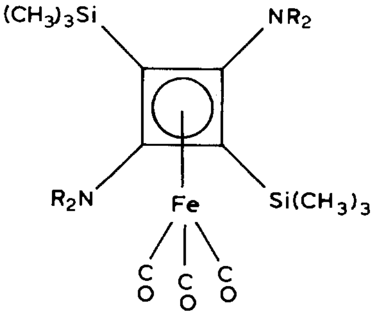
Results and discussion

The major organometallic products from the reactions of the dialkylaminotrimethylsilylacetylenes, $(CH_3)_3SiC{\equiv}CNR_2$, with $Fe(CO)_5$ at elevated temperatures are yellow air-stable crystalline solids $[(CH_3)_3Si]_2(R_2N)_2C_4Fe(CO)_3$ inferred from their stoichiometries to be cyclobutadiene-iron tricarbonyl derivatives. In the cases of the acetylenes $(CH_3)_3SiC{\equiv}CNR_2$ (R = methyl, ethyl, or R_2N = piperidino) these products were isolated in 12 to 23% yields from reactions conducted in boiling heptane (98 °C) whereas in the case of the much more sterically hindered $(CH_3)_3SiC{\equiv}CN[CH(CH_3)_2]_2$ no reaction occurred in boiling heptane and even in boiling decalin (190 °C) the yield of $[(CH_3)_3Si]_2\{[(CH_3)_2CH]_2N\}_2C_4Fe(CO)_3$ was only ~ 1%. The formation of cyclobutadiene-iron tricarbonyl derivatives from reactions of the unsymmetrical acetylenes $(CH_3)_3SiC{\equiv}CNR_2$ with iron carbonyls contrasts with the corresponding reactions of the symmetrical acetylenes $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ and $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ with iron carbonyls. Thus $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ reacts with $Fe(CO)_5$ to give the alkyne dichotomy product $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$ (I) and the cyclopentadienone complex $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ whereas $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ reacts with $Fe(CO)_5$ to give the acetylene complex $[(CH_3)_3Si]_2C_2Fe(CO)_4$ [7].

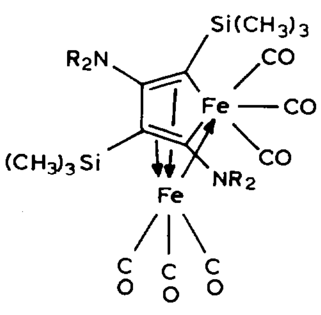
The spectroscopic properties of the complexes $[(CH_3)_3Si]_2(R_2N)_2C_4Fe(CO)_3$ are suggestive of cyclobutadiene-iron tricarbonyl derivatives. Their infrared ν(CO) spectra (Table 2) exhibit an A_1 band at 2020 cm^{-1} and a split E band around 1950 cm^{-1} indicating the expected deviation from C_{3v} symmetry accentuated by the unsymmetrical pattern of substituents on the cyclobutadiene ring. Their NMR spectra indicate both trimethylsilyl groups and both dialkylamino groups as well as the carbon atoms to which they are bonded (C–Si and C–N, respectively, in Table 3) to be equivalent in accord with a cyclobutadiene-iron tricarbonyl structure. However, the spectroscopic data do not distinguish between the two possible geometrical isomers, namely 1,2-$[(CH_3)_3Si]_2$-3,4-$(R_2N)_2C_4Fe(CO)_3$ and 1,3-$[(CH_3)_3Si]_2$-2,4-$(R_2N)_2C_4Fe(CO)_3$ formed by head-to-head and head-to-tail dimerization, respectively, of the acetylene. Therefore, the structure of the piperidino complex $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$ was determined by X-ray diffraction as summarized in Table 5.

The structural study on $[(CH_3)_3Si]_2(C_5H_{10}N)_2C_4Fe(CO)_3$ clearly indicates the 1,3-structure II (R_2N = piperidino) as depicted in Figs. 1 and 2. As Fig. 1 shows, the piperidino ring at C(5) is rotated almost perpendicular to the C_4 ring, while that at C(7) is almost parallel. Thus the ring at C(7) is very demanding sterically in the plane of the C_4 ring, while that at C(5) takes up as little space as possible in that plane. The two $Si(CH_3)_3$ groups are both rotated so that the equatorial H atoms on the "parallel" piperidino group (at C(7)) fit in the cleft between pairs of methyl groups (C(9)/C(10)) and C(12)/C(13)). This places the other methyl groups C(11) and C(8) closer to the plane of the C_4 ring and points them toward the "perpendicular" piperidino group (at C(5)). In both piperidino rings, the N atoms are clearly pyramidal with the average bond angle at N(1) 114.0 and at N(2) 117.4°. This difference in average bond angles may be due to the differences in interaction of N lone pair orbitals with the cyclobutadiene π-system, resulting from the two $C_5H_{10}N$ ring orientations. This overlap is presumably more favorable for the "parallel" ring (N(2) with C(7)) than for the "perpendicular" ring (N(1) with C(5)), allowing a slightly higher degree of sp^2 character at N(2). The deviation of the cyclobutadiene ring from a perfect square is significant with acute angles (86.85(15) at C(4) and 87.57(15)° at C(6)) at the carbon atoms bearing trimethylsilyl substituents and obtuse angles (91.49(17) at C(5) and 94.00(18)° at C(7)) at the carbon atoms bearing piperidino substituents indicative of the expected different interactions of these rather diverse substituents with the cyclobutadiene ring.

Figure 1 indicates that the $Fe(CO)_3$ group has a staggered rather than eclipsed orientation with respect to the cyclobutadiene ring [17] as might be expected in light of the relatively large trimethylsilyl and piperidino substituents. This is expressed in the quantitative terms as defined in Ref. 17: (i) The distance between projection of Fe onto the ring and the ring carbon centroid position (offset) is 0.27 Å. (ii) The



(II)



(III)

angle between the axis of the cone defined by the three Fe–C_{CO} bonds and the normal to the mean plane of the ring carbons (tilt) is 7.5°. (iii) The individual minimum torsion angles (MTA) involving (C_{CO}–Fe–centroid–C_{ring}) are C(3)–Fe–X–C(7) −13.78°, C(1)–Fe–X–C(4) −19.14°, and C(2)–Fe–X–C(5) 45.01°. This corresponds to a group torsion angle, ϕ (ref. 17) equal to 13.2°.

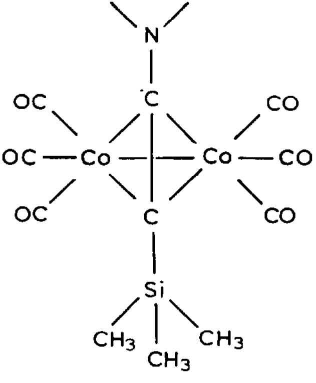
The reactions of $(CH_3)_3SiC{\equiv}CNR_2$ (NR_2 = diethylamino and piperidino) with $Fe(CO)_5$ give not only the corresponding cyclobutadiene-iron tricarbonyl derivatives II but also very low yields of red more strongly adsorbed complexes of the stoichiometry $[(CH_3)_3Si]_2(R_2N)_2C_4Fe_2(CO)_6$. These are formulated as the tricarbonylferrole-ion tricarbonyl derivatives III, a common type of product from reactions of acetylenes with iron carbonyls [18]. The arrangement of trimethylsilyl and dialkylamino substituents in structure III is suggested not only in accord with head-to-tail dimerization of the acetylene as found for the cyclobutadiene complex II (R_2N = piperidino) by the X-ray diffraction structure determination but also on the basis of NMR observations (Table 3) of two non-equivalent diethylamino or piperidino groups and four non-equivalent ferrole ring carbons indicating no symmetry in the system.

Several unsuccessful attempts were made to liberate the free cyclobutadiene or its dimer from the complex $[(CH_3)_3Si]_2[C_2H_5)_2N]_2C_4Fe(CO)_3$ by various oxidative degradation methods which are successful for other cyclobutadiene-iron carbonyl derivatives. Thus, treatment of $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$ at room temperature with ammonium hexanitratocerate (IV) in ethanol or trimethylamine *N*-oxide hydrate in acetone or benzene resulted in recovery of most of the iron carbonyl complex. Extended treatment of $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$ at room temperature in acetone solution with ammonium hexanitratocerate (IV) or ferric chloride or reaction of the iron carbonyl complex with anhydrous trimethylamine *N*-oxide in boiling benzene failed to give any evidence for $[(CH_3)_3SiC_2\text{-}N(C_2H_5)_2]_n$ oligomers as indicated by gas chromatography/mass spectrometry analysis of the crude oily products. We suspect that the bulky $(CH_3)_3Si$ and $(C_2H_5)_2N$ substituents in $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$ shield the iron atom thereby hindering clean oxidative removal of the $Fe(CO)_3$ group in contrast to other cyclobutadiene-iron tricarbonyl derivatives [16].

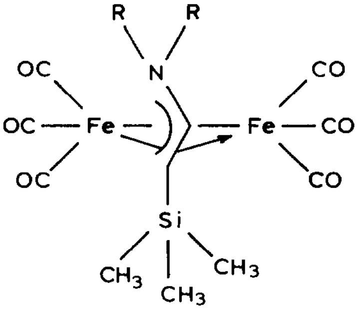
The formation of the cyclobutadiene derivatives II and the tricarbonylferrole-iron tricarbonyl derivatives III from reactions of the acetylenes $(CH_3)_3SiC{\equiv}CNR_2$ with

$Fe(CO)_5$ involve dimerization of the acetylene. Reactions of the acetylenes $(CH_3)_3SiC{\equiv}CNR_2$ with the binuclear metal carbonyls $M_2(CO)_n$ ($M = Mn$, $n = 10$; $M = Fe$, $n = 9$; $M = Co$, $n = 8$) under milder conditions (ambient temperature except for $Mn_2(CO)_{10}$ where ultraviolet irradiation is needed) result in products containing a monomeric $(CH_3)_3SiC_2NR_2$ unit. The deep green rather air-sensitive cobalt carbonyl derivatives $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ are suggested to have structures IV (R = methyl, ethyl, or isopropyl or R_2N = piperidino) similar to those of the many other known acetylene-dicobalt hexacarbonyl derivatives [19]. The deep green colors of the $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ are rather unusual since almost all known [19] $RC_2R'Co_2(CO)_6$ derivatives have colors ranging from light red to dark violet. However, some (1,3-diyne)$[Co_2(CO)_6]_2$ derivatives are also dark green [20] indicating that the observed dark green color of the $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ derivatives is not unprecedented. The $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ formulations of these complexes are supported by their mass spectra which show the complete series of $(CH_3)_3SiC_2NR_2Co_2(CO)_n^+$ ($n = 6, 5, 4, 3, 2, 1, 0$) ions. The infrared $\nu(CO)$ spectra of these complexes not only indicate an absence of bridging $\nu(CO)$ frequencies but exhibit patterns of terminal $\nu(CO)$ frequencies similar to those found for other (alkyne)$Co_2(CO)_6$ derivatives (Table 2). The ^1H and ^{13}C NMR spectra (Tables 3 and 4) of the $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ complexes indicate both alkyl groups of the R_2N moiety to be equivalent in accord with structure IV. However, the ^{13}C resonances of the carbons in the Co_2C_2 tetrahedron as well as the carbonyl groups could not be observed, possibly owing to broadening through coupling with the quadrupolar cobalt atoms.

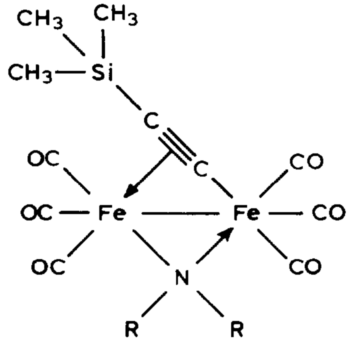
The remaining products of the type $(CH_3)_3SiC_2NR_2M_2(CO)_n$ ($M = Mn$, $n = 8$; $M = Fe$, $n = 6$) represent compound types previously [3] found for other aminoalkynes (e.g., $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$, $(C_2H_5)_2NC_2N(C_2H_5)_2Mn_2(CO)_8$, and $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$) but not for acetylenes without dialkylamino substituents [18]. The implied direct involvement of the R_2N group in the bonding to the dimetal system is supported by the non-equivalence of the two R groups in the ^1H and ^{13}C NMR spectra of these complexes (Tables 3 and 4) in contrast to the $(CH_3)_3SiC_2NR_2Co_2(CO)_6$ derivatives (IV) discussed above. For example, the diethylamino group in $(CH_3)_3SiC_2N(C_2H_5)_2Fe_2(CO)_6$ exhibits two CH_2 resonances at



(IV)

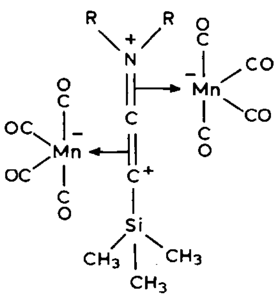


(Va)

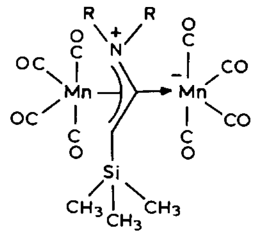


(Vb)

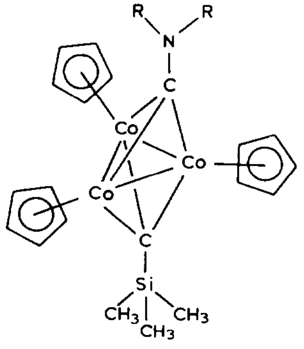
δ 67.2 and δ 52.2 and two CH_3 resonances at δ 21.4 and δ 20.9 (Table 4). Similarly, the diethylamino group in $(CH_3)_3SiC_2N(C_2H_5)_2Mn_2(CO)_8$ exhibits two CH_2 resonances at δ 51.2 and δ 50.8 and two CH_3 resonances at δ 13.4 and δ 12.7. Possible structures for the iron complexes $(CH_3)_3SiC_2NR_2Fe_2(CO)_6$ in which the iron atoms have the favored rare gas electronic configuration include Va analogous to that originally [3] proposed for $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$ and Vb subsequently proposed for this complex in a review article. Possible structures for the manganese complexes $(CH_3)_3SiC_2NR_2Mn_2(CO)_8$ (R_2N = diethylamino or piperidino) in which the manganese atoms have the favored rare gas electronic configuration include VIa similar to that originally [3] proposed for $(C_2H_5)_2NC_2N(C_2H_5)_2$-$Mn_2(CO)_8$ and $CH_3C_2N(C_2H_5)_2Mn_2(CO)_8$ and a fairly closely related VIb in which the C_2N moiety from the aminoalkyne is bonded to one $Mn(CO)_4$ unit as a trihapto 1-azaallyl ligand and to the other $Mn(CO)_4$ unit through the center carbon atom as an aminocarbene ligand. The relatively low chemical shift (δ 231 to 234) of one of the two C_2N carbon atoms is consistent with an aminocarbene carbon atom such as that required for structure VIb. We have not yet been in a position to



(VIa)



(VIb)



(VII)

undertake the X-ray diffraction studies required for more definitive structural information on these binuclear complexes.

The reactions of $(CH_3)_3SiC{\equiv}CNR_2$ with $C_5H_5Co(CO)_2$ do not proceed in a manner analogous to those of $(CH_3)_3SiC{\equiv}CNR_2$ with $Fe(CO)_5$ discussed above but instead give the black trinuclear derivatives $(CH_3)_3SiC_2NR_2Co_3(C_5H_5)_3$. A related product, $[(C_2H_5)_2N]_2C_2Co_3(C_5H_5)_3$, was first found [3] in the closely related reaction of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with $C_5H_5Co(CO)_2$. Analogy with structures determined by X-ray diffraction on this complex and on $[(CH_3)_3SiC_2]$-$[(CH_3)_3Si]C_2Co_3(C_5H_5)_3$ [22] suggest structures VII for the $(CH_3)_3SiC_2NR_2Co_3$-$(C_5H_5)_3$ complexes reported in this paper.

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References

1 For part XII of this series see R.B. King and K.N. Chen, Inorg. Chem., 16 (1977) 3372.

2 Portions of this work were presented at the XI International Conference on Organometallic Chemistry, Callaway Gardens, Georgia, October 1983: abstracts, p. 110.

3 R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879.

4 G.G. Cash, R.C. Pettersen, and R.B. King, Chem. Comm., (1977) 30.

5 R.C. Petterson and G.G. Cash, Acta Crystallogr., Sect. B, 34 (1978) 3086.

6 Y. Sato, Y. Kobayashi, M. Sugiura, and H. Shirai, J. Org. Chem., 43 (1978) 199.

7 K.H. Pannell and G.M. Crawford, J. Coord. Chem., 2 (1973) 251.

8 E. Braye and W. Hübel, Inorg. Synth., 8 (1966) 178.

9 R.B. King, Organomet. Synth., 1 (1965) 95.

10 M.D. Rausch and R.A. Genetti, J. Org. Chem., 35 (1970) 3888.

11 R.B. King, J.C. Stokes, and T.F. Korenowski, J. Organomet. Chem., 11 (1968) 641.

12 A.J. Speziale and L.R. Smith, J. Am. Chem. Soc., 84 (1962) 1868.

13 P.E. Riley and R.E. Davis, Acta Crystallogr., Sect. B, 32 (1976) 381.

14 Principal computer programs: least-squares lattice parameters, LSLAT by K.N. Trueblood; absorption correction, SYABS, a local version of ORABS by W.R. Busing and H.A. Levy as modified by J.M. Williams; full-matrix least-squares and Fourier calculations, SHELX-76 by G.M. Sheldrick; thermal ellipsoid plot, ORTEP-II by C.K. Johnson. Various data processing programs of local origin including: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON by R.E. Davis; preparation of structure amplitude tables, FTABLE by R.E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, and bond angles, FUER by S.B. Larson.

15 Scattering factors for H, C, N, O, and Si were used as programmed in SHELX-76. Values for Fe were obtained from "International Tables for X-Ray Crystallography" Kynoch Press: Birmingham, England, 1974; Vol. IV.

16 A. Efraty, Chem. Rev., 77 (1977) 691.

17 R.E. Davis and P.E. Riley, Inorg. Chem., 19 (1980) 674.

18 F.L. Bowden and A.B.P. Lever, Organomet. Chem. Revs., 3 (1968) 227.

19 R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 12 (1974) 323.

20 R.S. Dickson and G.R. Tailby, Austr. J. Chem., 22 (1969) 1143.

21 L.F. Dahl and co-workers, private communication, 1975.

22 J.R. Fritch, K.P.C. Vollhardt, M.R. Thompson, and V.W. Day, J. Am. Chem. Soc., 101 (1979) 2768.