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Synthesis and structure of well-defined tricarbonyl iron(0) complexes with multivinylsilicon ligands

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ABSTRACT

In this paper the synthesis of new iron(0) carbonyl complexes with π-bonded ligands containing at least two silicon-vinyl groups of formula [$Fe(CO)_3L$] and [$\{Fe(CO)_3\}_2L'$] are described. The synthesis is done *via* UV light initiated substitution of carbonyl ligands in [$Fe(CO)_5$] or [$Fe_2(CO)_9$] precursors by organosilicon dienes, trienes, vinyl functional silicones (L), tetraenes (L′). The spectroscopic study (^1H and ^{13}C NMR) and X-ray analysis of these novel complexes showed that they are all 5 coordinate exhibiting two geometric environments, i.e. trigonal bipyramidal or tetragonal pyramidal.

1. Introduction

Mono-, bi- and trinuclear iron(0) carbonyl complexes are well known as pre-catalysts in organic synthesis including processes such as addition and substitution reactions as well as hydrogenation, isomerization, polymerization and oxidation of unsaturated compounds (for a review see Ref. [1]). Research in the 1960's on the reactivity of iron(0) carbonyl complexes led to the synthesis of a large number of organometallic compounds by the substitution of carbonyl ligands with olefins, dienes and alkyne (for review see Ref. [2]). UV-irradiation of [$Fe(CO)_5$] in the presence of a diene in a solvent at −60 to +20 °C has been reported as an efficient method for the preparation of iron(0) complexes in which the metallic center is stabilized both by carbonyl ligands and diene molecules, e.g. butadiene [3], cyclobutadiene and its derivatives [4], cyclohexadienes [3b,5], cyclooctatetraene [4b,6], cyclooctatriene, cycloheptatriene [7 and references therein] or heterodienes [8]. In contrast to unsaturated organic compounds, commonly used in the preparation of iron organometallic derivatives [7], vinyl functionalized silicon compounds were not widely applied as ligands in iron chemistry at this time. There are few examples of the use of vinylsubstituted silicon compounds such as vinylsilanes [9] or siloles [10] being used as ligands to stabilize the iron(0) carbonyl system. The above-mentioned examples of iron(0)–(diene) complexes as well as research performed by Wrighton [11] concerning the catalytic activity of iron carbonyls [12], confirmed the formation *in situ* of complexes of the type FeL_3, in which the reactive species [$Fe(CO)_3$] is stabilized by dienes. This is analogous to Karstedt's platinum complex [$Pt_2\{(H_2C{=}CHSiMe_2)_2O\}_3$], a common hydrosilylation catalyst. In this paper detailed procedures for the synthesis of a whole family of new iron(0) carbonyl complexes with π-bonded ligands containing at least two terminal vinyl-silicon groups such as organosilicon dienes, trienes, tetraenes or vinyl functionalized polyorganosilicones using [$Fe(CO)_5$] and [$Fe_2(CO)_9$] iron precursors are described.

2. Experimental section

All manipulations were carried out under dry argon using standard Schlenk's and vacuum techniques. The chemicals were purchased from Aldrich or ABCR. Reagent grade pentane and benzene were distilled from sodium hydride under argon. The UV light source

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was an LQ-400 lamp (Gröbel UV-Elektronik GmbH), equipped with two liquid light guides (1 m long, diameter 8 mm) with a lamp power of 400 W (irradiance: 1.5 mW/cm^2 (UV-A); 200 mW/cm^2 (UV-B), luminance: 3.500 kLx, range of wavelengths: 280–600 nm).

Liquid state NMR spectra were recorded in chloroform-d_1 or benzene-d_6 using a Bruker Ultra Shield spectrometer (600 MHz) or Varian Mercury spectrometer (300HMz) and referred to the residual protonated solvent peaks (^{1}H δ_H = 7.26 ppm, ^{13}C δ_C = 77.0 ppm for $CDCl_3$ and ^{1}H δ_H = 2.16 ppm, ^{13}C δ_C = 128.05 ppm for benzene-d_6). Elemental analyses were performed on Vario EL Elementar (Germany).

2.1. X-ray crystallography

Crystals of the complexes were mounted in glass capillaries in order to avoid decomposition. Diffraction data were collected at room temperature (**Fe-1**, **Fe-2**, **Fe-4**, **Fe-11**) and at 100(1)K (**Fe-9**) by the ω-scan technique, on an Agilent Technologies kappa-geometry diffractometer: Eos with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å, **Fe-1**, **Fe-2**, **Fe-4**, **Fe-9**), and SuperNova with mirror-monochromatized CuK_α radiation (λ = 1.54178 Å, **Fe-11**). The temperature was controlled by an Oxford Instruments Cryosystems cooling device. The data were corrected for Lorentz-polarization effects as well as for absorption [13]. Accurate unit-cell parameters were determined by a least-squares fit of 6713 (**Fe-1**), 7266 (**Fe-2**), 7349 (**Fe-4**), 2368 (**Fe-9**), and 1942 (**Fe-11**). The structures were solved with SIR92 [14] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [15]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the idealized positions and refined 'riding' on their parent atoms with U_{iso} set at 1.2 times U_{eq} of appropriate carrier atom (1.5 for methyl groups). The crystals of complex **Fe-9** turned out to be twinned and were appropriately treated during both data reduction and refinement; the relative contents of both twin fragments refined at 56/44%. Relevant crystal data are listed in Table 1, together with refinement details.

2.2. General procedure for synthesis of complexes (*Fe-1* to *Fe-12*)

Complexes **Fe-1** to **Fe-12** were synthesized by reacting the calculated amounts of $[Fe(CO)_5]$ (method A) or $[Fe_2(CO)_9]$ (method B) and corresponding amount of vinyl silicon compound in pentane (see Scheme 1). The mixture was irradiated with UV light for 2–3 h under flow of argon at room temperature. After this time the mixtures were filtered by a cannula system, the solvent was evaporated from a yellow solution and materials obtained were dried under vacuum.

2.2.1. Procedures for synthesis of complex $[Fe(CO)_3\{(H_2C{=}CHSiMe_2)_2O\}]$ (*Fe-1*)

2.2.1.1. Method A. A Schlenk's tube (Pyrex glass) equipped with a magnetic stirrer and condenser with oil valve was charged with 13.79 g (74 mmol) of 1,3-divinyltetramethyldisiloxane, 1.45 g (7.4 mmol) of $[Fe(CO)_5]$ and 100 mL of pentane. The mixture was irradiated with UV light for 3 h under flow of argon. After filtration *via* a cannula system the solvent was evaporated from a yellow solution and the yellow crystals were dried under vacuum.

2.2.1.2. Method B. A Schlenk's tube (Pyrex glass) equipped with magnetic stirrer and condenser with oil valve was charged with 2.56 g (13.74 mmol) of 1,3-divinyltetramethyldisiloxane, 0.5 g (1.37 mmol) of $[Fe_2(CO)_9]$ and 100 mL of pentane. The mixture obtained was mixed overnight and then irradiated with UV light for 3 h under flow of argon. After filtration *via* a cannula system the solvent was evaporated from the yellow solution and yellow crystals were dried under vacuum.

Anal. calc. for $C_{11}H_{18}FeO_4Si_2$ C 40.49; H 5.56; found C 40.53; H 5.61. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ(ppm) = 3.06 (s, 2H), 2.65 (s, 2H), 2.40 (s, 2H) ($H_2C{=}CH-$ coordinated); 0.35 (s, 6H, −Me), −0.10 (s, 6H, −Me). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ(ppm) = 211.86 (CO); 46.47; 44.11 ($H_2C{=}CH-$ coordinated); 2.45, −1.91 (−Me). ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ(ppm) = 3.95.

2.2.2. Procedure for the synthesis of $[Fe(CO)_3\{(H_2C{=}CHSiMe_2)_2NH\}]$ (*Fe-2*)

Synthesis of complex **Fe-2** was performed using method B with 2.55 g (13.74 mmol) of 1,3-divinyltetramethyldisilazane, 0.5 g (1.37 mmol) of $[Fe_2(CO)_9]$ and 100 mL of pentane giving 0.71 g of complex **Fe-2**, Yield = 80%.

Anal. calc. for $C_{11}H_{19}FeNO_3Si_2$; C 40.62; H 5.89; N 4.31 found C 40.65; H 5.94; N 4.25. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 3.05 (d, 2H, $H_2C{=}CH-$); 2.62 (d, 2H, $H_2C{=}CH-$); 2.32 (t, 2H, $H_2C{=}CH-$); 0.27 (s, 6H, Me−); −0.17 (s, 6H, Me−). ^{13}C NMR

Table 1
Crystallographic data for iron(0) carbonyl complexes.

Complex	**Fe-1**	**Fe-2**	**Fe-4**	**Fe-9**	**Fe-11**
Molecular formula	$C_{11}H_{18}FeO_4Si_2$	$C_{11}H_{19}FeNO_3Si_2$	$C_{19}H_{16}FeO_3Si$	$C_{14}H_{12}Fe2O_6Si$	$C_{18}H_{24}Fe_2N_4O_6Si_4$
Molecular weight	326.28	325.63	376.26	416.03	616.47
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	Iba2	P-1	$P2_1/c$
a (Å)	9.1975(9)	13.4483(7)	22.493(5)	6.960(2)	8.6578(4)
b (Å)	18.140(2)	7.3989(4)	24.805(4)	10.637(2)	23.5345(12)
c (Å)	9.5588(10)	16.4133(9)	7.1216(12)	11.941(2)	13.9715(6)
α (°)	90	90	90	110.87(2)	90
β (°)	97.861(9)	96.212(5)	90	96.96(2)	105.519(4)
γ (°)	90	90	90	99.02(2)	90
V (Å^3)	1579.8(3)	1623.58(15)	3973.3(12)	800.7(3)	2743.0(2)
Z	4	4	8	2	4
d_x (g cm^{-3})	1.37	1.33	1.26	1.73	1.49
F(000)	680	680	1552	420	1464
μ (mm^{-1})	1.11	1.08	0.83	1.91	10.50
Number of reflections measured	8688	29,440	4132	5004	9054
Symmetrically independent (R_{int})	2769 (0.032)	5715 (0.080)	2363 (0.049)	5004 (0.0)	4637 (0.054)
With $I > 2\sigma(I)$	1874	4309	1183	4044	2655
R(F) $[I > 2\sigma(I)]$	0.033	0.056	0.043	0.038	0.075
$wR(F^2)$ $[I > 2\sigma(I)]$	0. 067	0.108	0.068	0. 092	0. 172
S	1.02	1.05	0.87	1.00	1.05
max/min $\Delta\rho$ (e Å^3)	0.29/−0.29	0.53/−0.27	0.34/−0.42	0.64/−0.54	0.69/−0.40