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Carbonyl Nitrosyl Clusters. Syntheses and Structures of $[Fe_5C(CO)_{13}(NO)]^-$, $[Fe_6C(CO)_{13}(NO)_2]^{2-}$, and $[Fe_3(CO)_8(NO)(NH)]^-$

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The reaction of $Fe_5C(CO)_{15}$ with $[Fe(CO)_3(NO)]^-$ in dichloromethane results in formation of $[Fe_5C(CO)_{13}(NO)]^-$ and $[Fe_6C(CO)_{13}(NO)_2]^{2-}$. $[Fe_3(CO)_{11}]^{2-}$ reacts with $Fe(CO)_2(NO)_2$ to give the carbonyl nitrosyl imido cluster $[Fe_3(CO)_8(NO)(NH)]^-$ after hydrogen abstraction from the solvent. The clusters have been characterized by X-ray crystallography. Crystal data for $[PPN][Fe_5C(CO)_{13}(NO)]\cdot 0.5CH_2Cl_2$ (PPN = $N(P(C_6H_5)_3)_2$): M_r 1266.44, space group $P2_1/n$, $Z = 4$, $a = 16.47$ (1) Å, $b = 17.66$ (1) Å, $c = 17.97$ (1) Å, $\beta = 91.47$ (5)°, $V = 5230$ Å^3; $R = 0.063$ for 4815 reflections having $F > 3\sigma(F)$. Crystal data for $[PPh_4]_2[Fe_6C(CO)_{13}(NO)_2]$: M_r 1450.03, $C2/c$, $Z = 4$, $a = 37.05$ (1) Å, $b = 12.635$ (5) Å, $c = 18.728$ (6) Å, $\beta = 137.04$ (3) Å, $V = 6007$ Å^3; $R = 0.055$ for 2210 reflections having $F > 3\sigma(F)$. Crystal data for $[PPN][Fe_3(CO)_8(NO)(NH)]$: M_r 975.23, $P\bar{1}$, $a = 11.949$ (4) Å, $b = 13.789$ (4) Å, $c = 14.278$ (3) Å, $\alpha = 112.35$ (2)°, $\beta = 90.66$ (3)°, $\gamma = 93.51$ (3), $V = 2170$ Å^3, $Z = 2$; $R = 0.051$ for 4749 reflections with $F > 3\sigma(F)$.

Introduction

Nitrosyl-containing metal clusters are currently attracting attention due to their greater reactivity compared with binary carbonyl clusters.[1] Recent work has shown that the coordinated NO ligand is susceptible to hydrogenation,[2] electrophilic attack,[3] and deoxygenation to yield nitrido clusters.[4]

Recently we reported the syntheses of the hexairon nitrosyl clusters $[Fe_6C(CO)_{15}(NO)]^-$ and $Fe_6C(CO)_{11}(NO)_4$[5] by substitution of CO with NO^+ (from $NOBF_4$). In order to avoid problems encountered with this ligand[6,7] — difficult to purify, reactive toward some solvents, and able to oxidize the clusters—we used $Fe(CO)_2(NO)_2$ and $[X][Fe(CO)_3(NO)]$ [X = PPN or $(Ph)_4P$] as nitrosyl sources.[8] The original goal of this work was to obtain nitrosyl-containing carbido clusters which might serve as possible precusors for carbido nitrido clusters and dianionic nitrido clusters which could prove to be reactive at the nitride ligand. In this paper we report syntheses and X-ray structures of three nitrosyl iron clusters: $[PPN][Fe_5C(CO)_{13}(NO)]$ (**1**), $[PPh_4]_2[Fe_6C(CO)_{13}(NO)_2]$ (**2**), and $[PPN][Fe_3(CO)_8(NO)(NH)]$ (**3**).

Experimental Section

General Data. Inert-atmosphere[9] and drybox techniques were used in handling the iron clusters. Dichloromethane was distilled over P_2O_5 under nitrogen. MeOH and EtOH were distilled from Mg/I_2 and Et_2O from sodium benzophenone. $[PPh_4]Br$ (Aldrich) was used without further purification. $[PPN]Cl$[10] [PPN = bis(triphenylphosphine)nitrogen(1+)], $[PPN]_2[Fe_3(CO)_{11}]$,[11] $Fe(CO)_2(NO)_2$,[12] $[PPN][Fe(CO)_3(NO)]$[13] were synthetized by literature procedures. $[PPN]_2[Fe_6C(CO)_{16}]$ was obtained by cation exchange in CH_2Cl_2/MeOH from the sodium salt[14] and recrystallized in this mixed solvent. $[PPh_4][Fe(CO)_3(NO)]$ was obtained from a procedure similar to that described in ref 13. IR spectra were obtained by using a Perkin-Elmer 597. ^1H NMR spectra were recorded at 18 °C in $CDCl_3$ and in acetone-d_6 on a Bruker WP-80 spectrometer.

Synthesis of $[X][Fe_5C(CO)_{13}(NO)]$ and $[X]_2[Fe_6C(CO)_{13}(NO)_2]$ (X = PPN and PPh_4). To a solution of $Fe_5C(CO)_{15}$ (1.0 g, 1.41 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of $[X][Fe(CO)_3(NO)]$ (X = PPN, 1.04 g; X = PPh_4, 0.747 g, 1.47 mmol) in CH_2Cl_2 (50 mL). After the mixture was stirred for 1 h at room temperature, the dichloromethane was evaporated under vacuum. The dark brown residue was washed with hexane until colorless. IR spectra showed that this solution contained mainly $Fe_3(CO)_{12}$. The ether soluble product was extracted from the dried reaction mixture by 100-mL aliquots of ether. The solvent was then pumped off, and the compound was recrystallized from CH_2Cl_2/EtOH. X-ray suitable crystals of $[PPN][Fe_5C(CO)_{13}(NO)]\cdot 0.5CH_2Cl_2$ were obtained from layered CH_2Cl_2/hexane.

The remaining ether insoluble product was dissolved in CH_2Cl_2 and recrystallized twice from CH_2Cl_2/MeOH. Crystals were grown by slow cooling of a 1:1 CH_2Cl_2/MeOH solution. Crystals of $[PPN]_2[Fe_6C(CO)_{13}(NO)_2]$ were found twinned, and X-ray analysis was performed with $[PPh_4]_2[Fe_6C(CO)_{13}(NO)_2]$.

$[PPN][Fe_5C(CO)_{13}(NO)]\cdot 0.5CH_2Cl_2$: 360 mg, 0.28 mmol, yield 20%; IR (CH_2Cl_2): ν(CO) 1815 (w br), 1990 (w sh), 2005 (vs), 2020 (w) cm^{-1}; ν(NO) 1740 (w) cm^{-1}. The presence of volatile CH_2Cl_2 in the solid prevented accurate microanalyses.[15] Anal.[15] Calcd for $C_{50.5}H_{31}N_2ClFe_5O_{14}P_2$: C, 47.9; H, 2.5; N, 2.2; P, 4.9. Found: C, 47.1; H, 2.3; N, 2.6; P, 4.7.

$[X]_2[Fe_6C(CO)_{13}(NO)_2]$: yield for X = PPN, 470 mg, 0.25 mmol based on $Fe_5C(CO)_{15}$, 18%. IR (CH_2Cl_2): X = PPN and PPh_4 ν(CO) 1780 (w), 1808 (m), 1910 (w), 1960 (vs br), 2020 (m) cm^{-1}; ν(NO) 1710 (m) cm^{-1}. Anal.[15] Calcd (X = PPN) for $C_{66}H_{60}N_4Fe_6O_{15}P_4$: C, 55.9; H, 3.3; N, 3.0; P, 6.7. Found: C, 54.9; H, 3.3; N, 2.3; P, 6.7.

Synthesis of $[PPN][Fe_3(CO)_8(NO)(NH)]$. A 20-mL CH_2Cl_2 solution of freshly distilled $Fe(CO)_2(NO)_2$ (945 mg, 5.5 mmol) was added dropwise over 15 min to a stirred 70 mL of CH_2Cl_2 solution of $[PPN]_2[Fe_3(CO)_{11}]$ (5.7 g, 3.67 mmol). After the solution was stirred for 30 min, the infrared spectra indicated complete consumption of the reactants (1640 (s), 1700 (sbr), 1780 (m), 1890 (vs), 1960 (s), 1990 (vs) cm^{-1}). After evaporation of the solvent, the brown residue was washed with hexane until colorless. The product was then extracted with ether (3 × 100 mL), recovered by evaporation of the diethyl ether under vacuum, and recrys-

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[15] Microanalyses were found not very reproducible, perhaps due to the high air-sensitivity of these compounds. The results quoted are the mean values from different analyses.

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Table I. Summary of the Crystallographic Data for the Compounds [PPN][$Fe_5C(CO)_{13}(NO)$]•$0.5CH_2Cl_2$ (1), [PPh_4][$Fe_6C(CO)_{13}(NO)_2$] (2), and [PPn][$Fe_3(CO)_8(NO)NH$] (3)

	1	2	3
formula	$C_{50.5}H_{31}N_2ClFe_5O_{14}P_2$	$C_{62}H_{40}N_2Fe_6O_{15}P_2$	$C_{44}H_{31}N_3Fe_3O_9P_2$
M_r	1266.44	1450.03	975.23
space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	16.47 (1)	37.05 (1)	11.949 (4)
b, Å	17.66 (1)	12.635 (5)	13.789 (4)
c, Å	17.97 (1)	18.728 (6)	14.278 (3)
α, deg			112.35 (2)
β, deg	91.47 (5)	137.04 (3)	90.66 (3)
γ, deg			93.51 (3)
Z	4	4	2
V, Å^3	5230	6007	2170
d(calcd), g cm^{-3}	1.61	1.60	1.49
radiatn		^{1}Mo Kα (λ = 0.71069 Å)	
μ(Mo Kα), cm^{-1}	15.78	15.71	11.49
orientation reflctns: no.; range	9; $16 < 2\theta < 25$	25; $20 < 2\theta < 28$	25; $24 < 2\theta < 30$
data collectn range 2θ, deg	4–46	3–48	3–48
no. of unique data with $F_o < 3\sigma(F_o)$	4915	2210	4749
no. of parameters refined	486	275	374
R	0.063	0.055	0.051
R_w	0.066	0.056	0.053

tallized from CH_2Cl_2/EtOH. Some more product of good purity could be obtained by cooling the recrystallization filtrate after concentration under vacuum (390 mg, yield 11% based on [PPN]$_2$[$Fe_3(CO)_{11}$]). IR (CH_2Cl_2): ν(CO) 1945 (w), 1955 (s), 1990 (s) cm^{-1}; ν(NO) 1700 (s) cm^{-1}. IR (KBr plates, Mujol mull): 1845 (m), 1890 (m), 1925 (s), 1940 (vs), 1960 (vs), 1990 (vs), 2050 (m), (NO) 1700 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 18 °C): no signal in addition to the PPN multiplet. Anal.[15] Calcd for $C_{44}H_{31}N_3Fe_3O_9P_2$: C, 54.2; H, 3.2; N, 4.3; P, 6.3. Found: C, 54.0; H, 3.3; N, 4.1; P, 6.2.

X-ray Structure Determinations. Crystals were mounted under dry argon in capillaries. After survey photography by precession methods, selected crystals of **1** and **3** were set upon an Enraf-Nonius CAD-4 diffractometer and a crystal of **2** on a laboratory-made automated three-circle diffractometer. Unit-cell dimensions and orientation matrices were obtained from the least-squares method from the setting angle of reflections for which 8° < θ < 15°. Crystal data and data collection parameters are summarized in Table I. Intensities of two standard reflections were monitored every 100 reflections. These showed no change during data collection. For **1** and **3** empirical absorption were applied.[16] Some reflections, for which the attenuator was mispositioned during data collection, were not included in refinements.

Computations were performed on a VAX 11/725 and a GOULD CONCEPT 32/87 with the Oxford CRYSTALS package.[17] Atomic scattering factors were taken from ref 18 and those for H were taken from Stewart et al.;[19] anomalous dispersion for Fe, P, and Cl was included.[18] The iron atoms positions were determined from Patterson maps and direct methods using MULTAN 80.[20] The remaining non-hydrogen atoms were obtained from successive difference electron maps. Slack constraints were applied to the carbon atoms of the phenyl rings which were refined isotropically. The phenyl group H atoms were positioned geometrically, their positions recalculated after each refinement cycle.

Table II. Selected Atomic Positional Parameters for 1

atom	*x*/*a*	*y*/*b*	*z*/*c*
Fe(1)	0.34365 (8)	0.30377 (7)	0.17749 (7)
Fe(2)	0.19853 (9)	0.27231 (8)	0.12764 (7)
Fe(3)	0.22082 (8)	0.35413 (9)	0.25046 (7)
Fe(4)	0.31295 (8)	0.44746 (7)	0.17244 (8)
Fe(5)	0.28886 (9)	0.36377 (9)	0.05489 (7)
C(1)	0.2469 (5)	0.3650 (5)	0.1509 (5)
C(11)	0.3611 (6)	0.2140 (6)	0.1376 (6)
O(11)	0.3779 (6)	0.1573 (5)	0.1118 (6)
C(12)	0.3530 (6)	0.2727 (6)	0.2710 (6)
O(12)	0.3715 (4)	0.2475 (5)	0.3282 (4)
C(13)	0.4462 (7)	0.3405 (6)	0.1734 (5)
O(13)	0.5118 (4)	0.3567 (5)	0.1715 (5)
C(21)	0.1927 (8)	0.1776 (7)	0.1587 (6)
O(21)	0.1908 (8)	0.1172 (6)	0.1779 (6)
C(22)	0.0935 (7)	0.2849 (7)	0.1129 (6)
O(22)	0.0253 (6)	0.2928 (7)	0.1020 (6)
C(25)	0.2223 (7)	0.2547 (6)	0.0302 (6)
O(25)	0.2179 (6)	0.2220 (5)	−0.0242 (4)
C(31)	0.1307 (7)	0.4083 (9)	0.2446 (6)
O(31)	0.0734 (5)	0.4435 (7)	0.2394 (5)
C(32)	0.1798 (6)	0.2741 (8)	0.2971 (7)
O(32)	0.1518 (6)	0.2259 (6)	0.3297 (6)
C(33)	0.2630 (6)	0.3973 (7)	0.3310 (6)
O(33)	0.2910 (5)	0.4235 (6)	0.3836 (4)
C(41)	0.2458 (7)	0.5269 (6)	0.1746 (6)
O(41)	0.2027 (6)	0.5774 (5)	0.1756 (6)
C(42)	0.3852 (6)	0.4796 (5)	0.2407 (5)
O(42)	0.4305 (4)	0.4975 (5)	0.2850 (4)
C(43)	0.3652 (7)	0.4748 (7)	0.0871 (6)
O(43)	0.4030 (5)	0.5082 (5)	0.0479 (4)
N(1)	0.2424 (6)	0.4109 (5)	−0.0194 (5)
O(1)	0.2147 (6)	0.4405 (5)	−0.0697 (5)
C(52)	0.3771 (8)	0.3290 (6)	0.0131 (6)
O(52)	0.4336 (7)	0.3086 (6)	−0.0142 (5)
N(2)	0.7672 (4)	0.0820 (4)	0.0979 (4)
P(1)	0.6958 (1)	0.1406 (1)	0.0938 (1)
P(2)	0.8063 (1)	0.0200 (1)	0.1515 (1)

In a first step, all the cluster ligands were refined as carbonyl groups. Analyses of isotropic temperature factors, bonding distances, and coordination numbers of metal atoms to which they are bonded allowed nitrosyl group distinction: in all three cases, the ligands with the shortest metal–ligand bond lengths are linked to the iron atoms with the lowest coordinate. When refined as carbon atoms, they had isotropic thermal parameters (*U* = 0.039 Å^2 in **1**, 0.033 Å^2 in **2**, and 0.022 Å^2 in **3**) significantly lower than any other carbon atom (lowest: 0.048 Å^2 in **1**, 0.042 Å^2 in **2**, and 0.062 Å^2 in **3**). Attempts to refine the nitrogen atoms in other positions were unsuccesful, leading to unrealistic temperature factors. For **1**, electron density maps revealed a CH_2Cl_2 molecule disordered around the origin. The occupation factor of this molecule refined to 0.5 and was then fixed to this value. Slack constraints were applied to the geometry of the Cl–C–Cl group, and this carbon atom was refined with an isotropic temperature factor, *U* = 0.05 Å^2. For **3**, the imido hydrogen atom position was directly obtained from difference electron density maps. It was refined with an isotropic temperature factor, *U* = 0.08 Å^2.

Refinements were carried out with large block approximation. Unit weights were used throughout. For each structure, refine-

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Table III. Selected Fractional Atomic Coordinates for 2

atom	*x/a*	*y/b*	*z/c*
Fe(1)	0.04574 (5)	0.2347 (1)	0.3949 (1)
Fe(2)	0.04276 (7)	0.1279 (1)	0.2732 (1)
Fe(3)	–0.04130 (7)	0.3413 (1)	0.2339 (1)
C(1)	0.0000	0.237 (1)	0.2500
C(11)	0.0351 (4)	0.1618 (9)	0.4578 (9)
O(11)	0.0308 (3)	0.1126 (7)	0.5029 (7)
C(12)	0.0937 (4)	0.1286 (8)	0.4263 (9)
O(12)	0.1328 (3)	0.0844 (7)	0.4965 (6)
C(13)	0.0981 (5)	0.314 (1)	0.5026 (9)
O(13)	0.1338 (4)	0.3624 (8)	0.5739 (6)
N(21)	0.0747 (4)	0.0660 (8)	0.2552 (7)
O(21)	0.0960 (4)	0.0258 (9)	0.2384 (8)
C(22)	0.0000	0.012 (2)	0.2500
O(22)	0.5000	0.420 (1)	0.2500
C(31)	–0.0568 (5)	0.465 (1)	0.174 (1)
O(31)	–0.0667 (4)	0.5445 (8)	0.1329 (8)
C(32)	–0.1045 (5)	0.307 (1)	0.178 (1)
O(32)	–0.1460 (3)	0.2958 (9)	0.1400 (8)
C(33)	–0.0118 (5)	0.386 (1)	0.3595 (9)
O(33)	–0.0039 (4)	0.4295 (7)	0.4221 (7)
P(1)	0.32388 (9)	0.2382 (2)	0.9809 (2)

Table IV. Selected Fractional Atomic Coordinates for 3

atom	*x/a*	*y/b*	*z/c*
Fe(1)	0.07871 (7)	0.15519 (7)	0.20749 (7)
Fe(2)	0.01415(7)	–0.00409 (7)	0.24719 (6)
Fe(3)	0.16138 (7)	–0.02077 (7)	0.11494 (6)
N(1)	0.0135 (4)	0.0225 (4)	0.1283 (4)
H(1)	–0.040 (6)	0.003 (5)	0.082 (5)
C(11)	–0.0387 (7)	0.2263 (5)	0.2586 (5)
O(11)	–0.1127 (5)	0.2764 (4)	0.2934 (4)
C(12)	0.1049 (6)	0.2126 (6)	0.1155 (6)
O(12)	0.1196 (5)	0.2470 (5)	0.0555 (5)
C(13)	0.1670 (6)	0.2327 (5)	0.3139 (6)
O(13)	0.2225 (5)	0.2843 (5)	0.3834 (5)
C(21)	–0.0309 (5)	–0.1396 (5)	0.2071 (5)
O(21)	–0.0609 (4)	–0.2261 (4)	0.1801 (4)
C(22)	–0.1160 (6)	0.0413 (6)	0.2959 (6)
O(22)	–0.2010 (5)	0.0675 (5)	0.3278 (5)
C(23)	0.0809 (6)	0.0242 (5)	0.3694 (5)
O(23)	0.1228 (5)	0.0407 (5)	0.4465 (4)
N(2)	0.1900 (4)	–0.0966 (4)	–0.0008 (4)
O(2)	0.2274 (5)	–0.1494 (5)	–0.0791 (4)
C(31)	0.2716 (6)	0.0809 (6)	0.1576 (5)
O(31)	0.3570 (4)	0.1297 (4)	0.1733 (5)
C(32)	0.1989 (5)	–0.0821 (5)	0.2010 (5)
O(32)	0.2413 (4)	–0.1292 (4)	0.2410 (4)
N(3)	0.2911 (4)	–0.6727 (3)	–0.2778 (3)
P(1)	0.4184 (1)	–0.6970 (1)	–0.2734 (1)
P(2)	0.2244 (1)	–0.5725 (1)	–0.2628 (1)

ment was continued until the sum of the squares of the shift/esd ratios was less than 0.05. Final *R* values are given in Table I.

Selected atomic positional parameters are given in Tables II–IV. Important bond lengths and angles are in Tables V–VII. Full data are available in the supplementary material.

Results and Discussion

[X][Fe(CO)$_3$(NO)] (X = PPh$_4$ or PPN) react rapidly with Fe$_5$C(CO)$_{15}$ in CH$_2$Cl$_2$ at room temperature affording approximately equal amounts of [X][Fe$_5$C(CO)$_{13}$(NO)] (1) and [X]$_2$[Fe$_6$C(CO)$_{13}$(NO)$_2$] (2). In contrast with the reaction of [PPN][Fe(CO)$_3$(NO)] with Fe$_3$(CO)$_{12}$ which produces [PPN][Fe$_4$N(CO)$_{12}$] in high yield,[8,21] we did not obtain any nitrido species. Attempts to prepare from [Fe$_5$C(CO)$_{14}$]$^{2-}$ and NOBF$_4$ have been unsuccessful, leading to the oxidative degradation of the cluster. Preparation of the ruthenium analogue [Ru$_5$C(CO)$_{13}$(NO)]$^-$ from Ru$_5$C(CO)$_{15}$ and [PPN][NO$_2$] was reported recently.[22]

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

	Bond Lengths		
Fe(1)–Fe(2)	2.591 (2)	Fe(3)–C(1)	1.861 (8)
Fe(1)–Fe(3)	2.596 (2)	Fe(3)–C(12)	2.63 (1)
Fe(1)–Fe(4)	2.589 (2)	Fe(3)–C(31)	1.77 (1)
Fe(1)–Fe(5)	2.586 (2)	Fe(3)–C(32)	1.78 (1)
Fe(1)–C(1)	1.975 (9)	Fe(3)–C(33)	1.76 (1)
Fe(1)–C(11)	1.77 (1)	Fe(4)–Fe(5)	2.600 (2)
Fe(1)–C(12)	1.77 (1)	Fe(4)–C(1)	1.852 (9)
Fe(1)–C(13)	1.81 (1)	Fe(4)–C(41)	1.79 (1)
Fe(2)–Fe(3)	2.656 (2)	Fe(4)–C(42)	1.78 (1)
Fe(2)–Fe(5)	2.575 (2)	Fe(4)–C(43)	1.84 (1)
Fe(2)–C(1)	1.864 (9)	Fe(5)–C(1)	1.875 (8)
Fe(2)–C(21)	1.77 (1)	Fe(5)–C(25)	2.25 (1)
Fe(2)–C(22)	1.76 (1)	Fe(5)–C(43)	2.39 (1)
Fe(2)–C(25)	1.83 (1)	Fe(5)–N(1)	1.73 (1)
Fe(3)–Fe(4)	2.663 (2)	Fe(5)–C(52)	1.76 (1)
	Bond Angles		
Fe(3)–Fe(1)–Fe(2)	61.59 (5)	Fe(2)–Fe(3)–Fe(1)	59.12 (5)
Fe(4)–Fe(1)–Fe(2)	91.17 (6)	Fe(4)–Fe(3)–Fe(1)	58.95 (5)
Fe(4)–Fe(1)–Fe(3)	61.82 (5)	Fe(4)–Fe(3)–Fe(2)	88.15 (6)
Fe(5)–Fe(1)–Fe(2)	59.65 (5)	Fe(3)–Fe(4)–Fe(1)	59.22 (5)
Fe(5)–Fe(1)–Fe(3)	91.75 (6)	Fe(5)–Fe(4)–Fe(1)	59.79 (5)
Fe(5)–Fe(1)–Fe(4)	60.33 (6)	Fe(5)–Fe(4)–Fe(3)	89.93 (6)
Fe(3)–Fe(2)–Fe(1)	59.29 (5)	Fe(2)–Fe(5)–Fe(1)	60.27 (5)
Fe(5)–Fe(2)–Fe(1)	60.08 (5)	Fe(4)–Fe(5)–Fe(1)	59.88 (5)
Fe(5)–Fe(2)–Fe(3)	90.65 (6)	Fe(4)–Fe(5)–Fe(2)	91.27 (6)

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

	Bond Lengths		
Fe(1)–Fe(2)	2.590 (2)	Fe(2)–Fe(3′)	2.696 (2)
Fe(1)–Fe(2′)	2.720 (2)	Fe(2)–C(1)	1.90 (1)
Fe(1)–Fe(3)	2.664 (2)	Fe(2)–C(12)	1.98 (1)
Fe(1)–Fe(3′)	2.671 (2)	Fe(2)–N(21)	1.65 (1)
Fe(1)–C(1)	1.884 (1)	Fe(2)–C(22)	1.96 (1)
Fe(1)–C(11)	1.76 (1)	Fe(3)–Fe(3′)	2.648 (3)
Fe(1)–C(12)	1.94 (1)	Fe(3)–C(1)	1.86 (1)
Fe(1)–C(13)	1.77 (1)	Fe(3)–C(31)	1.75 (1)
Fe(1)–C(33)	2.56 (1)	Fe(3)–C(32)	1.78 (1)
Fe(2)–Fe(2′)	2.598 (3)	Fe(3)–C(33)	1.82 (1)
	Bond Angles		
Fe(2)–Fe(1)–Fe(2′)	58.52 (7)	Fe(3′)–Fe(2)–Fe(1)	58.92 (6)
Fe(3)–Fe(1)–Fe(2)	91.35 (7)	Fe(3)–Fe(2′)–Fe(2)	90.46 (6)
Fe(3)–Fe(1)–Fe(2′)	60.11 (5)	Fe(1)–Fe(3)–Fe(1′)	89.86 (7)
Fe(3′)–Fe(1)–Fe(2)	61.64 (6)	Fe(2′)–Fe(3)–Fe(1)	60.97 (6)
Fe(3′)–Fe(1)–Fe(2′)	88.42 (6)	Fe(2′)–Fe(3)–Fe(1′)	57.71 (6)
Fe(3)–Fe(1)–Fe(3′)	59.52 (7)	Fe(3′)–Fe(3)–Fe(1)	60.38 (6)
Fe(1)–Fe(2)–Fe(1′)	90.36 (8)	Fe(3′)–Fe(3)–Fe(1′)	60.10 (6)
Fe(2)–Fe(2)–Fe(1)	63.23 (7)	Fe(3′)–Fe(3)–Fe(2′)	89.39 (6)
Fe(2′)–Fe(2)–Fe(1)	58.25 (6)	O(33)–C(33)–Fe(3)	162.9 (11)
Fe(3′)–Fe(2)–Fe(1′)	60.66 (7)		

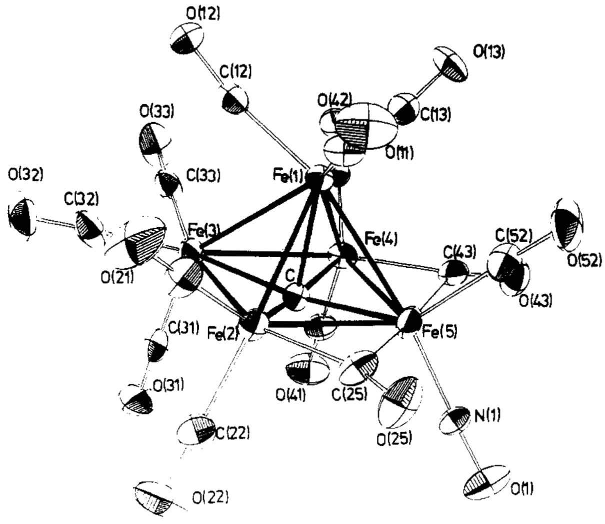

Figure 1. Structure of the [Fe$_5$C(CO)$_{13}$(NO)]$^-$ anion.

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Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Bond Lengths			
Fe(1)-Fe(2)	2.547 (1)	Fe(3)-C(31)	1.782 (7)
Fe(1)-Fe(3)	2.548 (1)	Fe(3)-C(32)	1.802 (7)
Fe(1)-N(1)	1.861 (5)	N(1)-H(1)	0.87 (7)
Fe(1)-C(11)	1.763 (8)	C(11)-O(11)	1.153 (8)
Fe(1)-C(12)	1.795 (8)	C(12)-O(12)	1.136 (8)
Fe(1)-C(13)	1.776 (7)	C(13)-O(13)	1.149 (8)
Fe(2)-Fe(3)	2.551 (1)	C(21)-O(21)	1.138 (7)
Fe(2)-N(1)	1.868 (5)	C(22)-O(22)	1.140 (8)
Fe(2)-C(21)	1.779 (7)	C(23)-O(23)	1.139 (8)
Fe(2)-C(22)	1.762 (7)	N(2)-O(2)	1.188 (6)
Fe(2)-C(23)	1.802 (8)	C(31)-O(31)	1.158 (8)
Fe(3)-N(1)	1.888 (5)	C(32)-O(32)	1.150 (7)
Fe(3)-N(2)	1.638 (6)		

Bond Angles			
Fe(3)-Fe(1)-Fe(2)	60.09 (3)	N(2)-Fe(3)-N(1)	113.9 (2)
N(1)-Fe(1)-Fe(2)	47.0 (2)	Fe(2)-N(1)-Fe(1)	86.2 (2)
N(1)-Fe(1)-Fe(3)	47.6 (1)	Fe(3)-N(1)-Fe(1)	85.6 (2)
Fe(3)-Fe(2)-Fe(1)	59.97 (3)	Fe(3)-N(1)-Fe(2)	85.6 (2)
N(1)-Fe(2)-Fe(1)	46.8 (1)	H(1)-N(1)-Fe(1)	131.6 (47)
N(1)-Fe(2)-Fe(3)	47.6 (1)	H(1)-N(1)-Fe(2)	126.1 (47)
Fe(2)-Fe(3)-Fe(1)	59.94 (3)	H(1)-N(1)-Fe(3)	126.8 (47)
N(1)-Fe(3)-Fe(1)	46.7 (1)	O(2)-N(2)-Fe(3)	169.9 (5)
N(1)-Fe(3)-Fe(2)	46.9 (2)	O(31)-C(31)-Fe(3)	165.3 (7)
N(2)-Fe(3)-Fe(1)	138.9 (2)	O(32)-C(32)-Fe(3)	164.8 (6)
N(2)-Fe(3)-Fe(2)	140.5 (2)		

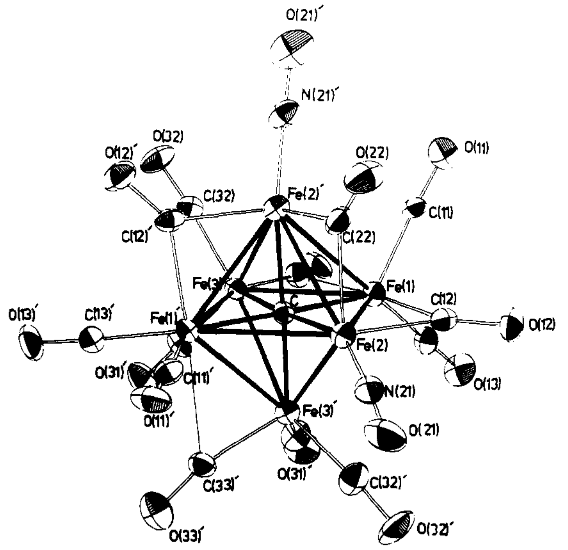

Figure 2. A view of the $[Fe_6C(CO)_{13}(NO)_2]^{2-}$ anion. The atoms with superscript' are related to the corresponding atoms without superscript by a crystallographic twofold axis.

A view of the pentanuclear anion 1 is shown in Figure 1. The overall geometry is very similar to that observed in $[Fe_5C(CO)_{14}]^{2-}$.[23] The iron skeleton has a square-based pyramid geometry according to Wade's rules.[24] The nitrosyl ligand occupies an axial position on the Fe(5) atom of the basal plane. In the ruthenium analogues $Ru_5C(CO)_{13}(NO)(\mu_2\text{-}AuPEt_3)$ and $Ru_5C(CO)_{13}(NO)(\mu_3\text{-}AuPEt_3)$,[22] the NO ligand occupies an equatorial position of a ruthenium atom of the basal plane. Two carbonyl ligands [(25) and (43)] are semibridging over to adjacent basal Fe–Fe bonds [Fe(2)–Fe(5) and Fe(5)–Fe(4)] as shown from the Fe–C–O angles [(25), 154.0 (10)°; (43), 160.2 (11)°] and the α values[25] [α(25), 0.23; α(43), 0.30]. This interaction is weaker than in $[Fe_5C(CO)_{14}]^{2-}$ due to the better π-acceptor character of NO. The carbide atom is located 0.11 Å below the iron basal mean plane, a value in good agreement with other carbido and nitrido iron clusters.

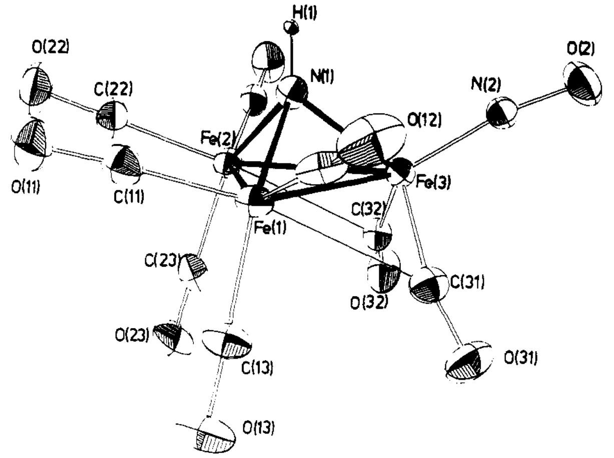

Figure 3. An ORTEP drawing of $[Fe_3(CO)_8(NO)(NH)]^-$.

The anion $[Fe_6C(CO)_{13}(NO)_2]^{2-}$ is shown in Figure 2. The cluster has a crystallographic twofold symmetry with respect to an axis going through C(1), C(22), and O(22). There is no distortion of the iron octahedron to D_3 symmetry as in the Ru_6[26] and Os_6[27] analogues. The nonbridged Fe–Fe bonds range from 2.648 (3) to 2.720 (2) Å and the bridged ones from 2.590 (2) to 2.598 (3) Å. As observed in other carbonyl nitrosyl octahedral cluster,[5,26,28] each nitrosyl ligand is bonded to a metal atom which shares two μ-CO groups with adjacent metal atoms of one triangular face. Contrary to $[Ru_6C(CO)_{14}(NO)_2]$,[26] in which the nitrosyl ligands are attached to opposite vertices, in 2 the nitrosyl ligands are bonded to adjacent iron atoms. A semibridging interaction Fe(1)–C(33) compensates for the electrons in excess on Fe(1) [Fe(3)–C(33)–O(33) = 162.9 (11)°, α = 0.41]. As noted by others,[26,29] the presence of two nitrosyl ligands on one face of a carbonyl cluster may have some relevance to the surface-catalyzed reduction of the nitric oxide by carbon monoxide to give CO_2 and N_2O. Although this may not prove to be a sound analogy, recent studies[4] have shown that it is the N–O bond cleavage of a coordinated nitrosyl ligand that yields nitrido clusters. Further work is in progress to study the possible deoxygenation of this compound to give a carbido nitrido cluster.

Other important surface-catalyzed reactions known to occur via adsorbed nitrogen atoms are hydrogenations of N_2 and NO. During our studies of the reactivity of $Fe(CO)_2(NO)_2$ with anionic clusters, we obtained the nitrosyl imido cluster anion 3, $[Fe_3(CO)_8(NO)(NH)]^-$, as a side product (yield 11%). This anion contains both NO and NH functional groups involved in NO reduction.

The reaction of $Fe(CO)_2(NO)_2$ with $[PPN]_2[Fe_3(CO)_{11}]$ proceeds readily at room temperature in CH_2Cl_2. Infrared spectroscopic monitoring of the reaction showed that 1.5 equiv of the dinitrosyl complex are necessary in order to obtain complete consumption of the anionic cluster. After removal of small amounts of $Fe_3(CO)_{12}$, the only ether-soluble product obtained from the reaction solution was

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[25] The semibridging character of carbonyl groups can be estimated from the α value defined as $(d_2 - d_1)/d_1$ with d_1 and d_2 as the shorter and the longer M–CO distances, respectively. Values with $0.1 < \alpha < 0.6$ are considered "semibridging"; see, for example; Yeh, W. Y.; Shapley, J. R.; Li, Y.; Churchill, M. R. *Organometallics* **1985**, *4*, 767. Footnote 12 on p 770.

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determined by X-ray crystallography to be [PPN][$Fe_3(CO)_8(NO)(NH)$] (**3**). The remaining products showed absorption bands in CH_2Cl_2 at 1645 (s), 1710 (m), 1780 (m), 1880 (vs), and 1990 (s) cm^{-1}; although they were not fully characterized, the bands at 1645, 1880, and 1990 cm^{-1} suggest the presence of $[Fe(CO)_3(NO)]^-$ (1650, 1875, and 1980 cm^{-1}).

Figure 3 shows a view of the anion illustrating the atomic numbering scheme. The Fe_3 triangle is symmetrically capped with a μ_3-NH imido group. This overall geometry is very similar to that observed for $FeCo_2(CO)_9(NH)$[7] and to that advanced from mass spectrometry for $Fe_3(CO)_{10}(NH)$.[21] The three iron atoms form an approximately equilateral triangle with a short average bond length of 2.549 (1) Å, if compared to other μ_3-bridged Fe_3 clusters.[30] The bonding angle Fe(3)–N(2)–O(2) of 169.9 (5)°, the relatively low value of ν(NO) (1700 cm^{-1}) and the short Fe(3)–N(2) bond length (1.638 (6) Å) suggest[31] a rather strong back-bonding from Fe(3). Two semibridging interactions, Fe(2)–C(32) and Fe(1)–C(31) [Fe(3)–C(31)–O(31) = 165.3 (7)°, α = 0.45; Fe(3)–C(32)–O(32) = 164.8 (6)°, α = 0.39], compensate for the imbalanced charges on Fe(1) and Fe(3). The three Fe–N(1) bond distances (mean 1.872 (5) Å) are similar to that in $Fe_3(CO)_{10}(NSiMe_3)$[32] (1.899 Å) and in $FeCo_2(CO)_9(NH)$ (1.86 Å). Contrary to $Fe_3(CO)_{10}(NH)$ and $H_2Ru_3(CO)_9(NH)$,[2b] we did not observe any ^1H NMR signal from the imido hydrogen atom, probably because of lower symmetry and/or proton exchange with the solvent as observed in $[Fe_3(CO)_{10}(CH)]^-$.[33] However, the imido hydrogen atom has been located from a difference Fourier map at 0.87 (7) Å from N(1). This distance is very similar to the N–H in $FeCo_2(CO)_9$ (NH) (0.83 (3) Å). As for this latter compound, prepared from $[FeCo_3(CO)_{12}]^-$ and NO^+ in CH_2Cl_2, the origin of the imido hydrogen atom is puzzling. The surprisingly high yield of the reaction rules out the possibility of a protonation from residual water in CH_2Cl_2 or in $Fe(CO)_2(NO)_2$ (both have been dried over P_2O_5). We consider that this hydrogen atom has been abstracted from the solvent, which suggests highly basic intermediate species in the reaction schemes.

Registry No. 1, 104716-28-1; 2, 104738-06-9; 3, 104716-30-5; $Fe_5C(CO)_{15}$, 11087-47-1; [PPN)[$Fe(CO)_3(NO)$], 61003-17-6; [PPh_4][$Fe(CO)_3NO$], 104716-31-6; $[PPN]_2[Fe_6C(CO)_{13}(NO)_2]$, 104716-33-8; $Fe(CO)_2(NO)_2$, 13682-74-1; $[PPN]_2[Fe_3(CO)_{11}]$, 66039-65-4; CH_2Cl_2, 75-09-2.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths, and bond angles (27 pages); listing of structure factor amplitudes (96 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of [*cyclo*-$(PhAs)_6Mo(CO)_4$] Containing a 1,4-Bidentate Coordinated Cyclohexaarsine Ring in a Twisted Boat Conformation

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The crystal and molecular structure of [*cyclo*-$(PhAs)_6Mo(CO)_4$] has been determined: monoclinic, $P2_1/c$, a = 11.850 (3) Å, b = 15.085 (3) Å, c = 25.302 (9) Å, β = 115.75 (3)°, V = 4074 (2) $Å^3$, Z = 4, R_F = 4.16%, T = 295 K. The structure contains a 1,4-bidentate coordinated molecule of *cyclo*-$(AsPh)_6$ in a previously unknown twisted boat conformation. The overall complex possesses approximate C_2 symmetry. The boat conformation provides a short As···As separation (3.196 (1) Å) needed for complex formation. The structure of the complex is compared to that of its uncoordinated precursor, *cyclo*-$(PhAs)_6$, which crystallizes in a chair conformation.

Introduction

One of the most striking features of reactions of homoatomic cyclopolyphosphines and arsines, *cyclo*-$(RE)_n$, with metal carbonyls is the variety of ring and chain dimensions found in the products.[1] There is the appearance of a seemingly free ability of the group-15 rings either to expand or contract the number of catenated units and either to retain a cyclic structure or open to form chains. This freedom contrasts sharply with the high specificity found in the ring dimensions of the uncoordinated precursors; for a particular R group, usually only a single (occasionally two) stable ring size is known.[2] More familiar to most chemists is the eventual conversion of all sulfur allotropes to *cyclo*-S_8; in this comparison it may be noted that S and RE units are isolobal.

Nearly 20 years ago, West et al. reported the synthesis of [$(PhAs)_6Mo(CO)_4$] (I) from the combination of *cyclo*-$(PhAs)_6$ (II) and $Mo(CO)_6$.[3] They proposed a structure based on 1,3-ring coordination of the known chair conformation of uncoordinated *cyclo*-$(PhAs)_6$.[4] No confirming

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