Basic Cluster Reactions. 2.[1] Reversible CO Additions to Fe_4 Clusters

Heinrich Vahrenkamp* and Doris Wolters

Institut für Anorganische Chemie der Universität Freiburg
D-7800 Freiburg, Germany

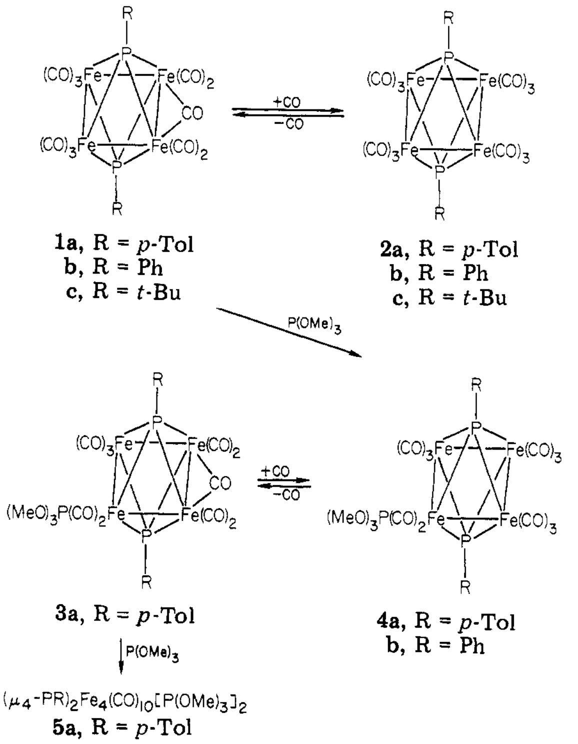
Received January 29, 1982

Summary: The doubly phosphorus-bridged quadrangular clusters $Fe_4(CO)_{11}(PR)_2$ (**1**, R = *t*-Bu, Ph, *p*-Tol) reversibly add CO to form the clusters $Fe_4(CO)_{12}(PR)_2$ (**2**). Addition of $P(OMe)_3$ yields the clusters $Fe_4(CO)_{11}(PR)_2{\cdot}P(OMe)_3$ (**4**, R = Ph, *p*-Tol) from which one CO ligand can be removed reversibly.

The high expectations for homogeneous catalysis by organotransition-metal clusters rest on two specific cluster properties. First, the binding to several metal atoms may modify the reactivity of ligating substrates in a way not obtainable in mononuclear complexes.[2] Second, the accumulation of metal atoms in the cluster core may cause unusual core properties.[3] Among these are the basic cluster reactions like two-center oxidative additions[2] or framework changes due to changes in the ligand or electron count.[1,4] Another basic cluster reaction results from the fact that some unsaturated clusters exist[4] which bear the possibility for substrate addition without gross changes in core geometry. We have found a group of tetrairon clusters of composition $Fe_4(CO)_{11}(PR)_2$[5] whose unsaturation caused us to investigate the possibility and reversibility of ligand additions to them.

During their synthesis,[5] the unsaturated $Fe_4(CO)_{11}$ clusters **1** are accompanied by their saturated $Fe_4(CO)_{12}$ analogues **2**. This indicates the possibility of CO addition to **1** and of decarbonylation of **2** (cf. Scheme I). In fact both reactions proceed easily and quantitatively at room temperature accompanied by a color change between red (for **2**) and black (for **1**). Thus, *n*-hexane solutions of **1a–c**[5], stirred under an atmosphere of CO, are completely converted in 3–5 h to **2a–c**[5] isolated in 70–90% yield by crystallization at −30 °C. And stirring in benzene under vacuum reconverts **2a–c** quantitatively in 1 day to **1a–c**, isolated in 85–95% yield by crystallization from benzene/*n*-hexane (1:2) at −30 °C. This is one of the simplest organometallic addition/elimination reactions.

Scheme I



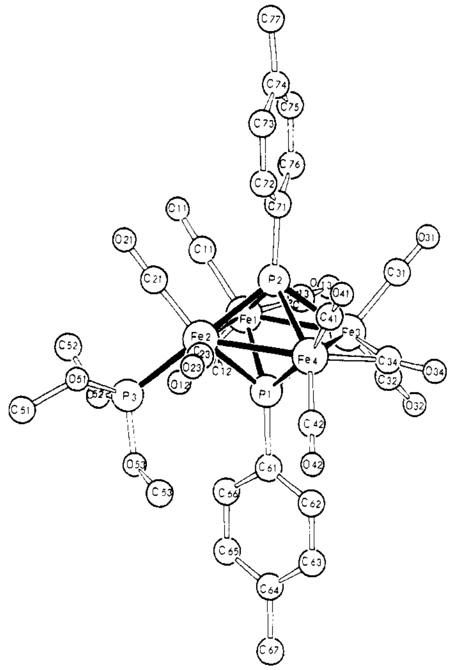


Figure 1. Molecular structure of $Fe_4(CO)_{10}(P\text{-}p\text{-}Tol)_2{\cdot}P(OMe)_3$ (**3a**).

Trimethyl phosphite, a better donor than CO, is added instantaneously to the clusters **1a** and **1b**, as again observed by a color change from black to red. From stoichiometric reactions in benzene, **4a**[6] and **4b**[7] are obtained in 80–90% yield by crystallization from benzene/*n*-hexane (1:2) at −30 °C. Of these saturated clusters, **4a** quantitatively eliminates one molecule of CO under vacuum as above to form **3a**[8] which in turn is reconverted under CO as above to **4a**. And yet another addition cycle was performed as above with **3a** and trimethyl phosphite resulting in the bis(phosphite)-substituted cluster **5a**.[9] Further

---

[1] Part 1: Richter, F.; Vahrenkamp, H. *Organometallics*, **1982**, *1*, 756.

[2] Cf. the reviews by: Deeming, A. J.; Whyman, R. In Johnson, B. F. G. "Transition Metal Clusters"; Wiley: New York, 1980; pp 391, 545.

[3] Cf. Vahrenkamp, H. In Müller, A.; Diemann, E. "Transition Metal Chemistry", Verlag Chemie: Weinheim, 1981, p 35.

[4] Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

[5] Vahrenkamp, H.; Wolters, D. *J. Organomet. Chem.*, **1982**, *224*, C17.

[6] $Fe_4(CO)_{11}(P\text{-}p\text{-}Tol)_2{\cdot}P(OMe)_3$ (**4a**): red-black crystals, decomposition above 60 °C; IR (cyclohexane) 2060 (w), 2038 (sh), 2024 (vs), 2016 (s), 1988 (s), 1980 (sh), 1955 (w), 1934 (w) cm^{-1}; ^1H NMR ($CDCl_3$) 2.47 (6 H), 3.48 (9 H, *J* = 11.0 Hz), 7.37 (m, 4 H), 8.17 (m, 4 H), ppm. Anal. Calcd for [$C_{28}H_{23}Fe_4O_{14}P_3$]: C, 37.37; H, 2.58; Fe, 24.83. Found: C, 37.57; H, 2.43; Fe, 24.51.

[7] $Fe_4(CO)_{11}(PPh)_2{\cdot}P(OMe)_3$ (**4b**): red-black crystals, decomposition above 50 °C; IR (cyclohexane) 2060 (w), 2024 (vs), 2015 (s), 1991 (s), 1958 (vw), 1935 (vw) cm^{-1}; ^1H NMR ($CDCl_3$) 3.50 (9 H, *J* = 11.1 Hz), 7.67 (br, 6 H), 8.40 (br, 4 H) ppm. Anal. Calcd for [$C_{26}H_{19}Fe_4O_{11}P_3$]: C, 35.82; H, 2.20; Fe, 25.63. Found: C, 35.61; H, 1.93; Fe, 26.41.

[8] $Fe_4(CO)_{10}(P\text{-}p\text{-}Tol)_2{\cdot}P(OMe)_3$ (**3a**) 95% from benzene/*n*-hexane): black crystals, decomposition above 90 °C; IR (cyclohexane) 2050 (w), 2013 (vs), 1983 (sh), 1979 (s), 1968 (sh), 1823 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 2.15 (6H), 3.57 (9H), *J* = 11.1 Hz), 6.6 (m, 8 H), ppm. Anal. Calcd for [$C_{27}H_{23}Fe_4O_{13}P_3$]: C. 37.19; H, 2.66; Fe, 25.63. Found: C, 37.49; H, 2.58; Fe, 25.76.

[9] $Fe_4(CO)_{10}(P\text{-}p\text{-}Tol)_2{\cdot}2P(OMe)_3$ (**5a**) (82% from benzene/*n*-hexane): black crystals, mp 120 °C dec; IR (cyclohexane) 2038 (w), 2018 (sh), 2000 (s), 1980 (m), 1970 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 1.50 (3 H), 2.15 (3 H), 3.48 (9 H, *J* = 11.0 Hz), 3.53 (9 H, *J* = 10.9 Hz), 6.75 (br, 8 H) ppm. Anal. Calcd for [$C_{30}H_{32}F_4O_{16}P_4$]: C, 36.18; H, 3.24; Fe, 22.43. Found: C, 36.18; H, 3.30; Fe, 21.82.

0276-7333/82/2301-0874$01.25/0

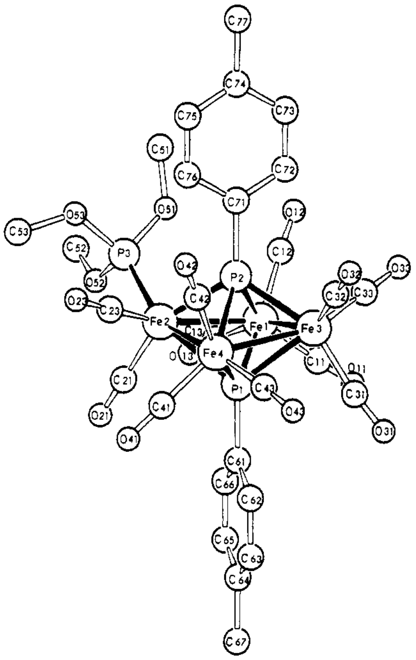


Figure 2. Molecular structure of $Fe_4(CO)_{11}(P\text{-}p\text{-}Tol)_2{\cdot}P(OMe)_3$ (**4a**).

"loading" of these tetrairon clusters with PR_3 ligands seems possible.

The compositions and structures of **3a** and **4a**, two representative addition/elimination products, were proved by crystal structure analyses[10] (cf. Figures 1 and 2 and Table I). The overall similarity of both compounds is obvious. It corresponds to, but does not explain, their facile interconversion. The main difference between both structures lies in the metal atom arrangement and the CO orientations. The Fe_4 unit in **3a** is practically planar as evidenced by the nearly equidistant Fe–P1 and Fe–P2 bonds. Its geometry with one Fe–Fe bond shortened by a CO bridge closely resembles that of **1a**.[5] In contrast the Fe_4 unit in **4a** is significantly nonplanar with a folding angle along the Fe1···Fe4 diagonal of 163°. This difference seems to result from the optimization of the terminal ligand orientations. In **3a** each iron atom has one ligand in the tetrametal plane, one above and one below, whereas in **4a** the iron atoms alternatively have one ligand above and two ligands below the tetrametal plane and vice versa.

The structures of **3a** and **4a** suggest one explanation for the ease of their interconversions: the crowding of ligands in **4a** may favor CO elimination whereas the unsaturation of **3a** may favor CO addition. Another explanation is offered by electron bookkeeping: the clusters **2**, **4**, and **5** have the correct electron count for a Fe_4 quadrangle according to the 18-electron rule. The clusters **1** and **3**, however, have the correct electron count for a closo Fe_4P_2 unit according to Wade's rules.[11]

Table I. Important Bond Lengths (pm) and Angles (Deg) in 3a and 4a

	3a	4a
Fe1-Fe2	275.5 (3)	271.0 (2)
Fe1-Fe3	264.2 (3)	266.6 (2)
Fe2-Fe4	267.1 (3)	268.7 (2)
Fe3-Fe4	245.8 (3)	266.8 (2)
Fe1-P1	226.4 (5)	221.5 (2)
Fe2-P1	225.6 (5)	235.1 (2)
Fe3-P1	234.6 (5)	237.7 (2)
Fe4-P1	232.3 (5)	221.5 (3)
Fe1-P2	225.3 (5)	235.5 (2)
Fe2-P2	223.2 (5)	219.7 (2)
Fe3-P2	230.1 (5)	223.4 (2)
Fe4-P2	231.9 (5)	240.6 (2)
P1···P2	264.6 (8)	259.8 (3)
$Fe\text{-}C_{term.}$	175-184 (2)	175-184 (1)
$C_{term.}\text{-}O_{term.}$	110-116 (2)	111-116 (1)
Fe2-P3	217.0 (5)	218.4 (2)
P1-Fe-P2	69.4-72.2 (2)	68.3-69.6 (1)
Fe1-P1-Fe4	108.5 (2)	117.2 (1)
Fe2-P1-Fe3	107.6 (2)	105.5 (1)
Fe1-P2-Fe4	109.1 (2)	105.2 (1)
Fe2-P2-Fe3	110.0 (2)	116.4 (1)
$Fe\text{-}C_{term.}\text{-}O_{term.}$	177-178 (2)	174-180 (1)
Fe1-C13-O13	168 (2)	175 (1)
Fe2-C23-O23	171 (2)	178 (1)

The addition of substrates to metal–metal double bonds has only sparsely been investigated.[12] In cluster chemistry only the Os–Os double bond in $H_2Os_3(CO)_{10}$ is well studied.[2,4] Unsaturation, however, is more often found in clusters of nuclearity 4 and above. Some clusters, like the ones described here, offer the possibility for this type of basic cluster reaction which consists of the binding and activation of a substrate without opening up the cluster and without replacing other ligands. This reaction which also bears significance in the context of the cluster–surface analogy is another demonstration of the unique possibilities in cluster chemistry.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Rechenzentrum der Universität Freiburg.

Registry No. 1a, 81534-74-9; **1b**, 81534-73-8; **1c**, 81534-72-7; **2a**, 81447-26-9; **2b**, 81456-90-8; **2c**, 81478-18-4; **3a**, 81534-75-0; **4a**, 81478-19-5; **4b**, 81478-20-8; **5a**, 81505-77-3.

Supplementary Material Available: Listings of the complete crystallographic details, all positional and anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors for both structures (30 pages). Ordering information is given on any current masthead page.

---

[10] Crystals of **3a** were obtained from toluene/hexane (1:2), those of **4a** from benzene/hexane (1:2). The crystal quality was checked by Weissenberg photographs; all other measurements were done on a Nonius CAD 4 diffractometer. **3a**: orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 1289.0$ (8) pm, $b = 1478.5$ (4) pm, $c = 1819.7$ (3) pm. **4a**: triclinic, space group $P\bar{1}$, $a = 1300.0$ (2) pm, $b = 1506.9$ (3) pm, $c = 944.52$ (2) pm, $\alpha = 100.65$ (1)° $\beta = 107.35$ (1)°, $\gamma = 84.43$°. The structures were solved by Patterson and Fourier methods. Blocked matrix refinement (rigid body and isotropic for phenyl C and H atoms, anisotropic for all other nonhydrogen atoms) using unit weights resulted in R values of 0.045 for **3a** and 0.055 for **4a**. All details of the crystallographic work are documented in the supplementary material: Table A contains all crystallographic data; Tables B and C list all atomic parameters for **3a** and **4a**. Table D lists all bond lengths and angles for both compounds: Tables E and F give the F_o/F_c listings.

[11] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[12] Cf. Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. In Chisholm, M. H. "Reactivity of Metal-Metal Bonds"; American Chemical Society: Washington, D.C. 1981; *ACS Symp. Ser.* No. 155, p 221.

Metal-Silicon Bonded Compounds. 16. The Structure of $(LiSiMe_3)_2{\cdot}(Me_2NCH_2CH_2NMe_2)_3$, a Highly Reactive Silylating Agent

Berhan Teclé, William H. Ilsley, and John P. Oliver*

Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received March 5, 1982

Summary: The structure of the highly reactive silylating agent, $(LiSiMe_3)_2{\cdot}(Me_2NCH_2CH_2NMe_2)_3$, has been determined from single-crystal X-ray diffraction data collected