Kurzmitteilung / Short Communication

Synthesis of the Novel μ-(Phosphanoalkylidene) Complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_2\}]$ (PR_2 = PEt_2, PHCy, PHPh) and Molecular Structure of the PEt_2 Derivative[☆]

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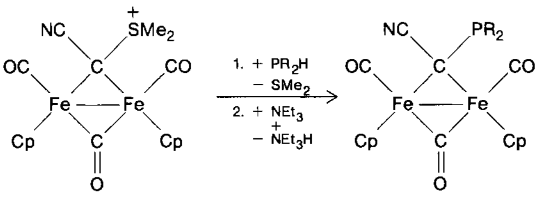
Replacement of SMe_2 at the pseudo-alkylidyne μ-carbon atom of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]SO_3CF_3$ by PR_2H (PR_2 = PEt_2, PCyH, PPhH) results in the formation of the phosphonium salts $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PHR_2\}]SO_3CF_3$ which upon deprotonation with NEt_3 yield the corresponding neutral complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_2\}]$. These μ-(phosphanoalkylidene) complexes have been characterized on the basis of IR, $^{31}P\{^1H\}$-, ^1H-, and $^{13}C\{^1H\}$-NMR spectra and by the X-ray molecular structure of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PEt_2\}]$.

The stability of dinuclear complexes with bridging alkylidene ligands containing π-donor heteroatoms has recently been proved by the synthesis of a variety of diiron derivatives $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)E\}]$ (E = SR, OR, NR_2) obtained by treating the alkylidyne-like sulfonium salt $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)\text{-}SMe_2\}]SO_3CF_3$ (**1**) with the appropriate nucleophile[1–3]. The general applicability of this method as well as the demonstrated role of the cyano group in stabilizing the poorly explored class of μ-(aminoalkylidene) ligands[4] prompted us to extend our investigation to the synthesis of other group-15 heteroatom-substituted μ-alkylidene complexes.

Here we report on the reactions of **1** with phosphanes (PEt_2H), $PCyH_2$, $PPhH_2$) which, in the presence of NEt_3, lead to the first examples of μ-(phosphanoalkylidene) complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_2\}]$ (PR_2 = PEt_2, **2a**; PCyH, **2b**; PPhH, **2c**).



(1)

1

2	PR_2
a	PEt_2
b	PCyH
c	PPhH

3: **2** with $\overset{+}{P}R_2H$ instead of PR_2

Cy: cyclohexyl

Treatment of a CH_3CN solution of **1** with 1 equiv. of phosphane and subsequent addition of a slight excess of triethylamine led to the formation of compounds **2a–c** [Eq. (1)].

Compounds **2a–c** were purified by column chromatography and isolated as red crystalline solids. Their IR spectra {e.g., **2a**: ṽ = 2139 cm^{-1} [ν(CN)]; 1994, 1963, 1801 [ν(CO)]} closely resemble those of the related complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NR_2\}]$ which have been shown to exist as *cis* isomers (Cp ligands *cis* to each other)[1]. The presence of the μ-$C(CN)PR_2$ group is clearly indicated by the occurrence of the doublet for the μ-carbon atom [e.g., **2a**: δ = 120.1 (J_{PC} = 61.9 Hz)] in the ^{13}C-NMR spectra.

It has been reported that the terminally coordinated carbyne complex $[ReM(CO)_9(CPh)]$ (M = Cr, W) undergoes PR_3 addition to give the metal-substituted ylides $[ReM(CO)_9\{\mu\text{-}C(Ph)PR_3\}]$[5]. Moreover the addition of phosphanes to the alkylidyne carbon atom of the cations $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CX)]^+$ (X = H, Me) and $[MPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2Cp]^+$ (M = Mn, Re; PR_3 = PMe_3, PMe_2Ph) has been proved to afford the phosphonium ions $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(X)PR_3\}]^+$[6] and $[MPt\{\mu\text{-}C(PR_3)C_6H_4Me\text{-}4\}(CO)_2(PR_3)_2Cp]^+$[7], respectively. Likewise, when the reaction described in Eq. (1) was performed in the absence of triethylamine, the cationic intermediates $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)PR_2H\}]^+$ were isolated (PR_2 = PEt_2, **3a**; PCyH, **3b**) or detected (PR_2 = PPhH, **3c**). The IR spectra of **3a–c** exhibit the same band pattern observed in **2a–c**, but with higher frequency absorbances {e.g., ṽ = 2165 cm^{-1} [ν(CN)]; 2007, 1977, 1837 [ν(CO)]}. The ^{13}C-NMR spectrum of **3a** shows a doublet for the μ-carbon atom at δ = 81.4 (J_{PC} = 41.1 Hz) which is strictly comparable to the value reported for the μ-carbon atom of its sulfonium precursor **1** (δ = 84.5). Compound **3a** was also obtained in almost quantitative yield by addition of HSO_3CF_3 to a CH_2Cl_2 solution of **2a** demonstrating that deprotonation of **3a** by NEt_3 can be reversed upon treatment with acids.

The molecular geometry of **2a** is shown in Figure 1. Most atoms in the molecule conform to an idealized mirror plane bisecting the iron–iron bond except for the ethyl groups bound to the phosphorus atom. Their different orientations around the P–C(ethyl) axes, probably motivated by the optimization of the H···H contacts, make the molecule asymmetric in the crystal. The geometric evidence [P–C1–C2 angle 110.2(2)°] would indicate tetrahedral hybridization of “carbenic” carbon orbitals, but a value narrower than the expected 120° can be justified in terms of repulsions among the electrons in the P–C bonds and those in the π μ-C-Fe_2 orbital which can induce some closure of the P–C1–C2 angle.

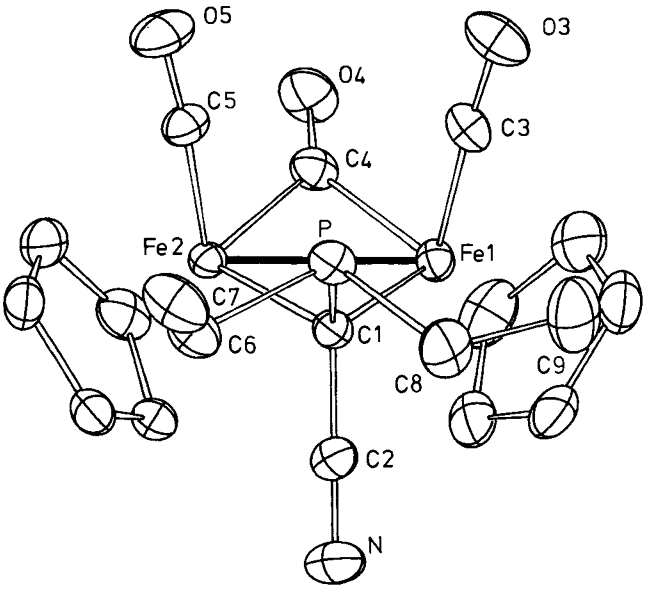


Figure 1. ORTEP drawing (30% probability) of **2a**; the hydrogen atoms have been omitted; selected bond lengths [Å] and angles [°]: Fe1–Fe2 2.534(1), Fe1–C1 2.004(3), Fe2–C1 2.008(2), P–C1 1.853(3), P–C6 1.851(3), P–C8 1.846(4), C1–C2 1.428(4), C2–N 1.151(4), Fe1–C4 1.926(3), Fe2–C4 1.910(3), C4–O4 1.178(4), Fe1–C3 1.765(3), C3–O3 1.137(4), Fe2–C5 1.766(3), C5–O5 1.150(4); P–C1–C2 110.2(2), C6–P–C8 98.8(2), C1–P–C6 100.7(1), C1–P–C8 105.3(2), C2–C1–Fe1 114.7(2), C2–C1–Fe2 115.0(2), C1–C2–N 179.1(4), Fe1–C1–Fe2 78.3(1), P–C1–Fe1 120.8(1), P–C1–Fe2 114.6(1)

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Experimental

All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. – IR: Perkin-Elmer 983-G. – NMR: Varian Gemini 200. – Elemental analyses: Pascher Microanalytical Laboratory (Remagen, Germany). – Compound **1** was prepared according to a published method[8].

[$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PEt_2\}$] (**2a**): To a solution of **1** (230 mg, 0.40 mmol) in CH_3CN (15 ml) was added PEt_2H (38 mg, 0.42 mmol). The mixture was stirred for 15 min and treated with a slight excess of NEt_3 (0.08 ml, 57 mmol). The solvent was then removed in vacuo. The residue was redissolved in CH_2Cl_2 and the solution filtered through an alumina pad (3 × 3 cm). The filtered, red solution was reduced to a minimum volume, layered with *n*-pentane and cooled to –20°C affording red crystals of complex **2a** (158 mg, 87%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2139 cm^{-1} w (CN); 1994 s, 1963 w, 1801 m (CO). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 4.84 (s, 10H, Cp), 1.98 (q, $J_{H,H}$ = 7.7 Hz, 4H, CH_2CH_3), 1.21 (dt, $J_{P,H}$ = 14.8 Hz, 6H, CH_2CH_3). – ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 266.2 (d, $J_{P,C}$ = 3.7 Hz, μ-CO), 209.9 (d, $J_{P,C}$ = 13.5 Hz, CO), 133.0 (CN), 120.1 (d, $J_{P,C}$ = 61.9 Hz, μ-C), 91.1 (Cp), 26.0 (d, $J_{P,C}$ = 19.7 Hz, CH_2CH_3), 11.0 (d, $J_{P,C}$ = 17.4 Hz, CH_2CH_3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ = 33.3.

$C_{19}H_{20}Fe_2NO_3P$ (453.0) Calcd. C 50.37 H 4.45
Found C 50.21 H 4.49

[$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PR_2\}$] (PR_2 = PCyH, **2b**; PPhH, **2c**): These complexes were prepared as described for **2a** starting from 230 mg (0.40 mmol) of **1**.

2b: Yield 65 mg (34%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2143 cm^{-1} w (CN); 1996 s, 1964 w, 1804 m (CO). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 4.87 (dd, $J_{P,H}$ = 198.0 Hz, $J_{H,H}$ = 3.2 Hz, 1H, PH), 4.80 (s, 5H, Cp), 4.76 (s, 5H, Cp), 2.2–1.1 (m, 11H, Cy). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 265.6 (μ-CO); 209.3 (d, $J_{P,C}$ = 13.1 Hz, CO); 208.8 (d, $J_{P,C}$ = 11.5 Hz, CO); 136.1 (CN); 110.9 (d, $J_{P,C}$ = 56.9 Hz, μ-C); 91.47 (Cp); 91.26 (Cp); 39.37 (d, $J_{P,C}$ = 16.4 Hz), 31.64 (d, $J_{P,C}$ = 28.4 Hz), 31.52, 27.36 (d, $J_{P,C}$ = 11.8 Hz) (Cy). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ = 18.0.

$C_{21}H_{22}Fe_2NO_3P$ (479.1) Calcd. C 52.65 H 4.63
Found C 53.02 H 4.74

2c: Yield 47 mg (25%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2146 cm^{-1} w (CN); 1996 s, 1965 w, 1806 m (CO). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.83–7.40 (m, 5H, Ph), 6.02 (d, $J_{P,H}$ = 204 Hz, 1H, PH), 4.88 (s, 5H, Cp), 4.60 (s, 5H, Cp). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 265.35 (μ-CO); 209.7, 209.6, 209.2 (CO); 136.0 (CN); 140.7 (d, $J_{P,C}$ = 21.5 Hz), 135.15 (d, $J_{P,C}$ = 19.5 Hz), 129.1, 129.0 (d, $J_{P,C}$ = 5 Hz) (Ph); 113.86 (d, $J_{P,C}$ = 56 Hz, μ-C); 91.15 (Cp). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ = 10.6.

$C_{21}H_{16}Fe_2NO_3P$ (473.0) Calcd. C 53.32 H 3.41
Found C 53.19 H 3.56

[$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PEt_2H\}$]SO_3CF_3 (**3a**): To a solution of **1** (230 mg, 0.40 mmol) in CH_3CN (15 ml) was added PEt_2H (38 mg, 0.42 mmol). The mixture was stirred for 15 min and evaporated to dryness in vacuo. The oily, red residue was washed with *n*-pentane (3 × 5 ml) and crystallized from CH_2Cl_2/*n*-pentane at –20°C yielding red crystals of **3a** (225 mg, 89%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2165 cm^{-1} w (CN); 2007 s, 1977 w, 1837 m (CO). – ^1H NMR (CD_3CN, 200 MHz): δ = 5.11 (dm, $J_{P,H}$ = 488.2 Hz, 1H, PH), 5.34 (s, 10H, Cp), 2.75 (m, 4H, PCH_2CH_3), 1.52 (dt, $J_{P,H}$ = 19.4 Hz, 6H, PCH_2CH_3).

$C_{20}H_{21}F_3Fe_2NO_6PS$ (603.1) Calcd. C 39.83 H 3.50
Found C 40.03 H 3.72

$Fe_2Cp_2(CO)_2(\mu$-$CO)\{\mu$-$C(CN)PR_2H\}SO_3CF_3$ (PR_2 = PCyH, **3b**; PPhH, **3c**): These complexes were prepared as described for **3a** starting from 230 mg (0.40 mmol) of **1**.

3b: Yield 125 mg (50%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2167 cm^{-1} w (CN); 2008 s, 1978 w, 1833 m (CO). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 5.41 (br. s, 10H, Cp), 5.18 (m, 2H, PH), 2.6–1.3 (m, 11H, Cy).

$C_{22}H_{23}Fe_2F_3NO_6PS$ (629.1) Calcd. C 42.00 H 3.69
Found C 42.09 H 3.86

3c: Compound **3c** was always obtained in mixture with **2c**. – IR (CH_3CN): $\tilde{\nu}$ = 2170 cm^{-1} w (CN); 2005 s, 1973 w, 1833 m (CO).

X-ray Crystallographic Studies: Crystallographic data for **2a** at room temperature: Crystal dimensions: 0.15 × 0.25 × 0.40 mm; M_r = 453.0; triclinic; *P*1 (No. 1); *a* = 7.716(1), *b* = 8.524(1), *c* = 8.972(1) Å; α = 63.50(1), β = 65.66(1), γ = 77.38(1)°; *V* = 480.7 $Å^3$; *Z* = 1, $d_{calcd.}$ = 1.56 g cm^{-3}; μ(Mo-K_α) = 15.3 mm^{-1}. Data measured with an Enraf-Nonius CAD4 diffractometer by using Mo-K_α radiation (λ = 0.71069 Å) (graphite-monochromated); ω-scan mode with 2Θ > 50°; *hkl* ranges –9 to 9, –10 to 10, 0 to 10, respectively. 2795 reflections measured and 2684 with F_o > $4\sigma(F_o)$ used for the structure determination; empirical absorption

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters [Å^2] for **2a**

Atom	x	y	z	U_{eq}
Fe(1)	0.57948	0.41791	0.25151	0.0304(2)
Fe(2)	0.43025(5)	0.43775(5)	0.55286(5)	0.0262(1)
P	0.79821(11)	0.16488(10)	0.54052(11)	0.0324(3)
N	0.3805(6)	-0.0331(5)	0.6127(6)	0.061(2)
C(1)	0.5763(4)	0.2359(3)	0.4908(3)	0.028(1)
C(2)	0.4667(5)	0.0877(4)	0.5585(5)	0.040(1)
C(6)	0.6996(5)	0.0496(5)	0.7866(5)	0.043(1)
C(7)	0.8510(6)	-0.0415(6)	0.8690(6)	0.054(2)
C(8)	0.8940(7)	-0.0277(5)	0.4836(6)	0.050(2)
C(9)	0.9838(9)	0.0204(7)	0.2826(7)	0.074(3)
C(3)	0.8117(4)	0.4815(4)	0.1854(4)	0.034(1)
O(3)	0.9598(4)	0.5329(4)	0.1267(4)	0.050(1)
C(4)	0.4856(4)	0.6159(4)	0.3166(4)	0.034(1)
O(4)	0.4699(5)	0.7696(3)	0.2444(4)	0.048(1)
C(5)	0.6238(4)	0.5123(4)	0.5572(5)	0.039(1)
O(5)	0.7353(4)	0.5745(4)	0.5663(5)	0.064(2)
C(11)	0.3529(3)	0.3361(4)	0.2268(4)	0.062(2)
C(12)	0.5233(3)	0.2381(4)	0.1730(4)	0.059(2)
C(13)	0.6611(3)	0.3578(4)	0.0274(4)	0.062(2)
C(14)	0.5757(3)	0.5297(4)	-0.0088(4)	0.064(2)
C(15)	0.3853(3)	0.5163(4)	0.1144(4)	0.074(3)
C(21)	0.2228(3)	0.2736(2)	0.7867(3)	0.038(1)
C(22)	0.1450(3)	0.3616(2)	0.6500(3)	0.037(1)
C(23)	0.1469(3)	0.5449(2)	0.5986(3)	0.044(1)
C(24)	0.2258(3)	0.5702(2)	0.7036(3)	0.054(2)
C(25)	0.2728(3)	0.4026(2)	0.8198(3)	0.052(2)

correction (DIFABS[9]). Structure solution with direct methods; full-matrix least-squares refinement (SHELX-76[10]) using anisotropic temperature factors for the nonhydrogen atoms. Rigid model for C_5H_5 groups (C–C = 1.42 Å). Hydrogen atoms in calculated positions (C–H = 1.08 Å) with common isotropic temperature factor (U = 0.08 Å^2). R = 0.027; R_w = 0.031, $w = 4/[\sigma(F_o)^2 + 0.003F_o^2]$; goodness of fit: 1.60; highest residual density peak: 0.48 eÅ^{-3}; positional and equivalent isotropic thermal parameters are listed in Table 1. Agreement indices for the inverted structure R = 0.032 and R_w = 0.037. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD-56040, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 60th birthday.

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