

Synthesis and X-Ray Crystal Structure of [(thf)₄Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}₂]

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Abstract

The reactions of [(thf)₄Ca(PPh₂)₂] with the iron carbonyls Fe₂(CO)₉ and Fe₃(CO)₁₂ in THF yield mixtures of iron carbonyl-containing phosphanides which transform upon prolonged heating into [(thf)₄Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}₂] (**1**) with a chemical shift of δ(³¹P) = 127.9 ppm. The distorted octahedrally coordinated calcium atom binds to four THF molecules (av. Ca-O 234.0 pm) and the bridging carbonyl ligand of the complex anions {Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}⁻ [Ca-O 229.8(4), Fe-Fe 257.9(2) pm].

Keywords: Iron; Calcium; Carbonyl complexes; Phosphanides; Coordination chemistry.

Introduction

The dinuclear anion [Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂]⁻ (**A**⁻) (Figure 1) can be obtained from the reaction of Na₂[Fe₂(CO)₈] with either R₂PCl^[1,2] or its nickel complex [Ni(CO)_{4-n}(R₂PCl)_n]^[3] yielding the sodium salt Na[Fe₂(CO)₆(μ-CO)(μ-PR₂)]. A similar reaction with the ammonium salt (NEt₄)₂[Fe₂(CO)₈] leads to the formation of the corresponding NEt₄[Fe₂(CO)₆(μ-CO)(μ-PR₂)].^[4] Heating of NEt₄[HFe(CO)₃(PPh₃)] in ethanol and recrystallization gave NEt₄[Fe₂(CO)₆(μ-CO)(μ-PPh₂)] with a rather poor yield.^[5] The anion is isoelectronic to the neutral dinuclear mixed-metal complex [FeCo(CO)₇(μ-PR₂)] (**B**) which was obtained from the metalation of (OC)₄Fe-PR₂H with (η³-C₃H₅)Co(CO)₃.^[6] However, the latter complex is not isostructural to the homonuclear iron anion because the six-coordinate iron atom is coordinated to four terminally bound CO groups, the bridging phosphanide group and the cobalt atom, whereas the cobalt atom shows a coordination number of five where it is bonded to three terminally bound CO ligands, the iron atom and the phosphanide ligand. Oxidation of the anion [Fe₂(CO)₆(μ-CO)(μ-PR₂)]⁻ (**A**⁻) with ferrocenium tetrafluoroborate produces the paramagnetic 33 electron complex [Fe₂(CO)₆(μ-CO)(μ-PR₂)] (**A**) which has a similar structure to the heteronuclear FeCo compound.^[1,2] Protonation of Na[Fe₂(CO)₆(μ-CO)(μ-PR₂)] yields a complex, [Fe₂(CO)₆(μ-CO)(μ-H)(μ-PR₂)] (**C**), with a bridging hydrogen atom^[3] and an iron-iron distance of 260.34(4) pm.^[7] The exchange of the sodium cation by bulky [(Ph₃P)₂N]⁺ leads to the formation of an ion pair without

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short contacts between cation and anion.^[7] The reaction of $\text{NEt}_4[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PR}_2)]$ with the PPh_3 adducts of CuI , AgI and AuCl yields the trinuclear complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PR}_2)\{\mu\text{-M}(\text{PPh}_3)\}]$ (**D**) with a Fe_2M triangle ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$).^[8] The formation of these heteronuclear clusters was verified by X-ray structure determinations.^[3,8,9]

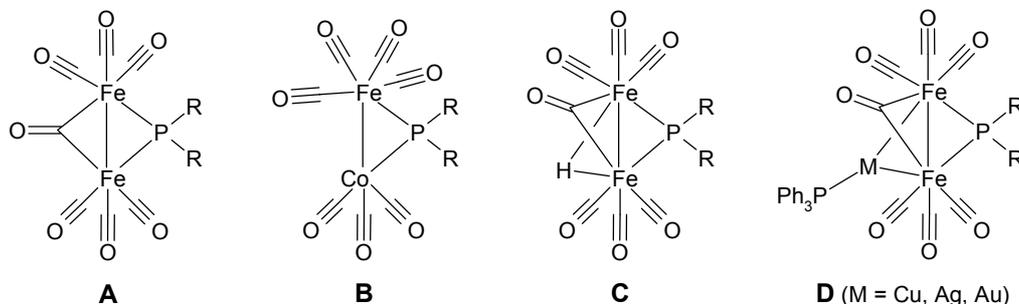


Figure 1: Schematic representations of **A**, **B**, **C**, and **D**.

Experimental

General remarks: All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were dried over sodium, degassed, and saturated with argon. NMR spectra were obtained on a Bruker AC 400 MHz spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 710 system, and IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. For the elemental analysis V_2O_5 was added to the samples in order to enhance combustion. Large H values were obtained because **1** is hygroscopic. Starting $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ was prepared from KPh_2 and anhydrous CaI_2 according to literature procedures.^[10,11]

*Synthesis of $[(\text{thf})_4\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\}_2]$ (**1**):*

Method A: A solution of 0.16 g of $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ (0.229 mmol) in 15 ml of THF was added dropwise at 0°C to a solution of 0.17 g of $\text{Fe}_2(\text{CO})_9$ (0.458 mmol) in 35 ml of THF. The color of the solution changed from yellow to red. After complete addition, the solution was warmed to r.t. and stirred for several hours. After reduction of the volume and storage at -25°C , 0.23 g of red crystals of **1** (0.17 mmol, 77%) precipitated.

Method B: A solution of 0.21 g of $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ (0.30 mmol) in 15 ml of THF was added dropwise at 0°C to a solution of $\text{Fe}_3(\text{CO})_{12}$ (0.30 g, 0.60 mmol) in 35 ml of THF. The color of the solution changed from yellow to red. After complete addition, the solution was warmed to r.t. and stirred for several hours. In order to complete the reaction, the solution was heated under reflux for 4 h. After reduction of the volume and storage at -25°C , 0.29 g of red crystals of **1** (0.22 mmol, 73%) precipitated.

Physical data of **1**: M.p. 206-209°C (dec.). Elemental analysis (C₅₄H₅₂CaFe₄O₁₈P₂, 1314.38): Calc.: C 49.34, H 3.99; found: C 48.36, H 4.88. ¹H NMR: δ (ppm) = 1.73 and 3.58 (THF), 7.1-7.8 (phenyl). ³¹P{¹H} NMR: δ (ppm) = 127.9. IR: 3051 w (C-H); 2027 s (CO), 1979 s, 1951 s (CO), 1934 vs (CO), 1915 s (CO), 1770 m (sh, broad, μ-CO), 1596 s, 1460 vs, 1377 s, 1305 w, 1260 sh, 1170 w, 1128 w, 1093 w, 1026 m, 998 w, 917 w, 874 m, 742 m, 722 m, 698 m, 659 m, 633 m, 625 w, 608 w, 592 s, 548 w, 511 m. MS (DEI, m/z, %): 28 (CO, 38), 42 (100), 72 (THF, 56), 78 (C₆H₆, 25), 242 (HFePPh₂, 39), 482 (Fe₂P₂Ph₄, 37), 510 (Fe₂P₂Ph₄CO, 43), 566 (Fe₂P₂Ph₄C₃O₃, 6), 622 (Fe₂P₂Ph₄C₅O₅, 20), 650 (Fe₂P₂Ph₄C₆O₆, 5).

X-Ray structure determinations

Intensity data for **1** (orange prism, size 0.04 x 0.04 x 0.04 mm³) was collected in the range 1.87° ≤ Θ ≤ 27.46° (completeness Θ_{max} = 97%) on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data was corrected for Lorentz and polarization effects but not for absorption effects.^[21,22] The structure was solved by direct methods (SHELXS)^[23] and refined by full-matrix least squares techniques against F_o² (SHELXL-97)^[24] (Table 2). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen and non-disordered atoms were refined anisotropically.^[24] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Table 2: Crystal data and refinement details for the X-ray structure determinations of the contact ion pair [(thf)₄Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}] (**1**).

Compound	1
formula	C ₅₄ H ₅₂ CaFe ₄ O ₁₈ P ₂
fw (g·mol ⁻¹)	1314.38
T/°C	-90(2)
crystal system	triclinic
space group	P $\bar{1}$
a/ Å	10.097(2)
b/ Å	11.905(2)
c/ Å	13.314(3)
α/°	101.07(3)
β/°	95.11(3)
γ/°	109.51(3)
V/Å ³	1460.0(6)
Z	1
ρ (g·cm ⁻³)	1.495
μ (cm ⁻¹)	11.86
measured data	9765
parameters	353
data with I > 2σ(I)	3490
unique data / R _{int}	6492/0.0491
wR ₂ (all data, on F ²) ^{a)}	0.1694
R ₁ (I > 2σ(I)) ^{a)}	0.0723
s ^{b)}	1.019
Res. dens./e·Å ⁻³	0.441/-0.424
CCDC No.	720836

^{a)} Definition of the R indices: $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$

$wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

^{b)} $s = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

Supporting Information

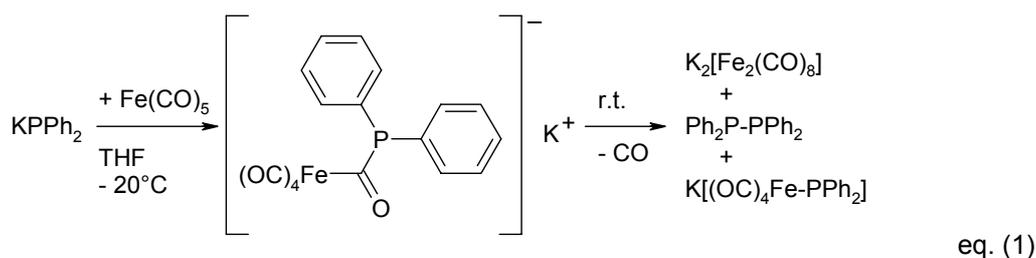
CIF files giving data collection and refinement details as well as positional coordinates of all atoms have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-720836 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, home page: www.ccdc.cam.ac.uk].

Results and Discussion

Synthesis

We are interested in the reaction behaviour of the easily accessible [(thf)₄Ca(PPh₂)₂].^[10,11] This complex shows an enormous reactivity as a catalyst in hydrophosphanylation reactions.^[12] The coordination behaviour of the nucleophilic phosphanide anion offers various possibilities in coordination chemistry.

Petz and Weller^[13] investigated the reaction of KPh₂ with Fe(CO)₅ in THF at -20°C. The first reaction step consisted of an addition of the PPh₂ nucleophile to a carbonyl group leading to the formation of K[(OC)₄Fe-C(O)-PPh₂] at δ(³¹P) = 46.4 ppm with a C=O stretching frequency of 1670 cm⁻¹ for the keto group. However, this compound decomposed at room temperature *via* a radical mechanism yielding [Fe(CO)₈]²⁻, Ph₂P-PPh₂ {δ(³¹P) = -14.4 ppm}, and K[(OC)₄Fe-PPh₂] {δ(³¹P) = -2.4 ppm} as is shown in equation 1. In addition, it was reported that complexes with the anion [K[(OC)₄Fe]₂PPh₂]^(E⁻) (which show a ³¹P NMR resonance at a position approximately 75 ppm to higher field than **A⁻**) decarbonylate readily yielding quantitatively the heptacarbonyl anion [Fe₂(CO)₆(μ-CO)(μ-PPh₂)]^(A⁻)^[14,15] with a ³¹P NMR shift of approximately δ(³¹P) = 125 ppm.^[3]



We present here a new access route to [(thf)₄Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}] (**1**) with a yet unknown coordination behaviour of the anion *via* the oxygen atom of the bridging carbonyl ligand.

The reaction of [(thf)₄Ca(PPh₂)₂] with excess of iron carbonyls Fe(CO)₅, Fe₂(CO)₉, or Fe₃(CO)₁₂ proceeded stepwise, finally leading to the formation of [(thf)₄Ca{Fe₂(CO)₆(μ-CO)(μ-PPh₂)₂}] (**1**). The ³¹P NMR spectroscopic pursuit of these reactions showed at the beginning resonances at δ(³¹P) = 43 ppm and at δ(³¹P) = 61 ppm with varying intensity ratios and the starting compound [(thf)₄Ca(PPh₂)₂] at δ(³¹P) = -13 ppm. In figure 2 the ³¹P{¹H} NMR spectra at the beginning of the reaction and

after heating for several hours are shown. Removal of the solvent or prolonged heating of the reaction mixtures led to extensive conversion of the intermediates at $\delta(^{31}\text{P}) = 43$ ppm and $\delta(^{31}\text{P}) = 61$ ppm to **1** at $\delta(^{31}\text{P}) = 128$ ppm. Our observations can be explained in terms of simultaneous formation of $[(\text{OC})_4\text{Fe}-\text{C}(\text{O})-\text{PPh}_2]^-$ and $[(\text{OC})_4\text{Fe}]_2\text{PPh}_2^+$ (**E**) in analogy to published investigations.^[13-15] Prolonged heating of these reaction mixtures led to liberation of carbon monoxide which drives the reaction toward the formation of the orange-red contact ion pair $[(\text{thf})_4\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\}_2]$ (**1**) which showed a six-coordinate calcium atom in the solid state and the carbonylferrate units in a trans position (equation 2). Compound **1** was only slightly air sensitive but hygroscopic.

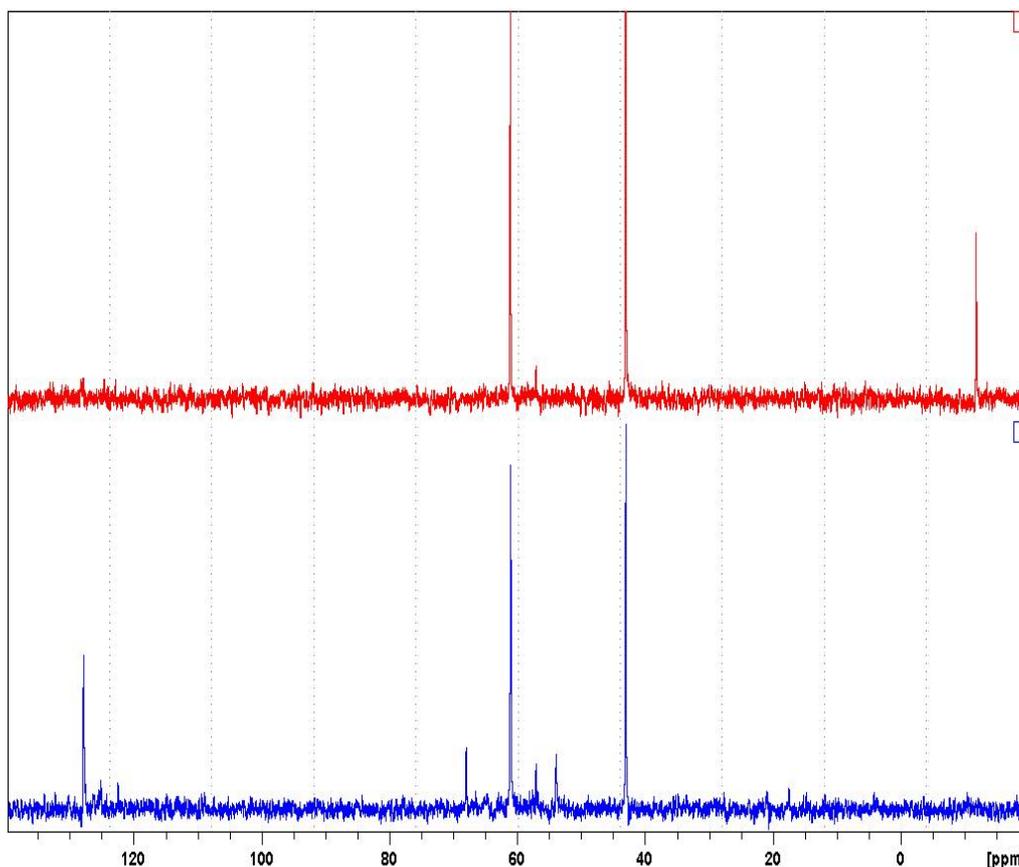
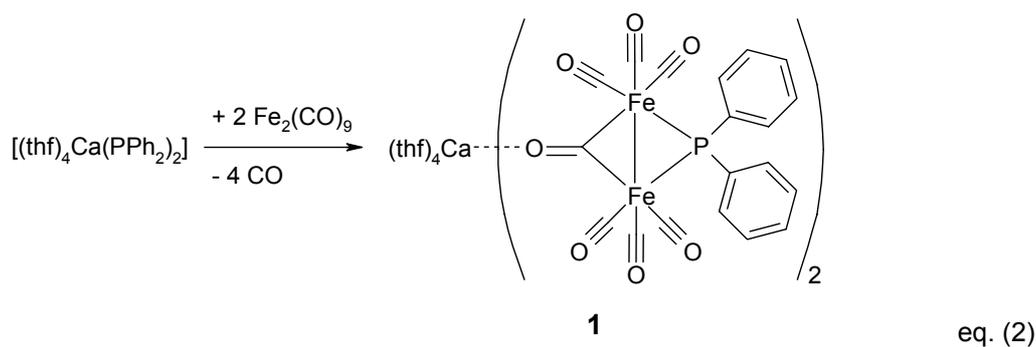


Figure 2: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction product of $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ [$\delta(^{31}\text{P}) = -13$ ppm] with $\text{Fe}_3(\text{CO})_{12}$ in THF immediately after addition (upper spectrum) and after 4 hours of heating under reflux (lower spectrum) (81.014 MHz, $[\text{D}_8]\text{THF}$).

Molecular Structure

Molecular structure and numbering scheme of **1** are shown in Figure 3. The calcium center shows a distorted octahedral environment with rather short Ca-O distances of 229.8 and 234.0 pm (average values) to the bridging carbonyl and to the THF molecules, respectively. The lower value is partly a consequence of less steric strain around the oxygen atom of the carbonyl group.

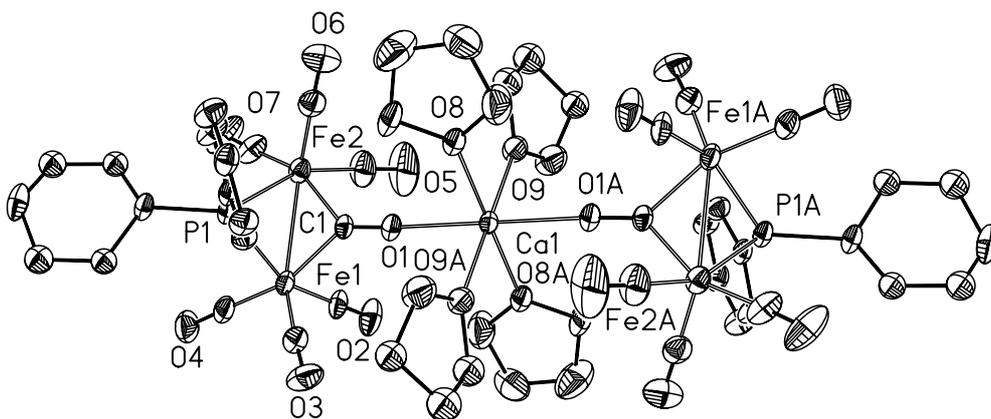


Figure 3: Molecular structure and numbering scheme of $[(\text{thf})_4\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\}(\mu\text{-PPh}_2)_2]$ (**1**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Symmetry related atoms ($-x+2, -y+2, -z$) are marked with the letter "A". Selected bond lengths (pm): Ca1-O1 229.8(4), Ca1-O8 233.5(4), Ca1-O9 234.5(4), Fe1-Fe2 257.9(2), Fe1-C1 192.7(6), Fe1-C2 176.4(6), Fe1-C3 176.4(7), Fe1-C4 180.8(7), Fe1-P1 221.9(2), Fe2-C1 192.2(6), Fe2-C5 176.4(7), Fe2-C6 176.1(8), Fe2-C7 179.8(7), Fe2-P1 222.5(2), C1-O1 122.1(6), C2-O2 115.9(7), C3-O3 115.4(7), C4-O4 115.5(7), C5-O5 114.6(8), C6-O6 114.9(8), C7-O7 114.5(7).

Selected structural parameters of the $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PR}_2)]^-$ anions (**A**⁻) are summarized in Table 1. In order to compare the Fe-P distances the influence of the P-bound groups has to be considered. In $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-PtBu}_2)]$ all carbonyl ligands are terminally coordinated and both phosphanide anions occupy bridging positions.^[19] The dialkyl substituted phosphanide shows a larger average Fe-P distance of 227.0 pm than the Fe($\mu\text{-PPh}_2$) moiety (av. 225.5 pm). In the structure of $[\text{Fe}_2(\text{CO})_5(\text{NO})(\text{PPh}_3)(\mu\text{-PtBu}_2)]$ ^[20] the Fe-P bond lengths to terminally bound PPh_3 and to bridging PtBu_2 are very similar suggesting that the coordination number of the phosphorus atom is the major influence on the Fe-P bond lengths. In the anion $[(\text{OC})_4\text{Fe-PPh}_2]^-$ repulsive forces between the phosphanide anion and the rather electron-rich iron center lead to large Fe-P distances of 235.9 pm despite the low coordination number of three for the P atom.^[13] The rather weak interaction between iron and phosphorus in this solvent-separated ion pair allows short Fe-C bonds to the

carbonyl ligands. The coordination of another $\text{Fe}(\text{CO})_4$ moiety and the formation of $[\{(\text{OC})_4\text{Fe}\}_2\text{PPh}_2]$ leads to a shortening of the Fe-P bonds despite the enhancement of the coordination number of the phosphorus atom and an enlargement of the Fe-C distances.^[2]

Table 1: Selected structural parameters (average values) for iron carbonyl complexes with additional phosphanide substituents. For comparison purposes, $[(\text{OC})_4\text{Fe}-\text{PPh}_3]$ and $[\text{FeCo}(\text{CO})_7(\mu\text{-PR}_2)]$ are included.

Compound ^a	Fe-P	Fe-Fe	Fe-C _t	Fe-C _b	Ref.
$[(\text{OC})_4\text{Fe}-\text{PPh}_3]$	224.4	-	179.5	-	[16]
$[(\text{OC})_4\text{Fe}-\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2]$	224.6	-	178.6	-	[17]
$[\text{K}(18\text{C}6)][(\text{OC})_4\text{Fe}-\text{PPh}_2]$	235.9	-	175.6	-	[13]
$[\text{Fe}_2(\text{CO})_6(\text{NO})(\mu\text{-PPh}_2)]$	222.6	269.9	179.9	-	[18]
$[\text{FeCo}(\text{CO})_7(\mu\text{-PMe}_2)]$	222.8	266.6 ^b	181	-	[6]
$[\{(\text{OC})_4\text{Fe}\}_2\text{PPh}_2]^-$ ^c	232.5	-	176.2	-	[2]
$[(\text{thf})_4\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\}_2]$ (1)	222.2	257.9	177.7	192.5	This work
$[\text{NEt}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]$	221.0	260.1	177.8	196.4	[5]
$[(\text{Ph}_3\text{P})_2\text{N}][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PtBu}_2)]$	224.9	262.7	177.1	196.4	[7]
$[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})(\mu\text{-PtBu}_2)]$	227.4	260.3	180.6	197.7	[7]
$[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\{\mu\text{-Cu}(\text{PPh}_3)\}]$	222.8	262.7	178.2	197.3	[8]
$[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PtBu}_2)\{\mu\text{-Ag}(\text{PPh}_3)\}]$	227.3	265.6	178.3	196.4	[3]

a) Methyl, Me; phenyl, Ph; *tert*-butyl, *t*Bu; 18-crown-6, 18C6. b) Fe-Co bond length. c) Counter cation: $[\text{Fe}_2(\text{CO})_5(\text{PMe}_3)_3(\mu\text{-PPh}_2)]^+$.

The C-O bond lengths strongly depend on the coordination mode. The C1-O1 bond of the bridging carbonyl ligand is elongated compared to the bond lengths in terminally bound carbonyl groups. This fact is in agreement with the expectation that bridging carbonyl groups should exhibit a C=O bond order of two (comparable to ketones), whereas terminally bound carbonyl groups should show a higher bond order (comparable to the isoelectronic cyanide). Within the group of terminally bound carbonyl ligands, significant differences can be noticed. The Fe1-C4 and Fe2-C7 bonds in trans-position to the bridging carbonyl group C1-O1 show significantly larger Fe-C distances due to the trans influence of the bridging carbonyl ligand.

Conclusion

The reaction of $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ with the iron carbonyls at room temperature in THF yields mixtures of iron carbonyl-containing phosphanides. Attempts to isolate intermediates from these reaction solutions were unsuccessful because CO was liberated during removal of solvent or heating under reflux. In both cases the intermediates were extensively converted into orange-red $[(\text{thf})_4\text{Ca}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)\}_2]$ (**1**) with satisfactory yields. The X-ray structure determination verified the proposed structure with the carbonyl ferrate anions in trans positions.

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