

Gmelin Handbook of Inorganic Chemistry

8th Edition

Fe Organoiron Compounds

Part B11

Mononuclear Compounds 11

With 29 illustrations

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B1



LITERATURE CLOSING DATE: END OF 1979
IN MANY CASES MORE RECENT DATA HAVE BEEN CONSIDERED

Library of Congress Catalog Card Number: Agr 25-1383

ISBN 3-540-93473-1 Springer-Verlag, Berlin · Heidelberg · New York
ISBN 0-387-93473-1 Springer-Verlag, New York · Heidelberg · Berlin

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Printing: Universitätsdruckerei H. Stürtz AG, Würzburg

R
54.4073
G 1-17
t-590-B11

Gmelin Handbuch der Anorganischen Chemie

Achte völlig neu bearbeitete Auflage

BEGRUNDET VON

Leopold Gmelin

ACHTE AUFLAGE BEGONNEN

im Auftrag der Deutschen Chemischen Gesellschaft
von R.J. Meyer

FORTGEFÜHRT VON

E.H.E. Pietsch und A. Kotowski
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HERAUSGEGEBEN VOM

Gmelin-Institut für Anorganische Chemie
der Max-Planck-Gesellschaft zur Förderung der Wissen-
schaften
Direktor: Ekkehard Fluck



Springer-Verlag 27
Berlin Heidelberg New York 1983

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Preface

The present volume is a continuation of Series B on the mononuclear organoiron compounds. It covers the literature completely to the end of 1979 and includes occasional references to the literature up to 1982.

This volume begins the description of compounds with ^5L ligands, i.e., ligands bonded to the iron atom by five carbon atoms. ^5LFe compounds are numerous particularly those where ^5L is cyclopentadienyl. The stability of a ^5LFe unit permits many different ligands at the other three coordination sites of the iron atom. Thus the present volume can only cover a part of the ^5L compounds. Main sections of the volume deal with ^5LFe compounds containing other ligands of the D and X type and ^5LFe compounds with an additional ^1L ligand, which include compounds with $^5\text{LFe}(\text{CO})$ units (complete in this volume) and $^5\text{LFe}(\text{CO})_2$ units (to be continued in B 12).

Series B so far comprises volumes B 1 to B 7, and a survey of this series has been given in the preface to B 7 (1981). The missing parts, B 8 to B 10, describe the remaining ^4LFe compounds and will appear in the near future.

Formulas and symbols have been explained in the prefaces to "Kobalt-Organische Verbindungen" 1, New Suppl. Ser., Vol. 5, and "Nickel-Organische Verbindungen" 1, New Suppl. Ser., Vol. 16. Much of the data, particularly in tables, is given in abbreviated form without dimensions; for explanations see p. 375. Additional remarks, if necessary, are given in the texts heading the tables. The location of substances in other organoiron volumes is given in the form "B 4, 1.1.6.1", i.e., Series B (mononuclear compounds), Volume 4, Chapter 1.1.6.1, or "C 3, 2.4.1.1.1", i.e., Series C (polynuclear compounds), Volume 3, Chapter 2.4.1.1.1.

The volume contains an empirical formula index on p. 376 and a ligand formula index on p. 398.

Frankfurt am Main
December 1982

Ulrich Krüerke

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Organoiron Compounds, Part B

Mononuclear Compounds 11

1.5 Compounds with Ligands Bonded by Five C Atoms

1.5.1 Compounds with One ^5L Ligand

$[\text{C}_5\text{H}_5\text{Fe}]^+\text{C}_6\text{H}_5\text{COO}^-$ forms in solution by photolysis ($\lambda = 359$ and 466 nm) of benzoylferrocene and an excess of water in $(\text{CH}_3)_2\text{SO}$, pyridine, or dimethylformamide. The ^1H NMR spectrum of a $\text{C}_5\text{D}_5\text{N}$ solution shows a C_5H_5 resonance at $\delta = 3.8$ ppm along with signals of $\text{C}_6\text{H}_5\text{COO}^-$ and cyclopentadiene. Characteristic IR absorptions indicate the presence of a carboxylate group. Admission of oxygen produces a purple solution ($\lambda_{\text{max}} = 550$ nm), which displays the ESR spectrum of high-spin Fe^{III} . Benzoic acid was isolated after acidification [1].

$[\text{C}_5\text{H}_5\text{Fe}]^+$ can be produced in the gas phase from ferrocene by electron impact, and generally it is an abundant fragment ion in the mass spectra of cyclopentadienyliron compounds. An ion cyclotron resonance investigation of the alkylation of $[\text{C}_5\text{H}_5\text{Fe}]^+$ by CH_3X ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) revealed sequential alkylation steps, $[\text{C}_5\text{H}_5\text{Fe}]^+ + n\text{CH}_3\text{X} \rightarrow [(\text{CH}_3)_n\text{C}_5\text{H}_{5-n}\text{Fe}]^+ + n\text{HX}$ with $n = 1$ to 4 , but significant product yields were obtained only in the case of CH_3Br [2].

$[\text{C}_5\text{H}_5\text{FeH}]^+$ was recently observed along with $[\text{C}_5\text{H}_5\text{Fe}]^+$ ($\sim 1:3$ mole ratio) in ion-molecule reactions of Fe^+ with cyclopentane ($< 10^{-6}$ Torr). It presumably forms by initial insertion of Fe^+ into a C-H bond followed by the stepwise loss of 2H_2 . The five-membered carbon ring remains intact [3].

References:

- [1] L.H. Ali, A. Cox, T.J. Kemp (J. Chem. Soc. Chem. Commun. **1972** 265/6). – [2] R.R. Corderman, J.L. Beauchamp (Inorg. Chem. **17** [1978] 68/70). – [3] G.D. Byrd, R.C. Burnier, B.S. Freiser (J. Am. Chem. Soc. **104** [1982] 3565/9).

1.5.1.1 Compounds with $[\text{}^5\text{LFe}(\text{}^2\text{D})_2]^-$ Anions

The two following salts represent singular cases since $[\text{}^5\text{LFe}(\text{}^2\text{D})_2]^-$ anions with ^2D ligands other than PF_3 have so far not been reported. The preparation of the salts below is based on the proton abstraction from $\text{C}_5\text{H}_5\text{Fe}(\text{PF}_3)_2\text{H}$, see 1.5.1.3, p. 16.

$\text{K}[\text{C}_5\text{H}_5\text{Fe}(\text{PF}_3)_2]$ was formed on slow addition of $\text{KOC}(\text{CH}_3)_3$ in THF to an excess of $\text{C}_5\text{H}_5\text{Fe}(\text{PF}_3)_2\text{H}$ in THF. The excess hydride prevented the easy exchange of $\text{OC}(\text{CH}_3)_3$ for F on the PF_3 ligand. Concentration of the solution and addition of pentane gave a white precipitate, which was purified by repeated washing with pentane, 86% yield.

IR spectrum (KBr): $\nu(\text{P-F})$ bands at 798 (sh), 820 (vs, br), 838 (vs, br), 852 (vs), and 878 (s) cm^{-1} ; $\delta(\text{PF})$ bands at 537 (vs) and 554 (sh) cm^{-1} . The $\nu(\text{P-F})$ frequencies are shifted to lower wave numbers relative to the hydride because the

negative charge enhances the Fe-PF₃ backbonding and thus reduces the P-F double-bond fraction.

$[(C_2H_5)_3NH][C_5H_5Fe(PF_3)_2]$ was obtained as a by-product in the synthesis of $C_5H_5Fe(PF_3)_2H$ from $C_5H_5Fe(PF_3)_3$ and $N(C_2H_5)_3$. After vacuum distillation of the hydride, repeated recrystallization of the residue from THF/pentane gave colorless crystals of the salt, 1 to 5% yield.

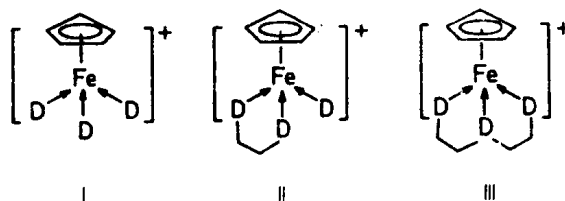
IR spectrum (KBr): 529 (s), 550 (m), 792 (vs. sh), 809 (vs. br), 817 (vs. sh), 833 (vs. sh), and 882 (m, br) cm⁻¹.

Reference:

T. Kruck, L. Knoll (Chem. Ber. **105** [1972] 3783/8).

1.5.1.2 Compounds with $[^5LFe(^2D)_3]^{n+}$, $[^5LFe(^2D)_2(^2D')]^+$, $[^5LFe(^2D-^2D)(^2D')]^+$, and $[^5LFe^2D-^2D-^2D]^+$ Cations

This chapter describes cationic compounds of the types represented by Formulas I to III. Much of the material is summarized in Table 1. ⁵L is always C₅H₅ and the only two compounds with a substituted C₅H₅ ring are described outside the table. With one exception (on p. 3) all cations are singly charged, i.e., n = 1. ²D represents phosphine, arsine, stibine, or another nitrogen- or oxygen-containing ligand. ²D-²D stands for diphosphine, o-phenanthroline, or 2,2'-bipyridyl; and ²D-²D-²D stands for polyphosphine ligands.



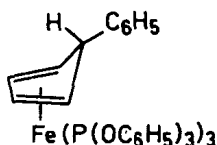
The ionic nature of these compounds is responsible for their conductivity in solution which shows that there are two ions per molecule. Molar conductivities have been determined in acetone, nitromethane, and methanol but only for a few complexes. For the compounds No. 9, 16, and 17 to 24 the molar conductivities were reported to be 82 to 89 Ω⁻¹·cm²·mol⁻¹ but neither solvent nor temperature was given [5]. The complexes No. 25 to 30 have Λ values of 95 to 99 (in methanol at 33 °C) [11], and the polyphosphine-containing compounds No. 41 to 49 have conductivities of 90 to 140 (in acetone) and 60 to 95 Ω⁻¹·cm²·mol⁻¹ (in nitromethane) [1 to 3, 8].

$[CH_3-C_5H_4Fe(P(OC_2H_5)_3)_3]PF_6$ is obtained in a 36% yield when the cationic arene complex $[CH_3-C_5H_4FeC_6H_5NO_2]PF_6$ is heated under reflux at 130 to 140 °C with 4 equivalents of $P(OC_2H_5)_3$ for 18 h. A 60% yield is obtained when the same reaction is carried out with $[CH_3-C_5H_4FeC_6H_5NH_2]PF_6$ as the starting material at 145 to 150° for 20 h. The excess phosphine is removed, the solid residue taken up in acetone, and the solution chromatographed on Al₂O₃ with CH₃COCH₃/CH₂Cl₂ (1:1).

The ^1H NMR spectrum (in CD_3COCD_3) exhibits signals at $\delta=1.17$ (t, CH_3 in C_2H_5), 1.93 (s, CH_3 on C_5H_4), 3.97 to 4.45 (m, CH_2), and 4.52 to 4.82 ppm (m, C_5H_4) [19].

$[\text{C}_6\text{H}_5\text{-C}_5\text{H}_4\text{Fe}(\text{P}(\text{OC}_6\text{H}_5)_3)_3]\text{I}$ is prepared by the action of iodine on $\text{C}_6\text{H}_5\text{-C}_5\text{H}_5\text{Fe}(\text{P}(\text{OC}_6\text{H}_5)_3)_3$ (see Formula IV) in CH_2Cl_2 . After 3 h the mixture is concentrated and the solution chromatographed on Al_2O_3 with petroleum ether. Two bands can be eluted, the first with ether/ CH_2Cl_2 to give the neutral $\text{C}_6\text{H}_5\text{-C}_5\text{H}_4\text{-Fe}(\text{P}(\text{OC}_6\text{H}_5)_3)_2\text{I}$ (p. 16), the second with acetone/methanol, followed by recrystallization from CH_2Cl_2 /ether, to give yellow crystals of the compound in a 30% yield. The crystals are the monoetherate $[\text{C}_6\text{H}_5\text{-C}_5\text{H}_4\text{Fe}(\text{P}(\text{OC}_6\text{H}_5)_3)_3]\text{I} \cdot (\text{C}_2\text{H}_5)_2\text{O}$ [5].

The ^1H NMR spectrum exhibits the signals $\delta=4.83$, 5.54 (m, C_5H_4) and 6.6 to 7.6 (m, C_6H_5), which are consistent with a substituted cyclopentadienyl ring [5].



IV

$[\text{C}_5\text{H}_5\text{Fe}(\text{P}(\text{CH}_3)_3)_3][\text{PF}_6]_2$ (Formula I, $n=2$) is prepared by addition of an equimolar amount of NOPF_6 to a solution of $[\text{C}_5\text{H}_5\text{Fe}(\text{P}(\text{CH}_3)_3)_3]\text{PF}_6$ (Table 1, No. 4) in acetone. Gas evolves immediately, and the color of the solution changes from orange to red. After 1 h the volume is reduced, and ether added to the mixture. This precipitates an orange powder, which is then dissolved in CH_3CN and filtered. The pure product is obtained from this solution, in a 68% yield, upon addition of ether [17].

The product melts at 180°C (dec.) and is paramagnetic, μ_{eff} : 2.12 B.M. [17].

The complexes described in Table 1 can be prepared by the following methods.

- Method I: The neutral complex of the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ type is irradiated for several hours in CH_3CN or benzene in the presence of excess ligand ^2D , $^2\text{D}-^2\text{D}$, or $^2\text{D}-^2\text{D}-^2\text{D}$ [1, 15, 17].
- Method II: The monocarbonyl complex of the $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})(^2\text{D}')_2]\text{X}$ type is irradiated in the presence of the ligand ^2D in acetone, THF, or CH_3CN or in ^2D as the solvent [13, 17].
- Method III: An excellent leaving group, such as $^2\text{D}' = \text{CH}_3\text{CN}$ or CH_3COCH_3 , in the cationic complex $[\text{C}_5\text{H}_5\text{Fe}(^2\text{D}'')_2^2\text{D}']\text{X}$ is replaced by the new ligand ^2D [13, 17].
- Method IV: Addition of the ligand ^2D to the neutral complex $\text{C}_5\text{H}_5\text{Fe}(^2\text{D}')_2\text{X}$. The ligands $^2\text{D}'$ of the starting material also may be partially replaced during the reaction [5].
- Method V: Metathesis between the cationic complex $[\text{C}_5\text{H}_5\text{Fe}(^2\text{D})_3]\text{X}$ and NH_4BF_4 , NH_4PF_6 , AgBF_4 , or AgPF_6 in a polar solvent such as methanol or water [1, 3].

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Table 1
Compounds with $[\text{C}_5\text{H}_5\text{Fe}(\text{}^2\text{D})_3]^+$, $[\text{C}_5\text{H}_5\text{Fe}(\text{}^2\text{D})_2\text{}^2\text{D}]^+$, $[\text{C}_5\text{H}_5\text{Fe}(\text{}^2\text{D})_2\text{}^2\text{D}]^+$, and $[\text{C}_5\text{H}_5\text{Fe}^2\text{D}-^2\text{D}-^2\text{D}]^+$ Cations.
Further information for all compounds (except for No. 16) is given at the end of the table.
For abbreviations and dimensions, see p. 375

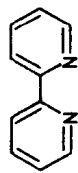
No.	donor ligands method of preparation (yield in %)	anion	properties and remarks	Ref.
$[\text{C}_5\text{H}_5\text{Fe}(\text{}^2\text{D})_3]^+$ type				
1	$\text{P}(\text{CH}_3)_3$ I (87)	Br	yellow, m.p. 250° ^1H NMR (CD_3SOCD_3): 1.45 (m, PCH_3), 4.40 (q, C_5H_5 , $\text{J}(\text{P}, \text{H}) = 1.9$)	[17]
2	$\text{P}(\text{CH}_3)_3$ II (29)	I	no properties reported	[17]
3	$\text{P}(\text{CH}_3)_3$ III	BF_4	no properties reported	[17]
4	$\text{P}(\text{CH}_3)_3$ V (93)	PF_6	m.p. 181° (dec.)	[17]
5	$\text{P}(\text{OCH}_3)_3$ see further information	PF_6	light yellow powder, m.p. 265 to 268° (dec.) ^1H NMR (CD_3COCD_3): 3.79 (m, CH_3 , $\text{J}(\text{P}, \text{H}) = 10.8$), 4.84 (q, C_5H_5 , $\text{J}(\text{P}, \text{H}) = 1.2$)	[18]
6	$\text{P}(\text{OC}_2\text{H}_5)_3$ see further information	PF_6	yellow powder, m.p. 254 to 255° (dec.) ^1H NMR (CD_3COCD_3): 1.33 (t, CH_3 , $\text{J}(\text{H}, \text{H}) = 7$), 4.18 (m, CH_2 , $\text{J}(\text{H}, \text{H}) = 7$, $^3\text{J}(\text{P}, \text{H}) = 4.1$), 4.73 (q, C_5H_5 , $\text{J}(\text{P}, \text{H}) = 1.3$)	[18, 19]
7	$\text{P}(\text{OC}_6\text{H}_5)_3$ IV, V (98)	BF_4	bright yellow, with 0.5 mol ether ^1H NMR (CD_3COCD_3): 5.03 (q, C_5H_5 , $\text{J}(\text{P}, \text{H}) = 1.6$), 7.1 (m, C_6H_5)	[5, 7]
8	$\text{P}(\text{OC}_6\text{H}_5)_3$ IV, V	PF_6	yellow, with 1 mol ether ^1H NMR: 4.78 (q, C_5H_5 , $\text{J}(\text{P}, \text{H}) = 1.5$), 6.81 to 7.17 (m, C_6H_5)	[5]

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9	$P(OC_6H_5)_3$ see further information	SCN	yellow, with 1 mol ether, m.p. 146 to 147° IR (Nujol): $\nu(SCN)$ 2050	[5]
[C ₅ H ₅ Fe(2D) ₂ ² D'] ⁺ type				
10	$P(CH_3)_3$ see further information	BF ₄	¹ H NMR (CD ₃ SOCD ₃): 1.52 (m, PCH ₃), 4.54 (t, C ₅ H ₅)	[17]
11	$P(CH_3)_3$ IV, V (74)	PF ₆	yellow, m.p. 283 to 286° (dec.) ¹ H NMR: 1.52 (m, PCH ₃), 3.23 (s, SCH ₃), 4.54 (t, C ₅ H ₅ , J(P,H) = 2)	[17]
12	$P(CH_3)_3$ IV	I	no properties reported	[17]
13	$P(CH_3)_3$ II (94)	BF ₄	orange, m.p. 168 to 175° (dec.)	[17]
14	$P(CH_3)_3$ II (96)	PF ₆	m.p. 300° (dec.) ¹ H NMR (CD ₃ SOCD ₃): 1.55 (m, PCH ₃), 2.05 (s, CH ₃ CN), 4.60 (t, C ₅ H ₅ , J(P,H) = 1.5) IR: $\nu(CN)$ 2260	[17]
15	$P(CH_3)_3$ III (67)	BF ₄	orange, m.p. 185 to 190° ¹ H NMR (CD ₂ Cl ₂): 1.37 (m, PCH ₃), 4.25 (q, C ₅ H ₅ , J(P,H) = 1.8), 7.42 (m, C ₆ H ₅)	[17]
16	$P(C_2H_5)_3$ IV, V	PF ₆	orange ¹ H NMR: 1.21 (t, CH ₃ , J(H,H) = 6), 1.93 (m, CH ₂), 4.56 (s, C ₅ H ₅), 6.98 to 7.10 (m, C ₆ H ₅)	[5]
17	$P(OC_6H_5)_3$ IV, V	PF ₆	yellow, with 1 mol ether ¹ H NMR: 4.94 (s, C ₅ H ₅), 7.33 (m, C ₆ H ₅) IR (Nujol): $\nu(SO)$ 1298	[5]
18	$P(OC_6H_5)_3$ IV, V	PF ₆	orange, m.p. 126 to 130° ¹ H NMR: 2.11 (s, CH ₃), 4.21 (s, C ₅ H ₅), 7.04 to 7.16 (m, C ₆ H ₅)	[5]

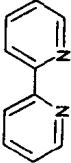
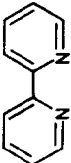
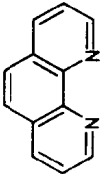
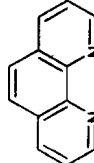
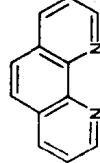
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Table 1 [continued]

No.	donor ligands method of preparation (yield in %)	anion	properties and remarks	Ref.
19	$P(OC_6H_5)_3$ IV, V	$NCCH_2CH_3$ PF_6	orange, m.p. 124 to 125° 1H NMR: 1.15 (t, CH_3 , $J(H,H)=6$), 2.61 (q, CH_2 , $J(H,H)=6$), 4.23 (s, C_5H_5), 7.06 to 7.34 (m, C_6H_5) IR (Nujol): $\nu(CN)$ 2267	[5]
20	$P(OC_6H_5)_3$ IV, V	$NCCH_2Cl$ PF_6	orange, m.p. 148 to 151° 1H NMR: 4.38 (t, C_5H_5 , $J(P,H)=1.5$), 4.90 (t, CH_2 , $J(P,H)=1$), 7.36 to 7.43 (m, C_6H_5) IR: $\nu(CN)$ 2271	[5]
21	$P(OC_6H_5)_3$ IV, V	$NCCH_2CH_2Cl$ BF_4	orange, m.p. 110 to 113° 1H NMR: 3.09 (t, $NCCH_2$, $J(H,H)=5$), 3.68 (t, CH_2Cl , $J(H,H)=5.6$), 4.23 (s, C_5H_5), 7.09 to 7.29 (m, C_6H_5) IR: $\nu(CN)$ 2278	[5]
22	$P(OC_6H_5)_3$ IV, V	$NCN(CH_3)_2$ BF_4	orange, m.p. 111 to 112° 1H NMR: 2.83 (s, CH_3), 4.19 (s, C_5H_5), 7.12 to 7.23 (m, C_6H_5) IR: $\nu(CN)$ 2292	[5]
23	$P(OC_6H_5)_3$ IV, V	$NCCH_2CONH_2$ BF_4	orange, m.p. 123 to 125° 1H NMR: 3.74 (s, CH_3), 4.16 (t, C_5H_5 , $J(P,H)\sim 1$), 5.67 (s, NH_2), 7.13 to 7.28 (m, C_6H_5) IR (Nujol): $\nu(C=O)$ 1716	[5]
24	$P(OC_6H_5)_3$ IV, V	$NCCH_2COOH$ BF_4	orange, m.p. 128 to 131° IR (Nujol): $\nu(CN)$ 2280	[5]
[$C_5H_5Fe(^2D-^2D)^2D^+$] type				
25		$P(C_6H_5)_3$ I	red violet	[11]

see further information

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26		$\text{As}(\text{C}_6\text{H}_5)_3$	I	red violet	[11]
	see further information				
27		$\text{Sb}(\text{C}_6\text{H}_5)_3$	I	red violet	[11]
	see further information				
28		$\text{P}(\text{C}_6\text{H}_5)_3$	I	orange red	[11]
	see further information				
29		$\text{As}(\text{C}_6\text{H}_5)_3$	I	orange red	[11]
	see further information				
30		$\text{Sb}(\text{C}_6\text{H}_5)_3$	I	orange red	[11]
	see further information				
31	$(\text{P}(\text{CH}_3)_2\text{CH}_2)_2$	$(\text{CH}_3)_2\text{CO}$	BF_4	brown crystals IR (Nujol): $\nu(\text{C}=\text{O})$ 1650	[4]
32	$(\text{P}(\text{CH}_3)_2\text{CH}_2)_2$ IV (51)	$\text{P}(\text{OC}_6\text{H}_5)_3$	I	yellow ^1H NMR (CDCl_3): 4.38 (C_5H_5)	[12]
33	$(\text{P}(\text{CH}_3)_2\text{CH}_2)_2$ V (82)	$\text{P}(\text{OC}_6\text{H}_5)_3$	BF_4	yellow	[12]
34	$(\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2)_2$	$(\text{CH}_3)_2\text{CO}$	Cl	see further information	[13]
35	$(\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2)_2$ II (70)	$(\text{CH}_3)_2\text{CO}$	PF_6	graphite, dec. p. 80 to 85° ^1H NMR (CD_3COCD_3): 2.20 (s, CH_3), 2.63, 2.73 (CH_2), 4.56 (t, C_5H_5), 7.70 (m, C_6H_5) IR (KBr): $\nu(\text{C}=\text{O})$ 1710	[10, 13]

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Table 1 [continued]

No.	donor ligands method of preparation (yield in %)	anion	properties and remarks	Ref.
36	(P(C ₆ H ₅) ₂ CH ₂ -) ₂ C ₄ H ₈ O (THF) II (15)	PF ₆	blue, dec. p. 80 to 85° not sufficiently soluble for ¹ H NMR	[13]
37	(P(C ₆ H ₅) ₂ CH ₂ -) ₂ NH ₃ III (10)	PF ₆	red crystals, with 1 mol THF, dec. p. 200 to 205° ¹ H NMR (CD ₃ COCD ₃): 0.75 (NH ₃), 2.81, 2.92 (CH ₂), 4.53 (t, C ₆ H ₅), 7.75 (C ₆ H ₅) IR (KBr): ν(NH) 3285, 3350	[13]
38	(P(C ₆ H ₅) ₂ CH ₂ -) ₂ N ₂ H ₄ III (55)	PF ₆	red crystals, with 1 mol THF, dec. p. 160 to 165° ¹ H NMR (CD ₃ COCD ₃): 2.66, 2.90 (CH ₂), 4.63 (t, C ₆ H ₅), 7.82 (m, C ₆ H ₅) IR (KBr): ν(NH) 3185, 3270	[13]
39	(P(C ₆ H ₅) ₂ CH ₂ -) ₂ NCCH ₃ I (87)	Br	red, dec. p. ~118 to 125° ¹ H NMR (CDCl ₃): 1.77 (s, CH ₃), 2.45 to 2.55 (m, CH ₂), 4.36 (t, C ₆ H ₅ , J(P,H) = 1.2), 7.0 to 7.8 (m, C ₆ H ₅)	[15]
40	(P(C ₆ H ₅) ₂ CH ₂ -) ₂ NCCH ₃ see further information	B(C ₆ H ₅) ₄	orange red, m.p. 190° (dec.) ¹ H NMR (CD ₃ COCD ₃): 1.40 (m, CH ₃), 2.40 (m), 2.62 (m), 4.40 (t, C ₆ H ₅), 6.85 (m, BC ₆ H ₅), 7.90, 7.52 (m, PC ₆ H ₅) ¹³ C NMR (CD ₃ COCD ₃): 79.7 (C ₆ H ₅), 129.9, 131.2, 131.5, 132.3, 132.5, 133.5, 133.7 (C ₆ H ₅) IR (CH ₂ Cl ₂): ν(CN) 2270	[14]
[C ₅ H ₅ Fe ²⁺ D ⁻² D] ⁺ type, R = C ₆ H ₅				
41	RP $\begin{array}{c} \text{C}_2\text{H}_4-\text{P}(\text{CH}_3)_2 \\ \\ \text{C}_2\text{H}_4-\text{P}(\text{CH}_3)_2 \end{array}$ I	I	yellow, m.p. 268 to 270° ¹ H NMR (CDCl ₃): 1.30 (m, CH ₃), 1.4 to 2.7 (br, CH ₂), 4.20 (s, C ₆ H ₅), 7.47 (m, C ₆ H ₅) ³¹ P NMR (CH ₂ Cl ₂): 76.1 (d, PCH ₃), 120.4 (t, PC ₆ H ₅ , J(P,P) = 37)	[8, 9]

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42	$\begin{array}{c} \text{C}_2\text{H}_4-\text{P}_a(\text{CH}_3)_2 \\ \\ \text{RP}-\text{C}_2\text{H}_4-\text{P}_a\text{R}_2 \\ \\ \text{I} \end{array}$	I	^{31}P NMR (CH_2Cl_2): 68.7 (m, PCH_3 , $\text{J}(\text{P}_b, \text{P}_a) = 39$), 104.3 (m, PR_2 , $\text{J}(\text{P}_a, \text{P}_c) = 44$, $\text{J}(\text{P}_b, \text{P}_c) = 29$), 123.1 (m, PR)	[9]
43	$\begin{array}{c} \text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{RP}-\text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{I (52)} \end{array}$	Br	yellow, m.p. 240 to 242° (dec.)	[2]
44	$\begin{array}{c} \text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{RP}-\text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{V} \end{array}$	PF_6	yellow, m.p. 253 to 255° ^1H NMR (CDCl_3): 2(CH ₂), 4.23 (C ₅ H ₅), 7.3 (C ₆ H ₅)	[2, 16]
45	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{PR}_2 \\ \quad \quad \\ \text{CH}_2-\text{PR}_2 \quad \text{CH}_2-\text{PR}_2 \\ \\ \text{I (33)} \end{array}$	Cl	yellow, 2-H ₂ O solvate, m.p. 139 to 141°	[1]
46	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{PR}_2 \\ \quad \quad \\ \text{CH}_2-\text{PR}_2 \quad \text{CH}_2-\text{PR}_2 \\ \\ \text{I (50)} \end{array}$	Br	yellow, m.p. 127 to 130°	[1]
47	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{PR}_2 \\ \quad \quad \\ \text{CH}_2-\text{PR}_2 \quad \text{CH}_2-\text{PR}_2 \\ \\ \text{V (93)} \end{array}$	PF_6	yellow, m.p. 298° (dec.) ^1H NMR (CD_3COCD_3): 5.06 (C ₅ H ₅)	[1]
48	$\begin{array}{c} \text{RP}-\text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{C}_2\text{H}_4 \\ \\ \text{RP}-\text{C}_2\text{H}_4-\text{PR}_2 \\ \\ \text{I (77)} \end{array}$	I	green, m.p. 211 to 214°	[3]

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