

Insertion of Diazoacetic Ester into the P–H Bond of the Cationic Primary and Secondary Phosphane-Substituted Iron Complexes $[\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{Ph})(\text{R})\text{H}]^+$ ($\text{R} = \text{Ph}, \text{Me}$) and $[(\text{R}'\text{C}_5\text{H}_4)(\text{OC})_2\text{Fe}-\text{P}(\text{R})\text{H}_2]^+$ [$\text{R} = t\text{Bu}, \text{Ph}, \text{Mes}$; $\text{R}' = \text{H}, \text{Neomenthyl (NM)}$]

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Treatment of the cationic secondary (phosphane)iron complexes $[\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{Ph})(\text{R})\text{H}]\text{BF}_4$ ($\text{R} = \text{Ph}, \text{Me}$) (**1a, b**) with diazoacetic ester (**2**) yields the novel complex salts $\{\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{Ph})(\text{R})[\text{N}(\text{H})-\text{N}=\text{C}(\text{H})\text{CO}_2\text{Et}]\}\text{BF}_4$ ($\text{R} = \text{Ph}, \text{Me}$) (**3a, b**) by insertion of the terminal nitrogen atom of **2** into the P–H bond of **1a, b**. Reaction of the primary (phosphane)iron

complexes $[(\text{R}'\text{C}_5\text{H}_4)(\text{OC})_2\text{Fe}-\text{P}(\text{R})\text{H}_2]\text{BF}_4$ [$\text{R} = t\text{Bu}, \text{Ph}, \text{Mes}$; $\text{R}' = \text{H}, \text{neomenthyl (NM)}$] (**4a–e**) with **2** affords the complex salts $\{(\text{R}'\text{C}_5\text{H}_4)(\text{OC})_2\text{Fe}-\text{P}(\text{R})(\text{H})[\text{N}(\text{H})-\text{N}=\text{C}(\text{H})\text{CO}_2\text{Et}]\}\text{BF}_4$ (**5a–d**) or $\{(\text{R}'\text{C}_5\text{H}_4)(\text{OC})_2\text{Fe}-\text{P}(\text{R})[\text{N}(\text{H})-\text{N}=\text{C}(\text{H})\text{CO}_2\text{Et}]\}_2\text{BF}_4$ (**6a–d**), depending on the molar ratio. The structures of **5c** and **6b** are proved by X-ray analysis.

Introduction

Our investigations into the reactivity of primary phosphane-substituted iron complexes of the type $[\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{R})\text{H}_2]\text{BF}_4$ ($\text{R} = \text{alkyl}, \text{aryl}$) towards organoisothoncyanates have revealed that in the presence of Et_3N the corresponding ferriophosphanes $\text{Cp}(\text{CO})_2\text{Fe}-\text{P}(\text{H})\text{R}$ are formed as intermediates. This will subsequently lead to the product of a P–H insertion^[2] or a combination of P–H insertion and [2+3] cycloaddition^[1]. This result clearly contrasts with the reactivity of ferriodiorganophosphanes $\text{Cp}(\text{OC})_2\text{Fe}-\text{PR}_2$ which in all cases were found to form the [2+3] cycloadducts $\text{Cp}(\text{OC})\text{Fe}-\text{PR}_2-\text{C}(\text{S})-\text{N}(\text{R}')-\text{C}^{\text{a}}(=\text{O})(\text{Fe}-\text{C}^{\text{a}})^{[3\text{a}]}$ with the heterocumulenes. A comparable reaction was observed with electron-deficient alkynes^{[3b][3c][3d][3e]}.

Now we have utilized this synthetic strategy for functionalization of phosphane ligands by transformation of metal-coordinated primary and secondary phosphanes with diazoacetic ester.

Results

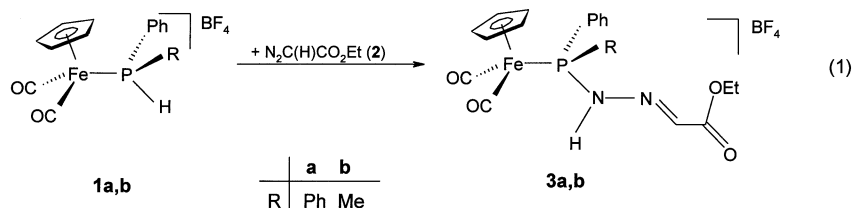
Preferentially, the complex salts $\{\text{Cp}(\text{OC})_2[\text{H}(\text{R})(\text{R}')\text{P}]\text{Fe}\}\text{BF}_4$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$; $\text{R}' = t\text{Bu}, \text{Ph}, \text{Mes}$) were used, which feature a simple structure and are easily accessible by thermal carbon monoxide/phosphane exchange from the cation $[\text{Cp}(\text{OC})_3\text{Fe}]^+$.

Reaction of **1a, b** with diazoacetic ester (**2**) in dichloromethane at room temperature yields the insertion products **3a, b** after 24 h which are obtained as yellow, microcrystalline powders in high yields (87%) after precipitation with ether [Eq. (1)].

The cation of **3a, b** bears a functional phosphane ligand characterized by a hydrazone unit formed by insertion of the terminal nitrogen atom of **2** into the P–H bond of **1a, b**. The constitution of **3a, b** is deduced from the NMR spectroscopic data that show a doublet resonance for the N–H proton [$\delta = 8.61$ (**3a**)/8.43 (**3b**); $^2J(\text{PNH}) = 16.7$ (**3a**)/22.0 Hz (**3b**)] and a singlet resonance for the $\text{CH}(\text{=N})$ proton [$\delta = 7.35$ (**3a**)/7.31 (**3b**)] in the ^1H -NMR spectra. The insertion of **2** causes a significant low-field shift of the ^{31}P -NMR resonance from $\delta = 31.8/10.8$ for the secondary phosphane in the starting material **1a, b** to $\delta = 114.1/108.0$ for the phosphanylhydrazone in the product **3a, b**. The IR spectra show the expected $\nu(\text{CO})_{\text{sym}}$ and $\nu(\text{CO})_{\text{asym}}$ absorptions at approximately 2050 and 2020 cm^{-1} .

In contrast to the insertion reaction of the metal-coordinated secondary phosphanes $\{\text{Cp}(\text{OC})_2\text{Fe}-\text{PR}_2\text{H}\}^+$ ($\text{R} = \text{alkyl}, \text{aryl}$) with isothiocyanates which requires a base (e.g. Et_3N)^[3a] the insertion of diazoacetic ester according to Eq. (1) proceeds without an auxiliary base. Since metallodiorganophosphanes, formed by deprotonation of secondary cationic phosphane complexes, have been shown to be essential intermediates for the insertion process, diazoacetic ester itself must act as the base. In accordance with this experience a reaction sequence for the formation of **3a, b** appears reasonable in which primarily the cation of **1a, b** is

[◇] Part LXI: Ref. [1].



deprotonated by diazoacetic ester to generate the phosphido species **A** followed by coupling between the terminal nitrogen atom and the phosphido phosphorus atom leading to intermediate **B** (Scheme 1). Protonation at the *P*-bound nitrogen atom gives **3a, b** under release of diazoacetic ester.

An insertion into one or both of the *P*–*H* bonds can be expected in the reaction of **2** with coordinated primary phosphanes. Especially the monoinsertion is of interest as it generates a stereogenic functionalized phosphorus atom. From this point of view it appears attractive to study the possibility of its asymmetrically induced formation using a chirally modified Cp ligand. In a first approach we introduced the easily accessible neomenthyl cyclopentadienyl unit^{[4][5]}.

Reaction of the primary (phosphane)iron complexes **4a–d** with **2** in acetonitrile at room temperature in a molar ratio of 1:1 yields the phosphanylhydrazone complexes **5a–d** within 2 d [Eq. (2a)]. The analogous reaction of **4a–c, e** with two equivalents of **2** leads to the formation of the metallophosphanyldihydrazone species **6a–d** by insertion of **2** into both the *P*–*H* bonds [Eq. (2b)]. Complexes **5a–d** and **6a–d** are obtained in good yields as yellow, microcrystalline powders after precipitation with ether from the concentrated reaction mixture.

The monoinsertion products **5a–d** are of particular interest, since they do not only contain a chiral phosphorus atom but also offer the possibility of further derivatization of the *R*₂*P*–*H* moiety. The NMC₅H₄ substituted compound **5d** is obtained as a 1:1 mixture of two epimers, which means that the chiral ring ligand has no effect on the stereochemical course of the coupling process^[6]. Compound **5d**, however, should offer the possibility of separating the stereoisomers with (*R*) and (*S*) configuration at the phosphorus atom by chromatography^{[6][7]}.

In accordance with the postulated constitution the ¹H-NMR spectra of **5a–d/6a–d** show the resonances of the NH and CH protons in the typical ranges of δ = 8.20–8.98 (N–H) and 7.02–8.47 (C–H). The resonance of the *P*-bonded hydrogen atom in **5a–d** at δ = 7.68–8.59 shows a doublet splitting with a *P*–*H* coupling constant of about 400 Hz. The ³¹P-NMR resonances of the secondary phosphane ligands in **5a–d** at δ = 64.9–113.8 exhibit a signifi-

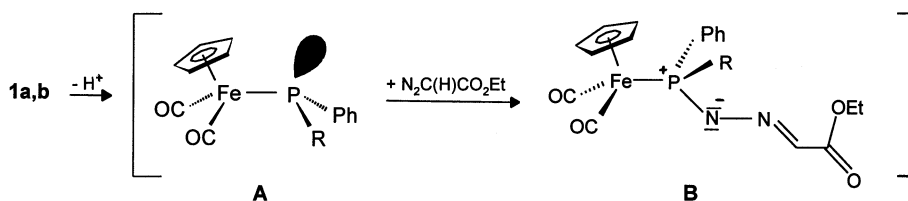
cant shift of about 120 ppm to lower field in relation to the starting materials **4a–d**. Relative to the secondary phosphane in **5a–c**, the tertiary phosphane in **6a–c** displays an additional shift of about 50 ppm (**5/6a**) or 80 ppm (**5/6b, c**).

The structures of the insertion products **5a–d/6a–d** deduced from the spectroscopic data are confirmed by X-ray analysis of **5c** and **6b**, demonstrating an exclusive formation of the (*E*) isomer at to the C=N double bond.

Molecular Structures of **5c** and **6b**

The complex salts **5c** (Figure 1) and **6b** (Figure 2) have an octahedral arrangement of the ligands CO, Cp, and P(H)(Mes)[N(H)–N=C(H)–C(O)OEt] or P(Ph)[N(H)–N=C(H)–C(O)OEt]₂, respectively, indicated by the bond angles of C1–Fe–C2 92.0(5)° (**5c**)/93.4(3)° (**6b**), C1–Fe–P 93.9(5)° (**5c**)/91.4(2)° (**6b**), and C2–Fe–P 95.0(8)° (**5c**)/95.0(2)° (**6b**). The Fe–C(O) distances of 1.757(12) Å (Fe–C1)/1.769(11) Å (Fe–C2) (**5c**), 1.753(7) Å (Fe–C1)/1.785(6) Å (Fe–C2) (**6b**) as well as the Fe–P distances [*d*(Fe–P) = 2.208(17) Å (**5c**)/2.1909(15) Å (**6b**)] are in good agreement with known values^{[1][2]}. The substituents at the phosphorus atom show a nearly perfectly staggered conformation of ligands at the iron atom. In **5c** the bulky mesityl unit adopts the *anti* position to the Cp ligand [Cp(Z)–Fe–P–C10 173.47°], while in compound **6b** this position is occupied by a hydrazone unit [Cp(Z)–Fe–P–N1 167.64°]. As a consequence the other two substituents in both molecules are oriented *trans* to the CO ligands [**5c**: H–P–Fe–C2 165.0(8)°, N1–P–Fe–C1–173.1(5)°; **6b**: C10–P–Fe–C2 175.7(3)°, N3–P–Fe–C1–159.4(3)°].

The phosphorus atoms exhibit a distorted tetrahedral conformation with the largest bond angles including the metal center [**5c**: N1–P–Fe 112.2(3)°, H–P–Fe 116.3(35)°, C10–P–Fe 118.7(2)°; **6b** N3–P–Fe 112.9(2)°, N1–P–Fe 113.8(2)°, C10–P–Fe 115.5(2)°]. The *P*–*H* distance of 1.39(8) Å is in good agreement with the expected values {[Cp(OC)(Me₃P)Fe–P(H)(*t*Bu)Me]I: 1.40(5) Å^[8]; PH₃: 1.439 Å^[9]}. The hydrazone units are characterized by N–N single bonds for N1–N2^[10] [1.374(9) Å (**5c**)/1.368(6)



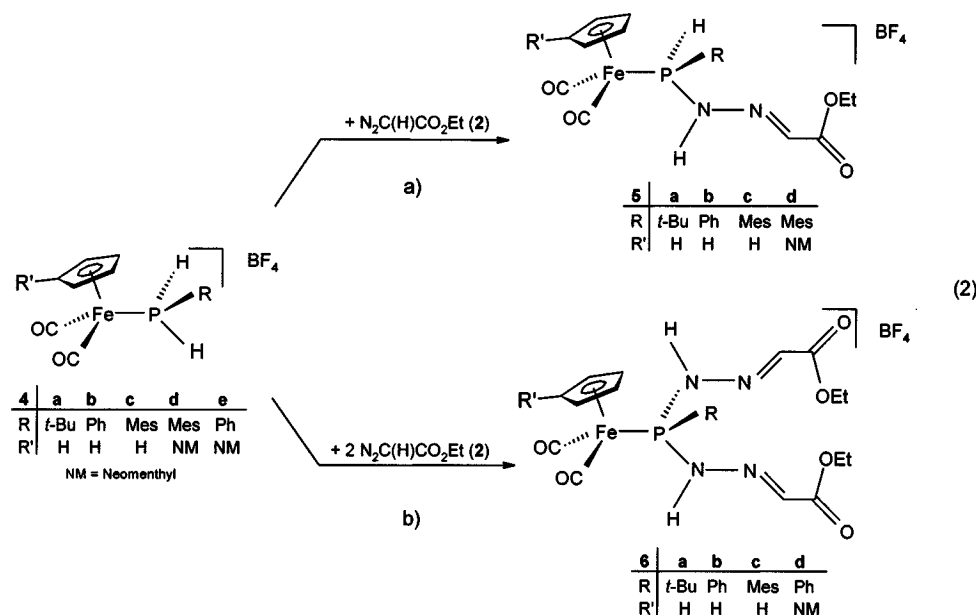
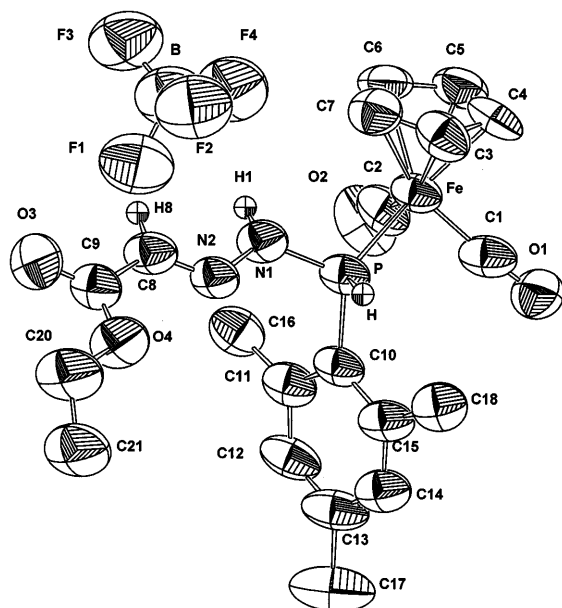


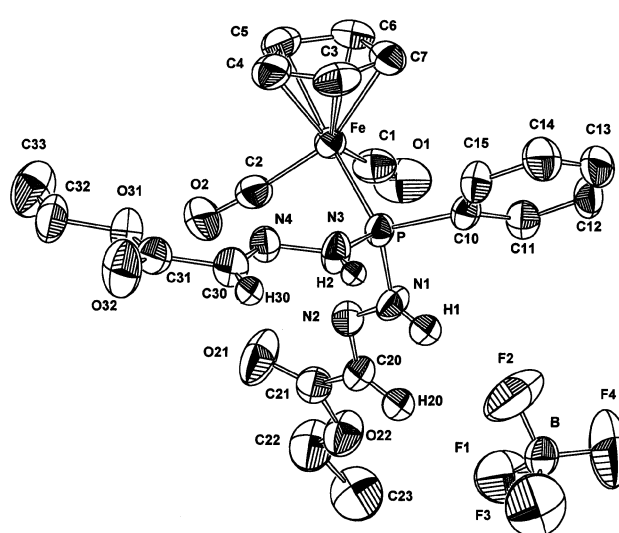
Figure 1. ORTEP plot of $\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{H})(\text{Mes})[\text{N}(\text{H})-\text{N}=\text{C}(\text{H})-\text{CO}_2\text{Et}]\text{BF}_4$ (**5c**)^[a]



^[a] Selected bond lengths [Å], bond and torsion angles [°]: Fe–P 2.208(17), Fe–C1 1.757(12), Fe–C2 1.769(11), P–N1 1.647(8), P–C10 1.807(8), N1–N2 1.374(9), N2–C8 1.254(11), P–H 1.39(8), N1–H1 0.85(8); C1–Fe–C2 92.0(5), C1–Fe–P 93.9(5), C2–Fe–P 95.0(8), N1–P–C10 109.8(4), N1–P–Fe 112.2(3), N2–N1–P 120.4(6), C8–N2–N1 117.2(7), N2–C8–C9 121.6(9), N2–C8–H8 119.2(5), C9–C8–H8 119.2(6), N1–P–H 99.9(34), Fe–P–H 116.3(35), N2–N1–H1 117.6(59), P–N1–H1 120.8(58); C1–Fe–P–N1 –173.1(5), C2–Fe–P–N1 –80.8(5), N2–C8–C9–O3 177.8(9), N1–P–C10–C15 –137.5, Fe–P–C10–C15 91.3(6).

Å (**6b**) and N3–N4 (**6b**) [1.367(5) Å], and values typical of a C=N double bond^[11] for N2–C8 (**5c**) [1.254(11) Å], N2–C20 (**6b**) [1.263(6) Å] and N4–C30 (**6b**) [1.256(6) Å]. The structural units N(H)–N=C(H)C–(O)OEt are nearly planar [N–N–C–C: –178.5(8)° (**5c**), –174.5(4)° and 176.7(5)° (**6b**)] and exhibit (*E*) configuration; the *P*-bound

Figure 2. ORTEP plot of $\{\text{Cp}(\text{OC})_2\text{Fe}-\text{P}(\text{Ph})[\text{N}(\text{H})-\text{N}=\text{C}(\text{H})-\text{CO}_2\text{Et}]\}_2\text{BF}_4$ (**6b**)^[a]



^[a] Selected bond lengths [Å], bond and torsion angles [°]: Fe–C1 1.753(7), Fe–C2 1.785(6), Fe–P 2.1909(15), P–N3 1.667(4), P–N1 1.670(5), P–C10 1.796(5), N1–N2 1.368(6), N2–C20 1.263(6), N3–N4 1.367(5), N4–C30 1.256(6); C1–Fe–C2 93.4(3), C1–Fe–P 91.4(2), C2–Fe–P 95.0(2), N3–P–N1 108.9(2), N3–P–Fe 112.9(2), N1–P–Fe 113.8(2), C10–P–Fe 115.5(2), C20–N2–N1 117.8(4), N4–N3–P 118.0(4), C30–N4–N3 118.5(4); N3–P–N1–N2 96.1(4), C10–P–N1–N2 –155.4(4), P–N1–N2–C20 180.0(4), N1–P–N3–N4 –96.5(4), C10–P–N3–N4 156.2(4), P–N3–N4–C30 173.9(4), N2–C20–C21–O22 163.5(5), N4–C30–C31–O32 –170.2(6).

nitrogen atoms N1 (**5c**, **6b**) and N3 (**6b**) as well as the sp^2 -hybridized C=N carbon atoms C8 (**5c**) and C20, C30 (**6b**) show nearly ideal planarity (sum of angles: 358.8°–360.0°).

We have demonstrated that diazoacetic ester is a reagent which easily inserts into P–H bonds of metal-coordinated primary and secondary phosphanes. This procedure can be used to build up novel phosphane ligands at the metal center. Controlled monoinsertion in the case of primary

phosphanes leads to chiral secondary phosphane ligands which possess a high synthetic potential because of the P–H moiety which is useful for further derivatization.

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Experimental Section

General: All manipulations were performed under purified nitrogen with standard Schlenk techniques. Solvents were rigorously dried with an appropriate drying agent and distilled under nitrogen prior to use. — ^1H -, ^{13}C -, and ^{31}P -NMR spectra were obtained with a Bruker AMX 400 spectrometer. — Infrared spectra were recorded in solution with a Perkin-Elmer 283 grating spectrometer in NaCl cells with 0.1 mm path lengths. — Melting points were determined by Differential Thermo Analysis (DTA) with a Du Pont Thermal Analysis System 9000. — Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie*. — $[\text{Cp}(\text{OC})_3\text{Fe}] \text{BF}_4$ [12] and $[(\text{NMC}_5\text{H}_4)(\text{OC})_3\text{Fe}] \text{BF}_4$ [6] were prepared according to literature procedures. $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ was obtained commercially and used without further purification.

1) *General Procedure for the Preparation of $\{\text{Cp}(\text{OC})_2[\text{H}(\text{R})\text{-(Ph)P}]\text{Fe}/\text{BF}_4$ [$\text{R} = \text{Ph, Me}$ (**1a, b**)], $\{\text{Cp}(\text{OC})_2[\text{H}_2(\text{R})\text{P}]\text{Fe}/\text{BF}_4$ [$\text{R} = \text{tBu, Ph, Mes}$ (**4a–c**)] and $\{(\text{NMC}_5\text{H}_4)(\text{OC})_2[\text{H}_2(\text{R})\text{P}]\text{Fe}/\text{BF}_4$ [$\text{R} = \text{Mes, Ph}$ (**4d, e**)]:* A cooled (0°C) solution of 3.50 mmol of $[\text{Cp}(\text{OC})_3\text{Fe}] \text{BF}_4$ or $[(\text{NMC}_5\text{H}_4)(\text{OC})_3\text{Fe}] \text{BF}_4$ in 20 ml of acetonitrile was combined with an equimolar amount of the appropriate phosphanes $\text{R}(\text{Ph})\text{PH}$ ($\text{R} = \text{Me, Ph}$) or RPH_2 ($\text{R} = \text{tBu, Ph, Mes}$). The mixture was stirred for 10 h at 60°C and then reduced in vacuo to a volume of 8 ml. Precipitation of the product was achieved by addition of 10 ml of ether. The product was separated by filtration, washed with 10 ml of ether and dried in vacuo. — Yield > 85%. — Yellow to orange microcrystalline powders. — M.p.: **1a**: 123°C ; **1b**: 143°C ; **4a**: $177\text{--}179^\circ\text{C}$ (dec.); **4b**: 178°C (dec.); **4c**: 137°C (dec.); **4d**: 76°C ; **4e**: 78°C .

1a: ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): $\delta = 8.02\text{--}7.62$ (m, 10 H, H_5C_6); 7.45 [d, $^1J(\text{PH}) = 418$ Hz, 1 H, H–P]; 5.50 [d, $^3J(\text{PFeCH}) = 2.0$ Hz, 5 H, H_5C_5]. — ^{13}C NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): $\delta = 209.8$ [d, $^2J(\text{PFeC}) = 24.4$ Hz, C=O]; 133.3 (s, C-4); 133.2 [d, $^2J(\text{PCC}) = 10.7$ Hz, C-2/6]; 130.8 [d, $^3J(\text{PCCC}) = 11.3$ Hz, C-3/5]; 129.9 [d, $^1J(\text{PC}) = 54.1$ Hz, C-1]; 89.1 (s, C_5H_5). — ^{31}P NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): $\delta = 31.8$. — IR (acetonitrile): $\nu(\text{PH}) = 2302$ (w); $\nu(\text{CO}) = 2054$ (s); 2016 (s) cm^{-1} . — $\text{C}_{19}\text{H}_{16}\text{BF}_4\text{FeO}_2\text{P}$ (449.96): calcd. C 50.72, H 3.58; found C 50.56, H 3.38.

1b: ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): $\delta = 7.80\text{--}7.55$ (m, 5 H, H_5C_6); 6.50 [dq, $^1J(\text{PH}) = 372$ Hz, $^3J(\text{HPCH}) = 6.18$ Hz, 1 H, H–P]; 5.45 [d, $^3J(\text{PFeCH}) = 2.1$ Hz, 5 H, H_5C_5]; 2.11 [dd, $^2J(\text{HCP}) = 12.1$ Hz, $^3J(\text{HCPH}) = 6.2$ Hz, 3 H, H_3CP]. — ^{31}P NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): $\delta = 10.8$. — IR (acetonitrile): $\nu(\text{CO}) = 2054$ (s); 2010 (s) cm^{-1} . — $\text{C}_{14}\text{H}_{14}\text{BF}_4\text{FeO}_2\text{P}$ (387.89): calcd. C 43.35, H 3.64; found C 43.90, H 3.71.

4a: ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): $\delta = 5.78$ (s, 5 H, H_5C_5); 5.12 [d, $^1J(\text{PH}) = 384.0$ Hz, 2 H, H–P]; 1.27 [d, $^3J(\text{PCCH}) = 21.3$ Hz, 9 H, $(\text{H}_3\text{C})_3\text{C}$]. — ^{13}C NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): $\delta = 209.5$ [d, $^2J(\text{PFeC}) = 24.1$ Hz, C=O]; 88.1 (s, C_5H_5); 31.7 [d, $^1J(\text{PC}) = 31.5$ Hz, $\text{C}(\text{CH}_3)_3$]; 29.4 [d, $^2J(\text{PCC}) = 3.7$ Hz, $\text{C}(\text{CH}_3)_3$]. — ^{31}P NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): $\delta =$

3.4. — IR (acetonitrile): $\nu(\text{PH}) = 2390$ (w); $\nu(\text{CO}) = 2057$ (vs); 2009 (vs) cm^{-1} . — $\text{C}_{11}\text{H}_{16}\text{BF}_4\text{FeO}_2\text{P}$ (353.87): calcd. C 37.33, H 4.56; found C 37.41, H 4.57.

4b: ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): $\delta = 7.71\text{--}7.52$ (m, 5 H, H_5C_6); 6.16 [d, $^1J(\text{PH}) = 407.8$ Hz, 2 H, H–P]; 5.42 [d, $^3J(\text{PFeCH}) = 2.1$ Hz, 5 H, H_5C_5]. — ^{13}C NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): $\delta = 209.0$ [d, $^2J(\text{PFeC}) = 24.9$ Hz, C=O]; 133.5 [d, $^2J(\text{PCC}) = 10.1$ Hz, C-2/6]; 132.1 [d, $^4J(\text{PCCCC}) = 2.9$ Hz, C-4]; 130.3 [d, $^3J(\text{PCCC}) = 11.5$ Hz, C-3/5]; 124.0 [d, $^1J(\text{PC}) = 57.2$ Hz, C-1]; 88.5 (s, C_5H_5). — ^{31}P NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): $\delta = -29.5$. — IR (acetonitrile): $\nu(\text{PH}) = 2398$ (w); $\nu(\text{CO}) = 2060$ (vs); 2015 (vs) cm^{-1} . — $\text{C}_{13}\text{H}_{12}\text{BF}_4\text{FeO}_2\text{P}$ (373.86): calcd. C 41.76, H 3.24; found C 41.53, H 2.93.

4c: ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): $\delta = 7.04$ (s, 2 H, H–C); 6.09 [d, $^1J(\text{PH}) = 400.4$ Hz, 2 H, H–P]; 5.49 [d, $^3J(\text{PFeCH}) = 2.3$ Hz, 5 H, H_5C_5]; 2.43 (s, 6 H, 2- H_3C); 2.27 (s, 3 H, 4- H_3C). — ^{13}C NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): $\delta = 209.3$ [d, $^2J(\text{PFeC}) = 24.1$ Hz, C=O]; 143.3 [d, $^4J(\text{PCCCC}) = 1.5$ Hz, C-4]; 141.6 [d, $^2J(\text{PCC}) = 8.0$ Hz, C-2/6]; 141.6 [d, $^3J(\text{PCCC}) = 9.0$ Hz, C-3/5]; 126.4 [d, $^1J(\text{PC}) = 58.4$ Hz, C-1]; 88.4 (s, C_5H_5); 21.6 [d, $^3J(\text{PCCC}) = 9.7$ Hz, 2/6- CH_3]; 20.9 (s, 4- CH_3). — ^{31}P NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): $\delta = -61.2$. — ^{19}F NMR ($[\text{D}_3]\text{acetonitrile}$, 376.5 MHz): $\delta = -150.2$. — IR (acetonitrile): $\nu(\text{PH}) = 2397$ (w); $\nu(\text{CO}) = 2058$ (vs), 2015 (vs) cm^{-1} . — $\text{C}_{16}\text{H}_{18}\text{BF}_4\text{FeO}_2\text{P}$ (415.94): calcd. C 46.20, H 4.36; found C 46.28, H 4.18.

4d: ^1H NMR (400.1 MHz, CDCl_3): $\delta = 6.90$ [s, 2 H, H–C]; 6.22 [s, $^1J(\text{HP}) = 407.5$ Hz, 1 H, H_2P]; 6.20 [s, $^1J(\text{HP}) = 405.8$ Hz, 1 H, H_2P]; 5.63/5.54/5.48/5.44 (s, 4 H, H_4C_5); 2.87 (s, 1 H, 6-H, $\text{H}_{19}\text{C}_{10}$); 2.40 (s, 6 H, $o\text{-H}_3\text{C}$); 2.24 (s, 3 H, $p\text{-H}_3\text{C}$); 0.90 (d, $^3J(\text{HCCH}) = 5.8$ Hz, 3 H, H_3C); 0.85 [d, $^3J(\text{HCCH}) = 5.9$ Hz, 3 H, H_3C]; 0.74 [d, $^3J(\text{HCCH}) = 5.9$ Hz, 3 H, H_3C]; 1.86–0.73 (m, 9 H, $\text{H}_{11}\text{C}_{10}$). — ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 209.13$ [d, $^2J(\text{CFeP}) = 23.7$ Hz, CO]; 142.23 [d, $^3J(\text{CCCCP}) = 2.1$ Hz, C-4, $\text{C}_6\text{H}_2(\text{CH}_3)_3$]; 140.69 [d, $^3J(\text{CCCCP}) = 8.6$ Hz, C-3, C-5, $\text{C}_6\text{H}_2(\text{CH}_3)_3$]; 130.12 [d, $^2J(\text{CCP}) = 9.00$ Hz, C-2, C-6, $\text{C}_6\text{H}_2(\text{CH}_3)_3$]; 117.39 [d, $^1J(\text{CP}) = 58.2$ Hz, C-1, $\text{C}_6\text{H}_2(\text{CH}_3)_3$]; 111.89 (s, C-1, C_5H_4); 90.44/90.17/88.10/84.56 (s, C-2, C-3, C-4, C-5, C_5H_4); 47.88 (s, C-6, $\text{C}_{10}\text{H}_{19}$); 43.72 (s, C-11, $\text{C}_{10}\text{H}_{19}$); 35.41 (s, C-7, $\text{C}_{10}\text{H}_{19}$); 34.78 (s, C-9, $\text{C}_{10}\text{H}_{19}$); 29.46 (s, C-10, $\text{C}_{10}\text{H}_{19}$); 27.91 (s, C-12, $\text{C}_{10}\text{H}_{19}$); 24.15 (s, C-8, $\text{C}_{10}\text{H}_{19}$); 22.27/21.80/21.70/21.60/21.13/20.51 (s, C-13, C-14, C-15, $\text{C}_{10}\text{H}_{19}$, $o\text{-CH}_3$, $p\text{-CH}_3$). — ^{31}P NMR (162.0 MHz, CDCl_3): $\delta = -60.24$. — IR (acetonitrile): $\nu(\text{CO}) = 2049$ (s), 2005 (s) cm^{-1} . — $\text{C}_{26}\text{H}_{36}\text{BF}_4\text{FeO}_2\text{P}$ (554.20): calcd. C 56.35, H 6.55; found C 56.51, H 6.74.

4e: ^1H NMR (400.1 MHz, CD_3CN): $\delta = 7.80\text{--}7.62$ (m, 5 H, H_5C_6); 6.25 [d, $^1J(\text{HP}) = 404.00$ Hz, 2 H, H_2P]; 5.79/5.49/5.33/5.22 (s, 4 H, $\text{H}_4\text{C}_5\text{NM}$); 2.98 (s, 1 H, 6-H, $\text{H}_{19}\text{C}_{10}$); 0.95 [d, $^3J(\text{HCCH}) = 6.4$ Hz, 3 H, H_3C]; 0.91 [d, $^3J(\text{HCCH}) = 6.2$ Hz, 3 H, H_3C]; 0.81 [d, $^3J(\text{HCCH}) = 6.5$ Hz, 3 H, H_3C]; 1.94–0.84 (m, 9 H, H_9C_7). — ^{13}C NMR (100.6 MHz, CD_3CN): $\delta = 208.93$ [d, $^2J(\text{CFeP}) = 24.7$ Hz, CO]; 208.90 [d, $^2J(\text{CFeP}) = 24.7$ Hz, CO]; 123.27 [d, $^2J(\text{CP}) = 57.2$ Hz, C-1, CP]; 132.78 [d, $^2J(\text{CCP}) = 10.5$ Hz, C-2, $\text{C}_6\text{H}_5\text{P}$]; 132.39 [d, $^3J(\text{CCCCP}) = 3.3$ Hz, C-3, C-6, $\text{C}_6\text{H}_5\text{P}$]; 129.97 [d, $^2J(\text{CCP}) = 12.1$ Hz, C-6, $\text{C}_6\text{H}_5\text{P}$]; 112.97 (s, C-1, C_5H_4); 90.85/90.76/96.67/84.11 (s, C-2, C-3, C-4, C-5, C_6H_4); 47.83 (s, C-6, $\text{C}_{10}\text{H}_{19}$); 43.34 (s, C-11, $\text{C}_{10}\text{H}_{19}$); 35.27 (s, C-7, $\text{C}_{10}\text{H}_{19}$); 34.89 (s, C-9, $\text{C}_{10}\text{H}_{19}$); 29.54 (s, C-10, $\text{C}_{10}\text{H}_{19}$); 27.76 (s, C-12, $\text{C}_{10}\text{H}_{19}$); 24.13 (s, C-8, $\text{C}_{10}\text{H}_{19}$); 21.82/21.40/20.10 (s, C-13, C-14, C-15, CH_3). — ^{31}P NMR (162.0 MHz, CD_3CN): $\delta = -28.87$. — IR (acetonitrile): $\nu(\text{CO}) = 2052$ (s), 2007 (s) cm^{-1} . — $\text{C}_{23}\text{H}_{30}\text{BF}_4\text{FeO}_2\text{P}$ (512.11): calcd. C 53.94, H 5.90; found C 54.06, H 6.03.

2) *Dicarbonyl*(η^5 -cyclopentadienyl)[(*ethoxycarbonylmethylenehydrazino*)diphenylphosphane]iron(II) Tetrafluoroborate (**3a**): 99 mg (0.87 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) was added to a solution of 300 mg (0.67 mmol) of $\{\text{Cp}(\text{OC})_2[\text{H}(\text{Ph})_2\text{P}]\text{Fe}\}\text{BF}_4$ (**1a**) in 11 ml of dichloromethane. After stirring for 24 h at room temperature, the reaction mixture was reduced in vacuo to a volume of 2 ml. Addition of 20 ml of ether afforded precipitation of **3a** which was separated by filtration, washed with three portions of 5 ml of ether, and dried in vacuo. – Yield 327 mg (87%). – Yellow microcrystalline powder. – M.p. 170 °C (dec.). – ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): δ = 8.61 [d, $^2J(\text{PNH})$ = 16.7 Hz, 1 H, HN], 7.62–7.46 (m, 10 H, H_5C_6), 7.35 (s, 1 H, HC), 5.25 [d, $^3J(\text{PFeCH})$ = 1.4 Hz, 5 H, H_5C_5], 4.14 [q, $^3J(\text{HCCH})$ = 7.1 Hz, 2 H, H_2C], 1.19 [t, $^3J(\text{HCCH})$ = 7.1 Hz, 3 H, H_3C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): δ = 208.4 [d, $^2J(\text{PFeC})$ = 26.6 Hz, CO], 162.2 (s, CO_2), 136.0–129.2 (m, C_6H_5 , C=N), 88.3 (s, C_5H_5), 60.8 (s, CH_2), 13.1 (s, CH_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): δ = 114.1 (s). – IR (acetonitrile): $\nu(\text{CO})$ = 2055 (s), 2009 (s); $\nu(\text{C}=\text{O})$ = 1740 (s) cm^{-1} . – $\text{C}_{23}\text{H}_{22}\text{BF}_4\text{FeN}_2\text{O}_4\text{P}$ (564.06): calcd. C 48.98, H 3.93, N 4.97; found C 48.60, H 3.70, N 4.61.

3) *Dicarbonyl*(η^5 -cyclopentadienyl)[(*ethoxycarbonylmethylenehydrazino*)(methyl)(phenyl)phosphane]iron(II) Tetrafluoroborate (**3b**): Prepared as described for **3a** from 250 mg (0.65 mmol) of $\{\text{Cp}(\text{OC})_2[\text{H}(\text{Me})(\text{Ph})\text{P}]\text{Fe}\}\text{BF}_4$ (**1b**) and 109 mg (0.96 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) in 10 ml of dichloromethane. – Yield 282 mg (87%). – Yellow microcrystalline powder. – M.p. 98 °C (dec.). – ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): δ = 8.43 [d, $^2J(\text{PNH})$ = 22.0 Hz, 1 H, HN], 7.52–7.39 (m, 5 H, H_5C_6), 7.31 (s, 1 H, HC), 5.28 [d, $^3J(\text{PFeCH})$ = 1.3 Hz, 5 H, H_5C_5], 4.14 [q, $^3J(\text{HCCH})$ = 7.2 Hz, 2 H, H_2C], 2.20 [d, $^2J(\text{PCH})$ = 10.1 Hz, 3 H, H_3CP], 1.19 [t, $^3J(\text{HCCH})$ = 7.2 Hz, 3 H, H_3C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): δ = 208.1 (d, $^2J(\text{PFeC})$ = 27.6 Hz, CO), 162.2 (s, CO_2), 136.2–128.7 (m, C_6H_5 , C=N), 87.7 (s, C_5H_5), 60.7 (s, CH_2), 19.2 [d, $^1J(\text{PC})$ = 39.2 Hz, CH_3P], 13.1 (s, CH_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): δ = 108.0 (s). – IR (acetonitrile): $\nu(\text{CO})$ = 2045 (s), 2000 (vs); $\nu(\text{C}=\text{O})$ = 1713 (s) cm^{-1} . – $\text{C}_{18}\text{H}_{20}\text{BF}_4\text{FeN}_2\text{O}_4\text{P}$ (501.99): calcd. C 43.06, H 4.02, N 5.58; found C 42.83, H 3.88, N 4.22.

4) *tert*-Butyl[(*E*)-ethoxycarbonylmethylenehydrazino]phosphane]dicarbonyl(η^5 -cyclopentadienyl)iron(II) Tetrafluoroborate (**5a**): 60 mg (0.53 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) was added to a solution of 200 mg (0.57 mmol) of $\{\text{Cp}(\text{OC})_2[\text{H}_2(\text{tBu})\text{P}]\text{Fe}\}\text{BF}_4$ (**4a**) in 10 ml of acetonitrile. After stirring for 48 h at room temperature, the solution was reduced in vacuo to a volume of 1 ml. Addition of 3 ml of ether afforded precipitation of **5a**, which was separated by filtration, washed with three portions of 5 ml of ether and dried in vacuo. – Yield 198 mg (74%). – Beige microcrystalline powder. – M.p. 113 °C (dec.). – ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): δ = 7.68 [d, $^2J(\text{PNH})$ = 19.8 Hz, 1 H, HN], 7.15 (s, 1 H, CH), 6.76 [d, $^1J(\text{PH})$ = 411.0 Hz, 1 H, HP], 5.51 [d, $^3J(\text{PFeCH})$ = 1.9 Hz, 5 H, H_5C_5], 4.26–4.17 (m, 2 H, H_2C), 1.39 [d, $^3J(\text{PCCH})$ = 18.4 Hz, 9 H, $(\text{H}_3\text{C})_3\text{C}$], 1.31 (m, 3 H, H_3C). – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): δ = 208.4 [d, $^2J(\text{PFeC})$ = 24.1 Hz, CO], 207.9 [d, $^2J(\text{PFeC})$ = 23.1 Hz, CO], 162.3 (s, CO_2), 134.4 [d, $^3J(\text{PNNC})$ = 14.1 Hz, C=N], 86.1 (s, C_5H_5), 60.3 (s, CH_2), 38.2 [d, $^1J(\text{PC})$ = 27.2 Hz, CP], 28.7 [d, $^2J(\text{PCC})$ = 3.0 Hz, $(\text{CH}_3)_3\text{C}$], 12.9 (s, CH_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): δ = 113.8 (s). – ^{19}F NMR ($[\text{D}_3]\text{acetonitrile}$, 376.5 MHz): δ = –149.9. – IR (acetonitrile): $\nu(\text{CO})$ = 2055 (s), 2013 (s); $\nu(\text{C}=\text{O})$ = 1713 (m) cm^{-1} . – $\text{C}_{15}\text{H}_{22}\text{BF}_4\text{FeN}_2\text{O}_4\text{P}$ (467.97): calcd. C 38.50, H 4.74, N 5.99; found C 39.01, H 4.92, N 6.21.

5) *Dicarbonyl*(η^5 -cyclopentadienyl)[(*E*)-ethoxycarbonylmethylenehydrazino](phenyl)phosphane]iron(II) Tetrafluoroborate (**5b**):

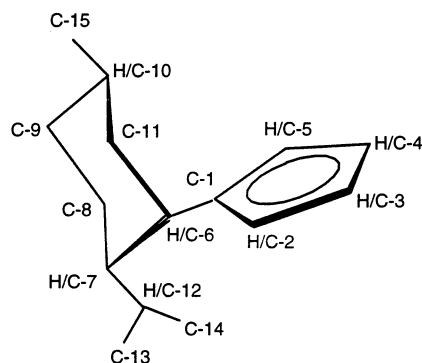
Prepared as described for **5a** from 200 mg (0.53 mmol) of $\{\text{Cp}(\text{OC})_2[\text{H}_2(\text{Ph})\text{P}]\text{Fe}\}\text{BF}_4$ (**4b**) and 57 mg (0.50 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) in 10 ml of acetonitrile. – Yield 191 mg (74%). – Yellow microcrystalline powder. – M.p. 106 °C (dec.). – ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): δ = 8.59 [d, $^1J(\text{PH})$ = 404.0 Hz, 1 H, HP], 8.47 [d, $^2J(\text{PNH})$ = 24.4 Hz, 1 H, HN], 7.75–7.22 (m, 5 H, H_5C_6), 7.19 (s, 1 H, CH), 5.27 [d, $^3J(\text{PFeCH})$ = 1.3 Hz, 5 H, H_5C_5], 4.20 [q, $^3J(\text{HCCH})$ = 7.2 Hz, 2 H, H_2C], 1.27 [t, $^3J(\text{HCCH})$ = 7.2 Hz, 3 H, H_3C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): δ = 209.3 [d, $^2J(\text{PFeC})$ = 29.6 Hz, CO], 208.7 [d, $^2J(\text{PFeC})$ = 29.7 Hz, CO], 163.5 (s, CO_2), 137.5 [d, $^3J(\text{PNNC})$ = 17.1 Hz, C=N], 133.5 [d, $^2J(\text{PCC})$ = 10.1 Hz, C-2/6], 133.1 [d, $^4J(\text{PCCCC})$ = 2.1 Hz, C-4], 131.6 [d, $^3J(\text{PCCC})$ = 11.1 Hz, C-3/5], 129.4 [d, $^1J(\text{PC})$ = 52.3 Hz, C-1], 88.6 (s, C_5H_5), 62.1 (s, CH_2), 14.4 (s, CH_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): δ = 86.6 (s). – ^{19}F NMR ($[\text{D}_3]\text{acetonitrile}$, 376.5 MHz): δ = –150.7. – IR (acetonitrile): $\nu(\text{CO})$ = 2058 (s), 2016 (s); $\nu(\text{C}=\text{O})$ = 1716 (m) cm^{-1} . – $\text{C}_{17}\text{H}_{16}\text{BF}_4\text{FeN}_2\text{O}_4\text{P}$ (487.97): calcd. C 41.84, H 3.72, N 5.74; found C 41.92, H 3.79, N 5.81.

6) *Dicarbonyl*(η^5 -cyclopentadienyl)[(*E*)-ethoxycarbonylmethylenehydrazino](2,4,6-trimethylphenyl)phosphane]iron(II) Tetrafluoroborate (**5c**): Prepared as described for **5a** from 200 mg (0.48 mmol) of $\{\text{Cp}(\text{OC})_2[\text{H}_2(\text{Mes})\text{P}]\text{Fe}\}\text{BF}_4$ (**4c**) and 55 mg (0.47 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) in 10 ml of acetonitrile. – Yield 201 mg (79%). – Yellow microcrystalline powder. – M.p. 135 °C (dec.). – ^1H NMR ($[\text{D}_3]\text{acetonitrile}$, 400.1 MHz): δ = 8.20 [d, $^2J(\text{PNH})$ = 24.0 Hz, 1 H, HN], 8.19 [d, $^1J(\text{PH})$ = 407.2 Hz, 1 H, HP], 7.26 (s, 1 H, HC), 7.03 [d, $^4J(\text{PCCCH})$ = 4.4 Hz, 2 H, *meta*-H], 5.45 [d, $^3J(\text{PFeCH})$ = 2.0 Hz, 5 H, H_5C_5], 4.20 [q, $^3J(\text{HCCH})$ = 7.2 Hz, 2 H, H_2C], 2.41 (s, 6 H, 2/6- H_3C), 2.29 (s, 3 H, 4- H_3C), 1.25 [t, $^3J(\text{HCCH})$ = 7.2 Hz, 3 H, H_3C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 100.6 MHz): δ = 209.3 [d, $^2J(\text{PFeC})$ = 25.2 Hz, CO], 208.4 [d, $^2J(\text{PFeC})$ = 23.1 Hz, CO], 163.0 (s, CO_2), 144.1 [d, $^4J(\text{PCCCC})$ = 1.1 Hz, C-4], 135.6 [d, $^3J(\text{PNNC})$ = 16.1 Hz, C=N], 134.8 (s, C-3/5), 130.6 (s, C-2/6), 123.7 [d, $^1J(\text{PC})$ = 59.4 Hz, C-1], 90.6 (s, C_5H_5), 61.6 (s, CH_2), 21.4 [d, $^3J(\text{PCCC})$ = 8.8 Hz, 2/6- CH_3], 20.7 (s, 4- CH_3), 13.9 (s, CH_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_3]\text{acetonitrile}$, 162.0 MHz): δ = 64.9 (s). – ^{19}F NMR ($[\text{D}_3]\text{acetonitrile}$, 376.5 MHz): δ = –151.1. – IR (acetonitrile): $\nu(\text{CO})$ = 2059 (s), 2017 (s); $\nu(\text{C}=\text{O})$ = 1736 (m) cm^{-1} . – $\text{C}_{20}\text{H}_{24}\text{BF}_4\text{FeN}_2\text{O}_4\text{P}$ (530.05): calcd. C 45.32, H 4.56, N 5.29; found C 45.57, H 4.71, N 5.45.

7) *Dicarbonyl*[(*E*)-ethoxycarbonylmethylenehydrazino](2,4,6-trimethylphenyl)phosphane][η^5 -(*c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-1-yl)cyclopentadienyl]iron(II) Tetrafluoroborate (**5d**): Prepared as described for **5a** from 150 mg (0.27 mmol) of $\{\text{NMC}_5\text{H}_4(\text{OC})_2[\text{H}_2(\text{Mes})\text{P}]\text{Fe}\}\text{BF}_4$ (**4d**) and 30 mg (0.27 mmol) of $\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}$ (**2**) in 10 ml of acetonitrile. – Yield 150 mg (83%). – Yellow microcrystalline powder. – M.p. 93 °C (dec.). – ^1H NMR (400.1 MHz, $[\text{D}_3]\text{acetonitrile}$): δ = 8.35 [dd, $^1J(\text{PH})$ = 434.2 Hz, $^3J(\text{HPNH})$ = 4.4 Hz, 1 H, HP], 8.34 [dd, $^1J(\text{PH})$ = 434.0 Hz, $^3J(\text{HPNH})$ = 4.4 Hz, 1 H, HP], 8.21 [d, $^2J(\text{PNH})$ = 24.8 Hz, 2 H, HN], 7.30 (s, 2 H, HC), 7.08 [d, $^4J(\text{PCCCH})$ = 4.00 Hz, 4 H, *meta*-H], 5.80 (m, 1 H, H_4C_5), 5.75 (m, 1 H, H_4C_5), 5.55 (m, 1 H, H_4C_5), 5.49 (m, 1 H, H_4C_5), 5.28 (m, 2 H, H_4C_5), 5.24 (m, 1 H, H_4C_5), 5.20 (m, 1 H, H_4C_5), 4.25 [q, $^2J(\text{HCCH})$ = 7.2 Hz, 2 H, $\text{H}_2\text{C}-\text{O}$], 4.24 [q, $^2J(\text{HCCH})$ = 7.2 Hz, 2 H, $\text{H}_2\text{C}-\text{O}$], 3.04 (m, 1 H, 6-H, NMH_4C_5), 3.01 (m, 1 H, 6-H, NMH_4C_5), 2.47 [s, 12 H, 2- CH_3 , 6- CH_3 , $(\text{H}_3\text{C})_3\text{C}_6\text{H}_2$], 2.34 [s, 6 H, 4- CH_3 , $(\text{H}_3\text{C})_3\text{C}_6\text{H}_2$], 1.86–1.84 (m, 2 H, 9/9'-H, NMH_4C_5), 1.84–1.82 (m, 2 H, 11/11'-H, NMH_4C_5), 1.73–1.71 (m, 2 H, 8/8'-H, NMH_4C_5), 1.69–1.66 (m, 2 H, 12-H, NMH_4C_5), 1.57–1.50 (m, 2 H, 11/11'-H, NMH_4C_5), 1.39–1.32 (m, 2 H, 7-H, NMH_4C_5), 1.32–1.29 (m, 2 H, 10-H,

NM₄C₅), 1.30 [t, $^2J(\text{HCCH}) = 7.2$ Hz, 6 H, OCH₂CH₃], 1.15–1.10 (m, 2 H, 8/8'-H, NM₄C₅), 1.10–0.94 (m, 2 H, 9/9'-H, NM₄C₅), 0.97 [d, $^3J(\text{HCCH}) = 6.0$ Hz, 3 H, 13-H, NM₄C₅], 0.96 [d, $^3J(\text{HCCH}) = 6.4$ Hz, 3 H, 13-H, NM₄C₅], 0.93 [d, $^3J(\text{HCCH}) = 6.4$ Hz, 3 H, 15-H, NM₄C₅], 0.92 [d, $^3J(\text{HCCH}) = 6.4$ Hz, 3 H, 15-H, NM₄C₅], 0.82 [d, $^3J(\text{HCCH}) = 6.8$ Hz, 3 H, 14-H, NM₄C₅], 0.81 [d, $^3J(\text{HCCH}) = 6.4$ Hz, 3 H, 14-H, NM₄C₅]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, [D₃]acetonitrile): $\delta = 210.32$ [d, $^2J(\text{CFeP}) = 26.16$ Hz, CO], 209.44 [d, $^2J(\text{CFeP}) = 22.14$ Hz, CO], 209.38 [d, $^2J(\text{CFeP}) = 23.14$ Hz, CO], 163.28 (s, CO₂), 144.24 [s, C-4, C₆H₂(CH₃)₃], 135.96 [s, CHC(O)OEt], 135.81 [s, CHC(O)OEt], 135.88 [m, C-2, C-6, C₆H₂(CH₃)₃], 131.77 [m, C-3, C-5, C₆H₂(CH₃)₃], 124.22 [d, $^1J(\text{CP}) = 58.36$ Hz, C-1, C₆H₂(CH₃)₃], 124.13 [d, $^1J(\text{CP}) = 59.36$ Hz, C-1, C₆H₂(CH₃)₃], 114.00 (s, C-1, C₅H₄), 113.78 (s, C-1, C₅H₄), 91.84 (s, C-2, C-3, C-4, C-5, C₅H₄), 91.30 (s, C-2, C-3, C-4, C-5, C₅H₄), 91.06 (s, C-2, C-3, C-4, C-5, C₅H₄), 90.99 (s, C-2, C-3, C-4, C-5, C₅H₄), 88.77 (s, C-2, C-3, C-4, C-5, C₅H₄), 88.72 (s, C-2, C-3, C-4, C-5, C₅H₄), 85.47 (s, C-2, C-3, C-4, C-5, C₅H₄), 84.55 (s, C-2, C-3, C-4, C-5, C₅H₄), 61.79 (s, OCH₂CH₃), 48.55 (s, C-7, NMC₅H₄), 48.43 (s, C-7, NMC₅H₄), 43.73 (s, C-11, NMC₅H₄), 43.43 (s, C-11, NMC₅H₄), 35.94 (s, C-6, NMC₅H₄), 35.84 (s, C-6, NMC₅H₄), 35.39 (s, C-9, NMC₅H₄), 30.07 (s, C-10, NMC₅H₄), 29.96 (s, C-10, NMC₅H₄), 28.35 (s, C-12, NMC₅H₄), 24.64 (s, C-8, NMC₅H₄), 22.35 (s, C-15, NMC₅H₄), 22.29 (s, C-15, NMC₅H₄), 21.93 (s, C-13, NMC₅H₄), 21.91 (s, C-13, NMC₅H₄), 21.76 (s, 2-CH₃, 6-CH₃, (CH₃)₃C₆H₂), 21.71 (s, 2-CH₃, 6-CH₃, (CH₃)₃C₆H₂), 21.67 [s, 2-CH₃, 6-CH₃, (CH₃)₃C₆H₂], 21.62 [s, 2-CH₃, 6-CH₃, (CH₃)₃C₆H₂], 20.94 [s, 4-CH₃, (CH₃)₃C₆H₂], 20.62 (s, C-14, NMC₅H₄), 20.59 (s, C-14, NMC₅H₄), 14.24 (s, OCH₂CH₃), 14.23 (s, OCH₂CH₃). – $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, [D₃]acetonitrile): $\delta = 65.48$ (s), 65.03 (s). – ^{19}F NMR (376.5 MHz, [D₃]acetonitrile): $\delta = -151.4$. – IR (acetonitrile): $\nu(\text{CO}) = 2049$ (s), 2008 (s) cm⁻¹. – C₃₀H₄₂BF₄FeN₂O₄P (668.30): calcd. C 53.92, H 6.33, N 4.19; found C 54.34, H 6.17, N 4.09.

Figure 3. Atom labeling in the neomenthylcyclopentadienyl ligand



8) *f*-(*tert*-Butyl)*bis*[(*E*)-ethoxycarbonylmethylenehydrazino]-phosphane/dicarbonyl(η^5 -cyclopentadienyl)iron(II) Tetrafluoroborate (**6a**): Prepared as described for **5a** from 200 mg (0.57 mmol) of {Cp(OC)₂[H₂(*t*Bu)P]Fe}BF₄ (**4a**) and 112 mg (0.98 mmol) of N₂C(H)CO₂Et (**2**) in 10 ml of acetonitrile. – Yield 212 mg (77%). – Beige microcrystalline powder. – M.p. 145°C (dec.). – ^1H NMR ([D₃]acetonitrile, 400.1 MHz): $\delta = 8.51$ [d, $^2J(\text{PNH}) = 13.2$ Hz, 2 H, HN], 7.32 (s, 2 H, HC), 5.44 (s, 5 H, H₅C₅), 4.21–4.09 (m, 4 H, H₂C), 1.31 [d, $^3J(\text{PCCC}) = 16.8$ Hz, 9 H, (H₃C)₃C], 1.27 [t, $^3J(\text{HCCH}) = 6.8$ Hz, 6 H, H₃C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 100.6 MHz): $\delta = 208.9$ [d, $^2J(\text{PFeC}) = 27.1$ Hz, CO], 166.0 (s, CO₂), 135.3 [d, $^3J(\text{PNNC}) = 16.1$ Hz, C=N], 85.6 (s, C₅H₅), 62.5 (s, CH₂), 40.9 [d, $^1J(\text{PC}) = 39.9$ Hz, CP], 25.7 [d, $^2J(\text{PCC}) =$

3.7 Hz, (CH₃)₃C], 13.6 (s, CH₃). – $^{31}\text{P}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 162.0 MHz): $\delta = 166.8$ (s). – ^{19}F NMR ([D₃]acetonitrile, 376.5 MHz): $\delta = -148.5$. – IR (acetonitrile): $\nu(\text{CO}) = 2058$ (s), 2019 (s); $\nu(\text{C=O}) = 1732$ (m) cm⁻¹. – C₁₉H₂₈BF₄FeN₄O₆P (582.08): calcd. C 39.21, H 4.85, N 9.63; found C 39.41, H 4.93, N 9.78.

9) *Dicarbonyl*(η^5 -cyclopentadienyl)*bis*[(*E*)-ethoxycarbonylmethylenehydrazino](phenyl)phosphane/iron(II) Tetrafluoroborate (**6b**): Prepared as described for **5a** from 200 mg (0.53 mmol) of {Cp(OC)₂[H₂(Ph)P]Fe}BF₄ (**4b**) and 114 mg (1.00 mmol) of N₂C(H)CO₂Et (**2**) in 10 ml of acetonitrile. – Yield 220 mg (75%). – Light yellow microcrystalline powder. – M.p. 176°C (dec.). – ^1H NMR ([D₃]acetonitrile, 400.1 MHz): $\delta = 8.86$ (s, 2 H, HN), 7.73–7.37 (m, 5 H, H₅C₆), 7.02 [d, $^4J(\text{PNNCH}) = 1.2$ Hz, 2 H, HC], 5.27 [d, $^3J(\text{PFeCH}) = 1.5$ Hz, 5 H, H₅C₅], 4.21 [q, $^3J(\text{HCCH}) = 7.2$ Hz, 4 H, H₂C], 1.27 [t, $^3J(\text{HCCH}) = 7.2$ Hz, 6 H, H₃C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 100.6 MHz): $\delta = 208.7$ [d, $^2J(\text{PFeC}) = 29.2$ Hz, CO], 163.4 (s, CO₂), 137.3 [d, $^3J(\text{PNNC}) = 17.1$ Hz, C=N], 134.1 [d, $^4J(\text{PCCCC}) = 1.7$ Hz, C-4], 133.1 [d, $^1J(\text{PC}) = 82.5$ Hz, C-1], 131.6 [d, $^2J(\text{PCC}) = 11.1$ Hz, C-2/6], 130.5 [d, $^3J(\text{PCCC}) = 12.1$ Hz, C-3/5], 89.1 (s, C₅H₅), 62.0 (s, CH₂), 14.3 (s, CH₃). – $^{31}\text{P}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 162.0 MHz): $\delta = 132.3$ (s). – ^{19}F NMR ([D₃]acetonitrile, 376.5 MHz): $\delta = -151.1$. – IR (acetonitrile): $\nu(\text{CO}) = 2059$ (s), 2018 (s); $\nu(\text{C=O}) = 1738$ (m) cm⁻¹. – C₂₁H₂₄BF₄FeN₄O₆P (602.05): calcd. C 42.03, H 3.70, N 9.34; found C 41.85, H 3.90, N 9.11.

10) *Dicarbonyl*(η^5 -cyclopentadienyl)*bis*[(*E*)-ethoxycarbonylmethylenehydrazino](2,4,6-trimethylphenyl)phosphane/iron(II) Tetrafluoroborate (**6c**): Prepared as described for **5a** from 200 mg (0.48 mmol) of {Cp(OC)₂[H₂(Mes)P]Fe}BF₄ (**4c**) and 112 mg (0.98 mmol) of N₂C(H)CO₂Et (**2**) in 10 ml of acetonitrile. – Yield 218 mg (69%). – Yellow microcrystalline powder. – M.p. 184°C (dec.). – ^1H NMR ([D₃]acetonitrile, 400.1 MHz): $\delta = 8.72$ (s, 2 H, HN), 7.16 (s, 2 H, HC), 6.88 [d, $^4J(\text{PNNCH}) = 4.0$ Hz, 2 H, *meta*-H], 5.17 (s, 5 H, H₅C₅), 4.03 [q, $^3J(\text{HCCH}) = 6.8$ Hz, 4 H, H₂C], 2.26 [d, $^4J(\text{PCCC}) = 1.0$ Hz, 6 H, 2-H₃C], 2.13 (s, 3 H, 4-H₃C), 1.09 [t, $^3J(\text{HCCH}) = 6.8$ Hz, 6 H, H₃C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 100.6 MHz): $\delta = 202.3$ [d, $^2J(\text{PFeC}) = 36.2$ Hz, CO], 156.2 (s, CO₂), 137.3 [d, $^4J(\text{PCCCC}) = 3.0$ Hz, C-4], 135.1 [d, $^3J(\text{PNNC}) = 20.0$ Hz, C=N], 128.8 [d, $^2J(\text{PCC}) = 17.1$ Hz, C-2/6], 126.3 [d, $^3J(\text{PCCC}) = 10.1$ Hz, C-3/5], 120.5 [d, $^1J(\text{PC}) = 66.4$ Hz, C-1], 82.2 (s, C₅H₅), 54.9 (s, CH₂), 17.4 [d, $^3J(\text{PCCC}) = 3.9$ Hz, 2-CH₃], 13.9 (s, 4-CH₃), 7.4 (s, CH₃). – $^{31}\text{P}\{^1\text{H}\}$ NMR ([D₃]acetonitrile, 162.0 MHz): $\delta = 139.14$ (s). – ^{19}F NMR ([D₃]acetonitrile, 376.5 MHz): $\delta = -149.0$. – IR (acetonitrile): $\nu(\text{CO}) = 2056$ (s), 2013 (s); $\nu(\text{C=O}) = 1730$ (m) cm⁻¹. – C₂₄H₃₀BF₄FeN₄O₆P (644.15): calcd. C 44.75, H 4.69, N 8.70; found C 44.57, H 4.71, N 8.53.

11) *Dicarbonyl*/*bis*[(*E*)-ethoxycarbonylmethylenehydrazino](phenyl)phosphane/ η^5 -(*c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-1-yl)-cyclopentadienyl]iron(II) Tetrafluoroborate (**6d**): Prepared as described for **5a** from 200 mg (0.36 mmol) of {NMC₅H₄(OC)₂[H₂(Ph)P]Fe}BF₄ (**4e**) and 117 mg (1.03 mmol) of N₂C(H)CO₂Et (**2**) in 10 ml of acetonitrile. – Yield 246 mg (81%). – Yellow microcrystalline powder. – M.p. 179°C (dec.). – ^1H NMR ([D₃]acetonitrile, 400.1 MHz): $\delta = 8.98$ (s, 2 H, HN), 7.78–7.61 (m, 5 H, H₅C₆), 7.40 (s, 2 H, HC), 5.58 (s, 1 H, H₄C₅), 5.30 (s, 1 H, H₄C₅), 5.07 (s, 1 H, H₄C₅), 4.93 (s, 1 H, H₄C₅), 4.22 [q, $^3J(\text{HCCH}) = 7.2$ Hz, 2 H, H₂C–O], 4.14 [q, $^3J(\text{HCCH}) = 7.2$ Hz, 2 H, H₂C–O], 2.63 (s, 1 H, 6-H, NM₄C₅), 1.87 (s, 1 H, 12-H, NM₄C₅), 1.81 (m, 2 H, 9/9'-H, NM₄C₅), 1.73 (m, 2 H, 11/11'-H, NM₄C₅), 1.63 (m, 2 H, 8/8'-H, NM₄C₅), 1.32 (s, 1 H, 7-H, NM₄C₅), 1.27 [t, $^3J(\text{HCCH}) = 7.2$ Hz, 6 H, H₃C], 0.86 [d, $^3J(\text{HCCH}) = 6.0$ Hz,

6 H, 13/14-H, NH_4C_5], 0.72 [d, $^3J(HCCH) = 6.4$ Hz, 3 H, 15-H, NH_4C_5]. – $^{13}C\{^1H\}$ NMR ($[D_3]$ acetonitrile, 100.6 MHz): $\delta = 205.8$ [d, $^2J(PFeC) = 26.7$ Hz, CO], 167.5 (s, CO_2), 133.4 [d, $^3J(PNNC) = 16.1$ Hz, C=N], 130.1 [d, $^4J(PCCCC) = 2.0$ Hz, C-4], 129.2 [d, $^1J(PC) = 82.0$ Hz, C-1], 127.8 [d, $^3J(PCCCC) = 11.0$ Hz, C-3/5], 126.6 [d, $^2J(PCC) = 12.0$ Hz, C-2/6], 112.1 (s, C-1, C_5H_4), 87.9 (s, C-2, C_5H_4), 87.2 (s, C-3, C_5H_4), 84.5 (s, C-4, C_5H_4), 82.5 (s, C-5, C_5H_4), 58.1 (s, CH_2-O), 57.8 (s, CH_2-O), 44.7 (s, C-7, NMC_5H_4), 39.8 (s, C-11, NMC_5H_4), 38.1 (s, C-6, NMC_5H_4), 31.8 (s, C-9, NMC_5H_4), 26.1 (s, C-10, NMC_5H_4), 24.6 (s, C-12, NMC_5H_4), 20.8 (s, C-8, NMC_5H_4), 18.7 (s, C-15, NMC_5H_4), 18.2 (s, C-14, NMC_5H_4), 16.8 (s, C-13, NMC_5H_4), 10.5 (s, CH_3). – $^{31}P\{^1H\}$ NMR ($[D_3]$ acetonitrile, 162.0 MHz): $\delta = 132.5$ (s). – ^{19}F NMR ($[D_3]$ acetonitrile, 376.5 MHz): $\delta = -150.8$. – IR (acetonitrile): $\nu(CO) = 2062$ (s), 2021 (s); $\nu(C=O) = 1740$ (m) cm^{-1} . – $C_{31}H_{42}BF_4FeN_4O_6P$ (740.32): calcd. C 50.29, H 5.72, N 7.57; found C 50.27, H 5.45, N 7.19.

12) *X-ray Analysis of 5c and 6b*: Yellow crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated solution of $\{Cp(OC)_2Fe-P(H)(Mes)[N(H)-N=C(H)-CO_2Et]\}BF_4$ (**5c**) or $\{Cp(OC)_2Fe-P(Ph)[N(H)-N=C(H)-CO_2Et]\}BF_4$ (**6b**), in acetonitrile at room temperature.

5c: $C_{20}H_{24}BF_4FeN_2O_4P$, $M_r = 530.05$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.490(3)$, $b = 22.433(5)$, $c = 11.483(7)$ Å, $\beta = 103.71(1)^\circ$, $V = 2375(2)$ Å³, $Z = 4$, $D_{calcd.} = 1.482$ g·cm⁻³, CAD4 diffractometer (Enraf-Nonius), radiation type: Mo- K_{α} , wavelength: $\lambda = 0.71073$ Å, graphite monochromator, crystal size: $0.20 \times 0.20 \times 0.15$ mm, temperature: 293(2) K, scale range: $1.81^\circ < \Theta < 24.96^\circ$, $F(000)$: 1088, total reflections: 5723, observed reflections: 2542 with $[I > 2.0 \sigma(I)]$, absorption coefficient: $\mu = 0.764$ mm⁻¹, semi-empirical absorption correction^[13] (T_{min}/T_{max} : 0.5586/0.9988), structure solution: SHELXS-86^[14] with Patterson methods, structure refinement: SHELXL-93^[15] (392 parameters), $R_1 = 0.1001$, $wR_2 = 0.3413$ ^[16].

6b: $C_{21}H_{24}BF_4FeN_4O_6P$, $M_r = 602.05$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.643(2)$, $b = 12.590(2)$, $c = 14.694(1)$ Å, $\alpha = 75.77(1)^\circ$, $\beta = 82.61(2)^\circ$, $\gamma = 82.88(2)^\circ$, $V = 1352.9(4)$ Å³, $Z = 2$, $D_{calcd.} = 1.478$ g·cm⁻³, CAD4 diffractometer (Enraf-Nonius), radiation type: Mo- K_{α} , wavelength: $\lambda = 0.71073$ Å, graphite monochromator, crystal size $0.25 \times 0.20 \times 0.15$ mm, temperature: 293(2) K, scale range: $1.67^\circ < \Theta < 23.92^\circ$, $F(000)$: 616, total reflections: 4048, observed reflections: 2623 with $[I > 2.0 \sigma(I)]$, absorption coef-

ficient: $\mu = 0.688$ mm⁻¹, semi-empirical absorption correction^[13] (T_{min}/T_{max} : 0.9564/0.9995), structure solution: SHELXS-86^[14] with Patterson methods, structure refinement: SHELXL-93^[15] (439 parameters), $R_1 = 0.0489$, $wR_2 = 0.1099$ ^[16].

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