A comparative study of biradicaloids as ligands in iron tetracarbonyl complexes

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Abstract

Iron tetracarbonyl complexes of the biradicaloids \([\text{P(}\mu\text{-N-Ter})_2] (\text{Ter: 2,6-dimesitylphenyl})\) and \([\text{P(}\mu\text{-C-IPr})_2] (\text{IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene})\) have been isolated. These two biradicaloids act here as \(\sigma\)-donating, monodentate ligands. Experimental and theoretical data suggest that they can best be described in their zwitterionic resonance structures in these complexes. Single-crystal XRD and IR spectroscopy reveal that the donor strength of both is comparable to \(N\text{-heterocyclic carbenes (NHCs). [P(}\mu\text{-C-IPr})_2\) is a slightly stronger donor than \([P(}\mu\text{-N-Ter})_2\). Furthermore, an improved, scalable, and facile synthesis of both biradicaloids is presented.

Keywords: Biradicaloids, coordination chemistry, iron complexes, \(N\text{-heterocyclic carbenes}
Introduction

Four-membered biradicaloids have gained significant attention over the last two decades. While biradicals based on carbon skeletons are elusive and highly reactive species, incorporation of main-group elements increases their stability and decreases their biradical character. These derivatives are often referred to as “biradicaloids”. A milestone has been the isolation of 1,3-diphospha-cyclobutane-2,4-diyl by Niecke. It is the first example of a stable biradicaloid that can be isolated in gram scale.

Scheme 1. Transition-metal complexes of the biradicaloids [P(μ-Nter)]₂ (1) and [P(μ-CIPr)]₂ (2). Coinage metal complexes of 1 (I, II) and 2 (III and IV)⁵; iron complexes of 2: VI: m = +1, VII: m = +2; VIII: n = +1, IX: n = 0. Partial charges in V – IX were omitted for clarity.⁸ Fe(CO)₄ complex of the biradicaloid [As(μ-C-IPr)]₂ (X).⁹

Further examples of biradicaloids were presented by Bertrand, Power, Schulz (1), Grützmacher (2) and others.⁶ Reactivities of 1 and 2 towards small molecules, alkenes, alkynes, oxidizing agents Lewis acids and Lewis bases were studied in detail. In these studies, it was shown that these species with a central 6π-electron system may react in the fashion of radicals, zwitterions or aromatic compounds. The combination of high reactivity and the presence of several potential donor atoms in 1 and 2 also make them intriguing ligands for transition metals. Indeed, it was found that 2 can act as a remarkable π-donating ligand (compare Scheme 1). Especially interesting is a series of Fe(CO)₄ (V, VI and VII) and Fe(CO)₃ (VIII and IX) complexes, which show a rich-redox chemistry. It was also shown that 2 can act as a redox non-innocent ligand and may change its hapticity from η³ to η⁴.

In contrast, the coordination chemistry of 1 is rather underexplored and is limited to gold chloride complexes I and II.⁷ Similar copper (III) and gold (IV) complexes are also known for 2. Only recently, an Fe(CO)₄ complex of the biradicaloid [As(μ-C-IPr)]₂ (X) was published by the Ghadwal group.⁹

Considering these findings, the further investigation of the coordination chemistry of biradicaloids 1 and 2 towards iron carbonyl fragments seemed worthwhile. The coordination of Fe(CO)₄ fragments is especially interesting since they are expected to bind to the phosphorus atoms in 1 and 2 in a mono-dentate fashion. To the best of our knowledge, no study has been published so far which directly compares the properties of the two biradicaloids in the same reaction or compound. This would yield additional insight into the π-donating
properties of the biradicaloids by comparison of the frequencies of the CO-stretching vibrations. In this paper, the results of these experimental efforts are reported.

Results and Discussion

The synthesis of 1 has been improved multiple times.\textsuperscript{17} Here, an upscaled procedure is given that makes it accessible on a multi-gram scale [see the experimental section] (yield for the reduction: 62%, overall yield starting from Ter–NH\textsubscript{2}: 47%). The original synthetic procedure for the synthesis of 2, in which an N-heterocyclic phosphane was used to scavenge an oxygen atom from sodium 2-phospha-ethynolate [Na(OCP)] under reductive conditions, is laborious. It is lengthy and does not scale to more than 150 mg of product.\textsuperscript{13} An improved procedure was published, which allows the synthesis of 2 on a larger scale, however, two very time consuming steps are still involved.\textsuperscript{18} In light of the increased number of interesting coordination compounds of 2, a facile synthesis is required to allow for a convenient exploration of their follow-up chemistry.

The protocol described here - in contrast to the original procedure - utilizes commercial Ph\textsubscript{3}SiCl to scavenge oxygen from Na(OCP). It had been reported already that Na(OCP) reacts with chloro(triphenyl)silane to form 3, and that 3 could then rearrange in the presence of the NHC-carbon atoms which initiate the rearrangement upon which the carbene becomes a substituent in the molecule to 4 (see Scheme 2).\textsuperscript{19}

\begin{center}
\begin{tikzpicture}
  % Diagram code
\end{tikzpicture}
\end{center}

\textbf{Scheme 2.} Top row: New reaction sequence for the synthesis of 2 and reaction with [Fe(CO)\textsubscript{5}] to form 6. Bottom row: reaction of 1 with iron carbyl([Fe(CO)\textsubscript{5}],[Fe\textsubscript{2}(CO)\textsubscript{9}],[Fe\textsubscript{3}(CO)\textsubscript{12}]) and the reaction times for quantitative formation of 5. For both biradicaloids the leading resonance structure is depicted.

Reduction of 4 also resulted in the formation of 2. The selectivity in the formation of 4 could be enhanced by using toluene with only small amounts of tetrahydrofuran (THF) as solvents at 80 °C. Subsequently, the reduction with KC\textsubscript{8} was best carried out in n-hexane at low temperature (~78 °C). Extraction of the crude product with diethyl ether gave a clean product without recrystallization (for details see experimental section). Under these reaction conditions, compound 2 is accessible in a one-step, one-pot reaction, and the product was obtained in 35% yield (calculated relative to IPr) on multi-gram scale. Furthermore, it avoids any olfactory irritation arising from the phosphino phosphaketene which is a reaction step in the old protocol.

To prepare a tetracarbonyl complex, 1 was treated with [Fe(CO)\textsubscript{5}] in toluene. The reaction proceeded very slowly (33% conversion after 7 days as monitored by \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy). The product showed doublet-of-doublets resonances at δ: 275.3 ppm and 357.1 ppm; \textsuperscript{2}J(\textsuperscript{31}P, \textsuperscript{31}P) 174 Hz, indicating that the two
phosphorus ring atoms became inequivalent in the reaction with pentacarbonyl iron(0). Using one equivalent of [Fe₂(CO)₉] as the source of the Fe(CO)₄ moiety gave full conversion after 16 h reaction time at room temperature. Fe(CO)₅ was acting as a leaving group in this reaction. No reaction could be observed between [Fe₃(CO)₁₂] and 1 (cf. Scheme 2).

When 2 was reacted with pentacarbonyl iron(0) at 130 °C, the tricarbonyl complex V was obtained. When the reaction was carried out at room temperature in toluene, the tetra-carbonyl complex (6, Scheme 2) was obtained. Within minutes, the color changed from moss green to dark purple via brownish red. An iron(tetracarbonyl) fragment coordinates to 2 via one phosphorus atom (as shown by X-ray crystallography, vide infra), and CO was liberated. The ³¹P{¹H} NMR spectrum of the reaction mixture showed a pair of doublet resonances at δ: 79.8 and 325.7 ppm [²J(³¹P, ³¹P) 119 Hz].

Figure 1. Solid-state structures of 5 and 6. Protons and solvents are omitted for clarity. Color code: carbon (grey), nitrogen (blue), phosphorus (orange), iron (dark blue), oxygen (red). Selected distances [Å]: 5: N1–P1 1.681(1), N2–P1 1.664(1), N1–P2 1.797(1), N2–P2 1.775(1), P2–Fe1 2.2657(4), O1–C1 1.147(2), O2–C2 1.148(2), O3–C3 1.147(2), O4–C4 1.149(2); 6: C1–C2 1.398(3), C3–C4 1.409(3), C1–P1 1.764(3), C3–P1 1.745(2), C1–P2 1.824(2), C3–P2 1.820(2), P2–Fe1 2.3648(7), O1–C5 1.143(3), O2–C6 1.159(3), O3–C7 1.158(3), O4–C8 1.149(3).

The structure of 5 (determined by X-ray diffraction methods (XRD)) shows evidence for the zwitterionic polarization of the radical electrons in the central ring (see Figure 1), which is in agreement with the NMR data discussed above. Distances from the coordinated P-atom to the nitrogen atoms in the ring are elongated in comparison to the starting material (Ø=1.786(1) Å vs. 1.717(1) Å) while distances of the non-coordinated P-atom are shortened compared to the starting material (Ø=1.673(1) Å vs. 1.717(1) Å). The P2–Fe1 bond towards the iron carbonyl moiety is bent out of the central N₂P₂ plane by 60°. The environment around the iron center can best be described as a distorted square pyramidal with ligand 1 in one of the basal positions, which is reflected by the structural parameter τ₂²º of 0.32 for 5 (see also Table S5, SM). In 6, the central four-membered C₂P₂ ring may be described in the same zwitterionic manner as above. The two distances from the coordinated phosphorus atom to the ring carbon atoms are elongated in comparison to the starting material (Ø=1.822 vs. 1.794 Å), while the distance from the non-coordinated P-atom to the ring-C-atoms are shortened (Ø=1.755 vs. 1.794 Å). The distances from the NHC-carbon atoms to the ring carbon atoms are slightly greater in comparison to the starting material (Ø=1.406 vs. 1.387Å), which is an indicator of
imidazolium character (a positive partial charge) of the NHC substituents. The P-Fe bond here is bent out of the C$_2$P$_2$ plane by 57°, which is slightly less than in 5. The P-Fe(CO)$_4$ moiety has a trigonal-bipyramidal shape at a structural parameter $\tau_{20}$ of 0.76 (see also Table S5, SM).

The average C-O distances are shorter in 5 ($\bar{\AA}$=1.148 Å) compared to 6 ($\bar{\AA}$ = 1.155 Å). The homologous C$_2$As$_2$ complex X has the same average CO bond distance as 6. This indicates that 1 acts as a weaker ligand than 2, and that IPr$_2$C$_2$As$_2$ in X is similar in donor strength to 2. This claim is supported by CO stretching frequencies in the IR spectra, which are lower for 6 [5: 2034, 1667, 1949 cm$^{-1}$ (overlap of two signals as indicated by calculations, see the SI, Figure S9 and S10), 6: 2001, 1928, 1900, 1886 cm$^{-1}$]. Classical metal carbonyl fragments exhibit lower CO stretching frequencies when bearing stronger ligands. For both 5 and 6 this holds true. The observation of 4 CO stretching frequencies is in accordance with a C$_1$-symmetric coordination environment. CO-stretching frequencies of iron(tetracarbonyl) complexes were collected from literature for a series of compounds (Figure 2). It shows that nitrogen substitution on phosphorus leads to higher stretching frequencies than carbon substitution (compounds A and B, C and D). This trend aligns well with the data reported here. It also appears that biradicaloids 1 and 2 are stronger ligands in iron(tetracarbonyl) complexes than the other phosphate complexes A - F listed in Figure 2. The weaker donor [P(µ-NTer)]$_2$ (1) can be compared in donor strength to complexes with N-heterocyclic carbenes (NHCs) as ligands (see G - K) while phosphate while 2 is has a stronger electron-donating effect in comparison to all complexes displayed in Figure 2.

![Figure 2. CO-stretching frequencies [cm$^{-1}$] of selected phosphane- and carbene iron(tetracarbonyl)-complexes. First column: comparison of carbon vs. nitrogen substitution; second column: increasing steric demand of phosphane substituent; third row: series of NHC complexes. Tris(dimethylamino)phosphane (A)$^{26}$, tris(tert-butyl)phosphane (B)$^{27}$, tris(N-pyrrolyl)phosphane (C)$^{28}$, tri(phenyl)phosphane (D)$^{29}$, tri(methyl)phosphane (E)$^{28}$, IPr (1,3-bis(6-diisopropylphenyl)imidazolium-2-ylidene, (G)$^{31}$, IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, (H)$^{31}$, IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, (J)$^{31}$, IPMe (1-(phenyl)-3-(methyl)imidazol-2-ylidene, (K)$^{31}$](https://www.chem.rutgers.edu/chemistry/chemistry/chemistry)
environments in 5 and 6 in the solid state are likely caused by the different steric demand of the terphenyl and diisopropylphenyl groups in ligands 1 and 2.

In addition, EDA-NOCV calculations\textsuperscript{32, 33} (ORCA program package,\textsuperscript{32} TPSS-D3BJ/def2-TZVP)\textsuperscript{34, 35, 36, 37} were carried out to get a deeper insight into the Fe-L interactions in 5 and 6. Both, 1 and 2 act as strong \(\sigma\)-donor and weak \(\pi\)-acceptor ligands in the tetracarbonyl complexes (see Figure S11 for a graphical representation). Thereby, in agreement with the conclusions drawn from IR-spectroscopy, 2 is a stronger \(\sigma\)-donor (68.3 vs. 50.6 kcal\(\cdot\)mol\(^{-1}\)) and weaker \(\pi\)-acceptor (6.5 vs. 13.6 kcal\(\cdot\)mol\(^{-1}\)) than 1.

**Conclusions**

A scaled procedure has been provided for biradicaloid [P(\(\mu\)-N-Ter)]\(_2\), and a new and improved synthetic route was presented for biradicaloid [P(\(\mu\)-C-IPr)]\(_2\). Their properties as ligands in the iron(tetracarbonyl) complexes were investigated and compared. It could be shown that both act as very strong \(\sigma\)-donor ligands to Fe(CO)\(_4\) complex fragments, as revealed by IR spectroscopy and XRD experiments performed with single crystals. While the donor strength of [P(\(\mu\)-N-Ter)]\(_2\) is comparable to phosphanes such as PPh\(_3\), the donor strength of [P(\(\mu\)-C-IPr)]\(_2\) exceeds the one of other phosphanes like PPh\(_3\) and Pt-Bu\(_3\) and even \(N\)-heterocyclic carbenes.

**Experimental Section**

**General.** All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified argon. CD\(_2\)Cl\(_2\) and C\(_6\)D\(_6\) were purchased from Cambridge Isotope Laboratories. CD\(_2\)Cl\(_2\) was dried over CaH\(_2\) and distilled and C\(_6\)D\(_6\) was distilled from sodium/benzophenone.

All glassware was either stored in a 130 °C oven for at least 16 hours and was degassed prior to use or flame dried. Solvents were degassed prior to the filtration over alumina in the PureSolv purification system and the water content was determined by Karl Fischer titration. DCM and acetonitrile were stored over molecular sieves (3 Å). For all other solvents, 4 Å molecular sieves were used.

1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IPr) was synthesized from 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr-HCl) according to literature procedures.\textsuperscript{38} 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr-HCl) was synthesized from 1,3-bis(2,6-diisopropylphenylimino)ethane according to literature procedures.\textsuperscript{38} 1,2-Bis(2,6-diisopropylphenylimino)ethane was synthesized from 1,3-bis(2,6-diisopropylphenyl)amine according to literature procedures.\textsuperscript{39} Fe(CO)\(_5\) (Sigma Aldrich, trace metal basis), Fe\(_2\)(CO)\(_9\), Fe\(_3\)(CO)\(_{12}\) and Ph\(_3\)SiCl (all abcr GmbH) were bought and used as received.

\(^1\)H NMR spectra were recorded on Bruker spectrometers operating at 200, 300, 400 or 500 MHz; \(^{13}\)C NMR spectra on Bruker spectrometers operating at 75.46, 100.61 or 125.758 MHz; \(^{31}\)P NMR spectra were recorded on Bruker spectrometers operating at 101.28, 121.494, 161.97, 202.457 or 283.419 MHz. All \(^1\)H and \(^{13}\)C NMR chemical shifts are reported relative to SiMe\(_4\) using the \(^1\)H (residual) and \(^{13}\)C chemical shifts of the solvent as a secondary standard (C\(_6\)D\(_6\): \(\delta\) 7.16 for \(^1\)H, \(\delta\) 128.06 for \(^{13}\)C; CD\(_2\)Cl\(_2\): \(\delta\) 5.32 for \(^1\)H, \(\delta\) 53.50 for \(^{13}\)C). \(^{31}\)P chemical shifts are reported relative to an 85% H\(_3\)PO\(_4\) solution in H\(_2\)O. Peak widths at half heights (in Hz) are given for broad signals. Data are reported as following: Chemical shift (\(\delta\)) in ppm, multiplicity (s: singlet, d: doublet, dd:
doublet of doublets, dt: doublet of triplets, t: triplet, td: triplet of doublets, q: quartet, qui: quintet, m: multiplet), coupling constants $J$ (Hz) and integration.

Infrared spectra were collected on a Bruker-Alpha FT-IR-spectrometer. The absorption bands are labeled as following: strong (s 70-100%), middle (m 40-70%) and weak (w 10-40%).

Single crystals suitable for X-ray diffraction were protected with polyisobutylene oil under argon and measured on the Bruker D8-Venture diffractometer or a Bruker Apex 2 diffractometer using molybdenum irradiation.

Elemental analyses were performed at the Mikrolabor of ETH Zürich.

Scaled synthesis of 1,3-Bis(2,2″,4,4″,6,6″-hexamethyl-[1,1′:3′,1″-terphenyl]-2′-yl)-1,3,2ℓ2,4ℓ2-diazadiphosphetyl (1).

$[\text{P}(\mu^N\text{-TerCl})_2]$ was synthesized according to a modified literature procedure.\(^{17}\)

Mg turnings can be activated by stirring under argon atmosphere for several days using a glass-covered magnetic-stirring bar. $[\text{P}(\mu^N\text{-TerCl})_2]$ (6.43 g, 8.16 mmol) and Mg turnings (2.87 g, 118 mmol) were combined in a Schlenk flask. **Attention:** It is paramount to ensure that no grease finds its way into the reaction vessel. It is paramount to ensure that no grease finds its way into the reaction vessel. Mg turnings can be activated by stirring under argon atmosphere for several days using a glass-covered magnetic-stirring bar. $[\text{P}(\mu^N\text{-TerCl})_2]$ (6.43 g, 8.16 mmol) and Mg turnings (2.87 g, 118 mmol) were combined in a Schlenk flask. **Attention:** It is paramount to ensure that no grease finds its way into the reaction vessel.

After activation, a modified literature procedure was used.\(^{17}\)

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After activation, a modified literature procedure was used.\(^{17}\)
vessel is removed, and the flask sealed with a stopcock. Afterwards, the reaction mixture is allowed to warm to room temperature. Stirring is continued.

After 16 h, a dark green mixture was obtained. It was transferred onto a G4 sintered frit, and packed with a generous pad of celite. The solution was collected. Volatiles were removed in vacuo via the tab on the receiver flask (1·10⁻³ mbar for 1 h, for a scheme of the setup see the SM). Afterwards, 150 ml of diethyl ether were added to the solid on top of the frit and filtered through. The stopcock on the frit was replaced with a reflux condenser, connected to a tap. The tab on the receiver flask was closed and the one on top of the reflux condenser opened. The flask was heated to 60 °C with an oil bath, so that the solvent evaporated, condensed in the reflux condenser, and extracted the solids on top of the frit (compare the scheme in the SM). The extraction was continued until the solution washing through the frit became almost colourless. (Towards the end, the solution went from green to slightly brown. At that point, the extraction was stopped.)

Subsequently, the receiver flask was disconnected from the extraction setup and sealed with a stopcock. Volatiles were removed in vacuo (1·10⁻³ mbar for 1 h). The remaining dark solid was suspended in 120 ml of acetonitrile and transferred onto another G4 sintered frit. Filtration gave a brown filtrate and a green solid. The solid was washed three times with 10 ml acetonitrile each. The receiver flask was then disconnected and the solid briefly dried in vacuo (1·10⁻³ mbar for 15 min).

Finally, a new receiver flask is connected to the frit. The solid is extracted with 100 ml of diethyl ether into the flask. Volatiles were removed in vacuo.

The product obtained via this route was of sufficient purity for follow-up reactions. Samples of very high purity may be obtained by recrystallization from hot n-hexane.

Yield: 6.0 g (6.989 mmol; 36%).

1H NMR (CD6, 500.1 MHz): δ [ppm] 1.19 (d, 1H, 1H) 6.6 Hz, 12 H, CH(CH3)2), 1.35 (d, 3J(1H, 1H) 6.5 Hz, 12 H, CH(CH3)2), 2.99 (m, 3J(1H, 1H) 6.7 Hz, 4 H, CH(CH3)2), 5.99 (s, 2H, NCH), 7.05 (d, 3J(1H, 1H) 7.7 Hz, 4H, meta-C₆H₄), 7.25 (t, 3J(1H, 1H) 7.7 Hz, 2H, para-C₆H₄). 13C{1H} NMR (CD6, 125.8 MHz): δ [ppm] 23.6 (s, 4C, CH(CH3)2), 25.0 (s, 4C, CH(CH3)2), 29.1 (s, 4C, CH(CH3)2), 118.3 (s, 4C, NCH), 123.4 (4C, para-C₆H₄), 129.7 (s, 8C, meta-C₆H₄), 131.0 (t, 1J(13C, 31P) 41 Hz, 2 C, CCP), 134.5 (s, 4C, ipso-C₆H₄), 147.7 (s, 8C, ortho-C₆H₄), 152.1 (t, 2J(13C, 31P) 14 Hz, 2 C, NCN). 31P{1H} NMR (CD6, 202.5 MHz): δ [ppm] 196.3 (s, 2P, CPC).

**Synthesis of 1,3-Bis(2,2",4,4",6,6"-hexamethyl-[1,1’:3’,1”-terphenyl]-2'-yl)-1,3,2,4λ²-2-diazadiphosphetidin-2-yl)tetracarboxylin (S)**

A round bottomed Schlenk flask was equipped with a stirrer bar and charged with 162 mg (0.226 mmol) [P(µ-NTer)]2 (Ter: 2,6-bis(2,4,6-trimethylphenyl)-phenyl), 82 mg (0.226 mmol) Fe₂CO₃ and 5 ml toluene. After stirring the mixture at room temperature for 20 h, volatiles were removed in vacuo (1·10⁻³ mbar for 1 h). The crude product was recrystallized from n-hexane by cooling a saturated solution from 60 °C to −20 °C, yielding a black, microcrystalline product.

Yield: 0.124 g (0.0140 mmol; 62%).

**Melting point:** 191 °C (dec.). **CHN** for C₅₂H₅₀Fe₂O₂P₂ (884.775 g·mol⁻¹) found (calc.): C 71.95 (70.59), H 5.81 (5.70), N 3.49 (3.17). 1H NMR (CDCl₃, 500.1 MHz): δ [ppm] 1.94 (s, 12H, Mes-ortho-CH₃), 1.97 (s, 12H, Mes-ortho-CH₃), 2.42 (s, 12H, Mes-para-CH₃), 6.80 (s, 4H, Mes-meta-H), 6.82 (s, 4H, Mes-meta-H), 6.87 (d, 3J(1H, 1H) 7.5 Hz, 4H, meta-CH₃), 7.13 (t, 3J(1H, 1H) 7.5 Hz, 2H, para-CH₃). 13C{1H} NMR (CDCl₃, 125.8 MHz) δ [ppm] 20.9 (s, 4C, para-CH₃), 21.5 (s, 4C, ortho-CH₃), 21.6 (s, 4C, ortho-CH₃), 125.5 (s, 2C, para-CH), 129.2 (s, 4C, Mes-meta-CH), 129.7 (s, 4C, Mes-meta-CH), 131.9 (s, 4C, meta-CH), 132.8 (s, 4C, ipso-C), 135.7 (s, 4C, ipso-C), 137.2 (s, 4C, ipso-C), 137.6 (s, 2C, NC), 138.3 (s, 4C, ipso-C), 138.5 (s, 4C, ipso-C), 217.4 (s, 4C, CO). 31P{1H} NMR (CDCl₃, 202.5 MHz): δ [ppm] 275.3 (d, 2J(31P, 31P) 174 Hz, 1P, N(Fe)P₃), 351.7 (d, 2J(31P, 31P) 174 Hz, 1P, NPN). IR (transmission, sat. n-hexane solution, 25 °C, 64 Scans): v [cm⁻¹]: 2034 (m), 1967 (m), 1949 (s). IR (ATR, 25 °C, Arkivoc 2022, iii, 327-338, M. T. et al. ©AUTHOR(S)}
64 Scans): v [cm⁻¹]: 2959 (w), 2908 (w), 2115 (w), 2025 (s), 1935 (s), 1610 (w), 1430 (w), 1404 (m), 1373 (w), 1336 (w), 1260 (m), 1235 (w), 1219 (s), 1160 (w), 1084 (w), 1015 (m), 947 (w), 930 (m), 912 (w), 872 (w), 842 (m), 795 (s), 761 (m), 745 (w), 734 (w), 686 (s), 631 (m), 618 (w), 607 (s), 572 (w), 548 (w), 521 (w), 509 (w), 474 (w), 456 (w), 428 (m).

**Synthesis of [2-(1,3-Bbis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)-4-(1,3-bis(2-isopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)-1,3λ²-diphosphetan-1-yl]tetracarboxyllirron (6)**

A Schlenk flask was equipped with a stirrer bar and charged with 400 mg (0.463 mmol) (IPrCP)₂, and 10 ml toluene. While being stirred at room temperature, Fe(CO)₅ (0.08 ml, 0.597 mmol, 1.3 eq) was added via microsyringe. The solution turned first brown, then intensely purple. Moderate gas development was observed at the pressure release valve of the Schlenk line. After stirring the mixture at room temperature for 20 h, volatiles were removed in vacuo (1·10⁻³ mbar for 1 h). The crude product was washed with hot n-hexane and dried in vacuo at ambient temperature (1·10⁻³ mbar for 3 h), yielding a black solid.

Yield: 276 mg (0.0278 mmol; 60%).

**Melting point:** 305 °C. CHN for C₆₀H₇₂FeN₄O₄P₂ (1031.053 g·mol⁻¹) found (calc.: C 70.12 (69.90), H 6.57 (7.04), N 5.42 (5.43). Ⅲ H NMR (C₆D₆, 500.1 MHz): δ [ppm] 0.96 (d, 3J(1H, 1H) 6.9 Hz, 6 H, CH(CH₃)₂), 0.99 (d, 3J(1H, 1H) 6.7 Hz, 6 H, CH(CH₃)₂), 1.06 (d, 3J(1H, 1H) 7.1 Hz, 6 H, CH(CH₃)₂), 1.08 (d, 3J(1H, 1H) 7.1 Hz, 6 H, CH(CH₃)₂), 1.22 (d, 3J(1H, 1H) 6.7 Hz, 6 H, CH(CH₃)₂), 1.29 (d, 3J(1H, 1H) 6.6 Hz, 6 H, CH(CH₃)₂), 1.37 (d, 3J(1H, 1H) 6.5 Hz, 6 H, CH(CH₃)₂), 1.81 (d, 3J(1H, 1H) 6.5 Hz, 6 H, CH(CH₃)₂), 2.65 (m, 3J(1H, 1H) 6.8 Hz, 2 H, CH(CH₃)₂), 3.07 (m, 3J(1H, 1H) 6.7 Hz, 2 H, CH(CH₃)₂), 3.33 (m, 3J(1H, 1H) 6.7 Hz, 2 H, CH(CH₃)₂), 3.60 (m, 3J(1H, 1H) 6.6 Hz, 2 H, CH(CH₃)₂), 6.04 (d, 3J(1H, 31P) 1.6 Hz, 2 H, NCH), 6.25 (d, 5J(1H, 31P) 1.4 Hz, 2 H, NCH), 6.92 (d, 3J(1H, 1H) 7.7 Hz, 2H, meta-C₆H₄), 7.01 (d, 3J(1H, 1H) 7.6 Hz, 2H, meta-C₆H₄), 7.1 (2H, meta-C₆H₄, overlap with solvent signal), 7.23 (d, 3J(1H, 1H) 7.7 Hz, 2H, meta-C₆H₄), 7.1 (2H, para-C₆H₄, overlap with solvent signal), 7.31 (t, 3J(1H, 1H) 7.7 Hz, 2H, para-C₆H₄).

**13C{¹H} NMR (C₆D₆, 125.8 MHz): δ [ppm] 22.8 (s, 1C, CH(CH₃)₂), 23.0 (s, 1C, CH(CH₃)₂), 23.2 (s, 1C, CH(CH₃)₂), 23.9 (s, 1C, CH(CH₃)₂), 25.5 (s, 2C, CH(CH₃)₂), 25.5 (s, 1C, CH(CH₃)₂), 27.9 (s, 1C, CH(CH₃)₂), 28.3 (s, 1C, CH(CH₃)₂), 28.5 (s, 1C, CH(CH₃)₂), 28.7 (s, 1C, CH(CH₃)₂), 29.3 (s, 1C, CH(CH₃)₂), 119.9 (s, 2C, NCH), 121.4 (s, 2C, NCH), 124.3 (1C, para-C₆H₄), 124.7 (1C, para-C₆H₄), 125.4 (1C, para-C₆H₄), 125.7 (1C, para-C₆H₄), 130.6 (s, 4C, meta-C₆H₄), 130.9 (s, 4C, meta-C₆H₄), 133.4 (s, 2C, ipso-C₆H₄), 143.3 (s, 2C, ipso-C₆H₄), 144.7 (t, 1J(13C, 31P) 38 Hz, 2 C, CCP), 145.1 (s, 2C, ortho-C₆H₄), 147.2 (s, 2C, ortho-C₆H₄), 147.2 (s, 2C, ortho-C₆H₄), 147.6 (s, 2C, ortho-C₆H₄), 151.6 (t, 2J(13C, 31P) 11 Hz, 2 C, NCH), 214.8 (s, 2C, CO, ν₁/₂ 50 Hz), 221.4 (s, 2C, CO, ν₁/₂ 130 Hz). 31P{¹H} NMR (C₆D₆, 202.5 MHz): δ [ppm] 79.8 (d, 2J(31P, 31P) 119 Hz, 1P, CP(Fe)C), 325.7 (d, 2J(31P, 31P) 119 Hz, 1P, CP(Fe)C). IR (transmission, sat. n-hexane solution, 25 °C, 64 scans): v [cm⁻¹]: 2001 (s), 1928 (w), 1890 (m), 1886 (s).

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**Supplementary Material**

A scheme of the apparatus for the synthesis of 2, detailed spectra, calculations and crystallographic data are available in the Supplementary Material associated with this paper.

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