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# Ligand Cleavage Put into Reverse: P–C Bond Breaking and Remaking in an Alkylphosphane Iron Complex

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*Dedicated to Professor Helmut Hartung on the occasion of his 70th birthday*

**Abstract:** Complex formation between $FeX_2{\cdot}6H_2O$ ($X = BF_4$ or $ClO_4$) and the pyridine-derived tetrapodal tetraphosphane $C_5H_3N[CMe(CH_2PMe_2)_2]_2$ (**1**) in methanol proceeds with solvent-induced cleavage of one $PMe_2$ group. Depending on the reaction temperature and the nature of the counterion, iron(II) is coordinated, in distorted square-pyramidal fashion, by the anionic remainder of the chelating ligand, $C_5H_3N[CMe(CH_2PMe_2)_2][CMe(CH_2PMe_2)(CH_2^-)]$ ($NP_3C^-$ donor set: $X = BF_4$, −50 °C: **2**; $X = ClO_4$, RT: **4**) or its protonated form $C_5H_3N[CMe(CH_2PMe_2)_2][CMe(CH_2PMe_2)(CH_3)]$, in which the methyl group is in agostic interaction with the metal centre ($X = BF_4$, RT: **3**; $X = ClO_4$, +50 °C: **5**). A monodentate phosphinite ligand $Me_2POMe$, formed from the cleaved $PMe_2$ group and methanol, completes the coordination octahedron in both cases. Working in $CD_3OD$ ($X = BF_4$, RT) gives the deuterium-substituted analogue of **3**, with ligands $L(CH_2D)$ (L = residual chelating ligand) and $Me_2POCD_3$. A mechanism for the observed phosphorus–carbon bond cleavage is suggested. Complex **2**, when isolated at −50 °C, is stable in the solid state even at room temperature. The reaction of **2** in methanol with carbon monoxide (10.5 bar) at elevated temperature forms, in addition to as yet unidentified side products, the carbonyl complex $[(\mathbf{1})Fe(CO)](BF_4)_2$ (**7**), in which the previous P–C bond cleavage has been reversed, reforming the original tetrapodal pentadentate $NP_4$ ligand **1**. All compounds have been fully characterised, including X-ray structure analyses in most cases.

**Keywords:** agostic interactions · iron · N,P ligands · P–C activation · tetrapodal ligands

## Introduction

Tertiary phosphanes are a ligand class of prime importance for well-defined molecular catalysis in homogeneous solution.[1] The reactivity of such compounds, both coordinated to transition metals and in their own right, has been the subject of intense scrutiny, in order to understand and control possible catalyst degradation.[2] Cleavage, or activation, of bonds within the ligand under reaction conditions is not uncommon. It was first reported for C–H bonds ("cyclometalation") and subsequently for C–P bonds.[3] In the latter case, the observed reactivity follows the order $P{-}C_{sp} > P{-}C_{sp^2} > P{-}C_{sp^3}$, and phosphanylacetylenes are the most reactive. The next in line, aryl phosphane ligands, have the largest number of reported C–P bond activations (which may be a reflection of their preferred use in catalysis). An external stimulus is usually required, such as the addition of acid.[2b] In only a handful of recently observed cases can C–P bond cleavage in such ligands be induced by the solvent acting as a nucleophile.[4] There appear to be no previous examples of solvent-induced C–P bond activation in alkyl phosphanes. The reverse reaction, that is, the specific remaking under different conditions of a C–P bond that was previously broken, has never been described.

We report here our first observations concerning the reactivity towards iron(II) of a novel pentadentate tetraphos-

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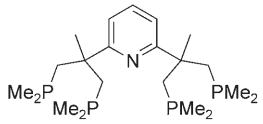
phane ligand derived from pyridine ($NP_4$ donor set).[5] Ligand **1** (systematic name: 2,6-bis(2-methyl-1,3-bis(dimethylphosphino)propan-2-yl)pyridine) has only phosphorus–carbon bonds of the P–$C_{sp^3}$ type. Complexation reactions with iron(II) in the presence of methanol or water lead to highly specific C–P bond cleavage, which can be reversed in a separate reaction by coordination of carbon monoxide, which leads to reformation of the intact ligand. The phenyl-substituted congener of **1**, $C_5H_3N$-$[CMe(CH_2PPh_2)_2]_2$, shows no such clear-cut reactivity.[6b]




**1**

## Results and Discussion

Tetraphosphane **1** can be prepared cleanly on a multigramme scale by reaction of the corresponding tetrabromide $C_5H_3N[CMe(CH_2Br)_2]_2$[6] with $LiPMe_2$[7] in diethyl ether. The ligand is obtained as a colourless oil in good yield (> 80%). When treated with a stoichiometric amount of $Fe(BF_4)_2 \cdot 6H_2O$ in methanol at room temperature, red microcrystalline **3** is formed within a few minutes. Its well-resolved $^1H$ NMR spectrum ([$D_6$]DMSO, RT, 200 MHz) has two striking features: The pyridine protons are separated into three signals (ABC, t/d/d between $\delta = 8.1$ and 7.5 ppm), and a singlet corresponding to 3H is observed at $\delta = -3.7$ ppm. In the $^{31}P$ NMR spectrum, one of the four phosphorus resonances is at very low field ($\delta = 174.5$ ppm relative to 85% $H_3PO_4$), separated by at least 125 ppm from the more closely spaced set of the three others (50.3–17.0 ppm). The original ligand has $C_{2v}$ symmetry, as indicated by its $^1H$, $^{13}C$, and $^{31}P$ NMR spectra, and we took the apparent loss of symmetry ($C_1$) as a first indication that cleavage of the ligand might have occurred.

Confirmation came from the structural characterisation of the product (Figure 1; **3**·0.5 MeOH; single crystals disintegrate upon drying in vacuo owing to loss of methanol of solvation to give **3**). The product has a tripodal tetradentate ligand coordinated to iron, in addition to an unusual monodentate methyl dimethylphosphinite ligand ($P(OMe)Me_2$, a constitutional isomer of trimethylphosphane oxide). Agostic interaction of one of the C–H bonds in what now is a $CH_3$ group (formerly P-bonded $CH_2$ in the ligand backbone) with iron completes the coordination sphere (all proton positions in the structure correspond to maxima in the difference Fourier synthesis which are reasonable both in terms of distance and angle relative to the carrier atom, with no residual electron density in the vicinity; see Experimental Section). The complex is chiral (as are all the other complexes in this series, see Experimental Section), and quaternary carbon atom C12 is a stereogenic centre. The coordination geometry at iron is distorted octahedral (see Table 1), with Fe–P bond lengths *d* varying from 2.1720(6) Å (P2) through 2.2041(6) Å (P4, phosphinite ligand) to 2.2681(6)/2.2710(6) Å (*trans* P1-Fe-P3). The observation that *d*(Fe–P2), *trans* to the agostic methyl group is the shortest iron–phosphorus distance correlates with the weak π-acceptor ability of the coordinated C–H bond. The resulting polarization of the iron d orbital towards the diametrically opposite phosphorus atom P2 helps to increase its π overlap with the metal centre. The distances in the arrangement P1-Fe-P3 are significantly longer and uniform, as bonding contributions are more evenly distributed. The Fe–N distance of 2.058(2) Å is similar to the corresponding value in the low-spin $Fe^{II}$ carbonyl complex of a related tetraamine imine ligand ($NN_4$ donor set),[8] but significantly shorter than in the $Fe^{II}$ carbonyl complex of tetraphosphane ligand **1** (2.143(2) Å, see below). In **3**, the agostic methyl group in

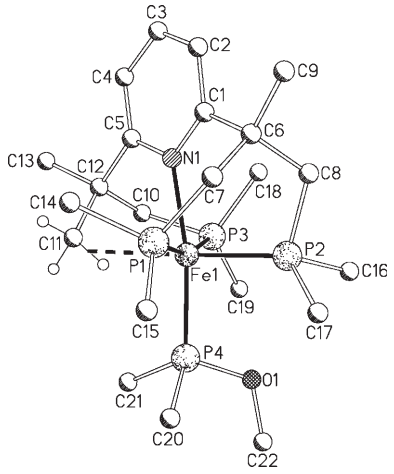



Figure 1. Structure of the dication in **3**·0.5 MeOH ($BF_4^-$ salt). Hydrogen atoms are shown only for the methyl group in agostic interaction with the metal centre.

Table 1. Selected bond lengths [Å] and angles [°] in **2**, **3**·0.5 MeOH, **4**, **6** and **7** (standard deviations in parentheses). Values in italics are parameters involving the "agostic" methyl carbon atom.

| | **2** | **3**·0.5 MeOH | **4** | **6**·$H_2O$ | **7**·2 MeOH |
|---|---|---|---|---|---|
| Fe1–N1 | 2.062(2) | 2.058(2) | 2.065(2) | 2.023(1) | 2.143(2) |
| Fe1–P1 | 2.2396(7) | 2.2681(6) | 2.2432(7) | 2.2766(5) | 2.2629(6) |
| Fe1–P2 | 2.2102(7) | 2.1720(6) | 2.2105(7) | 2.3127(5) | 2.2394(6) |
| Fe1–P3 | 2.2369(7) | 2.2710(6) | 2.2388(7) | 2.2945(5) | 2.2482(6) |
| Fe1–P4 | 2.1636(7) | 2.2041(6) | 2.1659(7) | 2.2353(6) | 2.2460(6) |
| Fe1···C11 (**3**); Fe1–C11 (**2**, **4**, **6**) | 2.068(2) | *2.643(2)* | 2.068(2) | 2.079(2) | – |
| Fe1–C22 | – | – | – | – | 1.739(2) |
| N1-Fe1-P4 | 170.81(6) | 168.97(5) | 170.81(5) | 160.55(4) | - |
| N1-Fe-C22 | – | – | – | – | 177.55(8) |
| Fe1-C22-O1 | – | – | – | – | 177.5(2) |
| P1-Fe1-P3 | 160.87(3) | 163.49(2) | 160.69(3) | 163.47(2) | 159.30(2) |
| P2-Fe1-C11 | 175.85(7) | *172.11(5)* | 175.93(7) | 175.91(6) | – |
| P2-Fe1-P4 | 91.49(2) | 91.74(2) | 91.46(2) | 97.71(2) | 165.53(2) |

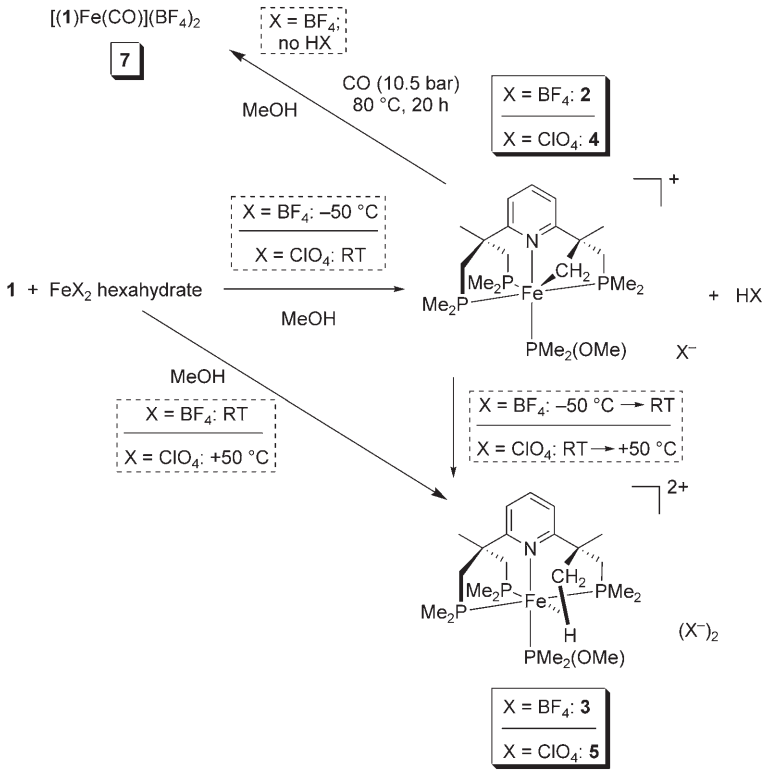
  

close proximity to the central iron ion is expected to give rise to a strongly shifted $^1$H NMR signal, as is indeed observed (rotation of this group, which is fast on the NMR timescale, causes the three protons to appear as a broadened singlet). Further, the methoxyl group of the phosphinite ligand should and does give a unique signal ($\delta = 3.42$ ppm, d, $^3J(P,H) = 11$ Hz; [D$_6$]DMSO, RT, 200 MHz). All other methyl resonances appear as a complex pattern which has been fully assigned by 2D techniques (see Experimental Section). When the complexation reaction is carried out in [D$_4$]methanol under otherwise identical conditions, the product contains the phosphinite ligand $Me_2POCD_3$ and a monodeuterated methyl group $CH_2D$, as deduced from a combination of NMR spectroscopic data and elemental analysis ($^1$H: no $OCH_3$ resonance, plus a broad singlet at $\delta = -3.7$ ppm corresponding to 2H; $^{31}$P: unchanged).

The reaction leading to **3** can thus be summarised as shown in Scheme 1. The complex is the sole product in the precipitate and forms in high yield (80%). It is soluble in water without decomposition. From the anion balance, the bond lengths, the diamagnetism as manifested in the NMR spectra, and the degree of saturation in the framework as determined by spectroscopic and structural analysis, we conclude that the iron centre has the oxidation state +II. The composition of the salt is $AB_2$ (A: dication; B: monoanion), and the elemental analysis (C/H/N) agrees with the predicted values.

The complexation of **1** with $Fe(ClO_4)_2 \cdot 6H_2O$ under otherwise identical conditions, particularly temperature, gives a strikingly different result. The solution turns orange but does not deposit a precipitate. After concentration, isothermal diffusion of diethyl ether produces an orange microcrystalline solid (**4**) which must be isolated with caution; while complexes containing organic ligands and perchlorates are potentially explosive, the material described here will explode, particularly when dry, if excessive pressure is exerted during handling, for example, with a spatula. It is therefore best prepared in amounts not greater than 40 mg. While $^1$H NMR spectra recorded at 200 MHz ([D$_4$]methanol, RT) are well resolved, they show only very broad lines at 500 MHz (RT). Obviously, the material is moderately paramagnetic at room temperature, which is more evident at higher field strength $B$, due to the quadratic dependence of the relaxation times $T_1$ and $T_2$ on $B$. We are currently investigating the origins of these phenomena (variable-temperature NMR studies) and will report our results in a forthcoming paper. In the 200 MHz $^1$H NMR spectrum of **4**, there are no signals at $\delta < 0$ ppm, which in **3** are diagnostic of an agostic interaction. Similar to the spectrum of **3**, the signals of the pyridine protons represent an ABC system, which indicates loss of $C_{2v}$ symmetry. The $^{31}$P NMR spectrum has four signals, one of which ($\delta = 178.6$ ppm) is again clearly separated from the rest ($\delta = 43.5$, 34.4, 18.4 ppm).

While the spectral data therefore suggest a structure largely similar to that of **3**, elemental analysis agrees only with the formulation of an AB salt, with one perchlorate ion (Scheme 1). In this case, as is evident from the X-ray crystal structure (Figure 2), one $PMe_2$ group has again been cleaved, as in **3**, but the $RCH_2^-$ "stump" of the ligand is now coordinated to the iron ion to give a monocationic complex. (All proton positions in the structure correspond to maxima of the difference Fourier synthesis which are reasonable both in terms of distance and angle relative to the carrier atom, with no residual electron density in the vicinity.) A phosphinite ligand was again formed, but the fate of the methanol proton is as yet undetermined (it likely produces 1 equiv of $HClO_4$). The geometry at iron is again distorted octahedral (see Table 1). While the Fe–N bond lengths in **3** and **4** are virtually identical, the patterns of Fe–P bond lengths are totally different: The shortest bond is now that which connects the phosphinite ligand in the axial position (highlighting the weak π-acceptor ability of the pyridine ring), while all




Scheme 1.

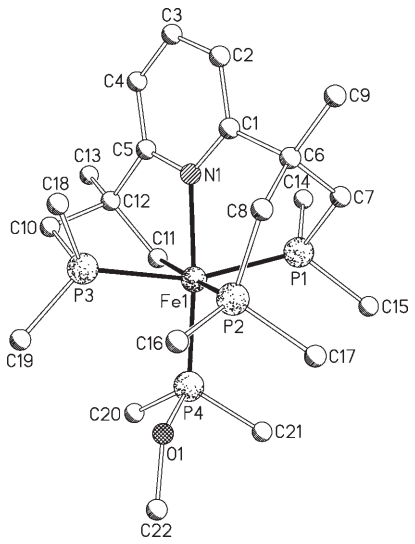



Figure 2. Structure of the monocation in **4** (hydrogen atoms omitted for clarity). The structure of the cation in **2** ($BF_4^-$ salt) is virtually identical.

three equatorial bonds are significantly longer but of overall similar length. Interestingly, carbanion coordination does not induce a significant lengthening of the bond in the *trans* position (Fe1–P2) compared to the two other equatorial Fe–P bonds; on the contrary, this bond is the shortest of the three, the diametrically opposed Fe-C unit being a very weak π acceptor at best. The electron density provided to the metal by the carbanionic ligand seems to be funnelled into the bond to the phosphane ligand in the *trans* position, through increased π backdonation.

The *trans* influence of the carbanionic ligand in **4** is clearly noticeable, however, when comparing *d*(Fe1–P2) in **4** (2.2105(7) Å) with the corresponding value in **3** (2.1720(6) Å). Based on reasoning similar to that used for **3**, we assign a +II oxidation state to the central iron ion. It is noteworthy that **4** dissolves in water without decomposition, even when no special precaution is taken to exclude atmospheric oxygen.

The outcome of the complexation reaction between iron(II) and **1** at room temperature thus appears to be controlled by the nature of the acid HX (Scheme 1) which is produced in the course of phosphinite formation and the solubility of the respective salt. Conversely, for one and the same counterion, protonation is temperature-dependent: when $Fe(BF_4)_2{\cdot}6H_2O$ reacts with **1** at −50 °C, the only isolable product (upon removal of the solvent and washing with diethyl ether; microcrystalline red solid, 75% yield) is the tetrafluoroborate salt **2** containing the carbanionic ligand (Scheme 1). Once isolated at −50 °C, this salt is stable even at room temperature; however, if it is not isolated, and the reaction mixture is allowed to warm to room temperature, the only detectable product is **3**, which has an agostic methyl group. Similar observations were made in the case of $X = ClO_4$, the only difference being that while "carbanionic" complex **4** forms at room temperature, preparation of "agostic" complex **5** requires heating (to +50 °C, Scheme 1). We have so far not succeeded in reversing either protonation reaction (at room temperature) by addition of a base such as lithium methoxide to agostic complexes **3** and **5** to reform complex **2** and **4**, respectively. The cation structures in the tetrafluoroborate salt **2** and the perchlorate salt **4** are virtually identical (Table 1), and the two compounds are isostructural.

However, quantitative deprotonation of the agostic group occurs when two equivalents of **3** react with 0.5 equiv of dioxygen [Eq. (1)], and products are the carbanionic iron(III) complex **6** and, remarkably, one equivalent of water. Compound $\mathbf{6}{\cdot}H_2O$, which is also soluble in bulk water without decomposition, was isolated as a crystalline green precipitate in 95% yield. In the solid-state structure of this dication bis(tetrafluoroborate) solvate (Figure 3 and Table 1), the

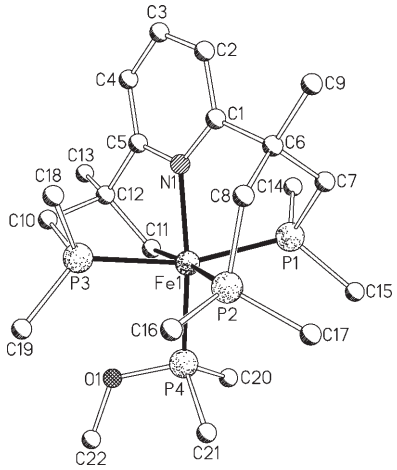
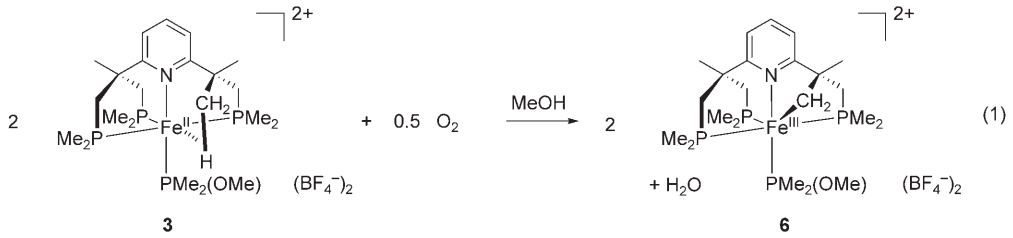



Figure 3. Structure of the dication in $\mathbf{6}{\cdot}H_2O$ (hydrogen atoms omitted for clarity).

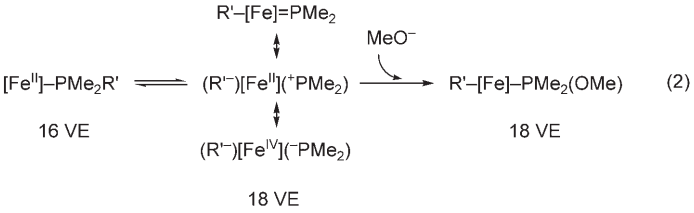
$Fe-N_{py}$ bond length is shorter than in **3** or **4**, as expected for a more highly oxidised metal centre and a ligand of predominantly σ-donor character; by contrast, all iron–phosphorus bonds are longer than in the iron(II) complexes, and this reflects strongly decreased π backdonation from iron(III).[9] While the two bond lengths in the P1-Fe1-P3 moiety are similar, as is the case in **4**, the iron–phosphorus bond *trans* to the carbanionic ligand (Fe1–P2) in **6** is significantly longer than the Fe1–P1/Fe1–P3 pair, whereas it is significantly shorter in **4** (Table 1). Decreased π backdonation from iron(III) to phosphorus seems to be the overriding influence here. The shortest iron–phosphorus bond in **6**, Fe1–P4, is that which connects the phosphinite ligand, as is the case in **4**.

Our rationalization of the ligand cleavage observed upon reaction of **1** with iron(II) is as follows: Given the topology of the ligand, which provides $5 \times 2 = 10$ valence electrons through its $NP_4$ donor set in a square-pyramidal arrangement, complexation to iron(II) with its $d^6$ electron configuration yields a 16-valence-electron (16-VE), and hence coordinatively unsaturated, complex. While this coordinative unsa-




**3** **6**




turation could be removed simply by coordination of the Lewis basic solvent MeOH, P–C bond activation is observed instead to give an 18-VE species as the result of nucleophilic attack of the solvent on one of the phosphorus atoms. Preliminary data indicate that other nucleophiles will induce ligand cleavage in the same way:[10] In THF solution, water of solvation from $FeX_2 \cdot 6H_2O$ produces the monodentate ligand $P(OH)Me_2$ exclusively. On the other hand, when acetonitrile is used as the (non-nucleophilic) solvent in conjunction with anhydrous iron(II) salts, such as iron(II) triflate, the product obtained is the regular complex $[(\mathbf{1})FeNCMe]^{2+}$, in which the ligand functions as a tetrapodal pentadentate "coordination cap".

As regards P–C bond breaking in **1** to give **3** or **4**, a plausible sequence of events may be as follows: Intermediate coordination of methanol forms the complex $[(\mathbf{1})FeHOMe]^{2+}$; binding to the metal helps to make the solvent more acidic, and intramolecular nucleophilic attack by methoxide then removes an adjoining $PMe_2$ substituent to produce a phosphinite ligand and a metal-coordinated alkyl residue. The nature of the acid (HX) formed in the process (Scheme 1) then controls the rate of protonation and crystallisation: With tetrafluoroborate, the protonated product precipitates at room temperature, whereas with perchlorate protonation/precipitation is not observed at room temperature. The overall process bears a distant resemblance to what has been termed a platinum alkoxide/phosphorus aryl metathesis, as reported by van Leeuwen, Orpen et al.[11] P–C bond activation in aryl phosphanes (M = Ru) has, however, been postulated to require the initial formation of an unsaturated precursor (16-VE), which undergoes insertion of the metal ion into a phosphorus–carbon bond to give a saturated (18-VE) system, which is then liable to attack by an incoming nucleophile.[4] As an alternative mechanism to that described above, this process may be operative in our case, too [Eq. (2)]. It is noteworthy that, depending on which resonance forms are drawn, this entails formal involvement of either an iron(IV) or a phosphenium ($R_2P^+$) ion.[12] A particularly striking aspect in our case is the specificity with which only that P–C bond is cleaved which links the dimethylphosphanyl unit to the rest of the ligand; metal insertion into a P–Me bond is not observed.

In the course of work aimed at the displacement of the agostic methyl group in **3** or the anionic methylene donor in **2**, we treated the latter with carbon monoxide (autoclave; $p_{CO} = 10.5$ bar, methanol solution, 80 °C, 20 h). We were surprised to find, upon workup of the resultant yellow solution, the isolated product to be the iron(II) carbonyl complex of the intact tetraphosphane ligand **1**, $[(\mathbf{1})Fe(CO)](BF_4)_2$ (**7**). This was obtained as a yellow, single-crystalline solid; while the yield of isolated product is still low (12% based on **2**), NMR spectroscopic analyses ($^1H$, $^{31}P$) of the mother liquor confirm that it contains a large amount of **7** in addition to other compounds ($^{31}P$ NMR) as yet unidentified. The NMR spectroscopic data of **7** ($^1H$, $^{31}P$, $^{13}C$; obtained from solutions of previously isolated pure **7** in [$D_4$]methanol) suggest $C_{2v}$ symmetry for the diamagnetic cation. Specifically, the spectra show an $AB_2$ pattern for the three pyridine protons $H^3$/$H^4$/$H^5$, equivalent *ortho* carbon atoms in the pyridine ring, and only one phosphorus resonance (singlet) at $\delta = 19$ ppm. The carbonyl carbon atom appears as a quintet at $\delta = 214.62$ ppm ($^2J(P,C) = 27.6$ Hz), in further support of the equivalence of all four phosphorus atoms. The carbonyl ligand gives rise to a prominent band in the solid-state IR spectrum (KBr; $\tilde{\nu} = 1969\ cm^{-1}$). In the mass spectrum (ESI), the molecular ion $[M]^{2+}$ is detected at $m/z$ 258.

In the solid state, the dication is distorted from octahedral geometry by displacement of diametrically opposite pairs of P donors from the equatorial plane, towards a tetrahedral $P_4$ arrangement (Figure 4, Table 1). The angles subtended by the iron–nitrogen bond and the iron–phosphorus bonds deviate from 90° in an alternating fashion: N1-Fe1-P1 79.54(4), N1-Fe1-P2 97.31(4), N1-Fe1-P3 79.77(4), N1-Fe1-P4 97.13(4)°. The pyridine-iron-carbonyl moiety is linear (N1-Fe1-C22 177.55(8)°, Fe1-C22-O1 177.5(2)°). Whereas the iron–carbon bond length ($d$(Fe1–C22) = 1.739(2) Å) is virtually the same as in the related low-spin iron(II) complex of a tetraamine imine ligand ($NN_4$ donor set; $d$(Fe–C) = 1.73(2) Å),[8] the iron–nitrogen bond ($d$(Fe1–N1) = 2.143(2) Å) in **7** is significantly longer than with $NN_4$ coordination ($d$(Fe–N) = 2.02(1) Å), most likely a consequence of the severe tetrahedral distortion of the basal donors in **7**. The reason for the observed reactivity of **2**, with the reformation under different conditions of a bond that was split when **1** first reacted with iron(II), is as yet unclear. Whether

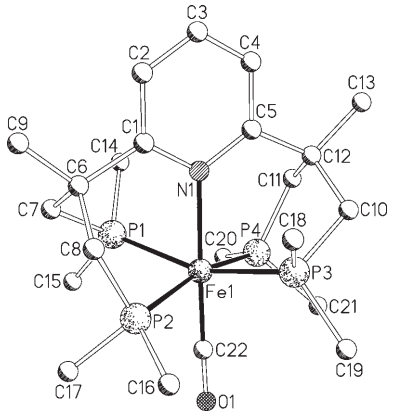



Figure 4. Structure of the dication in **7**·2 MeOH (hydrogen atoms omitted for clarity).

or not the process is intramolecular (and thereby entails breaking of the P–O bond in the phosphinite ligand, which, as such, should have considerable strength) or intermolecular (the required $PMe_2$ unit being provided by another equivalent of **2**, thereby explaining the presence of additional signals in the $^{31}P$ NMR spectrum of the mother liquor) is a question under current investigation.

## Conclusion

This study describes the unusual reactivity of the tetrapodal pentadentate phosphane ligand $C_5H_3N[CMe(CH_2PMe_2)_2]_2$ (**1**) towards iron(II). In methanol, the ligand undergoes selective cleavage of a methylene carbon–phosphorus bond, with concomitant formation of a phosphinite ligand, $Me_2POMe$. Given the relative inertness of tertiary alkyl phosphanes in other contexts (e.g., such compounds do not undergo alkali metal induced cleavage,[14] in contrast to aryl phosphanes or mixed aryl/alkyl phosphanes), the observed reactivity is all the more remarkable. The reaction product is an organometallic complex with a direct Fe–C bond or an agostic Fe-H-C interaction, depending on the reaction temperature and the nature of the counterion. The product containing the Fe–C bond reacts, in methanol under CO pressure, in such a way as to reform the intact ligand **1**, coordinated to iron(II), with a carbonyl ligand at the sixth coordination site. Current work is concerned with elucidating the mechanism of this unexpected reaction.

## Experimental Section

**Caution!** The perchlorate salt **4** is explosive in the solid state (see text). It should be prepared in quantities not exceeding 40 mg, and the utmost care must be exercised in its handling.

**Materials and instrumentation**: Unless noted otherwise, all reactions were carried out at room temperature in dried solvents under dry dinitrogen by using standard Schlenk techniques. $Fe(BF_4)_2 \cdot 6H_2O$ and $Fe(ClO_4)_2 \cdot 6H_2O$ were purchased from Aldrich and used without further purification. Carbon monoxide (99.997%) was purchased from Air Liquide. IR spectra of solids were measured by using KBr disks. IR spectra were assigned on the basis of literature data.[13] Spectroscopic data were obtained with the following instruments: IR spectroscopy: Nicolet Magna System 750; mass spectrometry: Varian 311 A and Spektrospin CMS FT-ICR; NMR spectroscopy: Bruker ARX 200 and Bruker ARX 400. Signs of coupling constants in the $^1H$, $^{13}C$, $^{19}F$ and $^{31}P$ spectra were not determined. Elemental analyses were carried out with a Thermo Finnigan, Flash EA, 1112 Series analyser. The superscripts for NMR assignments follow the numbering scheme adopted for the X-ray crystal structures (compounds **2**, **4**: Figure 2; compound **3**: Figure 1).

**X-ray crystallography**: Crystal data for **2**, **3**·0.5 MeOH, **4**, **6**·$H_2O$ and **7**·2 MeOH are given in Table 2, and selected distances and angles are listed in Table 1. Cation structures are presented in Figures 1–4. Compounds **2** and **4** are isostructural. Compounds **2**, **3** and **4** have centrosymmetric space groups (crystallisation of the racemate), whereas the space groups of compounds **6** and **7** are chiral (spontaneous resolution). Intensity data were collected at 100 K on a Bruker-Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, graphite monochromator). All structures were solved by direct methods and refined by full-matrix least-squares procedures on $F^2$ using SHELXTL NT 6.12 (Bruker AXS, 2002). All non-hydrogen atoms were refined anisotropically. Compounds **2**, **3**·0.5 MeOH (0.5 MeOH per formula unit) and **4** contain two symmetry-independent molecules in the asymmetric unit. Disorder: **2**: One of the $BF_4^-$ ions; two preferential orientations were refined (occupancy factors 72.8(8) and 27.2(8)%; atom pairs F23/F24 and F23′/F24′, respectively); **3**·0.5 MeOH: The O atom in the OMe group of one of the symmetry-independent cations; two preferential orientations refined (O2 28(2), O2′ 72(2)%); three $BF_4^-$ ions, two preferential orientations refined for each (see deposited CIF file); **4**: One of the $ClO_4^-$ ions; two preferential orientations refined (O23/O24 74.3(9), O23′/24′ 25.7(9)%); **7**: One of the $BF_4^-$ ions; two preferential orientations were refined (occupancy factors 69.7(8) and 30.3(8)%; atom pairs F23/F24 and F23′/F24′, respectively). Treatment of hydrogen atoms: **2**, **3**·0.5 MeOH, **4**, **6**: The positions of all H atoms were determined from a difference Fourier synthesis. The positional parameters were refined, and the isotropic displacement parameters tied to those of the respective carrier C atom or O atom by a factor of 1.2 or 1.5; **3**·0.5 MeOH: Only the H atoms of the methyl group (C44) bonded to the disordered O atom O2 and of the MeOH molecule of solvation were calculated in symmetry-optimised positions. **7**: All hydrogen atom positions were calculated by way of geometrical optimisation, and their isotropic displacement parameters tied to those of the respective carrier C atom or O atom by a factor of 1.2 or 1.5. CCDC-290737 (**2**), CCDC-275781 (**3**·0.5 MeOH), CCDC-275782 (**4**), CCDC-290738 (**6**·$H_2O$) and CCDC-290739 (**7**·2 MeOH) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**1**: A solution of $C_5H_3N[CMe(CH_2Br)_2]_2$[6] (5.1 g, 10 mmol) in diethyl ether (60 mL) was added from a dropping funnel to a suspension of $LiPMe_2 \cdot 0.5\,Et_2O$ (4.9 g, 47 mmol) in diethyl ether (80 mL) over 5 h at −70 °C. The mixture was allowed to warm to room temperature overnight. The colour changed from brown to red, and all solid dissolved. After distilling off the solvent, the yellow residue was treated with pentane (40 mL) and filtered. The light yellow solution was brought to dryness to yield a colourless oil (3.58 g, 83%). $^1H$ NMR (200 MHz, [D$_2$]dichloromethane, 25 °C, TMS): $\delta = 7.54$ (t, $^3J(H,H) = 7.8$ Hz, 1H; py-H$^4$), 7.12 (d, $^3J(H,H) = 7.9$ Hz, 2H; py-H$^{3,5}$), 1.87–2.14 (ddd, AB, $^2J(H,H) = 13.7$ Hz, $^2J(P,H) = 3.3$ Hz, 8H; $CH_2$), 1.53 (s, 6H; $CCH_3$), 0.76–0.91 ppm (2d, $^2J(P,H) = 2.8$ Hz, 24H; $PCH_3$); $^{13}C$ NMR (100.64 MHz, [D$_2$]dichloromethane, 25 °C, TMS): $\delta = 165.89$ (s, py-C$^{2,6}$), 136.12 (s, py-C$^4$), 117.79 (s, py-C$^{3,5}$), 48.67 (m, *C*CH$_3$), 44.41 (m, $CH_2$), 26.23 (s, *C*CH$_3$), 16.10 ppm (m, $PCH_3$); $^{31}P$ NMR (80.95 MHz, [D$_2$]dichloromethane, 25 °C, 85% $H_3PO_4$): $\delta = -59.69$ ppm (s, 4$PMe_2$); IR (KBr): $\tilde{\nu} = 2952$ (vs), 2893 (s), 1574 (s), 1429 (s), 1370 (s), 1292 (s), 939 (s), 903 (s), 703 cm$^{-1}$ (s); EI-MS (70 eV): *m/z* (%): 430 (100) [$M^+$–H].

**2**: A solution of $Fe(BF_4)_2 \cdot 6H_2O$ (205 mg, 0.607 mmol) in methanol (2.0 mL) was added over 10 min at −50 °C to a solution of **1** (262 mg, 0.607 mmol) in methanol (2.5 mL). The mixture was stirred at this tem-

Table 2. Crystal data for **2**, **3**·0.5 MeOH, **4**, **6**·$H_2O$ and **7**·2 MeOH.

| | **2** | **3**·0.5 MeOH | **4** | **6**·$H_2O$ | **7**·2 MeOH |
|---|---|---|---|---|---|
| molecular formula | $C_{22}H_{44}BF_4FeNOP_4$ | $C_{22.5}H_{47}B_2F_8FeNO_{1.50}P_4$ | $C_{22}H_{44}ClFeNO_5P_4$ | $C_{22}H_{46}B_2F_8FeNO_2P_4$ | $C_{24}H_{49}B_2F_8FeNO_3P_4$ |
| $M_r$ [g mol$^{-1}$] | 605.12 | 708.96 | 617.76 | 709.95 | 752.99 |
| crystal size [mm] | 0.23×0.23×0.14 | 0.33×0.24×0.19 | 0.20×0.17×0.15 | 0.21×0.14×0.10, green | 0.18×0.10×0.07 |
| colour | orange | red | orange | green | light yellow |
| $F$(000) | 2544 | 1476 | 2608 | 738 | 1568 |
| crystal system | monoclinic | triclinic | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) | $P2_1/c$ (no. 14) | $P2_1$ (no. 4) | $P2_12_12_1$ (no. 19) |
| $a$ [Å] | 11.129(1) | 10.2906(6) | 11.202(1) | 10.583(1) | 12.685(1) |
| $b$ [Å] | 13.350(2) | 15.4219(6) | 13.432(2) | 12.219(1) | 12.950(2) |
| $c$ [Å] | 38.271(2) | 19.7564(13) | 38.372(3) | 12.669(2) | 20.084(2) |
| $\alpha$ [°] | 90 | 91.306(5) | 90 | 90 | 90 |
| $\beta$ [°] | 95.598(6) | 90.493(6) | 95.447(5) | 110.149(7) | 90 |
| $\gamma$ [°] | 90 | 91.533(4) | 90 | 90 | 90 |
| $V$ [Å$^3$] | 5658.9(9) | 3133.3(3) | 5748(1) | 1538.0(3) | 3299.2(7) |
| $Z$ | 8 | 4 | 8 | 2 | 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.421 | 1.503 | 1.428 | 1.533 | 1.516 |
| $\mu$ [mm$^{-1}$] | 0.802 | 0.755 | 0.873 | 0.770 | 0.725 |
| absorption correction | SADABS | SADABS | numeric | SADABS | SADABS |
| $T_{min}/T_{max}$ | 0.843/1.000 | 0.874/1.000 | 0.859/0.901 | 0.863/1.000 | 0.929/1.000 |
| scan | $\phi$ and $\omega$ rotations with 0.6° and 72 s per frame | $\phi$ and $\omega$ rotations with 1.6° and 96 s per frame | $\phi$ and $\omega$ rotations with 0.6° and 57 s per frame | $\phi$ and $\omega$ rotations with 2.0° and 120 s per frame | $\omega$ rotations with 1.7° and 255 s per frame |
| 2$\theta$ range [°] | 6.4–54.2 | 7.0–55.8 | 6.8–54.2 | 6.6–57.4 | 6.6–55.0 |
| measured reflections | 41016 | 60891 | 62533 | 43654 | 42139 |
| unique reflections | 11137 | 14839 | 12364 | 7924 | 7553 |
| observed reflections[a] | 9054 | 12110 | 9639 | 7110 | 6657 |
| refined parameters | 896 | 1069 | 896 | 499 | 421 |
| w$R2$ (all data)[b] | 0.0781 | 0.0909 | 0.0777 | 0.0545 | 0.0581 |
| $R1$ (obsd data)[c] | 0.0381 | 0.0355 | 0.0375 | 0.0269 | 0.0272 |
| $\rho_{fin}$ (max/min) [e Å$^{-3}$] | 0.626/−0.489 | 0.897/−0.901 | 0.631/−0.448 | 0.318/−0.360 | 0.459/−0.303 |
| wighting scheme[d] | $k$=0.0267/$l$=7.0053 | $k$=0.0314/$l$=0.4873 | $k$=0.0317/$l$=4.6500 | $k$=0.0295/$l$=0 | $k$=0.0256/$l$=0.9662 |
| abs. struct. parameter | – | – | – | 0.013(7) | 0.01(1) |

[a] With $F_o \geq 4\sigma(F)$. [b] $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o \geq 4\sigma(F)$. [d] $w=1/[\sigma^2(F_o^2)+(kP)^2+lP]$ and $P=(F_o^2+2F_c^2)/3$.

perature for 1 h to give a red solution. After the solvent had been removed at this temperature, the residue was washed with diethyl ether (3×1 mL) and dried in vacuo to yield the product as a red powder (277 mg, 75%). $^1$H NMR (200 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$=7.77 (t, $^3J$(H,H)=7.8 Hz, 1H; py-H$^3$), 7.39 (d, $^3J$(H,H)=7.9 Hz, 1H; py-H$^2$), 7.27 (d, $^3J$(H,H)=7.9 Hz, 1H; py-H$^4$), 3.45 (d, $^3J$(P,H)=10.4 Hz, 3H; $OCH_3$$^{22}$), 2.14, 1.70 (m/m, 2H; $CH_2$$^7$), 2.10, 1.56 (m/m, 2H; $CH_2$$^{10}$), 2.01, 1.58 (m/m, 2H; $CH_2$$^8$), 1.93, 1.39 (m/m, 2H; $CH_2$$^{11}$), 1.69 (s, 3H; $CH_3$$^{13}$), 1.67 (s, 3H; $CH_3$$^9$), 1.64 (m, 3H; $PCH_3$$^{15}$), 1.62 (m, 3H; $PCH_3$$^{21}$), 1.55 (m, 3H; $PCH_3$$^{16}$), 1.54 (m, 3H; $PCH_3$$^{19}$), 1.52 (m, 3H; $PCH_3$$^{20}$), 1.47 (m, 3H; $PCH_3$$^{14}$), 0.52 (d, $^2J$(P,H)=6.5 Hz, 3H; $PCH_3$$^{17}$), 0.24 ppm (d, $^2J$(P,H)=6.5 Hz, 3H; $PCH_3$$^{18}$); $^{13}$C NMR (50.32 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$=176.80 (s, py-C$^5$), 169.77 (s, py-C$^1$), 138.50 (s, py-C$^3$), 120.48 (s, py-C$^4$), 119.93 (s, py-C$^2$), 55.88 (s, $C$$CH_3$$^{12}$), 50.75 (d, $^2J$(P,C)=63.8 Hz, $OCH_3$$^{22}$), 47.07 (m, $CH_2$$^{10}$), 45.50 (m, $CH_2$$^{11}$), 44.07 (m, $C$$CH_3$$^6$), 39.75 (m, $CH_2$$^8$), 39.50 (m, $CH_2$$^7$), 32.44 (m, $CH_3$$^{13}$), 30.88 (m, $CH_3$$^9$), 25.72 (m, $PCH_3$$^{15}$), 22.64 (m, $PCH_3$$^{20}$), 22.18 (m, $PCH_3$$^{21}$), 21.35 (m, $PCH_3$$^{14}$), 18.62 (m, $PCH_3$$^{16}$), 17.09 (m, $PCH_3$$^{18}$), 17.16 (m, $PCH_3$$^{19}$), 16.20 ppm (m, $PCH_3$$^{17}$); $^{31}$P NMR (80.95 MHz, [D$_4$]methanol, 25 °C, 85% $H_3PO_4$): $\delta$=178.18 (m, P$^4$Me$_2$OMe), 44.05 (m, P$^2$), 34.29 (m, P$^3$), 18.36 ppm (m, P$^1$); $^{19}$F NMR (188.31 MHz, [D$_4$]methanol, 25 °C, $CFCl_3$): $\delta$=−147.91 ppm (s, $BF_4^-$); IR (KBr): $\tilde{\nu}$=2974 (m), 2923 (m), 1598 (m), 1463 (s), 1296 (s), 1053 (vs) ($BF_4^-$), 935 (s), 912 (s), 731 cm$^{-1}$ (s); ESI MS: $m/z$ (%): 518 (100) [$M^+$], 87 (100) [$BF_4^-$]; elemental analysis (%) calcd for $C_{22}H_{44}BF_4FeNOP_4$ (605.1): C 43.67, H 7.33, N 2.31; found: C 43.88, H 7.19, N 2.17.

**3**: A solution of $Fe(BF_4)_2$·6$H_2O$ (28 mg, 0.08 mmol) in methanol (1.5 mL) was added over 30 min at room temperature to a solution of **1** (36 mg, 0.08 mmol) in methanol (2 mL). The reaction mixture was stirred for 4 h, during which it deposited a red microcrystalline precipitate. The product was filtered off and washed with methanol (2×1.5 mL) to yield a red solid (46 mg, 80%). $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta$=8.06 (t, $^3J$(H,H)=4.0 Hz, 1H; py-H$^3$), 7.70 (d, $^3J$(H,H)=3.9 Hz, 1H; py-H$^2$), 7.50 (d, $^3J$(H,H)=3.9 Hz, 1H; py-H$^4$), 3.42 (d, $^3J$(P,H)=11.4 Hz, 3H; $OCH_3$$^{22}$), 2.69, 2.28 (m/m, 2H; $CH_2$$^{10}$), 2.29, 1.88 (m/m, 2H; $CH_2$$^7$), 1.89, 1.70 (m/m, 2H; $CH_2$$^8$), 1.96 (m, 3H; $PCH_3$$^{21}$), 1.90 (m, 3H; $PCH_3$$^{20}$), 1.81 (m, 3H; $PCH_3$$^{15}$), 1.75 (s, 3H; $CH_3$$^9$), 1.69 (m, 3H; $PCH_3$$^{18}$), 1.58 (s,

3H; $CH_3$[13]), 1.43 (d, $^2J$(P,H) = 9.8 Hz, 3H; $PCH_3$[16]), 1.16 (d, $^2J$(P,H) = 10.0 Hz, 3H; $PCH_3$[17]), 0.63 (m, 6H; $PCH_3$[19,14]), −3.75 ppm (s, 3H; $CH_3$[11]); $^{13}$C NMR (50.32 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta$ = 168.32 (s, py-C[5]), 166.48 (s, py-C[1]), 140.36 (s, py-C[3]), 122.14 (s, py-C[4]), 121.82 (s, py-C[2]), 51.15 (d, $^2J$(P,C) = 57.7 Hz, $OCH_3$[22]), 42.85 (s, $CCH_3$[6]), 42.33 (s, $CCH_3$[12]), 41.03 (m, $CH_2$[10]), 35.82 (m, $CH_2$[8]), 32.73 (m, $CH_2$[7]), 32.68 (m, $CH_3$[9]), 30.00 (m, $CH_3$[11]), 26.92 (m, $CH_3$[13]), 20.98 (m, $PCH_3$[20,21]), 19.98 (m, $PCH_3$[16]), 16.49 (m, $PCH_3$[17]), 16.25 (m, $PCH_3$[14]), 15.22 (m, $PCH_3$[15]), 14.87 (m, $PCH_3$[19]), 12.95 ppm (m, $PCH_3$[18]); $^{31}$P NMR (80.95 MHz, [D$_6$]DMSO, 25 °C, 85 % $H_3PO_4$): $\delta$ = 174.50 (m, P$^4$Me$_2$OMe), 50.29 (m, P$^2$), 27.71 (m, P$^3$), 17.04 ppm (m, P$^1$); $^{19}$F NMR (188.31 MHz, [D$_4$]methanol, 25 °C, $CFCl_3$): $\delta$ = − 147.89 ppm (s, $BF_4^-$); IR (KBr): $\tilde{\nu}$ = 2966 (s), 2918 (s), 1598 m, 1462 (s), 1310 (s), 1054 (vs, $BF_4^-$), 940 (s), 917 (s), 733 cm$^{-1}$ (s); ESI MS: *m/z* (%): 518 (100) [$M^+$−H], 214 (10) [$M^{2+}$−PMe$_2$OMe], 87 (100) [$BF_4^-$]; elemental analysis (of single-crystalline material dried in vacuo to remove methanol of solvation) calcd (%) for $C_{22}H_{45}B_2F_8FeNOP_4$ (692.9): C 38.13, H 6.55, N 2.02; found: C 38.35, H 6.43, N 1.99.

**4**: A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (25 mg, 0.07 mmol) in methanol (1.5 mL) was added over about 10 min at room temperature to a solution of **1** (32 mg, 0.07 mmol) in methanol (2 mL). The solution spontaneously turned orange and was then stirred for a further 2 h at room temperature. The solvent was reduced in volume to about 1.5 mL. Isothermal diffusion of diethyl ether, filtration and washing with diethyl ether (3 × 1.5 mL) yielded the product as a microcrystalline orange powder (34 mg, 74 %). $^1$H NMR (200 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$ = 7.77 (t, $^3J$(H,H) = 7.9 Hz, 1H; py-H[3]), 7.41 (d, $^3J$(H,H) = 8.0 Hz, 1H; py-H[2]), 7.27 (d, $^3J$(H,H) = 8.0 Hz, 1H); py-H[4]), 3.50 (d, $^3J$(P,H) = 10.4 Hz, 3H; $OCH_3$[22]), 2.12, 1.68 (m/m, 2H; $CH_2$[7]), 2.08, 1.56 (m/m, 2H; $CH_2$[10]), 2.05, 1.62 (m/m, 2H; $CH_2$[8]), 1.95, 1.42 (m/m, 2H; $CH_2$[11]), 1.71 (s, 3H; $CH_3$[13]), 1.69 (s, 3H; $CH_3$[9]), 1.63 (m, 3H; $PCH_3$[15]), 1.62 (m, 3H; $PCH_3$[21]), 1.56 (d, $^2J$(P,H) = 6.5 Hz, 3H; $PCH_3$[16]), 1.55 (d, $^2J$(P,H) = 6.0 Hz, 3H; $PCH_3$[19]), 1.51 (d, $^2J$(P,H) = 6.5 Hz, 3H; $PCH_3$[20]), 1.46 (br, 3H; $PCH_3$[14]), 0.54 (d, $^2J$(P,H) = 6.4 Hz, 3H; $PCH_3$[17]), 0.25 ppm (d, $^2J$(P,H) = 6.6 Hz, 3H; $PCH_3$[18]); $^{13}$C NMR (50.32 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$ = 177.11 (s, py-C[5]), 169.98 (s, py-C[1]), 138.64 (s, py-C[3]), 120.71 (s, py-C[4]), 120.10 (s, py-C[2]), 56.19 (s, $CCH_3$[12]), 50.86 (d, $^2J$(P,C) = 63.7 Hz, $OCH_3$[22]), 47.28 (m, $CH_2$[10]), 45.50 (m, $CH_2$[11]), 44.37 (m, $CCH_3$[6]), 39.77 (m, $CH_2$[8]), 39.76 (m, $CH_2$[7]), 32.83 (m, $CH_3$[13]), 30.49 (m, $CH_3$[9]), 26.04 (m, $PCH_3$[15]), 22.80 (m, $PCH_3$[20]), 22.51 (m, $PCH_3$[21]), 21.55 (m, $PCH_3$[14]), 18.95 (m, $PCH_3$[16]), 17.42 (m, $PCH_3$[18]), 17.41 (m, $PCH_3$[19]), 16.50 ppm (m, $PCH_3$[17]); $^{31}$P NMR (80.95 MHz, [D$_4$]methanol, 25 °C, 85 % $H_3PO_4$): $\delta$ = 178.61 (m, P$^4$Me$_2$OMe), 43.51 (m, P$^2$), 34.42 (m, P$^3$), 18.44 ppm (m, P$^1$); IR (KBr): $\tilde{\nu}$ = 2919 (s), 1596 (m), 1461 (m), 1293 (m), 1095 (vs, $ClO_4^-$), 1025 (s), 897 (s), 716 cm$^{-1}$ (s); ESI MS: *m/z* (%): 518 (100) [$M^+$], 99 (100) [$^{35}ClO_4^-$], 101 (32) [$^{37}ClO_4^-$]; elemental analysis (%) calcd for $C_{22}H_{44}ClFeNO_5P_4$ (617.8): C 42.77, H 7.18, N 2.27; found C 42.55, H 7.03, N 2.13.

**6**: A stoichiometric amount of dioxygen (2.46 mL, 0.110 mmol) was injected by syringe into a solution of agostic iron complex **3** (305 mg, 0.440 mmol) in methanol (5.0 mL). The solution was stirred at room temperature for 10 min, during which time its colour changed from red to green. After removal of the solvent the residue was washed with diethyl ether (3 × 2 mL) to yield the product as a dark green microcrystalline powder (289 mg, 95 %). ESI MS: *m/z* (%): 259 (100) [$M^{2+}$], 87 (100) [$BF_4^-$]; elemental analysis (of single-crystalline material dried in vacuo to remove water of solvation) calcd (%) for $C_{22}H_{44}B_2F_8FeNOP_4$ (691.9): C 38.19, H 6.41, N 2.02; found: C 37.76, H 6.61, N 1.85.

**7**: An autoclave (volume: 200 mL) was charged with a red solution of **2** (95 mg, 0.16 mmol) in methanol (20 mL) and CO (10.5 bar), and the mixture heated to 80 °C for 12 h. After the mixture had been cooled to room temperature, the pressure was released; the yellow solution that had formed was reduced in volume to about 5 mL and cooled to 2 °C to precipitate a yellow single-crystalline solid (13 mg, 12 %). $^1$H NMR (200 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$ = 8.22 (t, $^3J$(H,H) = 7.4 Hz, 1H; py-H[4]), 8.08 (d, $^3J$(H,H) = 7.4 Hz, 2H; py-H[3,5]), 2.65–1.97 (dd, AB, $^2J$(H,H) = 18.0 Hz, 8H; $CH_2$), 1.95–1.43 (m, 24H; $PCH_3$), 1.28 ppm (s, 6H; $CCH_3$); $^{13}$C NMR (100.64 MHz, [D$_4$]methanol, 25 °C, TMS): $\delta$ = 214.62 (quintet, $^2J$(P,C) = 27.6 Hz, CO), 169.38 (s, py-C[2,6]), 142.84 (s, py-C[4]), 126.50 (s, py-C[3,5]), 46.48 (s, $CH_2$), 35.23 (s, $CCH_3$), 18.25 ppm (m, $PCH_3$), $CCH_3$ obscured by solvent signal; $^{31}$P NMR (80.95 MHz, [D$_4$]methanol, 25 °C, 85 % $H_3PO_4$): $\delta$ = 19.00 ppm (s, 4P$Me_2$); $^{19}$F NMR (188.31 MHz, [D$_4$]methanol, 25 °C, $CFCl_3$): $\delta$ = − 153.73 ppm (s, $BF_4^-$); IR (KBr): $\tilde{\nu}$ = 2980 (s), 2924 (s), 1969 (vs) (CO), 1596 (s), 1455 (s), 1322 (s), 1057 (vs) ($BF_4^-$), 947 (s), 918 cm$^{-1}$ (s); ESI MS: *m/z* (%): 258 (28) [$M^{2+}$], 244 (12) [$M^{2+}$−CO], 87 (100) [$BF_4^-$]; elemental analysis calcd (%) for $C_{22}H_{41}B_2F_8FeNOP_4$ (688.9): C 38.36, H 6.00, N 2.03; found C 38.69, H 5.91, N 1.93.

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