From Ylides to Doubly Yldiide-Bridged Iron(II) High Spin Dimers via Self-Protopolysis

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Supporting Information

ABSTRACT: A synthetic strategy for the preparation of novel doubly yldiide bridged iron(II) high spin dimers [(μ2-C)FeL]2, L = N(SiMe3)2, Mesityl) has been developed. This includes the synthesis of ylide-iron(II) monomers [(Ylide)-FeL] via adduct formation. Subsequent self-protolysis at elevated temperatures by in situ deprotonation of the ylide ligands results in a dimerization reaction forming the desired bridging μ2-C yldiide ligands in [(μ2-C)FeL]2. The comprehensive structural and electronic analysis of dimers [(μ2-C)FeL]2 including NMR, Mössbauer, and X-ray spectroscopy, as well as X-ray crystallography, SQUID, and DFT calculations, confirm their high-spin FeII configurations. Interestingly, the Fe2C2 cores display very acute Fe-C bond angles (averaged: 78.6°) resulting in short Fe–Fe distances (averaged: 2.588(2) Å). A remarkably strong antiferromagnetic coupling between the Fe centers has been identified. Strongly polarized Fe-C bonds are observed where the negative charge is mostly centered at the μ2-C yldiide ligands.

INTRODUCTION

Nitrogenases are the only enzymes that are capable of reducing atmospheric N2 to NH3. This conversion occurs at a heterometallic Fe3Mo7S9C cluster, known as FeMoco, which contains a very unique interstitial μ2-carbide ligand (Chart 1A).3 Biosynthetically, the carbide ligand originates from the iron sulfur cluster via a radical mechanism.3 While the role of the carbide ligand for the catalytic activity of the FeMoco is unknown, it has been postulated to function as a stabilizing anchor for the cluster,4 to allow for facile modulation of the belt iron interactions during substrate binding,5 and even to form transient C–H bonds during catalysis.6 However, a detailed understanding of the exact role of the carbide is in part limited by the absence of any synthetic models which support both a μ2-carbide ligand and locally high-spin ferrous (and ferric) iron atoms.7 In fact, synthetic strategies that allow the introduction of C-based ligands bonded to more than one Fe atom (μ2,μ3-C-based ligands) are very rare, explaining the lack of suitable model systems. Known strategies are, for example, the conversion or substitution of CO ligands in polyiron-carbonyl clusters into μ2, μ3, or μ3-C ligands to yield, e.g., clusters of type B (Chart 1).8 Interestingly, these clusters contain strong-field CO ligands and are low-spin complexes, in contrast to the sulfide ligated high spin iron sites in FeMoco. Carbido bridged, diamagnetic porphyrinato (C) and phthalocyanato Fe dimers have been synthesized using Cl4 as a μ2-C2− ligand source, yielding high-valent FeIV sites.9 In addition, a dimeric but low spin [1,2,4-Bu(C5H4)FeH(μ2-C2-C)]2 complex containing μ2-C ligands was synthesized by alkyne insertion into an Fe≡Fe double bond.10 In addition, a small number of low coordinated, high spin Fe dimers bridged by singly charged μ2-C− ligands were prepared by using (H2C)Li or ArylLi as [H2C]− and [Aryl]− sources functioning as two electron donor ligands.11–13 Recently, Holland and co-workers have reported on the synthesis of the singly alkylidene bridged high-spin FeII dimer of type D by using diazoalkanes as a μ2-C ligand source, formally having been a four electron donor ligand.14

In this contribution, we report on the development of a new synthetic strategy for generating μ2-C2− yldiide ligands that support the coordination of high-spin iron, which enabled the preparation of novel doubly yldiide-bridged iron(II) high spin complexes. This has been accomplished by starting from novel low-coordinated FeII–ylide complexes of type E containing both a strongly basic ligand (L) and a H-acidic ylide ligand facilitating self-protopolysis and subsequent dimerization yielding dinuclear complexes of type F. The well-established chemistry of isolable ylides containing, e.g., phosphonio or imidazoliumyl substituents as electron withdrawing groups (EWG) allows precise substituent adjustment,15 rendering these as potential precursors for μ2-C2− ligands.
RESULTS AND DISCUSSION

The reaction of the phosphorus ylides 1a and 1b or the related N-heterocyclic olefin (NHO) 1c with [Fe(N(SiMe3)2)2] results in the quantitative formation of the FeII−ylide adducts 2a−2c, which are isolated in good yields (Scheme 1). The molecular structures for all three congeners were determined by X-ray crystallography and show a distorted trigonal planar coordination environment around the Fe atom (Figure 1). The N−Fe−N angles decrease with higher steric demand of the ylide (1b > 1a > 1c, see Table 1).16

Interestingly, the Fe−C bonds in all three FeII−ylide complexes which are at 2.158(6) Å (2a), 2.176(2) Å (2b), and 2.159(3) Å (2c), respectively, are longer than the Fe−C bond distances in the related tricoordinated alkyl substituted [LFeR] complexes reported by the groups of Hessen and Holland (L = bulky β-diketiminate ligand, R = Me, iPr, CH2tBu, benzyl; Fe−C: 2.009(3)−2.048(3) Å)17 or in the anionic congener [(Me3Si)CH2Fe(N(SiMe3)2)2][Na(NHC Dipp)], which is at 2.065 Å.18 This observation points to a weaker donor strength of the ylide ligands. In the case of the Ph3P substituted complexes 2a and 2b, this can be explained by the strong negative hyperconjugation of the lone pair of the ylidic C atoms into the σ*−P−CPh bonds, as indicated by the shortened C−P bonds (∑covalent_radii(C,P): 1.83 Å) of 1.751(6) Å and 1.736(1) Å in 2a and 2b, respectively.19 In the NHO substituted complex 2c, the ylidic lone pair is strongly involved in forming the π−C−C2 bond at 1.417(5) Å, which is in between the expected values for a C−C single bond (1.54 Å) and a double (1.34 Å) bond.20 This delocalization decreases the overall ylide donor strength in 2c.15c The widened Fe−C−P angles of 133.4(5)° and 120.35(7)° in 2a and 2b, respectively, can be explained by the steric repulsion of the Ph3P and the N(SiMe3)2 groups.

The paramagnetic character of complexes 2a−2c is manifested in the broad and paramagnetically shifted resonances observed in their 1H NMR spectra. No resonances could be found in the 31P and 29Si NMR spectra of 2a and 2b due to paramagnetism. The solution magnetic susceptibilities determined at room temperature by Evan’s method21 are calculated to be 4.9 μB, 5.2 μB, and 5.5 μB for 2a−2c, respectively. These values are all close to the expected value of 4.9 μB for high-spin FeII complexes (S = 2). The 57Fe Mössbauer spectra of 2a−2c recorded at 80 K display isomer shifts ranging from δ = 0.51 to 0.55 mm/s (see Supporting Information (SI), Figures S9−S11), which are typical values for tricoordinated FeII centers in high-spin configurations and are comparable to the shift observed in [LFeMe] (L = bulky β-diketiminate ligand, δ = 0.48 mm/s).7c In contrast, the quadrupolar splittings of ΔEQ = 0.92, 0.73, and 1.14 mm/s for 2a−2c, respectively, deviate significantly from the quadrupole splitting of ΔEQ = 1.74 mm/s determined for [LFeMe]. We note that no Mössbauer has

Figure 1. Molecular structures of 2a−2c. Selected hydrogen atoms are omitted for clarity; thermal ellipsoids are displayed at 50% probability.
Table 1. Selected Geometrical Parameters for the Crystallographically Characterized Iron Complexes 2a–2c (Bond Lengths in Å and Angles in Degrees)

|       | Fe–C   | Fe–N   | C–P/C2  | N–Fe–N | Fe–C–P/C2  | angle sum Fe |
|-------|--------|--------|---------|---------|------------|-------------|
| 2a    | 2.158(6) | 1.963(5) | 1.962(5) | 1.751(6) | 127.8(4)   | 133.4(5)    |
| 2b    | 2.176(1) | 1.954(1) | 1.970(1) | 1.736(1) | 122.63(7)  | 120.35(7)   |
| 2c    | 2.159(3) | 1.939(3) | 1.950(3) | 1.417(5) | 133.6(2)   | 115.2(2)    |

aSix selected molecules in unit cell; only one molecule is considered due to nonsignificant differences in structural parameters. \( C_2 \) atom in complex 2c.

been reported for the other known dialkyl- or diaryl-bridged diiron compounds.\(^{11-13}\)

Complexes 2a–2c are extremely air and moisture sensitive and readily decompose in solvents such as CH\(_2\)Cl\(_2\), CHCl\(_3\), and CH\(_3\)CN, which is probably due to the high reactivity of the weak Fe–C bond in 2a–2c. This hypothesis is nicely corroborated by the formal insertion of benzonitrile into the Fe–C bond of 2a. Subsequent proton migration from the ylidy C atom to the nitrile N atom yields complex 3 (Scheme 2). Due to its high reactivity and thermal instability complex 2a is lost in the reaction mixture at ambient temperature, 3 was not isolated in larger amounts. However, suitable single crystals for X-ray crystallography of 3 were obtained from a PhCN/n-pentane mixture at \(-35 ^\circ C\) showing the E isomer with a distorted trigonal planar coordination environment around the Fe atom (angle sum around Fe: 359.8(2)°; Figure 2). Both, the

Figure 2. Molecular structure of 3 (selected hydrogen atoms omitted for clarity, thermal ellipsoids displayed at 50% probability). Selected bond lengths in Å and angles in degrees: Fe1–N1 2.018(1), Fe1–N51 1.949(1), Fe1–N61 1.945(1), N1–C2 1.328(2), C2–C3 1.398(2), C3–P4 1.723(1).

shortened N1–C2 (1.328(2) Å), C2–C3 (1.398(2) Å), and C3–P4 (1.723(1) Å) bond lengths in 3 as well as the planarity of the N1–C2–C3–P4 unit (torsion angle 0.1(3)°) indicate a significant \( \pi \)-delocalization over this fragment. The presence of basic amido- and a H-acidic ylide ligands in 2a–2c should allow for an intramolecular deprotonation reaction generating an additional donor site at the ylide–C atom. Attempts to induce such a self-protolysis reaction by refluxing solutions of 2a–2c in toluene, THF, or C\(_6\)H\(_5\)F were unsuccessful and yielded deep brown reaction mixtures of unidentifiable products. However, melting solid 2a at 135 °C results in condensation of a colorless liquid at the glass wall and the formation of a brown sticky residue. The colorless product is identified as HN-(SiMe\(_3\))\(_2\) (Scheme 3, 1), while recrystallization of the brown residue from CH\(_2\)Cl\(_2\) results in the formation of analytically pure, orange-brown block-like crystals which are composed of the desired doubly ylidiide-bridged Fe\(^{II}\) dimer 4 (isolated yield: 27%). Following the same synthetic approach for 2b and 2c resulted in the formation of an unidentifiable reaction mixture.

However, a second ylidiide-bridged iron dimer can be prepared by reacting a fluorobenzene solution of 1a with \([\text{Fe(Mes})\(_2\)]\(_2\)\(^{13}\) (Mes = 2,4,6-trimethylphenyl) instead of \([\text{Fe(N(SiMe})\(_3\))\(_2\])\(_2\)\) as an iron precursor. In analogy to the basic N(SiMe\(_3\))\(_2\) ligands, the mesityl ligands in \([\text{Fe(Mes})\(_2\)]\(_2\) act as proton acceptors inducing the self-protolysis reaction (Scheme 3, II). Upon the addition of two equivalents of 1a to a red solution of \([\text{Fe(Mes})\(_2\)]\(_2\), an immediate color change to yellow is observed. The \(^1\)H NMR spectrum of the reaction mixture shows the presence of four broad resonances, presumably due to the formation of monomer 5 (Scheme 3, see also SI, Figure S7). These resonances decrease in intensity upon heating to 85 °C accompanied by the appearance of eight new resonances with increasing intensity over time. Six of those rising resonances are assigned to the doubly yldiide-bridged Fe\(^{II}\) dimer 6, and the residual two resonances correspond to the couple product mesitylene. After 1 h,
quantitative conversion to 6 is observed, resulting in a deep brown reaction solution from which brown needle-shaped crystals are isolated after layering it with n-hexane (yield: 60%). Attempts to isolate analogous Fe$_2$C$_2$-dimers from reactions of 1b and 1c with with [Fe(Mes)$_2$]$_2$ were not successful. The molecular structures of 4 and 6 display centrosymmetric Fe dimers, containing a Fe$_2$C$_2$-diamond core (Figure 3). A distorted trigonal planar bonding environment is observed for the iron atoms (angle sum around Fe: 360°, see Table 2), whereas the endocyclic C atoms render a distorted tetrahedral geometry. The Fe–C bonds at 2.050(5) Å and 2.046(4) Å in 4 and 2.037(2) Å and 2.039(2) Å in 6 are slightly shorter than those found in the precursors 2a and 2b. However, they are significantly longer than those observed in the alkylidene bridged Fe$^0$ dimer D reported by Holland et al. (Chart 1, Fe–C 1.973(6) Å, 1.956(6) Å)$^{14}$ and are of a comparable length to those observed in the nitrogenase FeMoco (averaged: 2.00 Å).$^{25}$ Remarkable is the very acute Fe–C–Fe angle in 4 (78.58(16)$^\circ$) and 6 (78.64(6)$^\circ$). For comparison, the related and literature known thiolato- and amido-bridged Fe$^{II}$ dimers 7 and 8 (Figure 3) render slightly larger Fe–S–Fe (84.34(2)$^\circ$)$^{22}$ and Fe–N–Fe (79.4(1)$^\circ$)$^{23}$ angles, respectively.

The acute Fe–C–Fe angles in 4 and 6 result in a very short Fe···Fe distance of 2.5939(12) Å and 2.5826(5) Å, respectively, being far below the covalent radii of two Fe high spin atoms ($\sum_{\text{covalent radii}}$: 3.04 Å).$^{19a}$ Larger Fe···Fe distances are observed in 7 (3.209(4) Å) and 8 (2.715(1) Å). The $^1$H and $^{31}$C($^1$H) NMR spectra of 4 and 6 display broad and paramagnetically shifted resonances which are nevertheless unambiguously assignable (see SI).

Noticeably, the resonances of the ylidic C–H protons in 4 and 6 are strongly downfield shifted at $\delta = 131.58$ and 144.31 ppm, respectively. No resonances can be found in the $^{31}$P and $^{29}$Si NMR (for 4) spectra due to paramagnetism. The zero field $^{57}$Fe Mössbauer spectra of solid 4 and 6 at 80 K show a single quadrupole doublet at $\delta = 0.35$ and 0.24 mm/s with quadrupolar splittings of $\Delta E_Q = 1.75$ and 1.95 mm/s, respectively (Figure 4, top). The solid-state SQUID measure-

Table 2. Selected Geometrical Parameters for the Crystalllographically Characterized Iron Complexes 4 and 6 (Bond Lengths in Å and Angles in Degrees)

|              | Fe–Fe  | Fe–C    | Fe–N/C41$^a$ | C–P    | Fe–C–Fe | C1–Fe–C1$^b$ | angle sum (Fe) |
|--------------|--------|---------|-------------|--------|---------|-------------|---------------|
| 4            | 2.5939(12) | 2.050(5) | 2.046(4) | 1.94(4) | 1.695(4) | 78.58(16) | 101.42(16) |
| 6            | 2.5826(5) | 2.037(2) | 2.039(2) | 2.037(2) | 1.705(2) | 78.64(6) | 101.36(6) |

$^a$C41 atom in complex 6.

Figure 4. Top: Zero field $^{57}$Fe Mössbauer spectra of solid 4 (left) and 6 (right) recorded at 80 K. The solid lines represent fits with $\delta = 0.35$ mm/s and $\Delta E_Q = 1.75$ mm/s for 4 and $\delta = 0.24$ mm/s and $\Delta E_Q = 1.95$ mm/s for 6. Bottom: Temperature dependent $\mu_{\text{eff}}$ for 4 (left) and 6 (right) at a field of 1.0 T. The solid lines represent spin-Hamiltonian simulations (fit parameters for 4: $J = −219$ cm$^{-1}$, $g_1 = g_2 = 2.2$, $\Pi = 7.5$%, TIP = 1.284 × 10$^{-6}$ cm$^{-3}$ mol$^{-1}$; fit parameters for 6: $J = −262$ cm$^{-1}$, $g_1 = g_2 = 2.0$, $\Pi = 7.5$%, TIP = 165 × 10$^{-6}$ cm$^{-3}$ mol$^{-1}$).
The normalized XAS spectrum is displayed in Figure 5 and shows a pre-edge feature at 7112.4 eV originating from the dipole forbidden 1s to 3d transition typically observed for high-spin FeII centers.24 The additional intense feature at 7116.2 eV can be assigned to the dipole allowed Fe 1s to 4p transition, where the ligands around the Fe atoms lie in the xy plane. This transition is characteristic for the trigonal planar coordination environment of the Fe atoms.25 To obtain further insight into the electronic nature of 4 and 6, broken-symmetry DFT calculations have been performed using the TPSSh functional. The geometry optimized structures of the full models accurately reproduce the molecular structures derived from X-ray crystallography with calculated Fe···Fe distances of 2.568 and 2.557 Å for 4 and 6, respectively (2.5939(12) Å and 2.5826(5) Å found by X-ray crystallography). Localized magnetic molecular orbitals (LMMO)26 were chosen to investigate the antiferromagnetic coupling between both iron centers following the analysis concept of Ye et al.27 The frontier orbitals with significant d character are displayed in Figure 6 for compound 4 (for 6, see SI, Figure S12). Both iron centers reveal a doubly occupied dxy orbital, whereas each dxz, dyz, dx2−y2, and dz2 orbital is singly occupied, consistent with a high spin FeII assignment.

The LMMO (Figure 6) for the dxz and dyz pairs shows strong localized iron character (>95%) depending on their spin-state as a result of the antiferromagnetic coupling. In contrast to that, the high-valent dx2−y2 and dz2 pairs behave rather covalently with strong interaction between the metals and carbide ligands, respectively. A similar trend of increasing covalency of the high-valent MOs was previously studied by Ye and co-workers for antiferromagnetic coupled mononucleoid transition metal complexes.27,28 This indicates a mechanism for strong antiferromagnetic coupling in which the Fe···Fe interactions are formed by (a) direct σ-bond interaction of the dx2−y2 pair and (b) the Fe···C interactions provided over the ylide ligands for both the dxz and the dyz pair. This magnetic exchange coupling results in a diamagnetic ground state (S0 = 0), consistent with the SQUID measurements. The Yamaguchi spin-projection formula29 was used to calculate antiferromagnetic Heisenberg coupling constants of J = −372 cm−1 and J = −429 cm−1 for 4 and 6, respectively, which qualitatively fits with the values observed for the SQUID measurements. We note that a predicted overestimation of the computed J values relative to experiment is quite common for single reference DFT methods.30 The bonding interactions in 4 and 6 were analyzed by Pipek-Mezey localized orbitals displaying a strong Fe−C interaction (BFe-C > 0.65), whereas the Fe−Fe interaction (BFe-Fe < 0.18) is comparatively weak, additionally attested by the Mayer bond-order analysis (see SI, Table S2).21 The endocyclic Fe−C bonds reveal “pear shaped” localized orbitals that indicate a strong polarization of these bonds where the binding pairs of electrons are mainly localized on the bridging C atoms (Figure 7). This is further reflected by the position of the charge centroid depicted as small red dots centered at the carbon atoms. The depicted localized orbitals are comprised of 19−26% Fe character and 81−74% C character.

■ CONCLUSION

The synthesis of the doubly ylide bridged FeII dimers 4 and 6 is presented facilitated by the self-protolysis reaction of low coordinated ylide-FeII high-spin complexes 2a−2c. Dimers 4 and 6 represent the first examples of ylide-supported Fe2C2−...
clusters is an ongoing research subject in our group. Nitrogenase. The synthesis of such sulfur-ligated \(\text{[Fe}_2\text{C}_2]\) would yield very promising synthetic model systems for potassium) were employed. Deuterated benzene \((\text{C}_6\text{D}_6)\) was used to account for two electrons. Each dot accounts for two electrons.

**EXPERIMENTAL SECTION**

**General Remarks.** All manipulations were performed in a glovebox (MBrown Lahnmaster pro ECO) under an atmosphere of nitrogen or using Schlenk techniques under an atmosphere of purified argon. Dry, oxygen-free solvents \((\text{CH}_2\text{Cl}_2, \text{CH}_3\text{CN, CH}_4\text{F (distilled from CaH}_2); \text{Et}_2\text{O, toluene, THF (distilled from potassium/benzophenone); and n-hexane and n-pentane (distilled from potassium)}) were employed. Deuterated benzene \((\text{C}_6\text{D}_6)\) was purchased from Sigma-Aldrich. All distilled, recondensed, and degassed and recondensed prior to use. \([\text{Fe}(\text{N(SiMe}_3)_2)_2]\) were degassed and recondensed prior to use. \([\text{Fe}(\text{N(SiMe}_3)_2)_2]\)

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antiferromagnetic broken symmetry solution with \( M_0 = 0 \). The localised orbitals were calculated using the Pipek–Mezey scheme. X-ray Crystal Structure Determination. Suitable single crystals of 2a–2c, 3, 4, and 6 were coated with perfluoropolyether (PF0-4XR75), picked up with nylon loops, and immediately mounted in the nitrogen cold stream of the diffractometers at 100 K. A Bruker Nonius KappaCCD diffractometer with a Mo-rotating-anode X-ray source and Incoatec Helios focusing multilayer optics and a Bruker kappa Mach3 APEX-II diffractometer with a Bruker IGS and Incoatec Helios mirror was used (Mo Kα radiation; \( \lambda = 0.71073 \) Å). Final cell constants were obtained from least-squares fits of setting angles of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections using SADABS. The structures were readily solved by direct and Patterson methods and subsequent difference Fourier techniques. The Bruker SHEXL2010 software package was used for solution, refinement, and artwork of the structures. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystal and data collection details are given in Tables S3 and S4 (see SI). The \( \left[\left(\text{SiMe}_3\right)_2\text{Fe}\right]_2^+ \) unit of 2a was found to be severely disordered. A split atom model with restrained bond distances and displacement parameters using the EADP, SAME, and ISOR instructions of SHEXL was refined to account for the disorder (293 restraints; 0.52/0.48 occupation ratio). A SiMe\(_3\) group in the structure of 2c was also disordered and treated similarly (31 restraints; 0.67/0.33 occupation ratio). Crystals of 2c contained a severely disordered fluorobenzene molecule, which was removed using Platon/SQUEEZE.

Preparation of \([\text{Ph}_3\text{PCH}_2\text{Fe}(\text{N(SiMe}_3)_2)_2]\) (2a). A solution of \(\left[\text{Fe}(\text{N(SiMe}_3)_2)_2\right]\) (1.51 g, 4.00 mmol) in THF (5 mL) was added to a stirring solution of \(\text{Ph}_3\text{PCH}_2\) (1.11 g, 4.00 mmol) in THF (5 mL), and the resulting light green reaction mixture was stirred for 1 h at ambient temperature. All volatiles were removed in vacuo to afford a colorless solid. \(\text{Ph}_3\text{PCH}_2\) (2 mL) was added to give an almost clear solution that was filtered. (Me\(_3\)Si)\(_2\)O (2 mL) was added to the filtrate, and the mixture was stored at \(-35 \) °C for 7 days to give large amounts of crystalline material. The supernatant was removed by decantation, and the residue was dried in vacuo to give 2a as highly air sensitive colorless crystals. 2a slowly decomposes at ambient temperatures by changing its color to brown and therefore needs to be stored at low temperatures (\(-35 \) °C).

Yield: 154 mg (52%), mp: decomp. > 88 °C. IR (ATR, 298 K, in cm\(^{-1}\)): 406 (vw), 414 (vw), 421 (vw), 500 (vs), 554 (m), 625 (w), 638 (m), 658 (w), 705 (vw), 731 (w), 759 (w), 821 (w), 865 (w), 892 (w), 942 (w), 985 (w), 1049 (w), 1148 (w), 1203 (vs), 1231 (s), 1353 (vw), 1375 (s), 1476 (w), 1489 (w), 1502 (w), 1602 (w), 1625 (w), 2894 (w), 2945 (w); \(\text{H}\) NMR (CD\(_2\)\(_2\)CO, 298 K, in ppm): \(\delta = 0.6\) (12H, br, \(\text{Ph}_3\text{P}-\text{CH}\)), \(-0.18\) (36H, br, \(\text{CHCl}_3\)), \(-0.54\) (4H, br, CH-aryl), \(-9.16\) (2H, br, Ph-CH), the resonance for \(\text{CH}_2\) is not observed. 31P\({}^1\)H NMR (CD\(_2\)\(_2\)CO, 298 K, in ppm): R = 1.75 mm/s, \(\Delta E_p = 1.14 \) mm/s. Elemental analysis of sufficient quality could not be obtained due to rapid decomposition of 2a during sampling, preparation, and investigation.

Preparation of \([\text{Ph}_3\text{PCH}_2\text{Fe}(\text{N(SiMe}_3)_2)_2]\) (2c). Method A: Solid 2a (210 mg, 0.32 mmol) was heated to 135 °C for 12 h. The resulting brown melt containing crystalline material was stored for 24 h at \(-35 \) °C. The residue orange-brown crystalline material was washed with CH\(_2\)Cl\(_2\) (1 mL) and dried in vacuo (yield: 29 mg, 18%). Method B: A solution of Ph\(_3\text{PCH}_2\) (1.106 mg, 0.40 mmol) in THF (1 mL) was added to a stirring solution of \(\text{Fe}(\text{N(SiMe}_3)_2)_2\) (74.0 mg, 0.2 mmol) in THF (1 mL). The reaction mixture was stirred for 10 min followed by removal of all volatiles in vacuo. The yellow, sticky residue was heated to 135 °C for 24 h to give a brown residue. CH\(_2\)Cl\(_2\) (1 mL) was added, and the resulting suspension was stored for 1 week at \(-35 \) °C. The brown suspension was filtered, and the residue was washed with CH\(_2\)Cl\(_2\) (4 × 0.2 mL) and dried in vacuo to give an air sensitive, orange-red powder (yield: 27 mg, 28%). IR (ATR, 298 K, in cm\(^{-1}\)): 403 (vw), 411 (vw), 439 (w), 446 (w), 468 (w), 513 (vs), 536 (s), 579 (vs), 610 (w), 625 (w), 661 (m), 709 (vs), 743 (s), 788 (m), 817 (vs), 841 (s), 867 (vs), 885 (s), 918 (w), 929 (w), 980 (vs), 1003 (w), 1029 (w), 1100 (m), 1111 (w), 1183 (w), 1236 (m), 1251 (w), 1435 (m), 1482 (w), 1981 (w), 2891 (w), 2984 (w), 3052 (w). \(\text{H}\) NMR (CD\(_2\)\(_2\)CO, 298 K, in ppm): \(\delta = 1.31\) (8H, \(\text{CH}_2\)), \(6.66\) (12H, br, o-Me), \(6.13\) (6H, br, Ph-CH), \(4.84\) (12H, br, \(\text{Ph}_3\text{P}-\text{CH}\)), \(3.25\) (12H, br, SiMe\(_3\)). 31P\({}^1\)H NMR (CD\(_2\)\(_2\)CO, 298 K, in ppm): \(\delta = 133.0\) (12C, br, o-Me), \(132.9\) (6C, br, p-C), \(130.2\) (12C, br, o-Me). MMPS (80 K, 0.0 T): 0.35 mm/s \((\Delta E_p = 1.75 \) mm/s). Elemental analysis calculated for C\(_{104}\)H\(_{160}\)Fe\(_2\)N\(_{36}\)Si\(_{12}\): C, 61.09; H, 6.97; N, 2.85. Found: C, 60.95; H, 6.84; N, 2.90.
Preparation of \([\text{Fe}(\text{Mes})_2\text{PCH}(\text{SiMe}_3)_2]\_2\) (6). A solution of \(\text{Pb}, \text{CH}_3\_1, 111 \text{ mg}, 0.40 \text{ mmol}\) in \(\text{C}_6\text{H}_5\text{F}\) (1.5 mL) was added to a stirring solution of \([\text{Fe}(\text{Mes})_2]\_2\) (118 mg, 0.20 mmol) in \(\text{C}_6\text{H}_5\text{F}\) (1.5 mL) to give a yellow solution which was subsequently heated to 85 °C for 4 h. The resulting brown reaction mixture was cooled to ambient temperature and filtered to give a brown solution. Slow vapor diffusion of \(n\)-hexane into the brown solution yielded deep brown crystals. Yield: 109 mg (60%). mp: decomp. > 320 °C.

IR (ATR, 298 °C) (in KBr, in cm\(^{-1}\)): 738 (m), 748 (s), 837 (m), 882 (m), 896 (s), 978 (vs), 916 (s), 1026 (w), 1098 (vs), 1161 (w), 1186 (w), 1304 (w), 1363 (w), 1435 (s), 1481 (w), 1588 (w), 1967 (w), 2167 (w), 2898 (w), 3051 (w).

\(^1\text{H}\) NMR (CD\(_2\)CO 298 K, in ppm): \(\delta\) 144.32 (2H, br, CH-PPh\(_3\)), 13.60 (4H, br, \(-\text{CH}(\text{mesityl}))\), 11.09 (6H, br, \(-\text{CH}(\text{mesityl}))\), 6.32 (12H, br, \(-\text{CH}(\text{mesityl}))\), 6.06 (12H, br, \(-\text{CH}(\text{PPh}3))\), 5.98 (6H, t, \(J_{\text{HH}} = 7.0\) Hz, \(-\text{CH}(\text{PPh}3))\), \(-0.58\) (12H, br, \(-\text{CH}(\text{mesityl}))\). 13C\(_{(\text{H})}\) NMR (CD\(_2\)CO 298 K, in ppm): \(\delta\) 277.4 (4C, br, \(-\text{CH}(\text{mesityl}))\), 207.1 (6C, br, \(-\text{CH}(\text{PPh}3))\), 180.4 (2C, br, \(-\text{CH}(\text{PPh}3))\), 139.3 (12C, br, \(-\text{CH}(\text{PPh}3))\), 132.6 (6C, br, \(-\text{CH}(\text{mesityl}))\), 130.0 (12C, br, \(-\text{CH}(\text{PPh}3))\), 94.8 (4C, br, \(-\text{CH}(\text{mesityl}))\), 38.5 (4C, br, \(-\text{CH}(\text{mesityl}))\), 9.0 (2C, br, \(-\text{CH}(\text{mesityl}))\). 1\(^3\)P\(_{(\text{H})}\) NMR (CD\(_2\)CO 298 K, in ppm): \(\delta\) 19.55 ppm (2P, br, \(-\text{CH}(\text{mesityl}))\), 19.45 ppm (2P, br, \(-\text{CH}(\text{mesityl}))\), 19.35 ppm (2P, br, \(-\text{CH}(\text{mesityl}))\). Elemental analysis calculated for \(\text{C}_56\text{H}_54\text{Fe}_2\text{P}_2\): C, 74.68; H, 6.04. Found: C, 74.29; H, 6.49.

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