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Novel Straightforward Access to a 2,2′-Bipyridine Ligand Bearing Two “(η^2-dppe)(η^5-C_5Me_5)FeC≡C−” Redox-Active Substituents by Homocoupling of Mononuclear Organoiron(II) 2-Bromopyridyl Synthons

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We report in this contribution the synthesis and characterization of the two organoiron(II) (η^2-dppe)(η^5-C_5Me_5)FeC≡C−(5,2-C_5H_3N-X) compounds (X = Cl, **6a**; X = Br, **6b**) bearing a pendant halogenated *m*-pyridyl group. These new functional “metallo-ligands” allow for an original, convenient, and rapid synthetic access to the 2,2′-bipyridine (bipy) ligand (**3**) bearing two redox-active “(η^2-dppe)(η^5-C_5Me_5)FeC≡C−” organometallic moieties grafted to the 5,5′-positions of bipy via a Pd-catalyzed homocoupling procedure.

Judicious spatial or topologic arrangements of redox-active end groups can lead to molecular architectures presenting unique properties for information storage or information processing at the molecular level.[1] On the basis of that statement, we have previously reported on the synthesis of several ubiquitous chelating ligands incorporating redox-active “(η^2-dppe)(η^5-C_5Me_5)FeC≡C−” fragments such as **1**-**3** (Chart 1).[2,3] Related alkynyl electron-rich metallo-ligands bearing one redox-active site connected to a diimine unit have been scarce in the literature until now.[4] Moreover, to the best of our knowledge, with the exception of **2** and **3**, no other polydentate ligand carrying *several* such redox-active organometallic end groups has been reported so far.[5]

Compound **3** was previously isolated using a bis-Sonogashira coupling reaction between the known acetylide complex (η^2-dppe)(η^5-C_5Me_5)FeC≡CH (**4**) and 5,5′-dibromo-2,2′-bipyridine (**5**),[3] following a coupling protocol which had ample precedence in our group.[6,7] Although the targeted compound **3** could be isolated and characterized according to this synthesis, its yield as an isolated compound proved very poor (≤15%) due to its difficult purification, which was based on a repetitive fractional recrystallization procedure. Now, the exploration of the coordination chemistry of this fascinating “metallo-ligand” evidently requires its isolation in good yields. We therefore logically wondered if an alternative approach based on the catalytic coupling of organoiron synthons such as **6a**,**b** (Chart 1) might not provide an easier access to **3**. Moreover, such an approach in which the bipyridine moiety is formed in the last synthetic step should prevent to some extent any undesired side reaction that might happen between this chelating site and organoiron compounds present in the reaction medium.[8]

In this contribution, we disclose such a synthetic pathway. Remarkably, the fact that **3** could be straightforwardly obtained by extending a known Pd-based homocoupling procedure to the bromopyridyl compound **6b** emphasizes the interest of this class of functional organometallics as potent building blocks.

Results and Discussion

We initially started our investigations with the chloro complex **6a**, using a Ni-based protocol.[9,10] The synthesis of the required starting mononuclear precursor **6a** was readily achieved following the “so-called” metalla-Sonogashira approach from **4**

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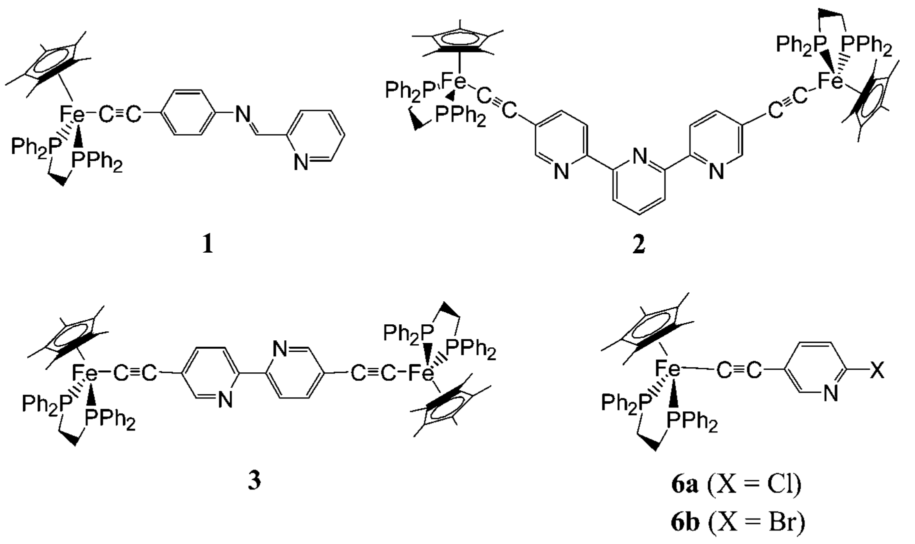
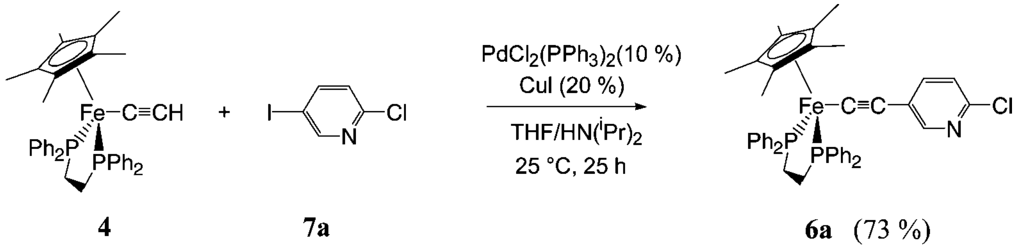
Chart 1. Selected Pyridine-Based Organometallic Complexes



1 **2** **3** **6a** (X = Cl) **6b** (X = Br)

Scheme 1. Synthesis of 6a



4 **7a** **6a** (73 %)

(Scheme 1) and the commercially available 2-chloro-5-iodopyridine (**7a**).[6,7] This reaction was performed at ambient temperature in order to avoid any undesired coupling at the carbon−chlorine bond. Good yields of the new compound **6a** were obtained. This key compound was fully characterized, and its solid-state structure was solved (Figure 1).

The Ni-based homocoupling of **6a** was subsequently attempted. However, the desired product **3** could not be isolated according to the classic procedure (see the Supporting Information).[10] We then tried a Pd-based homocoupling protocol recently reported by Lemaire and co-workers for a similar coupling reaction with organic 2-halopyridines.[11] In contrast to the former reaction, this alternative procedure slowly but selectively generated the desired complex **3**. The desired complex **3** is formed in a 2:1 ratio along with unreacted starting compound **6a** after ca. 50 h of reaction. However, the separation of **3** from **6a** proved to be quite difficult. At this stage, the next step in order to improve this homocoupling reaction and to obtain **3** in good yields was to repeat it with an organometallic substrate, such as **6b**, presenting a more reactive aryl−halogen bond toward oxidative addition than **6a**.

The synthesis of **6b** was therefore undertaken. However, considering the increased reactivity of the halogen atoms when appended in positions ortho to nitrogen in heterocycles along with the high reactivity of bromine−aryl bonds in Sonogashira couplings,[12] we feared that the metalla-Sonogashira coupling reaction between **4** and commercial 2-bromo-5-iodopyridine (**7b**) might prove less selective than in the case of **7a**. Thus, isolation of the compound **6b** was also attempted from the chloro complex **8** and the preformed organic alkyne **9** following the classic activation approach (Scheme 2).[6,13] By any of these routes, the desired compound was successfully isolated in more than 70% yield. In spite of slightly lower yields, the former route to **3** starting from the chloro complex **8** and the 2-bromo-5-ethynylpyridine **9** (reaction i, Scheme 2) is more easily amenable to large-scale syntheses than is the catalytic approach starting from **4** and **7b** (reaction ii, Scheme 2), especially when considering that the organic alkyne **9** can simply be isolated in good yields from the commercial 2-bromo-5-iodopyridine **7b** (>70%).[14] The new compound **6b** was characterized, and its solid-state structure was also solved (Figure 1).

The compound **6b** was then tested in the aforementioned Pd-based homocoupling reaction. As expected, **3** was quantitatively formed in the medium after 16 h (Scheme 3). Notably, when this reaction was repeated several times, the known *m*-pyridyl compound **10** was formed in low and variable amounts in some runs.[15] However, the desired complex **3** could be conveniently

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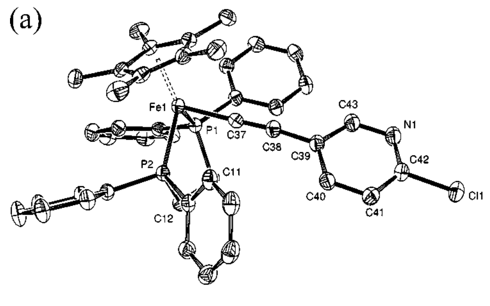
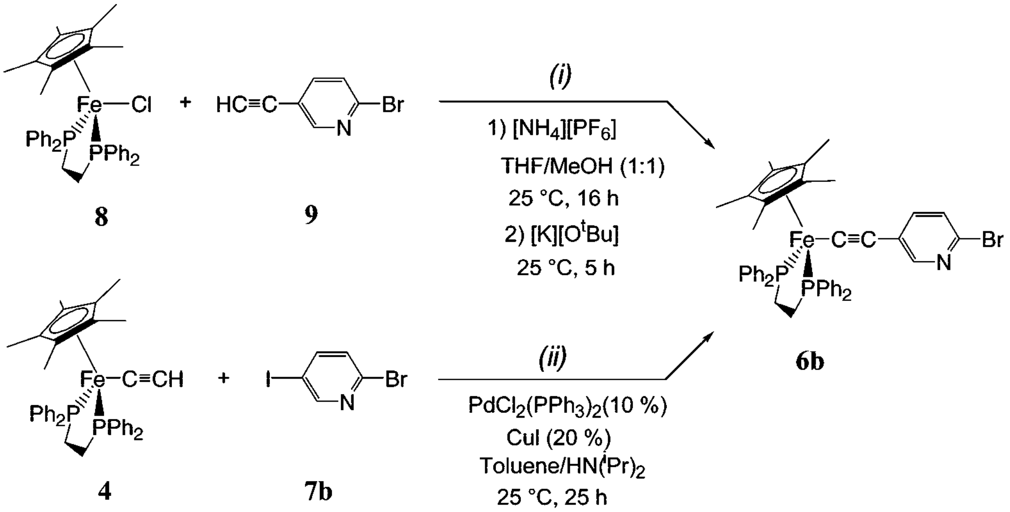


Figure 1. ORTEP representations of the complexes (a) **6a** and (b) **6b** with displacement ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): **6a**, Fe1−(Cp*)$_{centroid}$ = 1.733, Fe1−P1 = 2.1748(8), Fe1−P2 = 2.1808(8), Fe1−C37 = 1.899(3), C37−C38 = 1.217(4), C38−C39 = 1.433(4), C39−C40 = 1.404(4), C40−C41 = 1.378(4), C41−C42 = 1.379(4), C39−C43 = 1.397(4), N1−C42 = 1.315(4), N1−C43 = 1.347(4), Cl1−C42 = 1.755(3), P1−Fe1−P2 = 86.82(3), Fe1−C37−C38 = 178.1(2), C37−C38−C39 = 174.4(3), C43−C39−Fe1−(Cp*)$_{centroid}$ = −69.7; **6b**, Fe1−(Cp*)$_{centroid}$ = 1.743, Fe1−P1 = 2.1808(6), Fe1−P2 = 2.1888(6), Fe1−C37 = 1.894(2), C37−C38 = 1.217(3), C38−C39 = 1.435(3), C39−C40 = 1.382(3), C40−C41 = 1.378(4), C41−C42 = 1.360(3), C39−C43 = 1.386(3), N1−C40 = 1.343(3), N1−C41 = 1.306(4), Br1−C41 = 1.921(2), P1−Fe1−P2 = 86.68(2), Fe1−C37−C38 = 179.4(2), C37−C38−C39 = 173.6(2), C43−C39−Fe1−(Cp*)$_{centroid}$ = 117.3.

Scheme 2. Syntheses of 6b[a]



[a] Isolated yields: reaction i, 70%; reaction ii, 79%.

separated from this side product by exploiting their different solubilities in organic solvents.

Thus, this new route constitutes a convenient preparative access to the metallo-ligand **3**. Its overall yield over two steps (Schemes 2 and 3) compares very favorably with that of the previous synthesis (46% vs 15%). Then, recalling that **4** is itself isolated in two steps from the chloro complex **8**,[16] the isolation of **6b** in 70% yield from the same precursor constitutes a very appealing synthetic approach for obtaining large quantities of **3** via the organometallic precursor **6b**.[17] Moreover, this synthesis can be undertaken from commercially available precursors such as 2-bromo-5-iodopyridine (**7b**) or (trimethylsilyl)acetylene (**11**), in contrast to that previously reported requiring the more involved preparation of **5**.[18]

In conclusion, a new, original, and efficient synthetic homocoupling procedure involving mononuclear organoiron(II) intermediates could be devised, allowing us to isolate **3** in good yields following a quite straightforward workup. This reaction opens now the way to the exploration of the coordination chemistry of this fascinating metallo-ligand. Notably, only scant examples of such catalyzed couplings occurring in the coordination sphere of electron-rich metal centers present as substituents (spectators) on functional (hetero)aryl rings have been reported so far.[9,19] Thus, in line with these recent studies, it seems that Pd-catalytic procedures involving organometallic building blocks offer very appealing synthetic alternatives to more classic approaches, where introduction of the metal centers is usually performed at the end of the synthetic sequence. With this in mind, we now intend to explore the coupling chemistry of functional 2-bromo-5-pyridylacetylide complexes such as **6b** in a more systematic way.

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[17] The overall yield of **3** obtained from **4** and the noncommercial 5,5′-dibromo-2,2′-bipyridine **5** when the synthesis of **4** from **8** is taken into consideration is below 13%, vs 46% for the present route when the synthesis of **6b** is undertaken from **8** and **9**.

[18] Note also that the halogenated reactant **7b** can be obtained at the multigram scale in much better yields than **5** according to published procedures; see for instance: Bouillon, A.; Lancelot, J.-C.; Collot, V.; Bovy, P. R.; Rault, S. *Tetrahedron* **2002**, *58*, 2885–2890.

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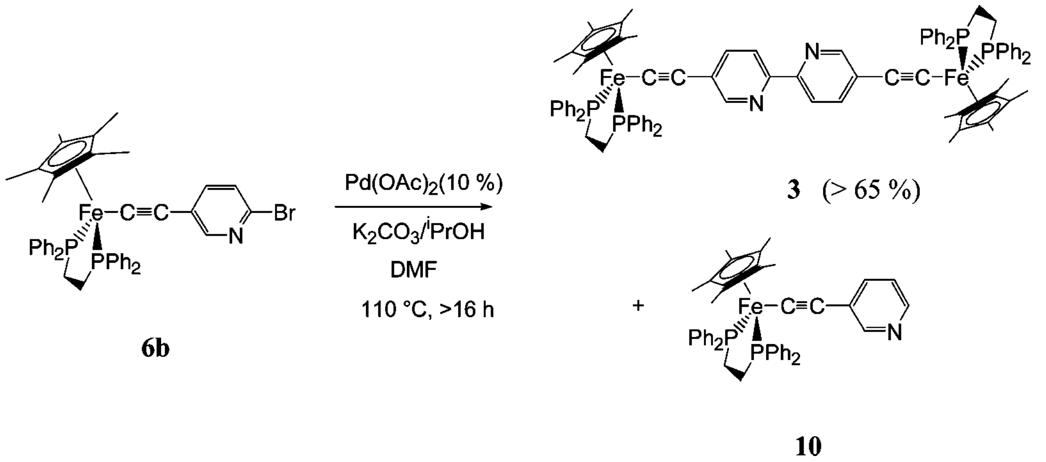
Scheme 3. Synthesis of 3 Based on the Pd-Homocoupling Reaction of 6b



Experimental Section

General Data. All manipulations were carried out under an inert atmosphere. Solvents and reagents were used as follows: THF, Et_2O, and *n*-pentane, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 and purged with Ar, opened/stored under Ar; DMF (extra dry, ACROS), distilled. High-field NMR spectra experiments were performed on a multinuclear Bruker 500, 300, or 200 MHz instrument (AVANCE 500, AM300WB, and 200DPX). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer (400−4000 cm^{-1}). UV−visible spectra were recorded using a Cary 5000 spectrometer. MS analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes) on a high-resolution MS/MS ZABSpec TOF Micromass spectrometer. Elemental analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes). The solid-state structures (X-ray) were resolved at the "Centre de Diffractométrie X" (UMR CNRS 6226, University of Rennes). The complexes $(\eta^5\text{-}C_5Me_5)Fe(\eta^2\text{-dppe})(C{\equiv}CH)$ (**4**) and $[(\eta^5\text{-}C_5Me_5)Fe(\eta^2\text{-dppe})Cl$ (**8**) were prepared according to published procedures.[16,20]

Synthesis of $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}C{-}(5,2\text{-}C_5H_3NX)$ (X = Cl, 6a; X = Br, 6b) from $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}CH$ (4) by the Metalla-Sonogashira Approach. In a Schlenk tube, the complex $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}CH$ (**4**; 0.400 g, 0.65 mmol), the $(PPh_3)_2PdCl_2$ catalyst precursor (0.045 g, 0.06 mmol; 10%), and CuI cocatalyst (0.025 g, 0.13 mmol; 20%) were introduced under argon. Subsequently, the desired 2-halogeno-5-iodopyridine **7a** (X = Cl; 0.188 g, 0.78 mmol) or **7b** (X = Br; 0.219 g, 0.78 mmol) was added to 70 mL of a $^iPr_2NH$/THF (3:4) mixture or of a $^iPr_2NH$/toluene (1:3) mixture, respectively, and the reaction medium was stirred for 25 h. The solvents were then cryogenically trapped, and the dark orange residue was extracted with toluene and filtered on an alumina/Celite pad. Evaporation of the toluene and washing with cooled pentane (−40 °C, 2 × 10 mL) yielded the desired complexes $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}C{-}(5,2\text{-}C_5H_3NX)$ (**6a**, X = Cl, 0.344 g, 0.47 mmol; **6b**, X = Br, 0.393 g, 0.51 mmol) as orange solids after drying in vacuo.

Compound 6a. Yield: 73%. Crystals were grown by slow diffusion of pentane in a toluene solution of **6a** (layer/layer). Anal. Calcd for $C_{43}H_{42}NClP_2Fe$: C, 71.13; H, 5.83; N, 1.93. Found: C, 70.76; H, 5.97; N, 1.87. MS (positive LSI, CH_2Cl_2): *m/z* 725.1832 $[M]^+$, *m/z* calcd for $[C_{43}H_{42}NClP_2Fe]$ 725.1830. FT-IR (ν, CH_2Cl_2/KBr, cm^{-1}): 2048/2051 (s, C≡C) and 2026/2019 (m, C≡C). ^{31}P NMR (δ, C_6D_6, 81 MHz): 100.8 (s, dppe). ^1H NMR (δ, C_6D_6, 200 MHz): 8.25 (s, 1H, H_{Py}), 7.85 (m, 4H, H_{Ar}), 7.30 (m, 4H, H_{Ar}), 7.10−6.94 (m, 13H, H_{Ar+Py}), 6.80 (d, $^3J_{HH}$ = 9 Hz, 1H, H_{Py}), 2.50 (m, 2H, $CH_{2/dppe}$), 1.77 (m, 2H, $CH_{2/dppe}$), 1.47 (s, 15 H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 50 MHz): 151.0 (t, $^2J_{CP}$ = 38 Hz, Fe*C*≡C), 151.3 (s, CH_{Py}), 143.9 (s, C_{Py}), 139.5−137.0 (m, CH_{Py} + C_{Py} + $C_{Ar/dppe}$), 134.4−123.4 (m, $CH_{Ar/dppe}$ + CH_{Py} + C_{Py}), 115.5 (s, FeC≡*C*), 88.2 (s, $C_5(CH_3)_5$), 31.2 (m, $(CH_2)_{dppe}$), 10.4 (s, $C_5(CH_3)_5$). UV−vis (CH_2Cl_2, λ_{max}/nm [$\epsilon/10^3$ dm^3 M^{-1} cm^{-1}]): 372 [12.9]. CV (CH_2Cl_2, 0.1 M *n*-$Bu_4N^+PF_6^-$, 20 °C, 0.1 V s^{-1}; $E°$ in V vs SCE (ΔE_p in V, $i_{p,a}/i_{p,c}$)): −0.07 (0.07, 1.0).

Compound 6b. Yield: 79%. Crystals were grown by slow diffusion of pentane in a dichloromethane solution of **6b** (layer/layer). Anal. Calcd for $C_{43}H_{42}NBrP_2Fe$: C, 67.03; H, 5.49; N, 1.82. Found: C, 66.92; H, 5.64; N, 1.80. MS (positive LSI, CH_2Cl_2): *m/z* 770.1372 $[M]^+$, *m/z* calcd for $[C_{43}H_{42}NBrP_2Fe]$ 770.1404. FT-IR (ν, CH_2Cl_2/KBr, cm^{-1}): 2054/2049 (vs, C≡C) and 2025/2022 (sh, C≡C). ^{31}P NMR (δ, C_6D_6, 81 MHz): 100.7 (s, dppe). ^1H NMR (δ, C_6D_6, 200 MHz): 8.21 (d, $^3J_{HH}$ = 2.0 Hz, 1H, H_{Py}), 7.84 (m, 4H, H_{dppe}), 7.40−7.05 (m, 16H, H_{dppe}), 6.97 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H_{Py}), 6.85 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, H_{Py}); 2.46 (m, 2H, $(CH_2)_{dppe}$), 1.77 (m, 2H, $(CH_2)_{dppe}$), 1.46 (s, 15H, $C_5(CH_3)_5$). UV−vis (CH_2Cl_2, λ_{max}/nm [$\epsilon/10^3$ dm^3 M^{-1} cm^{-1}]): 372 [12.0]. CV (CH_2Cl_2, 0.1 M *n*-$Bu_4N^+PF_6^-$, 20 °C, 0.1 V s^{-1}; $E°$ in V vs SCE (ΔE_p in V, $i_{p,a}/i_{p,c}$)): −0.06 (0.07, 1.0).

Synthesis of $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}C{-}(5,2\text{-}C_5H_3NBr)$ (6b) from $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeCl$ (8). In a Schlenk tube, $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeCl$ (**8**; 0.625 g, 1.0 mmol) was solubilized in 40 mL of a MeOH/THF (1:1) mixture. 2-Bromo-5-ethynylpyridine (**9**; 200 mg, 1.1 mmol) and NH_4PF_6 (0.180 g, 1,1 mmol) were subsequently added before stirring the reaction medium for 16 h at 25 °C. Then, ^{t}BuOK (0.134 g; 1.1 mmol) was added and the reaction was stirred for another 5 h. The volatiles were then removed in vacuo, and the solid residue was extracted with 3 × 30 mL of diethyl ether. Once the solvent was removed, the orange powder was washed with 2 × 30 mL of pentane to afford the desired compound $(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}C{-}(5,2\text{-}C_5H_3NBr)$ (**6b**; 0.540 g, 0.70 mmol; 70%).

Synthesis of 5,5′-$[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)FeC{\equiv}C]_2$-[2,2′-$(C_5H_3N)_2$] (3). In a Schlenk tube, **6b** (0.770 g, 1.0 mmol), K_2CO_3 (0.138 g, 1.0 mmol), and $Pd(OAc)_2$ (0.022 g, 0.1 mmol) were introduced in 5 mL of anhydrous DMF. A 150 μL portion of anhydrous ^{i}PrOH (2.0 mmol) was next syringed at once into the Schlenk tube, which was placed in a preheated oil bath at 110 °C with stirring. A rapid color change of the mixture from red to black took place. After 16 h, the reaction mixture was cooled back to room temperature and the solvents evacuated in vacuo. The residue was subsequently extracted with 3 × 30 mL of toluene, and the extract was evaporated to dryness. The resulting residue was then washed with 2 × 30

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for 6a,b

	6a	**6b**
formula	FeP$_2$NClC$_{43}$H$_{42}$	FeP$_2$NBrC$_{43}$H$_{42}$
fw	726.02	770.48
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	11.9115(3)	12.0155(5)
b (Å)	19.3856(3)	19.3821(8)
c (Å)	15.7925(3)	16.1491(7)
α (deg)	90.0	90.0
β (deg)	92.1160(10)	92.543(3)
γ (deg)	90.0	90.0
V (Å^3)	3644.2(1)	3757.5(3)
Z	4	4
D_{calcd} (g cm^{-3})	1.323	1.352
cryst size (mm)	0.35 × 0.15 × 0.12	0.35 × 0.32 × 0.32
F(000)	1520	1592
abs coeff (mm^{-1})	0.607	1.581
no. of total/unique rflns	8379/8379	8379/8379
no. of variables	434	433
final R	0.051	0.0312
R_w	0.130	0.0702
goodness of fit/F^2 (S_w)	1.075	0.909

mL of diethyl ether and 2 × 30 mL of pentane before being solubilized in 2 mL of THF. This solution was filtered through a plug compacted with silica gel and eluted with THF/toluene (1:1). After evacuation of the solvent, the desired bipy complex 5,5′-[(η^2-dppe)(η^5-C$_5$Me$_5$)FeC≡C]$_2$-[2,2′-(C$_5$H$_3$N)$_2$] (**3**) was obtained as an orange-brown powder (473 mg; 0.343 mmol; 68%). Preliminary characterization data have already been reported for this compound.[3]

Crystallography. Data collection of crystals of **6a** and **6b** was performed on an NONIUS Kappa CCD and on an Oxford Diffraction Xcalibur Saphir 3 diffractometer at 120 and 295 K, respectively, with graphite-monochromated Mo Kα radiation (Table 1). The cell parameters were obtained with Denzo and Scalepack with 10 frames (ψ rotation: 1° per frame).[21] The data collections[22] gave 64 195 ($2\theta_{\max} = 54°$, 298 frames via 1.4° ω rotation and 160 s per frame, *hkl* ranges h 0−15, k 0−25; l −20 to +20) and 26 498 ($2\theta_{\max} = 54°$, ω scan frames via 0.7° ω rotation and 10 s per frame, *hkl* ranges h 0−15, k 0−24, l −20 to +20) reflections, respectively. The data reduction with Denzo and Scalepack[21] led to 8379 (respectively 8132) independent reflections, from which 6733 (respectively 5091) had $I > 2.0\sigma(I)$. The structures were solved with SIR-97, which revealed the non-hydrogen atoms of these molecules.[21] After anisotropic refinement, many hydrogen atoms could be found by difference Fourier techniques. The entire structures were subsequently refined with SHELXL97 by full-matrix least-squares techniques (use of F^2 magnitude; x, y, z, β_{ij} for Fe, P, Br, Cl, C, and N atoms, x, y, z in riding mode for H atoms: 434 variables and 6733 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 4.72P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **6a** and 433 variables and 5091 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 1.1P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **6b**).[23] Atomic scattering factors were taken from ref 24. Ortep views were realized with PLATON98.[25]

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Supporting Information Available: CIF files giving crystallographic data for **6a**,**b** and text and figures giving additional synthesis details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles, and anisotropic thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre and were allocated the deposition numbers CCDC 221829 and CCDC 607551, respectively.

OM800388J

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