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$iPr_2N-P{=}Fe(CO)_4$ in Olefinic Solvents: A Reservoir of a Transient Phosphinidene Complex Capable of Substrate Hopping

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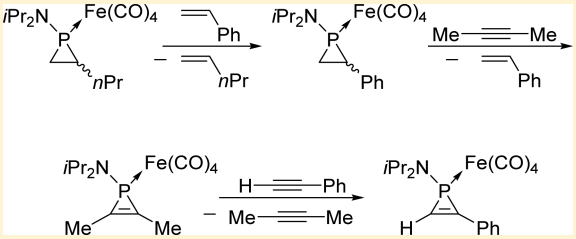
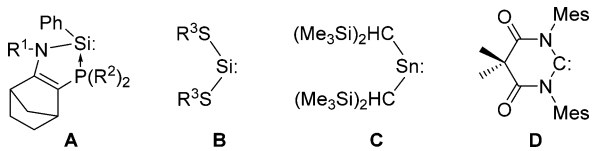
Supporting Information

ABSTRACT: The phosphinidene complex $iPr_2N-P{=}Fe(CO)_4$ was prepared as a storable phosphirane solution from Collman's reagent and iPr_2NPCl_2 in the olefins 1-pentene and 1-hexene. The carbene-like reagent is able to hop under very mild conditions (>−25 °C) from one olefin to another and to alkynes to give the more stable phosphirenes that likewise display dynamic covalent behavior. The olefinic solutions are effective reservoirs for the highly reactive phosphinidene complex, as is illustrated in its N−H and O−H insertion reactions with amines, alcohols, and carboxylic acids and in its P−C bond formation with Grignard reagents.



INTRODUCTION

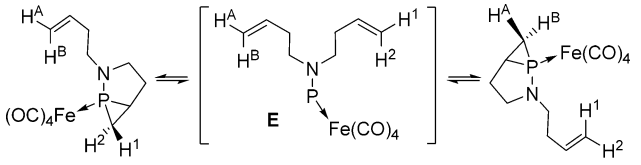
Reversible coordination of low-valent transition metal complexes to alkenes and alkynes is a key step in a plethora of homogeneous catalytic transformations.[1] The display of this behavior by some main group compounds signifies a valuable complementary toolbox.[2] Exemplary are the established low-valent carbenes (NHCs, CAACs),[3] their heavier homologues (tetrylenes: Si, Ge, Sn, Pb),[2a] and the fast growing class of FLPs that activate dihydrogen and small unsaturated molecules.[4] Reversible cycloadditions are known for silylenes and alkenes[5] and even ethylene when using **A**[6] or **B**,[7] not yet for germylenes,[8] but also stannylene **C** is in equilibrium with a stannacyclopropene.[9,10] Recently, even the stable carbene **D** was reported to give reversible cycloadditions with retro-addition requiring elevated temperatures.[11] Such dynamic covalent chemistry[12] under mild conditions has not yet been reported for the diagonally related phosphinidenes.[13,14]



We wondered whether this dynamic behavior could be achieved at ambient temperatures with fleeting neutral electrophilic phosphinidenes ($R-P{=}ML_n$). These transient reagents, which enable the synthesis of numerous organophosphorus compounds by cycloadditions and bond insertions,[15] are typically generated *in situ* by thermal expulsion from ML_n-complexed 7-phosphanorbornadienes[16] or 3*H*-3-benzophosphepines[17,18] and act as the P-analogues of carbenes to give [1+2]-cycloadducts with alkenes and alkynes.[19] They are extremely reactive, and only in a single case could one ($R-P{=}W(CO)_5$, R = p-$C_6H_4NH_3^+$) be detected spectroscopically in the gas phase.[20]

Herein we report that the phosphinidene complex $iPr_2N-P{=}Fe(CO)_4$ (**1**),[21] which is stabilized by an amino substituent and effective Fe→P back-bonding,[22] undergoes facile, reversible cycloadditions with alkenes and alkynes. An indication of such dynamic behavior came from the reported *intra*molecular phosphinidene transfer between the two olefinic groups of **E**, as was established at −10 °C by NMR magnetization transfer experiments between the hydrogens pairs H^A-H^1 and H^B-H^2 (Scheme 1).[23] When P-transfer would occur *inter*molecularly, it would mean that the transient reagent can be stored as a cycloadduct, in essence be "bottled", and serve as a phosphinidene reservoir for further reaction. This is precisely

Scheme 1. Intramolecular Phosphinidene Transfer



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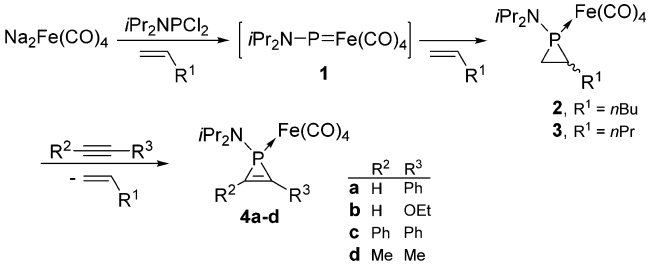
what occurs when the three-membered phosphiranes **2** and **3** are used in the solvents in which they are generated (Scheme 2).[24] A consequence of the dynamic covalent behavior is that

Scheme 2. Synthesis and Application of Phosphinidene $i\mathrm{Pr_2N{-}P{=}Fe(CO)_4}$ (1) in Olefinic Solvents



the readily accessible "stored" phosphinidenes can serve as convenient reagents for the synthesis of $Fe(CO)_4$ complexes of substituted phosphanes under very mild conditions.[25]

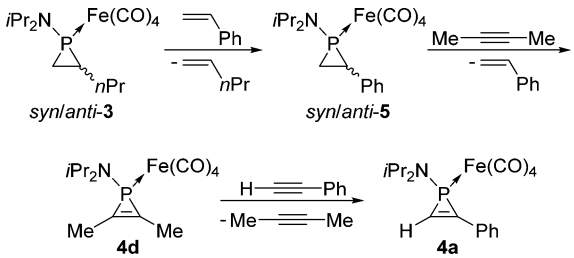
RESULTS AND DISCUSSION

The two $Fe(CO)_4$-complexed phosphiranes are generated in neat 1-hexene or 1-pentene at −78 °C by treating Collman's reagent ($Na_2[Fe(CO)_4]\cdot 1.5$dioxane) with dichloro(diisopropylamino)phosphane ($i\mathrm{Pr_2NPCl_2}$)[26] to afford after workup at −30 °C nearly quantitatively 4:1 mixtures of the *syn*- and *anti*-isomers of **2** and **3**, respectively (δ^{31}P **2**: −45.4 (*syn*), −44.8 (*anti*); **3**: −45.5 (*syn*), −44.9 (*anti*) ppm; Scheme 2). The three-membered rings **2** and **3** are stable for months at ambient temperature, but only in the olefinic solvent under an inert atmosphere. Suitable crystals for X-ray diffraction could not be obtained, as concentrating the solution led invariably to decomposition and formation of P/Fe clusters.[21,27] This sensitivity manifests itself when the cycloadditions were executed with, for example, only 3 equiv of 1-hexene in diethyl ether as solvent, in which case significant amounts of P/Fe clusters were detected according to ^{31}P NMR spectroscopy with reduced yields for **2** (41%). Under those conditions no cycloadducts were detected for the more congested olefins 2-methyl-1-hexene, 2-methyl-2-butene, 2,3-dimethylbutene, and *trans*-stilbene.

To corroborate whether $i\mathrm{Pr_2N{-}P{=}Fe(CO)_4}$ (**1**) retains its full reactivity as a "bottled" phosphinidene, we examined the reaction of **2** with four different alkynes. Satisfyingly, addition of 1 equiv of phenylacetylene, ethoxyacetylene, diphenylacetylene, or 2-butyne to a 0.1 M solution of **2** in 1-hexene at room temperature gave indeed in all cases within minutes quantitative conversion (>95% isolated) to the expected aminophosphirenes **4a**–**d** (δ^{31}P = −48.4 (**4a**),[21b] −10.4 (**4b**), −49.4 (**4c**),[21b] −54.4 (**4d**)[21b] ppm; Scheme 2).

To further probe the dynamic covalent chemistry of **1** toward alkenes and alkynes, we used a solution of **3** in the more volatile 1-pentene. Treatment of 3.0 mL of a 0.1 M solution of **3** with an equal amount of styrene at room temperature resulted in a 7:1 ratio of **3** and styrene cycloadduct **5** (*syn*:*anti* = 1:1; δ^{31}P = −39.3 (*syn*) and −39.0 (*anti*) ppm; Scheme 3). ^{31}P NMR monitoring of the reaction mixture showed quantitative **3** → **5** conversion on slow evaporation of 1-pentene. This result is remarkable, as calculations at the B3PW91/6-31+G(d,p) (LANL2DZ for Fe) level of theory (ZPE corrected) reveal **5** to be the less stable phosphirane ($\Delta\Delta E_{(5\text{-}2A)}$ = 4.1 (*syn*), 2.9 (*anti*) kcal·mol^{-1} (**2A**, R^1 = Me), which accentuates the

Scheme 3. Conversion of Phosphinidene Reservoir 3 into 4a, via Phosphiranes *syn*/*anti*-5 and Phosphirene 4d



dynamic covalent behavior of **1**. Subsequent treatment of the styrene solution of **5** with 2 equiv of 2-butyne afforded expectantly the more stable aminophosphirene **4d** (92% isolated; δ^{31}P = −50.8 ppm; isodesmic $\Delta\Delta E_{(4d\text{-}5syn)}$ = −9.7 kcal·mol^{-1}). With the reaction commencing already at −25 °C, it emphasizes the observed dynamics and the readiness of **1** to "hop" from one substrate to another. This became further evident on treating the reaction mixture with 1 equiv of phenylacetylene and heating it to 70 °C, upon which the more stable yellow crystalline **4a** resulted (79% isolated; δ^{31}P = −48.4 ppm; isodesmic $\Delta\Delta E_{(4a\text{-}4d)}$ = −2.8 kcal·mol^{-1}). This result shows that even unsaturated phosphirenes can serve as a reservoir of **1**. Crystals of **4a** could be obtained suitable for an X-ray crystal structure determination (see the Supporting Information) that compares well with the computed one.

Calculations at B3PW91/6-31+G(d,p) (LANL2DZ for Fe) reveal a lowest energy asynchronous concerted pathway for cycloaddition of $i\mathrm{Pr_2N{-}P{=}Fe(CO)_4}$ to propene (as alkene model) to give *anti*- and *syn*-phosphirane **2A** with a modest exothermicity of respectively 4.7 and 6.4 kcal·mol^{-1} with corresponding reaction barriers of 13.9 and 14.1 kcal·mol^{-1}; the asynchronicity is evident from the P···C1/P···C2 distances of 2.153/2.430 Å for the transition structure for *syn*-addition (Figure 1). The energy profile fully reflects the observed

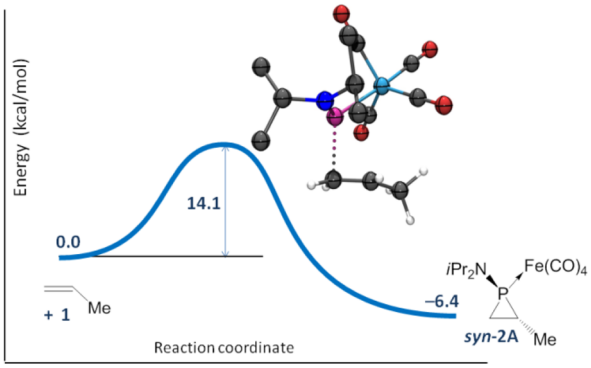


Figure 1. Potential energy surface for the cycloaddition of $Fe(CO)_4$-complexed phosphinidene **1** to propylene.

dynamic behavior of **2** and **3** at ambient temperatures—retroaddition from *syn*-**2A** requires 20.5 kcal·mol^{-1}, indicating a dissociative process[14c]—and underscores the storage ability of the olefins. Cycloaddition of **1** to 2-butyne and phenylacetylene is exothermic by 12.0 and 14.8 kcal·mol^{-1}, respectively, and concurs excellently with the observed more difficult retroaddition of the phosphirenes. In sharp contrast, **1** is not stabilized by diethyl ether, which explains the formation of P/Fe clusters in this solvent.

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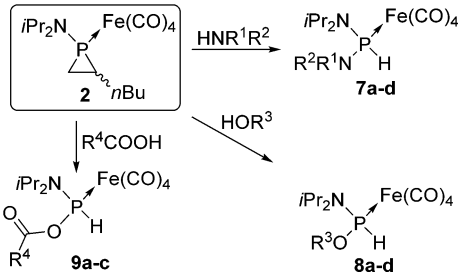
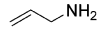
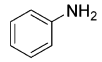
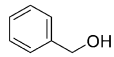
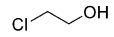
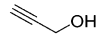
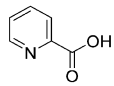
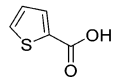
Reactions with "Bottled" iPr$_2$N−P═Fe(CO)$_4$. The remarkable dynamic behavior of the Fe(CO)$_4$-complexed aminophosphiranes and -phosphirenes[28] prompted an exploration of their reactivity as a reservoir of **1** toward amines, alcohols, and carboxylic acids for which N−H and O−H insertions are expected.[15] Treatment of phosphirane **2** (0.1 M in 1-hexene) with 1 equiv of allylamine, aniline, cyclopropylamine, or morpholine at room temperature (1 h) indeed afforded diaminophosphanes **7a−d** in 87−95% yield as yellow to orange oils (Table 1, entries 1−4). Reaction with methanol, benzyl alcohol, and 2-chloroethanol as substrate resulted in aminoalkoxyphosphanes **8a−c** in equally high yields of 71−95% (Table 1, entries 5−7). Reaction of **2** with propargyl alcohol shows competition between O−H insertion and cycloaddition to the C≡C triple bond in a 84:9 ratio, according to ^{31}P NMR spectroscopy, but because the cycloadduct (δ^{31}P = −44.4 ppm) is thermally labile (*vide supra*) still a 84% yield of **8d** is achieved (Table 1, entry 8). The reaction also extends to carboxylic acids, as shown by the facile formation of phosphanes **9a−c** on addition of 1 equiv of acetic acid, picolinic acid, or 2-thiophenecarboxylic acid to **2** (69−93%; Table 1, entries 9−11).[29] P-transfer from **2** to acetic acid starts at −10 °C and is complete at 0 °C within 4 h. These conditions are similar to those for the P-transfer of **1** from **2** to alkynes and supports the hopping process of the transient phosphinidene complex.

Table 1. Synthesis of Diaminophosphanes 7, Aminoalkoxy Phosphanes 8, and Carboxylate Phosphanes 9 from 2[a]

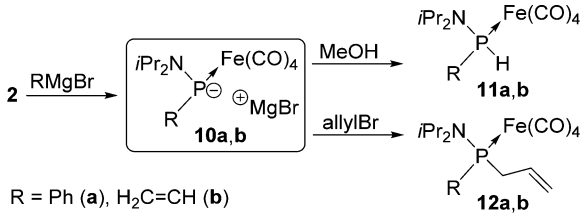


Entry	Substrate	Product[b]	δ^{31}P NMR	Yield [%][c]
1		**7a**	81.8	90
2		**7b**	82.6	95
3		**7c**	79.9	87
4		**7d**	105.9	93
5		**8a**	136.8	95
6		**8b**	134.4	71
7		**8c**	136.5	93
8		**8d**	135.4	84
9		**9a**	125.7	81
10		**9b**	127.6	93
11		**9c**	123.1	69

[a]Standard conditions: a 0.1 M 1-hexene solution of **2** (5.0 mL, 0.5 mmol) is reacted with the substrate (1 equiv, 0.5 mmol) at room temperature for 1 h. [b]**7a−c**, R^1 = H, R^2 = amine substituent; **7d**, R^1, R^2 = morpholine; **8a−d**, R^3 = alcohol substituent; **9a−c**, R^4 = carboxylic acid substituent. [c]Yields of isolated products.

Lastly, "bottled" iPr$_2$N−P═Fe(CO)$_4$ was reacted with Grignard reagents to demonstrate a novel approach to form P−C bonds.[30,31] Treating **2** (0.1 M in 1-hexene) with phenylmagnesium or vinylmagnesium bromide (1.0 M in THF) at room temperature yielded selectively Fe(CO)$_4$-complexed aminophosphides **10a,b** (**10a**: 1.5 h, δ^{31}P = 78.7 ppm; **10b**: 0.5 h, δ^{31}P = 63.5 ppm; Scheme 4); these reactions represent unique conversions of P^{I} fragments into P^{III} anions.[32] Subsequent quenching with methanol afforded the secondary aminophosphanes **11** as orange oils in 87−90% yield (δ^{31}P = 73.7 (**11a**), 67.3 (**11b**) ppm; Scheme 4), which are the formal phosphinidene C−H insertion products[33] of benzene and ethylene. Trapping the phosphide anions **10a,b** with allyl bromide instead resulted in the formation of the corresponding allyl-functionalized aminophosphanes **12a,b** in 69−85% yield (δ^{31}P = 125.7 (**12a**), 116.8 (**12b**) ppm; Scheme 4).

Scheme 4. Functionalization of Phosphinidene iPr$_2$N−P═Fe(CO)$_4$ (1) with Grignard Reagents



CONCLUSION

In summary, from Collman's reagent and iPr$_2$NPCl$_2$ we prepared the reactive phosphinidene complex iPr$_2$N−P═Fe(CO)$_4$, which is storable as a cycloadduct in the olefinic solvents 1-pentene and 1-hexene. The phosphirane cycloadducts show dynamic covalent behavior with the carbene-like reagent hopping under very mild conditions (>−25 °C) from one olefin to another and also to alkynes to give the thermodynamically more stable unsaturated phosphirenes that are still capable of undergoing retroaddition. The olefinic solutions are effective reservoirs for the transient phosphinidene complex that reacts cleanly and in high yield with amines, alcohols, and carboxylic acids to give the corresponding N−H and O−H insertion products, as well as with Grignard reagents, which represents a novel route to form P−C bonds.

EXPERIMENTAL SECTION

Computational Procedure. Density functional calculations were performed at the B3PW91 level of theory using Gaussian09, revision D.01.[34] Geometry optimizations were performed using the 6-31+G(d,p)[35] basis set with LANL2DZ for Fe, and the nature of each stationary point was confirmed by frequency calculations.

Preparation of Compounds. All experiments were performed under an atmosphere of dry nitrogen. Solids were dried *in vacuo*, and liquids were distilled (under N$_2$) prior to use. Solvents were distilled from LiAlH$_4$ (pentane, diethyl ether) and sodium benzophenone (THF). NMR spectra were recorded on Bruker AC 200, MSL 400

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(^{1}H, ^{13}C{^{1}H}), and WM 250 (^{31}P{^{1}H}) spectrometers using $SiMe_4$ (^{1}H, ^{13}C{^{1}H}) or 85% H_3PO_4 (^{31}P{^{1}H}) as external standards. High-resolution mass spectra (HR-MS) were recorded on a Finnigan MAT 90, UV/vis spectra on a Varian Cary, and FT-IR spectra on a Mattson 630 Galaxy spectrophotometer.

*Bottled Phosphinidene [iPr$_2$N−P═Fe(CO)$_4$] in 1-Hexene (**2**).* $Na_2Fe(CO)_4$·1.5dioxane (3.0 mmol, 1.05 g) is suspended in 1-hexene (30 mL) and cooled to −78 °C, after which iPr$_2$NPCl$_2$ (3.0 mmol, 0.45 mL) is added. The reaction mixture is allowed to warm to room temperature overnight, during which the nearly colorless solution turns orange-brown. After removal of the salts by filtration, the solution of **2** (0.1 M) is ready for use and is stable for months at room temperature under an inert atmosphere. For isolation of the thermally unstable phosphiranes **2**, all volatiles were evaporated at −30 °C to afford a 4:1 mixture of *syn*- and *anti*-**2** (1.11 g, 97%) as a thermally unstable reddish-brown oil. ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C): δ −45.4 (*syn*-**2**) and −44.8 (*anti*-**2**) in a 4:1 ratio. HRMS (CI): calcd for $C_{16}H_{26}FeNO_4P$ (M) 383.09810, found 383.09485. IR (1-hexene): 2050, 2022, 2000, 1976, 1942 (CO) cm^{-1}.

*Bottled Phosphinidene [iPr$_2$N−P═Fe(CO)$_4$] in 1-Pentene (**3**).* $Na_2Fe(CO)_4$·1.5dioxane (1.0 mmol, 0.35 g) is suspended in 1-pentene (10 mL) and cooled to −78 °C, after which iPr$_2$NPCl$_2$ (1.0 mmol, 0.15 mL) is added. The reaction mixture is allowed to warm to room temperature overnight, during which the nearly colorless solution turns orange-brown. After removal of the salts by filtration, the solution of **3** (0.1 M) is ready for use. For isolation of the thermally unstable phosphiranes **3**, all volatiles were evaporated at −30 °C to afford a 4:1 mixture of *syn*- and *anti*-**3** (0.36 g, 98%) as a thermally unstable red-brown oil. ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C): δ −45.5 (*syn*-**3**) and −44.9 (*anti*-**3**) in a 4:1 ratio. HRMS (CI): calcd for $C_{15}H_{24}FeNO_4P$ (M) 369.0792, found 369.0781. IR (1-pentene): 2050, 1999, 1976, 1942 (CO) cm^{-1}.

*Synthesis of Aminophosphirenes **4a**−**d**.* A 0.1 M solution of bottled phosphinidene [iPr$_2$N−P═Fe(CO)$_4$] in 1-hexene (**2**) is treated with 1 equiv of the desired acetylene (for **4a**: phenylacetylene, for **4b**: ethoxyacetylene, for **4c**: diphenylacetylene, and for **4d**: 2-butyne) at room temperature, which resulted in the quantative conversion (isolated yields > 95%) within minutes into the corresponding aminophosphirenes **4a**−**d**. For purification and characterization of the previously reported three-membered rings **4a** (^{31}P{^{1}H} NMR ($CDCl_3$): δ − 48.4), **4c** (^{31}P{^{1}H} NMR ($CDCl_3$): δ −49.4), and **4d** (^{31}P{^{1}H} NMR ($CDCl_3$): δ −54.4), see ref 21a.

*1-Diisopropylamino-2-ethoxyphosphirene Tetracarbonyliron(0), **4b**.* All volatiles are evaporated, and the crude mixture is dissolved in *n*-pentane at −20 °C and purified at this temperature by column chromatography (silica 60, 0.015−0.040 mm), resulting in a bright yellow oil. Yield: >95%. ^{1}H NMR (C_6D_6): δ 1.05 (d, ^3J(H,H) = 6.78 Hz, 6H; CH(CH_3)$_2$), 1.07 (d, ^3J(H,H) = 6.94 Hz, 6H; CH(CH_3)$_2$), 1.12 (t, ^3J(H,H) = 7.10 Hz, 3H; OCH$_2$CH_3), 3.87 (dsp, ^3J(H,P) = 17.1 Hz, ^3J(H,H) = 6.78 Hz, 2H; CH(CH$_3$)$_2$), 4.09 (dq, ^4J(H,P) = 1.82 Hz, ^3J(H,H) = 7.10 Hz, 2H; OCH_2CH$_3$), 6.29 (d, ^2J(H,P) = 10.8 Hz, 1H; HC═C). ^{13}C{^{1}H} NMR (C_6D_6): δ 15.0 (s; OCH$_2$CH_3), 22.2 (d, ^3J(C,P) = 3.0 Hz; CH(CH_3)$_2$), 23.8 (d, ^3J(C,P) = 3.7 Hz; CH(CH_3)$_2$), 47.4 (d, ^2J(C,P) = 5.9 Hz; CH(CH$_3$)$_2$), 70.1 (d, ^3J(C,P) = 5.6 Hz; OCH_2CH$_3$), 108.0 (d, ^1J(C,P) = 7.7 Hz; HC═C), 170.7 (d, ^1J(C,P) = 19.7 Hz; HC═COCH$_2$), 214.0 (d, ^2J(C,P) = 23.3 Hz; CO). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.2. IR (KBr): 2050, 1973, 1933 (CO) cm^{-1}. HRMS (CI): calcd for $C_{14}H_{20}FeNO_5P$ (M) 369.04282, found 369.045206.

*Phosphinidene Transfer Reactions: **3** → **5** → **4d** → **4a**.* A 3.0 mL amount of a 0.1 M solution of bottled phosphinidene [iPr$_2$N−P═Fe(CO)$_4$] in 1-pentene (*syn*-**3**, δ ^{31}P: −46.9; *anti*-**3**, δ ^{31}P: −45.4) is treated with an excess of styrene (3.0 mL) at room temperature for 1 h. After removal of 1-pentene by either applying reduced pressure or bubbling N_2 through the solution, the equilibrium is completely shifted to the right, affording quantitatively a 1:1 mixture of *syn*-**5** (δ ^{31}P: −39.3) and *anti*-**5** (δ ^{31}P: −39.0). Subsequently, the styrene solution of **5** is treated with 2 equiv of 2-butyne (0.6 mmol) to afford nearly quantitatively (92%) the corresponding aminophosphirene **4d** (δ ^{31}P: −50.8). In the last step, the reaction mixture is treated with 1 equiv (0.3 mmol) of phenylacetylene and heated to 70 °C, which allowed the evaporation of 2-butyne and resulted in the formation of the corresponding aminophosphirene **4a** (δ ^{31}P: −48.4). Evaporation of all volatiles, followed by crystallization from *n*-pentane at −76 °C, afforded **4a** as yellow crystals in 79% yield.

*Synthesis of Fe(CO)$_4$-Complexed Diaminophosphanes (**7a**−**d**), Phosphoramidites (**8a**−**d**), and Carboxylate Phosphanes (**9a**−**c**).* Procedure A: 0.5 mmol of the desired substrate (1°, 2° amine, alcohol, or carboxylic acid) is added to 5 mL of the 1-hexene solution **2** (0.1 M; 0.5 mmol) at room temperature. The resulting solution is stirred at ambient temperature for an additional hour, after which the solvent is evaporated. The crude reaction mixture is then dissolved in $CHCl_3$ and filtered over a short column (silica, 0.015−0.040 mm) to yield after solvent evaporation yellow to orange oils. The thermal stability of the products is limited in the nonpolar solvents pentane and 1-hexene. Procedure B: Because of the poor solubility of some of the substrates in 1-hexene, they can also be dissolved in $CHCl_3$, CH_2Cl_2, toluene, or THF, to which then the 1-hexene solution **2** is added in a dropwise manner. Further workup of the reaction is identical to **A**.

*N-Allyl-N′,N′-diisopropyldiaminophosphane Tetracarbonyliron-(0), **7a**.* Yield: 90%, yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.24 (d, ^3J(H,H) = 6.90 Hz, 6H; CH(CH_3)$_2$), 1.27 (d, ^3J(H,H) = 6.90 Hz, 6H; CH(CH_3)$_2$), 2.26 (br d, ^2J(H,P) = 21.9 Hz, 1H; HNCH$_2$), 3.58 (br d, ^3J(H,P) = 6.62 Hz, 2H; HNCH_2), 3.67 (dsp, ^3J(H,P) = 18.63 Hz, ^3J(H,H) = 6.90 Hz, 2H; CH(CH$_3$)$_2$), 5.17 (d, ^3J(H,H) = 10.4 Hz, 1H; (*Z*) HC═CH_2), 5.27 (d, ^3J(H,H) = 17.0 Hz, 1H; (*E*) HC═CH_2), 5.82 (m, 1H; HC═CH$_2$), 7.56 (dd, ^1J(H,P) = 410.2 Hz, ^3J(H,H) = 2.9 Hz, 1H; PH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.7 (s; CH(CH_3)$_2$), 23.5 (d, ^3J(C,P) = 2.1 Hz; CH(CH_3)$_2$), 46.2 (d, ^2J(C,P) = 5.5 Hz; CH(CH$_3$)$_2$), 46.4 (d, ^2J(C,P) = 9.3 Hz; HNCH_2), 115.9 (s; HC═CH_2) 136.0 (d, ^3J(C,P) = 4.5 Hz; HC═CH$_2$), 214.4 (d, ^2J(C,P) = 21.4 Hz; CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 81.8. IR (KBr): 2049, 1975, 1939 (CO) cm^{-1}. HRMS (CI): calcd for $C_{13}H_{22}FeN_2O_4P$ (M + H) 357.06420, found 357.06659.

*N,N-Diisopropyl-N′-phenyldiaminophosphane Tetracarbonyliron(0), **7b**.* Yield: >95%, orange-brown oil. ^{1}H NMR ($CDCl_3$): δ 1.01 (d, ^3J(H,H) = 6.78 Hz, 6H; CH(CH_3)$_2$), 1.23 (d, ^3J(H,H) = 6.76 Hz, 6H; CH(CH_3)$_2$), 3.64 (dsp, ^3J(H,P) = 13.77 Hz, ^3J(H,H) = 6.78 Hz, 2H; CH(CH$_3$)$_2$), 4.53 (dd, ^2J(H,P) = 16.57 Hz, ^3J(H,H) = 6.80 Hz, 1H; NH), 6.9−7.4 (m, 5H; PhH), 7.91 (dd, ^1J(H,P) = 426.0 Hz, ^3J(H,H) = 6.80 Hz, 1H; PH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.6 (s; CH(CH_3)$_2$), 23.7 (s; CH(CH_3)$_2$), 47.4 (s; CH(CH$_3$)$_2$), 122.6 (d, ^3J(C,P) = 2.4 Hz; *o*-PhC) 124.2 (s; *p*-PhC) 129.5 (s; *m*-PhC) 141.6 (d, ^2J(C,P) = 12.4 Hz; *ipso*-PhC), 214.1 (d, ^2J(C,P) = 22.1 Hz; CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 82.6. IR (KBr): 2049, 1971, 1937 (CO) cm^{-1}.

*N-Cyclopropyl-N′,N′-diisopropyldiaminophosphane Tetracarbonyliron(0), **7c**.* Yield: >87%, orange-brown oil. ^{1}H NMR ($CDCl_3$): δ 0.6−0.9 (m, 4H; H_2CCH$_2$), 1.26 (d, ^3J(H,H) = 6.9 Hz, 6H; CH(CH_3)$_2$), 1.33 (d, ^3J(H,H) = 6.8 Hz, 6H ; CH(CH_3)$_2$), 2.41 (br s, 1H; HCNH), 2.68 (br d, ^2J(H,P) = 22.3 Hz, 1H; HCNH), 3.71 (dsp, ^3J(H,P) = 14.8 Hz, ^3J(H,H) = 6.9 Hz, 2H; CH(CH$_3$)$_2$), 7.39 (dd, ^1J(H,P) = 422.6 Hz, ^3J(H,H) = 6.21 Hz, 1H; PH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.9 (s; CH_2CH_2), 22.6 (d, ^3J(C,P) = 4.3 Hz; CH(CH_3)$_2$), 23.0 (s; HCNH), 24.1 (d; CH(CH_3)$_2$), 48.7 (d, ^2J(C,P) = 3.7 Hz; CH(CH$_3$)$_2$), 213.4 (d, ^2J(C,P) = 21.6 Hz; CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 79.9. IR (KBr): 2048, 1969, 1937 (CO) cm^{-1}. HRMS (CI): calcd for $C_{13}H_{22}FeN_2O_4P$ (M + 1) 357.06363, found 357.06659.

*N,N-Diisopropylamino(morpholyl)phosphane Tetracarbonyliron-(0), **7d**.* Yield: 93%, yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.26 (d, ^3J(H,H) = 6.95 Hz, 6H; CH(CH_3)$_2$), 1.27 (d, ^3J(H,H) = 6.97 Hz, 6H; CH(CH_3)$_2$), 3.02 (dtd, ^2J(H,H) = 12.45 Hz, ^3J(H,P) = 4.75 Hz, ^3J(H,H) = 4.55 Hz, 2H; NCH_2CH$_2$O), 3.23 (dtd, ^2J(H,H) = 12.43 Hz, ^3J(H,P) = 5.01 Hz, ^3J(H,H) = 4.63 Hz, 2H; NCH_2CH$_2$O), 3.68 (t, ^3J(H,H) = 4.64 Hz, 4H; NCH$_2$CH_2O), 3.72 (dsp, ^3J(H,H) = 6.96 Hz, ^3J(H,P) = 15.8 Hz, 2H; CH(CH$_3$)$_2$), 7.50 (d, ^1J(H,P) = 418.8 Hz, 1H; PH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.4 (d, ^3J(C,P) = 1.9 Hz; CH(CH_3)$_2$), 24.0 (d, ^3J(C,P) = 1.9 Hz; CH(CH_3)$_2$), 47.8 (d, ^2J(C,P) = 5.2 Hz; CH(CH$_3$)$_2$), 48.0 (s; NCH_2CH$_2$O), 67.2 (d, ^3J(C,P)

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= 7.9 Hz; NCH_2CH_2O), 214.0 (d, ^2J(C,P) = 20.4 Hz; *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 105.9. IR (KBr): 2049, 1971, 1937 (CO) cm^{-1}. HRMS: calcd for $C_{14}H_{23}FeN_2O_5P$ 386.06934, found 386.06872.

N,N-Diisopropyl-O-methylphosphonamidite Tetracarbonyliron, ***8a.*** Yield: >95%, thermally unstable yellow oil. ^1H NMR ($CDCl_3$): δ 1.16 (d, ^3J(H,H) = 6.87 Hz, 6H; $CH(CH_3)_2$), 1.20 (d, ^3J(HH) = 7.01 Hz, 6H; $CH(CH_3)_2$), 3.43 (d, ^3J(H,P) = 14.62 Hz, 3H; CH_3O), 3.87 (sp, ^3J(H,H)= 6.94 Hz, 2H; $CH(CH_3)_2$), 7.83 (d, ^1J(H,P) = 439.6 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (d, ^3J(C,P) = 4.25 Hz; $CH(CH_3)_2$), 23.6 (d, ^3J(C,P) = 2.44 Hz; $CH(CH_3)_2$), 48.2 (d, ^2J(C,P) = 3.74 Hz; $CH(CH_3)_2$), 52.3 (d, ^2J(C,P) = 5.28 Hz; CH_3O), 213.3 (d, ^1J(C,P) = 34.7 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 136.8. IR (KBr): 2054, 1981, 1946 (CO) cm^{-1}. HRMS: calcd for $C_{11}H_{18}FeNO_5P$ 331.02713, found 331.02610.

N,N-Diisopropyl-O-benzylphosphonamidite Tetracarbonyliron(0), ***8b.*** Yield: 71%, dark brown oil. ^1H NMR ($CDCl_3$): δ 1.29 (dd, ^3J(H,H) = 6.95, ^3J(H,H) = 6.77 Hz, 12H; $CH(CH_3)_2$), 4.00 (sp, ^3J(H,H) = 6.86 Hz, 2H; $CH(CH_3)_2$), 4.80 (d, ^3J(H,P) = 8.03 Hz, 1H; OCH_2Ph), 4.81 (d, ^3J(H,P) = 7.95 Hz, 1H; OCH_2Ph), 7.2−7.4 (m, 5H; Ph*H*), 8.05 (d, ^1J(H,P) = 437.6 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.7 (d, ^3J(C,P) = 4.2 Hz; $CH(CH_3)_2$), 24.2 (d, ^3J(C,P) = 2.4 Hz; $CH(CH_3)_2$), 48.8 (d, ^2J(C,P) = 3.5 Hz; $CH(CH_3)_2$), 68.0 (d, ^2J(C,P) = 5.1 Hz; OCH_2Ph), 127.8 (s; *o*-PhC), 128.4 (s; *p*-PhC), 128.9 (s; *m*-PhC), 140.9 (d, ^2J(C,P) = 10.3 Hz; *ipso*-PhC), 213.3 (d, ^2J(C,P) = 21.6 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 134.4. IR (KBr): 2058, 2013, 1952 (CO) cm^{-1}. HRMS (CI): calcd for $C_{17}H_{23}FeNO_5P$ 408.06476 (M + 1), found 408.06628.

N,N-Diisopropyl-O-(2-Chloroethyl)phosphonamidite Tetracarbonyliron(0), ***8c.*** Yield: 93%, yellow oil. ^1H NMR ($CDCl_3$): δ 1.25 (d, ^3J(H,H) = 6.68 Hz, 6H; $CH(CH_3)_2$), 1.33 (d, ^3J(H,H) = 6.95 Hz, 6H; $CH(CH_3)_2$), 3.67 (t, ^3J(H,H) = 5.68 Hz, 2H; $ClCH_2CH_2O$), 3.95 (m, 4H; $CH(CH_3)_2$ + $ClCH_2CH_2O$), 8.09 (d, ^1J(H,P) = 399.82 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.7 (d, ^3J(C,P) = 4.2 Hz; $CH(CH_3)_2$), 24.2 (s; $CH(CH_3)_2$), 43.4 (d, ^3J(C,P) = 9.2 Hz; $ClCH_2CH_2O$), 48.8 (d, ^2J(C,P) = 2.8 Hz; $CH(CH_3)_2$), 66.1 (d, ^2J(C,P) = 4.1 Hz; $ClCH_2CH_2O$), 213.0 (d, ^2J(C,P) = 21.9 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 136.5. IR (KBr): 2056, 1975, 1942 (CO) cm^{-1}. HRMS (CI): calcd for $C_{12}H_{20}ClFeNO_5P$ (M + 1) 380.00991, found 380.01166.

N,N-Diisopropyl-O-2-propynephosphonamidite Tetracarbonyliron(0), ***8d.*** Yield: 84%, orange oil. ^1H NMR ($CDCl_3$): δ 1.25 (d, ^3J(H,H) = 6.71 Hz, 6H; $CH(CH_3)_2$), 1.33 (d, ^3J(H,H) = 6.84 Hz, 6H; $CH(CH_3)_2$), 2.54 (t, ^5J(H,H) = 2.38 Hz, 1H; *H*C≡CCH_2O), 3.95 (sp, ^3J(H,H) = 6.80 Hz, 2H; $CH(CH_3)_2$), 4.45 (dd, ^3J(H,P) = 13.87 Hz, ^5J(H,H) = 2.38 Hz, 2H; HC≡CCH_2O), 8.04 (d, ^1J(H,P) = 437.63 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.7 (d, ^3J(C,P) = 4.2 Hz; $CH(CH_3)_2$), 23.7 (d, ^3J(C,P) = 2.5 Hz; $CH(CH_3)_2$), 48.9 (d, ^2J(C,P) = 4.0 Hz; $CH(CH_3)_2$), 53.7 (d, ^3J(C,P) = 4.2 Hz; HC≡CCH_2O), 75.9 (s; HC≡CCH_2O), 78.4 (d, ^3J(C,P) = 6.8 Hz; HC≡CCH_2O), 212.9 (d, ^2J(C,P) = 21.5 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 135.4. IR (KBr): 2060, 1985, 1941 (CO) cm^{-1}. HRMS (CI): calcd for $C_{13}H_{18}FeNO_5P$ (M + 1) 356.03300, found 356.03497.

Acetoxy-(N,N-diisopropylamino)phosphane Tetracarbonyliron-(0), ***9a.*** Yield: 81%, orange oil. ^1H NMR ($CDCl_3$): δ 1.25 (d, ^3J(H,H) = 7.26 Hz, 6H; $CH(CH_3)_2$), 1.28 (d, ^3J(H,H) = 7.36 Hz, 6H; $CH(CH_3)_2$), 2.12 (s, 3H; CO_2CH_3), 4.02 (sp, ^3J(H,H) = 7.31 Hz, 2H; $CH(CH_3)_2$), 7.94 (d, ^1J(H,P) = 460.91 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (d, ^3J(C,P) = 4.9 Hz; $CH(CH_3)_2$), 22.7 (s; CO_2CH_3), 23.2 (d, ^3J(C,P) = 3.1 Hz; $CH(CH_3)_2$), 49.2 (d, ^2J(C,P) = 1.4 Hz; $CH(CH_3)_2$), 168.0 (d, ^2J(C,P) = 9.2 Hz; CO_2CH_3), 212.6 (d, ^2J(C,P) = 21.5 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 125.7. IR (KBr): 2059, 2025, 1982, 1942, 1743 (CO) cm^{-1}. HRMS (CI): calcd for $C_{12}H_{19}FeNO_6P$ (M + 1) 360.02648, found 360.02991.

N,N-Diisopropylamino-2-pyridylcarboxyphosphane Tetracarbonyliron(0), ***9b.*** Yield: 93%, dark red oil. ^1H NMR ($CDCl_3$): δ 1.30 (d, ^3J(H,H) = 6.92 Hz, 6H; $CH(CH_3)_2$), 1.34 (d, ^3J(H,H) = 7.05 Hz, 6H; $CH(CH_3)_2$), 4.14 (sp, ^3J(H,H) = 6.98 Hz, 2H; $CH(CH_3)_2$), 7.52 (dd, ^3J(H,H) = 4.64 Hz, ^3J(H,H) = 7.76 Hz, 1H; pyridyl-C5*H*), 7.88 (t, ^3J(H,H) = 7.76 Hz, 1H; pyridyl-C4*H*), 8.08 (d, ^3J(H,H) = 7.76 Hz, 1H; pyridyl-C3*H*), 8.40 (d, ^1J(H,P) = 455.09 Hz, 1H; P*H*), 8.81 (d, ^3J(H,H) = 4.64 Hz, 1H; pyridyl-C6*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (d, ^3J(C,P) = 4.9 Hz; $CH(CH_3)_2$), 23.3 (d, ^3J(C,P) = 3.4 Hz; $CH(CH_3)_2$), 49.5 (d, ^2J(C,P) = 2.3 Hz; $CH(CH_3)_2$), 125.9 (s; pyridyl-C3), 127.9 (s; pyridyl-C5), 137.7 (s; pyridyl-C4), 147.4 (s; pyridyl-C2), 150.8 (s; pyridyl-C6), 161.8 (d, ^2J(C,P) = 8.2 Hz; CO_2), 212.4 (d, ^2J(C,P) = 21.3 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 127.6. IR (KBr): 2058, 2026, 1977, 1948 (CO) cm^{-1}.

2-Thienylcarboxy-(N,N-diisopropylamino)phosphane Tetracarbonyliron, ***9c.*** Yield: 69%, orange oil. ^1H NMR ($CDCl_3$): δ 1.29 (d, ^3J(H,H) = 6.63 Hz, 6H; $CH(CH_3)_2$), 1.34 (d, ^3J(H,H) = 6.87 Hz, 6H; $CH(CH_3)_2$), 4.09 (sp, ^3J(H,H) = 6.70 Hz, 2H; $CH(CH_3)_2$), 7.15 (dd, ^3J(H,H) = 4.49 Hz, ^3J(H,H) = 4.12 Hz, 1H; SC=C*H*), 7.67 (dd, ^3J(H,H) = 4.12 Hz, ^4J(H,H) = 0.94 Hz, 1H; *H*C=CHS), 7.85 (dd, ^3J(H,H) = 4.12 Hz, ^4J(H,H) = 0.94 Hz, 1H; HC=C*H*S), 8.57 (d, ^1J(H,P) = 451.98 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.7 (d, ^3J(C,P) = 5.0 Hz; $CH(CH_3)_2$), 23.4 (d, ^3J(C,P) = 3.2 Hz; $CH(CH_3)_2$), 49.4 (d, ^2J(C,P) = 2.2 Hz; $CH(CH_3)_2$), 114.0 (s; SC=*C*H), 128.6 (s; HC=*C*HS), 134.6 (s; HC=CH), 135.4 (s; HC=*C*H), 212.4 (d, ^2J(C,P) = 21.4 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 123.1. IR (KBr): 2059, 2026, 1983, 1946, 1707 (CO) cm^{-1}. HRMS (CI): calcd for $C_{15}H_{19}FeNO_6PS$ (M + 1) 427.99916, found 428.00198.

Synthesis of Aminophosphanes ***11a,b*** *and* ***12a,b.*** The Grignard reagents are purchased as 1.0 M solutions in THF and added directly to the 1-hexene solution **2** in 2.2 molar equiv at room temperature. The resulting mixture is stirred for 20 min in the case of the vinyl Grignard reagent and 90 min for the phenyl Grignard reagent. The time is related to the steric congestion at the phosphorus reaction center. The progress of the reaction is monitored by $^{31}P\{^1H\}$ NMR spectroscopy; signals for the phosphorus anions **10a** and **10b** are $\delta^{31}P$ = 78.7 and 63.5 ppm, respectively. When the signals of **2** have disappeared, the reaction is quenched with (a) methanol to generate **11a,b** or (b) 1 equiv of allyl bromide to afford **12a,b**. After filtration of the salts and evaporation of the 1-hexene, the crude reaction mixture is dissolved in $CHCl_3$, filtered over a short column (silica, 0.015−0.040 mm), and concentrated to yield yellow to orange oils.

(N,N-Diisopropylamino)phenylphosphane Tetracarbonyliron(0), ***11a.*** Yield: 87%, orange oil. ^1H NMR ($CDCl_3$): δ 1.10 (d, ^3J(H,H) = 6.81 Hz, 6H; $CH(CH_3)_2$), 1.28 (d, ^3J(H,H) = 6.55 Hz, 6H; $CH(CH_3)_2$), 4.00 (sp, ^3J(H,H) = 6.70 Hz, 2H; $CH(CH_3)_2$), 7.2−7.7 (m, 5H; Ph*H*), 7.67 (d, ^1J(H,P) = 392.1 Hz, 1H; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.2 (d, ^3J(C,P) = 2.7 Hz; $CH(CH_3)_2$), 23.9 (d, ^3J(C,P) = 2.4 Hz; $CH(CH_3)_2$), 49.4 (d, ^2J(C,P) = 5.2 Hz; $CH(CH_3)_2$), 127.6 (d, ^2J(C,P) = 4.9 Hz; *o*-PhC), 129.2 (d, ^3J(C,P) = 2.3 Hz; *m*-PhC), 130.7 (d, ^4J(C,P) = 2.3 Hz; *p*-PhC), 141.7 (d, ^1J(C,P) = 13.2 Hz; *ipso*-PhC), 213.6 (d, ^2J(C,P) = 19.6 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.7. IR (KBr): 2049, 1969, 1937 (CO) cm^{-1}. HRMS: calcd for $C_{16}H_{20}FeNO_4P$ 377.0479, found 377.0486.

(N,N-Diisopropylamino)vinylphosphane Tetracarbonyliron(0), ***11b.*** Yield: 90%, orange oil. ^1H NMR ($CDCl_3$): δ 1.22 (d, ^3J(H,H) = 2.37 Hz, 6H; $CH(CH_3)_2$), 1.25 (d, ^3J(H,H) = 2.46 Hz, 6H; $CH(CH_3)_2$), 3.78 (dsp, ^3J(H,H) = 2.42 Hz, ^3J(H,P) = 21.84 Hz; $CH(CH_3)_2$), 5.87 (dd, ^3J(H,H) = 11.97 Hz, ^3J(H,P) = 21.56 Hz, 1H; (*Z*)-H_2C=CH), 5.91 (dd, ^3J(H,H) = 17.85 Hz, ^3J(H,P) = 23.70 Hz, 1H; (*E*)-H_2C=CH), 6.38 (m, ^3J(H,H) = 11.97 Hz, ^3J(H,H) = 17.85 Hz, ^3J(H,H) = 5.17 Hz, ^2J(H,P) = 45.36 Hz; H_2C=*C*H), 7.30 (dd, ^1J(H,P) = 393.2 Hz, ^3J(H,H) = 5.17 Hz; P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.1 (s; $CH(CH_3)_2$), 23.8 (s; $CH(CH_3)_2$), 48.3 (d, ^2J(C,P) = 4.5 Hz; $CH(CH_3)_2$), 128 (s; H_2C=CH), 137.7 (d, ^1J(C,P) = 36.5 Hz; H_2C=*C*H), 213.6 (d, ^2J(C,P) = 19.9 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 67.3. IR (KBr): 2049, 1972, 1933 (CO) cm^{-1}. HRMS (CI): calcd for $C_{12}H_{19}FeNO_4P$ (M + 1) 328.03756, found 328.04007.

Allyl(diisopropylamino)phenylphosphane Tetracarbonyliron(0), ***12a.*** Yield: 85%, orange oil. ^1H NMR ($CDCl_3$): δ 1.29 (d, ^3J(H,H) = 7.10 Hz, 6H; $CH(CH_3)_2$), 1.32 (d, ^3J(H,H) = 7.00 Hz, 6H; $CH(CH_3)_2$), 3.26 (ddd, ^2J(H,H) = 14.48 Hz, ^2J(H,P) = 15.87 Hz, ^3J(H,H) = 6.88 Hz, 1H; PCH_2), 3.49 (ddd, ^2J(H,H) = 14.48 Hz, ^2J(H,P) = 13.40 Hz, ^3J(H,H) = 7.61 Hz, 1H; PCH_2), 4.15 (sp, ^3J(H,H) = 7.05 Hz, 2H; $CH(CH_3)_2$), 6.06 (m, 1H; CH=CH_2), 5.38 (dd,

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^3J(H,H) = 9.07 Hz, ^3J(H,H) = 13.04 Hz, 2H; CH=CH_2), 7.3−7.9 (m, 5H; Ph*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.8 (d, ^3J(C,P) = 4.0 Hz; CH(CH_3)$_2$), 40.8 (d, ^1J(C,P) = 28.0 Hz; PCH_2), 51.2 (d, ^2J(C,P) = 6.3 Hz; CH(CH_3)$_2$), 120.5 (d, ^3J(C,P) = 22.3 Hz; CH=CH_2), 127.0 (s; *p*-PhC), 128.2 (d, ^2J(C,P) = 26.4 Hz; *C*H=CH_2), 130.1 (s; *m*-PhC), 130.7 (d, ^2J(C,P) = 2.9 Hz; *o*-PhC), 140.5 (d, ^1J(C,P) = 54.9 Hz; *ipso*-PhC), 213.5 (d, ^2J(C,P) = 17.9 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 125.7. IR (KBr): 2057, 1982, 1950 (CO) cm^{-1}. HRMS: calcd for $C_{19}H_{24}FeNO_4P$ 417.07922, found 417.07615.

*Allyl(diisopropylamino)vinylphosphane Tetracarbonyliron(0), **12b***. Yield: 69%, orange oil. ^1H NMR ($CDCl_3$): δ 1.31 (d, ^3J(H,H) = 3.65 Hz, 6H; CH(CH_3)$_2$), 1.33 (d, ^3J(H,H) = 3.68 Hz, 6H; CH(CH_3)$_2$), 3.02 (dd, ^2J(H,P) = 10.71 Hz, ^3J(H,H) = 7.67 Hz, 2H; PCH_2), 4.02 (sp, ^3J(H,H) = 3.66 Hz, 2H; CH(CH_3)$_2$), 5.2−5.4 (m, 2H; =CH_2), 5.8−6.1 (m, 3H; =CH_2 + CH_2C*H*=CH_2), 6.61 (dt, ^3J(H,H) = 12.37 Hz, ^2J(H,P) = 18.74 Hz, 1H; PC*H*=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.7 (d, ^3J(C,P) = 3.4 Hz; CH(CH_3)$_2$), 25.3 (d, ^3J(C,P) = 2.0 Hz, CH(CH_3)$_2$), 41.7 (d, ^1J(C,P) = 27.6 Hz; PCH_2), 51.0 (d, ^2J(C,P) = 5.8 Hz; CH(CH_3)$_2$), 120.5 (d, ^2J(C,P) = 12.0 Hz; PCH=CH_2), 126.8 (s; PCH_2CH=CH_2), 130.7 (d, ^2J(C,P) = 4.5 Hz; PCH_2CH=CH_2), 137.8 (d, ^1J(C,P) = 51.1 Hz; PCH=CH_2), 214.2 (d, ^2J(C,P) = 18.2 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 116.8. IR (KBr): 2048, 1965, 1933 (CO) cm^{-1}. HRMS (CI): calcd for $C_{15}H_{23}FeNO_4P$ (M + 1) 368.07139, found 368.07315.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00227.

Geometries of computed structures (PDF)
X-ray crystallographic data for **4a** (CCDC-1401129) (CIF)

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Notes

The authors declare no competing financial interest.

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