DOI: 10.1002/ejic.201100233

Synthesis, Characterization and Catalytic Application of Iron Complexes Modified by Monodentate Phosphane Ligands

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Keywords: Phosphanes / Monodentate ligands / Iron / Homogeneous catalysis

In the present study, the properties of new monodentate phosphane ligands with a *N*,*N*-diphenyl-1*H*-pyrrol-1-amine moiety have been investigated. The ligands are easily accessible by lithiation of *N*,*N*-diphenyl-1*H*-pyrrol-1-amine in the 2-position and by quenching with phosphane chlorides (**2**: R = *t*Bu, **3**: R = Ph). After characterization of the ligands, their coordination to iron carbonyls has been studied. The ligands coordinate through the phosphorus in a monodentate fashion to the iron to realize complexes with the (L)Fe(CO)$_4$ motif. Initial catalytic experiments have been performed; the iron-catalyzed reduction of alkynes to alkenes with excellent selectivities to the corresponding alkenes has been achieved.

Introduction

The advance of sustainable and more environmentally friendly techniques for the synthesis of high-value products is one of the central aims for industry as well as academia.[1] In this regard, transition-metal-catalyzed reactions offer an efficient and versatile approach and represent a key feature for the advancement of "green chemistry", specifically for waste prevention, achieving high atom economy and advantageous economics.[2] A current trend is the substitution of expensive and toxic metals (e.g., Rh, Ir, Ru) by cheap, abundant and less toxic metals.[3] Thus the use of biometals, e.g. iron, is of great importance. Over the last years, special attention was directed to iron catalysis.[4] Aside from the choice of the metal, the influence of the surrounding ligands is of importance.[5] In this context, phosphane ligands have been demonstrated as useful tools, with respect to catalyst activity and selectivity, in various iron-catalyzed reduction protocols, e.g. C=O, amides, imines, alkynes.[6] However, improvement of activity and selectivity still remains a challenge. On the basis of our ongoing interest in iron catalysis, we report herein the synthesis of easy accessible phosphanes, the synthesis and characterization of the corresponding iron complexes and the application in reduction chemistry, i.e. the selective reduction of alkynes to alkenes.[7]

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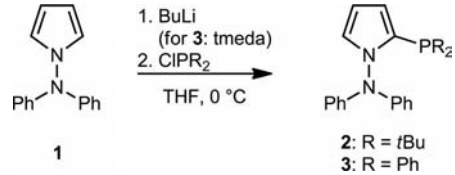
Results and Discussion

Synthesis of Phosphane Ligands

Recently, various groups reported the synthesis and application of 2-**p**hosphanyl-1-**a**ryl**p**yrrole ligands (PAP ligands).[8,9] By selective lithiation in the 2-position of *N*-substituted pyrroles with *n*BuLi/tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and subsequent reaction with phosphane chlorides, electron-rich and sterically demanding ligands were accessed. The ligands have been proven to be useful in the making of highly active catalysts with transition metals and have been applied in numerous catalytic transformations.[8,9] Further, the substituent connected to the pyrrole nitrogen atom has a crucial influence (electronic and steric) on catalysis. So far, most of the PAP ligands are based on aryl substituents that form a N–C bond. We were interested in knowing whether the carbon group can be replaced by an amine functionality to generate a N–N bond and allow a different electronic and steric situation. Furthermore, the amine-based group can be an additional donor, which can coordinate to the metal centre. On the basis of this concept, we developed a new type of pyrrole–phosphane ligand. The overall synthesis of phosphanes **2** and **3** proceeds in two steps and starts with the reaction of dimethoxytetrahydrofuran and *N*,*N*-diphenylhydrazine. Both compounds were heated at reflux in acetic acid to yield *N*,*N*-diphenyl-1*H*-pyrrol-1-amine (**1**). After



Scheme 1. Synthesis of **2** and **3**.

isolation, a selective lithiation in the 2-position of the pyrrole unit was performed with *n*-butyllithium in THF at 0 °C (Scheme 1).

Subsequently, chloro-di-*tert*-butylphosphane or chlorodiphenylphosphane, respectively, were added to allow C–P bond formation. In the case of phosphane **3**, lithiation was performed in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda). The ligands were purified by either column chromatography (**2**) or crystallization in acetone (**3**). It is noteworthy that phenyl-substituted phosphane **3** is highly air- and moisture stable (>6 month), while phosphane **2** is easily oxidized. The molecular structure of compound **2** is confirmed as the corresponding phosphane oxide (**2**-oxide) by X-ray crystallography and is depicted in Figure 1. The N–N distance (1.392–1.394 Å) of **2**-oxide and phosphane **3** (Figure 2) are quite similar. The phenyl groups at the phosphorus atom of compound **3** are slightly distorted compared to the *tert*-butyl groups of phosphane **2**.

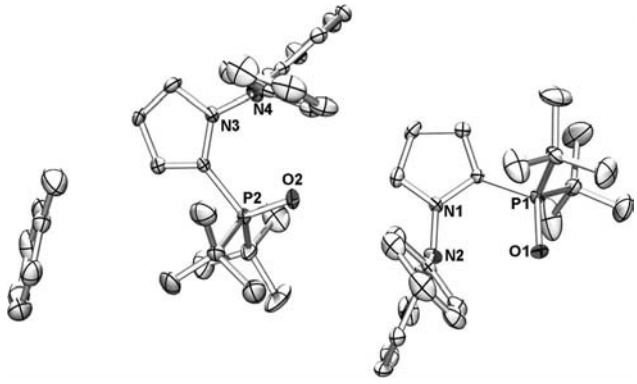


Figure 1. Molecular structure of **2**-oxide. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: N1–N2 1.394(4), P1–O1 1.477(2), N3–N4 1.392(4), P2–O2 1.488(2).

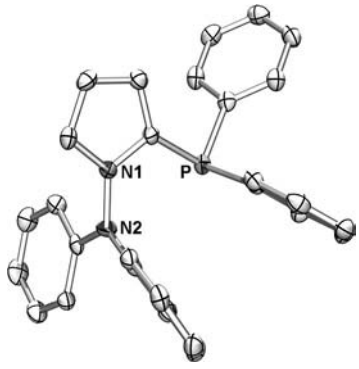
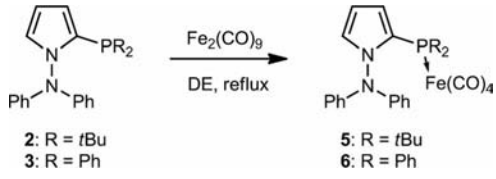


Figure 2. Molecular structure of **3**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: N1–N2 1.3919(18).

Synthesis of Iron Phosphane Complexes

Moreover, phosphanes **2** and **3** were treated with equimolar amounts of diiron nonacarbonyl in refluxing diethyl ether to yield the corresponding iron complexes **5** and **6** (Scheme 2).[10] In the case of **6**, suitable crystals for single-crystal X-ray diffraction analysis were obtained by slow cooling to room temperature and slow evaporation of the solvent (see Figure 3), while the reaction of **2** with $Fe_2(CO)_9$ was incomplete and only small amounts of the corresponding complex **5** was formed. In accordance with other monodentate iron phosphane complexes reported in the literature, four carbonyl groups are attached to the iron centre.[11,12] For the carbonyl ligand in the *trans* position with respect to the phosphane ligand, a shorter Fe–C distance (1.768 Å) could be observed because of the *trans*-effect of the phosphane ligand. The *cis*-positioned carbonyl ligands show almost equal Fe–C distances (1.784–1.794 Å). The Fe–P bond length (2.248 Å) is shorter in contrast to similar complexes in the literature. The bond angles between the carbonyl ligands in the equatorial position (116.06–122.18°) differ from the ideal angle of 120° because of steric hindrance of the phenyl groups at the phosphorus and at the nitrogen atoms. In addition, the carbonyl ligand in the axial position is nearly linearly coordinated (178.96°). The large N2–Fe distance (4.025 Å) neglects the coordination of nitrogen to the iron centre. Attempts to force the coordination of the nitrogen donor, by irradiation of the complex with light or addition of Me_3NO, failed so far. In the case of complex **5**, the IR spectra shows two strong absorption bands at 1962 and 1929 cm^{-1}, which can be attributed to the carbonyl ligands coordinated equatorially and axially to the iron, while for complex **6**, two strong bands at 1971 and 1938 cm^{-1} are observed. The signals in the ^1H NMR spectra for both compounds **5** and **6** are broad, because of the properties of iron. In contrast, the



Scheme 2. Synthesis of iron phosphane complexes **5** and **6**.

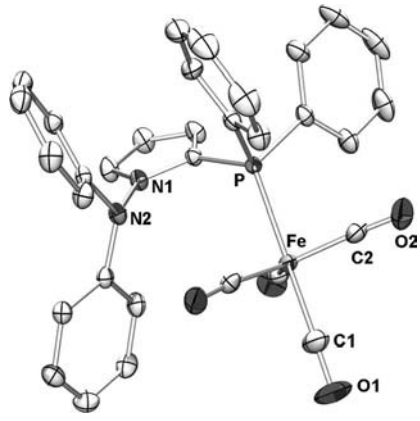


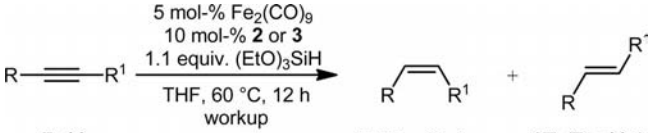
Figure 3. Molecular structure of **6**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Fe–C1 1.768(3), Fe–C 1.784(3)–1.794(3), Fe–P 2.2484(7).

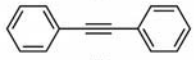
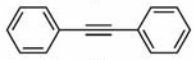
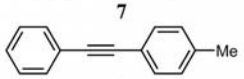
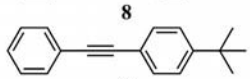
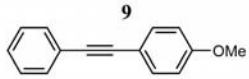
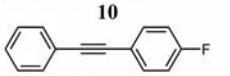
^{31}P NMR spectra show sharp signals – the coordinated and non-coordinated ligands can be determined conclusively. As expected, the signals for coordinated ligands are shifted to a lower field, 103.0 ppm for complex **5** (**2**: 1.3 ppm) and 55.3 ppm for complex **6** (**3**: –31.4 ppm).

Reduction of Alkynes to Alkenes

With these new ligands and complexes in hand, we were interested in the iron-catalyzed reduction of alkynes to alkenes, since alkenes have a wide range of applications in industry as well as in academic research, e.g. as synthons for bulk chemicals, pharmaceuticals, agrochemicals, polymers, natural product synthesis and as key intermediates in organic syntheses. Catalytic hydrogenation has been proven to be a method of choice.[13] However, over reduction to the corresponding alkanes often occurs, which reduces the impact of this method.[14] An alternative to hydrogenation is hydrosilylation, with the advantage of mild reaction conditions and a straightforward process. The group of Chirik applied well-defined iron complexes modified by tridentate nitrogen ligands on the reduction of alkynes with silanes to the corresponding alkenes at ambient temperature.[15] Recently, we have reported the application of a robust and easy-to-adopt iron-based catalyst for the selective reduction of alkynes to alkenes.[12] However, an unsolved challenge must be addressed to the (*E*)/(*Z*)-selectivity to obtain one isomer exclusively. In accordance to earlier reports, diphenylacetylene **7** was chosen as the model substrate. The precatalyst was formed in situ by reacting 5 mol-% of diiron nonacarbonyl with 10 mol-% of ligand **2** or **3** in THF. After addition of the reducing reagent $(EtO)_3SiH$, the reaction mixture was stirred for 12 h at 60 °C (Table 1). The reaction was then quenched under aqueous conditions. The best performance for the formation of stilbene was found for the catalyst containing ligand **3**, with yields of >99% and a (*Z*)-selectivity of 87%, while with ligand **2** a lower conversion and a (*Z*)-selectivity of 72% was obtained. Furthermore, the isolated complex **6** was applied as a precatalyst. However, a significant reduced yield and selectivity was observed relative to the in situ approach. Probably, in the in situ approach, complexes are formed along with **6**, which are catalytically active, which results in increased yields. Unfortunately, the complexes are so far unidentified. Moreover, various substituted diphenylacetylenes have been reduced in the presence of $Fe_2(CO)_9$ and ligand **3**, which results in the formation of the corresponding stilbenes in good yield and selectivities. It should be noted that in all cases, no over reduction was observed.

Table 1. Iron-catalyzed reduction of alkynes.



7–11		(*Z*)-(**7a–11a**)		(*E*)-(**7a–11a**)
Entry[a]	Substrate	Pre-catalyst	Yield [%][b,c]	(*Z*)/(*E*)[b]
1	 **7**	$Fe_2(CO)_9$ **2**	71	72:28
2	 **7**	**6**[d]	43	74:26
3	 **7**	$Fe_2(CO)_9$ **3**	>99 (93)	87:13
4	 **8**	$Fe_2(CO)_9$ **3**	83 (77)	86:14
5	 **9**	$Fe_2(CO)_9$ **3**	78 (74)	85:15
6	 **10**	$Fe_2(CO)_9$ **3**	55	85:15
7	 **11**	$Fe_2(CO)_9$ **3**	44	86:14

[a] Reaction conditions: Reactions were carried out with 0.036 mmol $Fe_2(CO)_9$ (5 mol-%), 0.072 mmol ligand, 0.72 mmol substrate, 0.79 mmol $(EtO)_3SiH$ (1.1 equiv.), 2.0 mL THF, 12 h at 60 °C. [b] The conversion was determined by GC (30 m Rxi-5ms column, 40–300 °C). For compound **7**, dodecane was applied as internal standard. [c] In brackets the isolated yield is stated. [d] The isolated complex **6** was applied as pre-catalyst.

Conclusions

In summary, we have presented the straightforward synthesis of monodentate phosphanes based on the *N*,*N*-diphenyl-1*H*-pyrrol-1-amine scaffold. The corresponding iron complexes have been obtained by reacting the phosphanes with diiron nonacarbonyl in a molar ratio of 1:1. The defined complexes consist of the structural motif $LFe(CO)_4$. The complexes have been applied as useful catalysts in the reduction of alkynes to alkenes with good selectivities. Contrary to case for the isolated complex, the in situ approach exhibited an increase in yield and selectivity. In future work, the composition of the in situ catalyst will be studied to understand the different behaviour.

Experimental Section

General: All manipulations with oxygen- and moisture-sensitive compounds were performed under dinitrogen by using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker AFM 200 spectrometer (^1H: 200.13 MHz; ^{13}C: 50.32 MHz) by using the proton signals of the deuterated solvents as reference. IR spectra were recorded either on a Nicolet Series II Magna-IR-System 750 FTR-IR or on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Electron-impact mass spectra (EI-MS) were recorded on a Finnigan MAT95S.

Safety Consideration: During our studies we used triethoxysilane as reducing reagent without incident. However, Buchwald et al. reported on difficulties when working with triethoxysilane.[16]

Synthesis of *N*,*N*-diphenyl-1*H*-pyrrol-1-amine: 1,1-Diphenylhydrazine (0.11 mol) was dissolved in 1,4-dioxane at room temperature. Dimethoxytetrahydrofuran (0.14 mol) was added, followed by acetic acid (100 mL). The solution was stirred and heated at reflux for

12 h, during which the colour changed to deep brown. After cooling to room temperature, dichloromethane was added, and the solution was filtered through a plug of silica. The solvent was removed in vacuo to yield a black oily residue, which was purified by vacuum distillation to give off-white crystals. Yield: 15.2 g (59%). M.p. 58 °C (off-white crystals). B.p. 138–140 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 6.24 (t, J = 2.31 Hz, 2 H, pyrrole), 6.86 (t, J = 2.31 Hz, 2 H, pyrrole), 6.94–7.07 (m, 6 H, C_6H_5), 7.23–7.34 (m, 4 H, C_6H_5) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 107.6, 119.1, 120.6, 123.1, 129.2, 130.6, 146.1 ppm. IR (KBr): $\tilde{\nu}$ = 3400 (w), 3027 (w), 1942 (w), 1727 (w), 1591 (s), 1495 (s), 1330 (m), 1313 (m), 1295 (m), 1195 (w), 1180 (w), 1156 (w), 1069 (m), 1061 (m), 997 (w), 973 (m), 890 (w), 747 (s), 717 (s), 691 (s), 643 (m), 507 (w) cm^{-1}. MS (ESI): m/z = 235 [M$^+$ + 1 H]. HRMS calcd. for [$C_{16}H_{14}N_2$ + H] 235.12298; found 235.12223.

Synthesis of *N*,*N*-Diphenyl-1*H*-pyrrol-1-amine-2-di-*tert*-butylphosphane (2): A solution of *N*,*N*-diphenyl-1*H*-pyrrol-1-amine (19.6 mmol) in dry THF (50 mL) was stirred under an atmosphere of dinitrogen. The mixture was cooled to 0 °C, and *n*-butyllithium [23.6 mmol (1.2 equiv.), 1.6 M in *n*-hexane] was added dropwise by syringe. The solution was stirred for additional 2 h at 0 °C, followed by the addition of di-*tert*-butylchlorophosphane (19.99 mmol) and stirring at room temperature for 8 h. After refluxing for 3 h, the solvent was removed in vacuo. The residue was dissolved in toluene (100 mL) and filtered. The solvent was removed, and, after drying, a white powder was obtained. Yield: 5.1 g (69%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 6.65–7.20 (m, 11 H), 6.48–6.54 (m, 1 H), 6.23–6.29 (m, 1 H), 1.03 (s, 9 H, *t*Bu), 0.97 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 146.8, 129.4, 128.7, 124.6, 123.0, 122.8, 119.2, 115.7, 115.6, 108.4, 107.9, 32.6, 32.2, 30.5, 30.2 ppm. ^{31}P NMR (50 MHz, C_6D_6, 25 °C): δ = 1.3 ppm. IR (KBr): $\tilde{\nu}$ = 3395 (w), 3133 (w), 3067 (w), 2939 (m), 2862 (m), 1939 (w), 1744 (w), 1590 (s), 1493 (s), 1456 (s), 1414 (m), 1361 (m), 1274 (s), 1209 (m), 1174 (m), 1097 (m), 1074 (m), 1028 (m), 1008 (m), 930 (w), 884 (w), 808 (w), 799 (w), 749 (s), 723 (s), 691 (s), 634 (m), 590 (w), 572 (w), 525 (w), 489 (w), 460 (w) cm^{-1}. MS (ESI): m/z = 379 [M$^+$ + 1 H]. HRMS calcd. for [$C_{24}H_{31}N_2P$ + H] 379.22976; found 379.22839.

Synthesis of *N*,*N*-Diphenyl-1*H*-pyrrol-1-amine-2-di-*tert*-butylphosphane Oxide (2-oxide): A solution of *N*,*N*-diphenyl-1*H*-pyrrol-1-amine (19.6 mmol) in dry THF (50 mL) was stirred under an atmosphere of dinitrogen. The mixture was cooled to 0 °C, and, in a sequence, *n*-butyllithium [23.6 mmol (1.2 equiv.), 1.6 M in *n*-hexane] and *N*,*N*-tetramethylethylenediamine (19.6 mmol) were added dropwise by syringe. The solution was stirred for additional 2 h at 0 °C, followed by the addition of di-*tert*-butylchlorophosphane (19.99 mmol) and stirring at room temperature for 8 h. After refluxing for 3 h, the solvent was removed in vacuo. The residue was dissolved in toluene (100 mL) and filtered. The volume was reduced to ca. 50 mL, and ethyl acetate was added in air. After several days, colourless crystals appeared. The crystals were removed by filtration and dried in vacuo. Yield: 7.3 g (95%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 6.90–7.29 (m, 11 H, C_6H_5), 6.53–6.59 (m, 1 H, pyrrol), 6.34–6.39 (m, 1 H, pyrrol), 1.15 (s, 9 H, *t*Bu), 1.08 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 146.1, 130.9, 128.6, 128.5, 128.4, 122.6, 119.9, 116.6, 116.3, 107.7, 107.5, 38.1, 36.8, 26.3 ppm. ^{31}P NMR (50 MHz, $CDCl_3$, 25 °C): δ = 48.7 ppm. IR (KBr): $\tilde{\nu}$ = 3430 (m), 3112 (w), 3082 (w), 3027 (w), 2963 (m), 2871 (m), 1728 (m), 1590 (m), 1496 (s), 1474 (m), 1460 (m), 1404 (m), 1387 (m), 1364 (m) 1331 (m), 1308 (m), 1279 (m), 1221 (m), 1197 (m), 1165 (s), 1121 (m), 1094 (m), 1081 (m), 1039 (m), 1017 (m), 931 (w), 874 (w), 811 (m), 762 (m), 742 (m), 701, 690 (m), 665 (m), 646 (m), 538 (w), 523 (w), 488 (w), 473 (m) cm^{-1}. MS (ESI): m/z = 395 [M$^+$ + 1 H]. HRMS calcd. for [$C_{24}H_{31}N_2OP$ + H] 395.22468; found 395.22321.

Synthesis of *N*,*N*-Diphenyl-1*H*-pyrrol-1-amine-2-diphenylphosphane (3): A solution of *N*,*N*-diphenyl-1*H*-pyrrol-1-amine (17.8 mmol) in dry THF (50 mL) was stirred under an atmosphere of dinitrogen. The mixture was cooled to 0 °C, and, in a sequence, *n*-butyllithium [20.5 mmol (1.2 equiv.), 1.6 M in *n*-hexane] and *N*,*N*-tetramethylethylenediamine (17.1 mmol) were added dropwise by syringe. The solution was stirred for additional 2 h at 0 °C, followed by addition of chlorodiphenylphosphane (17.8 mmol) and stirring at room temperature for 8 h. After refluxing for 3 h, the solvent was removed in vacuo. The residue was dissolved in toluene (100 mL) and filtered. The solvent was removed, and the residue dissolved in acetone in air. After several days, colourless crystals appeared. The crystals were removed by filtration and dried in vacuo. Yield: 6.2 g (83%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 6.80–7.30 (m, 21 H), 6.28–6.36 (m, 1 H), 6.02–6.09 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 145.9, 136.8, 136.7, 133.7, 133.3, 130.6, 129.0, 128.4, 128.2, 128.1, 124.8 (d, J = 1.66 Hz), 123.0, 119.4 (d, J = 1.28 Hz), 116.5 (d, J = 2.47 Hz), 109.2 (d, J = 1.07 Hz) ppm. ^{31}P NMR (50 MHz, $CDCl_3$, 25 °C): δ = –31.4 ppm. IR (KBr): $\tilde{\nu}$ = 3435 (m), 3112 (m), 3093 (m), 3068 (m), 3050 (s), 3009 (m), 2627 (w), 2346 (w), 1948 (w), 1888 (w), 1809 (w), 1743 (w), 1676 (w), 1587 (s), 1533 (m), 1492 (s), 1460 (s), 1432 (s), 1395 (m), 1329 (s), 1306 (s), 1281 (s), 1211 (m), 1191 (s), 1156 (m), 1120 (m), 1095 (m), 1079 (m), 1069 (m), 1027 (m), 1007 (m), 998 (m), 909 (w), 876 (m), 849 (w), 837 (m), 807 (m), 760 (s), 727 (s), 695 (s), 654 (m), 628 (m), 594 (w), 571 (w), 523 (s), 502 (s), 487 (m), 458 (w) cm^{-1}. MS (ESI): m/z = 419 [M$^+$ + 1 H]. HRMS calcd. for [$C_{28}H_{23}N_2P$ + H] 419.16716; found 419.16548.

General Synthesis of Iron Phosphane Complexes: A solution of the corresponding phosphane ligand (761 μmol) and diironnonacarbonyl (761 μmol) in diethyl ether (30 mL) was heated at reflux for 1–2 h. The solution was allowed to cool to room temperature. The volatiles were removed in vacuo to yield a brown foam. The products were purified by extraction and filtration through a pad of aluminium oxide. Coloured crystals were obtained by crystallization from diethyl ether.

5: (Reaction time: 1 d, deep red solid). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 7.40–5.80 (m), 4.91 (br. s), 1.88 (br. s), 1.00 (s) ppm. ^{31}P NMR (50 MHz, C_6D_6, 25 °C): δ = 103.0 ppm. IR (KBr): $\tilde{\nu}$ = 2968 (w), 2940 (w), 2894 (w), 2862 (w), 2348 (w), 2042 (m), 2000 (w), 1962 (s), 1929 (s), 1590 (m), 1494 (s), 1458 (w), 1391 (w), 1362 (w), 1312 (w), 1275 (w), 1175 (w), 1075 (w), 1028 (w), 809 (w), 750 (m), 724 (m), 693 (m), 635 (w), 490 (w) cm^{-1}. MS (70 eV, EI): m/z (%) = 490 (<1) [**5** – 2× CO], 462 (<1) [**5** – 3× CO], 434 (<1) [**5** – 4× CO], 378 (44), [**5** – Fe(CO)$_4$], 321 (16), 265 (46), 234 (19), 168 (100), 98 (18), (Molpeak was not detectable).

6: (Reaction time: 1 h, deep red crystals obtained from diethyl ether). M.p. 167 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.20–5.77 (m), 1.23 (s), 0.81 (s) ppm. ^{31}P NMR (50 MHz, $CDCl_3$, 25 °C): δ = 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 3114 (w), 3064 (w), 2049 (s), 1971 (s), 1930 (s), 1588 (m), 1492 (m), 1458 (w), 1437 (m), 1257 (m), 1210 (w), 1184 (w), 1095 (m), 1079 (m), 761 (m), 752 (m), 736 (m), 693 (m), 626 (s), 563 (w), 543 (w), 534 (w), 505 (m) cm^{-1}. MS (70 eV, EI): m/z (%) = 502 (40) [**6** – 3× CO], 474 (100) [**6** – 4× CO], 418 (18) [**6** – Fe(CO)$_4$], 172 (33), (Molpeak was not detectable).

Single-Crystal X-ray Structure Determination: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected by using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and re-

fined on F^2 with the SHELX-97 software package.[17] The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model. CCDC-815979, -815980 and -815981 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.

Compound 2-Oxide: Triclinic; space group $P\bar{1}$; a = 9.6130(6), b = 12.7465(5), c = 22.6180(10) Å; α = 95.731(4)°, β = 99.133(4)°, γ = 110.383(5)°; V = 2528.7(2) Å^3; Z = 2; $\rho_{calcd.}$ = 1.157 mg m^{-3}; absorption coefficient 0.130 mm^{-1}; F(000) 948; reflections collected: 19886; independent reflections: 8882 [R_{int} = 0.0579]; completeness to θ = 25.00° (99.7%); max. and min. transmission 0.9770 and 0.9524; goodness-of-fit on F^2 1.058; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0784, $wR2$ = 0.1553; R indices (all data): $R1$ = 0.1435, $wR2$ = 0.1754; largest diff. peak and hole 0.470 and –0.354 e Å^{-3}.

Compound 3: Triclinic; space group $P\bar{1}$; a = 10.0533(4), b = 10.9260(5), c = 11.2871(5) Å; α = 111.201(4)°, β = 100.956(4)°, γ = 101.463(4)°; V = 1085.29(8) Å^3; Z = 2; $\rho_{calcd.}$ = 1.281 mg m^{-3}; absorption coefficient 0.145 mm^{-1}; F(000) 440; reflections collected: 9345; independent reflections: 3806 [R_{int} = 0.0219]; completeness to θ = 25.00° (99.8%); max. and min. transmission: 0.9565 and 0.9004; goodness-of-fit on F^2 1.021; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0363, $wR2$ = 0.0765; R indices (all data): $R1$ = 0.0468, $wR2$ = 0.0797; largest diff. peak and hole 0.239 and –0.280 e Å^{-3}.

Compound 6: Monoclinic; space group $P2_1/n$; a = 16.3557(7), b = 10.8043(4), c = 17.0356(8) Å; α = 90°, β = 110.408(5)°, γ = 90°; V = 2821.4(2) Å^3; Z = 4; $\rho_{calcd.}$ = 1.380 mg m^{-3}; absorption coefficient 0.631 mm^{-1}; F(000) 1208; reflections collected: 10889; independent reflections: 4956 [R_{int} = 0.0346]; completeness to θ = 25.00° (99.7%); max. and min. transmission: 0.8789 and 0.7775; goodness-of-fit on F^2 0.940; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0372, $wR2$ = 0.0688; R indices (all data): $R1$ = 0.0585, $wR2$ = 0.0722; largest diff. peak and hole 0.273 and –0.346 e Å^{-3}.

General Procedure for the Reduction of Alkynes: A pressure tube was charged with diiron nonacarbonyl (0.036 mmol, 5.0 mol-%) and the corresponding ligand (0.072 mmol, 10 mol-%). The compounds were dissolved in freshly distilled tetrahydrofuran (2.0 mL). To this solution diphenylacetylene (0.72 mmol) and $(EtO)_3SiH$ (0.79 mmol) were added by syringe. The reaction mixture was stirred in a preheated oil bath at 60 °C for 12 h. The mixture was cooled down in an ice bath and was treated with dodecane (10 µL) as GC standard (for GC analysis) and aqueous sodium hydroxide solution (1.0 mL) with stirring. The reaction mixture was stirred for 60 min at room temperature and was then extracted with diethyl ether (2 × 10.0 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and filtered, and an aliquot was removed for GC analysis (30 m Rxi-5ms column, 40–300 °C). The obtained analytical data for all products are in agreement with literature reports.[18]

Acknowledgments

This work was supported by the Cluster of Excellence "Unifying Concepts in Catalysis" (sponsored by the Deutsche Forschungsgemeinschaft and administered by the Technische Universität Berlin). The author thanks Prof. Dr. Matthias Drieß (Technische Universität Berlin) for general discussion. Paula Nixdorf (Technische Universität Berlin) is acknowledged for analytical support.

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Received: March 7, 2011
Published Online: May 17, 2011

