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Discovery and Synthetic Value of a Novel, Highly Crowded Cyclopentadienylphosphane Ph_2P-$Cp^{TM}H$ and Its Ferrocenyl-Bisphosphane $dppf^{TM}$

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Base-catalysed condensation of Ph_2P–C_5H_5 (**1**) with an excess of acetone leads to a fulvene-like diphenyl(4,4,6-trimethyl-4,5-dihydropentalen-2-yl)phosphane Ph_2P-$C_{11}H_{13}$ (**3**) as a product of double condensation. Carbometallation of **3** with MeLi, followed by aqueous work-up, results in formation of a new cyclopentadienylphosphane bearing a highly sterically demanding, anellated 1,1,3,3-tetramethylcyclopentane moiety (**4**, Ph_2P-$Cp^{TM}H$). It reacts with chalcogene oxidants (H_2O_2, S_8, Se) to form the corresponding phosphane chalcogenides $Ph_2P(=X)Cp^{TM}H$, X = O (**5**), S (**6**), Se (**7**) in high yields. Quaternization of **4** with MeI gives the phosphonium salt **8** as a single isomer in high yield. Dehydrohalogenation of **8** by reaction with *n*BuLi gives Cp^{TM}-phosphonium ylide $Ph_2P(Cp^{TM})Me$ (**9**). An alternative protocol towards **9** that includes deprotonation of **8** with benzylpotassium followed by *P*-alkylation is superior and gives **9** in more than 95 % yield. Staudinger reaction of **4** with *t*BuN_3 gives only *P*-amino-cyclopentadienylidenephosphorane $Ph_2P(Cp^{TM})$-NH*t*Bu (**10**), whereas with Me_3SiN_3 only the tautomeric *P*-imino-cyclopentadienylphosphane $Ph_2P(NSiMe_3)Cp^{TM}H$ (**11**) was isolated. Hydrolysis of **11** with wet MeCN leads to the new parent *P*-amino-cyclopentadienylidenephosphorane Ph_2P-$(Cp^{TM})NH_2$ (**12**). Treatment of **4** with benzylpotassium followed by transmetallation with $FeCl_2$ leads to the sterically most crowded ferrocenyl-bisphosphane [{Ph_2P-Cp^{TM}}$_2$Fe] (**13**, $dppf^{TM}$) in high yield. Its X-ray diffraction analysis reveals an *anti*-orientation of phosphane functionalities at both cyclopentadienyl rings. However, upon reaction of $dppf^{TM}$ with [$PdCl_2(MeCN)_2$], a constrained *syn*-orientation is achieved in the product [{$dppf^{TM}$}$PdCl_2$] (**14**). Halogen exchange by reaction of **14** with NaI leads to the corresponding [{$dppf^{TM}$}PdI_2] (**15**). Molecular structures of **4**, **9**, **13** and **15** have been confirmed by XRD studies.

Introduction

Cyclopentadienylphosphane ligands [R_2P-{Cp}, {Cp} = (non)-substituted Cp, Ind or Flu] are useful building blocks, broadly applied in organometallic chemistry.[1] As structural motive they can be found in very useful ligands such as dppf [{Ph_2P-C_5H_4}$_2$Fe] or CTC-Q-Phos [{Ph_5C_5}Fe-{$C_5H_4P(tBu)_2$}]. Most frequently R_2P-{Cp} are represented in the literature by phosphanes R_2P-C_5H_5 (R = Me, Ph),[2] R_2P-C_5Me_4H (R = Me,[3] Ph[4]), ($tBu)_2P$-C_5H_5,[5] 3-indenyl-(Ph_2P-C_9H_7)[6] and 9-fluorenyl- (Ph_2P-$C_{13}H_9$),[7] that with exception of 9-fluorenyl derivatives, show fluxional behaviour in solutions and appear as mixtures of isomers.

Commonly R_2P-{Cp} are synthesized by nucleophilic substitution of R_2P–X (X = Hal, OAlk) with anionic forms of appropriate cyclopentadienes. Nevertheless, their further derivatization is very scarcely described in the literature.[2]

For our systematic investigation of chelating organophosphorus(V) ligands of the general type $[R_2P(X)Z]^-$ (X, Z = S, NR′, CH_2, CHR′, Cp, Ind, Flu; as for X = Z and X ≠ Z)[8,9] it was necessary to synthesize Ph_2P-{Cp} phosphanes, bearing sterically demanding substituents, e.g. a *tert*-butyl group, at the C_5 ring. Besides simple metathesis of *t*BuCp anion with Ph_2PCl, such ligand motive may be achieved by carbometallation with MeLi of corresponding 6,6-dimethylfulvene that is easily accessible by a condensation of acetone with {Cp}H using 5–10 mol-% of pyrrolidine, as a catalyst, in methanol. The reaction is highly chemoselective and, as a rule, high yields of fulvenes are reported.[10] However, even minor changes of the reaction conditions were found to be highly crucial to its further transformation. Here we report our discovery of a new, highly crowded cyclopentadienylphosphane, Ph_2P-$Cp^{TM}H$, its reactivity and synthetic potential.

Results and Discussion

Synthesis and Molecular Structure of Ph_2P-$Cp^{TM}H$

Condensation reaction of Ph_2P-C_5H_5 (**1**)[2] with one equivalent of acetone (MeOH, 10 mol-% pyrrolidine) leads

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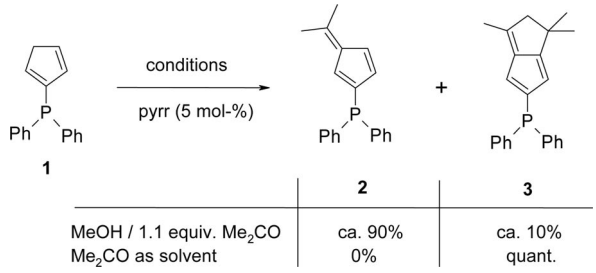
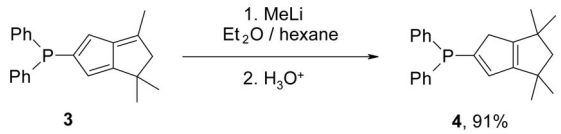
to the selective formation of the expected fulvenylphosphane Ph_2P-C_8H_9 (**2**) (Scheme 1). The product precipitates from the reaction mixture as a bright yellow, air-stable crystalline solid, ^{31}P NMR (C_6D_6): δ_P = –16.8 ppm. Monitoring of the reaction by ^{31}P NMR spectroscopy indicated formation of ca. 10% of an unidentified impurity (δ_P = –13.9 ppm). By working in acetone as solvent, formation of **2** was quantitative within minutes, however it was followed by conversion of **2** into this new compound **3** within 4 h as monitored by ^{31}P NMR spectroscopy. The structure and composition of thus formed Ph_2P-$C_{10}H_{13}$ (**3**) as annelated phosphane (Scheme 1) have been confirmed by multinuclear and 2D NMR spectroscopic techniques, mass spectra and elemental analysis.



Scheme 1.

Further carbometallation of **3** with MeLi in ether or hexane as solvent followed by protonation of thus derived carbanion leads to a new annelated tetramethylpentalenyl-substituted phosphane ($Ph_2PCp^{TM}H$) **4**, that, compared to its 3-*t*Bu-substituted analogue, is higher both by its steric impact and symmetry (Scheme 2). However, if the reaction with MeLi is performed in THF a deprotonation of the exocyclic fulvene methyl group of **3** rather than a carbometallation took place. Phosphane Ph_2P-$Cp^{TM}H$ (**4**) was purified by preparative flash chromatography under anaerobic conditions. This pale yellow needle-like crystalline material with a faint phosphane-like odour is fairly air-stable and can be handled and stored under aerobic conditions without decomposition for months. The solubility of **4** is very high in common organic solvents, but becomes moderate in those ones of the higher polarity (CH_3CN, MeOH) as well as in cold lower alkanes (pentane, hexane). The molecular structure of **4** was confirmed by multinuclear NMR spectroscopy, mass spectrometry, elemental and XRD single crystal structure analysis.



Scheme 2.

Crystals of the compound **4**, suitable for X-ray diffraction analysis, were obtained by slow cooling of its hot concentrated ethanol solution. It crystallizes in the monoclinic space group $P2_1/c$ with four molecules per cell unit. In the structure the bridging H_2C-group of the aliphatic ring is disordered with occupancies of 0.49/0.51; only one conformation is shown in Figure 1. As expected, the phosphorus atom is threefold coordinated by two phenyl groups and a $Cp^{TM}H$-moiety – all are twisted in a propeller-like arrangement. The unsaturated Cp ring is essentially planar [Δ_{max} = 0.0002(2) Å for C8]. The C4 and C6 atoms of the aliphatic ring deviate only by values of 0.053 and 0.073(2) Å from the $Cp^{TM}H$-ring plane.

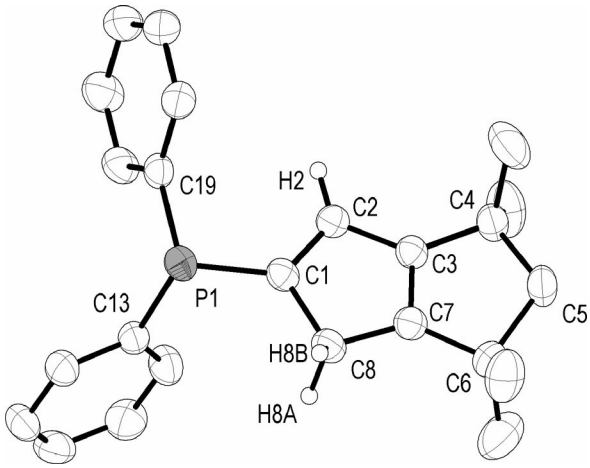
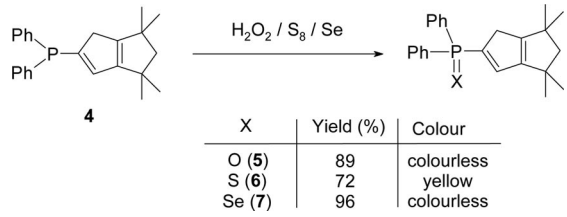


Figure 1. Molecular structure of compound **4**. All hydrogen atoms, except of those at the Cp-ring, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.807(2), P1–C13 1.832(2), P1–C19 1.833(2), C1–C2 1.348(2), C2–C3 1.475(2), C3–C7 1.334(2), C7–C8 1.487(2), C1–C8 1.517(2); C1–P1–C13 103.1(1), C13–P1–C19 102.3(1), C19–P1–C1 100.7(1), C1–C8–C7 102.7(1), C3–C2–C1–C8 0.2(2), C2–C3–C7–C8 0.2(2).

The average P–C_{Ph} bond length is of 1.832(3) Å and falls in the typical range of other phosphanes Ar_3P (1.82–1.84 Å).[11] However, the P–C1 bond length is slightly shorter [1.807(2) Å]. The olefinic bonds lengths are alternating and are shorter at C1–C2 and C3–C7 with 1.348(2) and 1.334(2) Å, respectively then other ones in the Cp ring [C2–C3 1.475(2), C7–C8 1.487(2), C1–C8 1.517(2) Å]. All C–P–C angles [100.7(1), 102.3(1) and 103.1(1) Å] lie in the typical range reported for triarylphosphanes.[11] Although several free indenyl- and fluorenylphosphanes are known,[12] to the best of our knowledge, **4** is the first free diorgano-cyclopentadienylphosphane characterized by X-ray crystallography.

Reactivity of Ph_2P-$Cp^{TM}H$ as Phosphane

The phosphane **4** is readily oxidized by H_2O_2 (30% solution in water) in THF, elemental sulfur in toluene and red selenium in $CHCl_3$ to form corresponding chalcogenido phosphanes as air-stable, crystalline solids in high yields (Scheme 3).

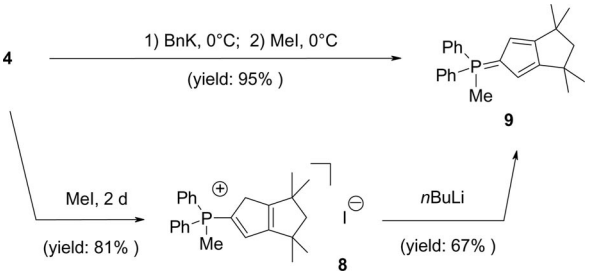


X	Yield (%)	Colour
O (**5**)	89	colourless
S (**6**)	72	yellow
Se (**7**)	96	colourless

Scheme 3.

As expected and confirmed by NMR spectroscopy, only one tautomeric form is observed for all these compounds. Steric hindrance of the tetramethyltrimethylene backbone prevents their dimerization by the Diels–Alder reaction typically found for the parent C5-unsubstituted derivatives $Ph_2P(X)C_5H_5$ (X = O, S).[2]

Quaternization of **4** with an excess of MeI leads to the expected phosphonium salt $[Ph_2P(Cp^{TM}H)Me]^+ I^-$ (**8**) (Scheme 4) as an air-stable, non-hygroscopic solid, that appears as a single isomer (δ_P = 12.2 ppm). It is worth to mention, that sterically less hindered Ph_2P-Cp and Ph_2P-Ind upon reaction with MeI lead to the mixtures of allylic and vinylic isomers; for the Cp-derivative, Diels–Alder type dimerization products were also obtained.[13,14] Dehydrohalogenation of the salt **8** with *n*BuLi leads to the formation of cyclopentadienyliden-phosphorane $Ph_2P(Cp^{TM})Me$ (**9**) as a pale yellow, crystalline solid in 67% yield. A superior protocol towards **9** includes deprotonation of **4** with BnK followed by in situ quaternization of thus obtained anionic derivative with an excess of MeI that chemoselectively leads to *P*-alkylation and gives **9** in almost quantitative yield.



Scheme 4. Two alternative reaction sequences toward synthesis of **9**.

Single crystals, suitable for X-ray diffraction analysis, were obtained by storing of concentrated ether solution to 0 °C. Compound **9** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. The molecular structure of one of these molecules is drawn in Figure 2.

The P1–C1 bond length in **9** is significantly shorter [1.714(2) Å] than in parent **4**, this is in good agreement with those in other cyclopentadienylidenephosphoranes.[15] An alternating order of C–C bond lengths at the C_5 ring was observed: the short bonds are C2–C3 and C7–C8 [1.373(3) and 1.385(3) Å], whereas C1–C2, C3–C7 and C1–C8, respectively, are long [1.425(3), 1.404(3) and 1.441(3) Å].

Earlier, we reported the Staudinger reactions of a series of R_2P–{Cp} with organic azides.[8] Successful formation of

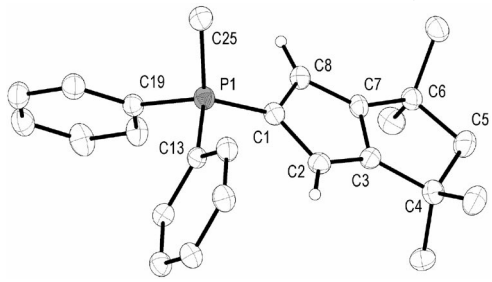
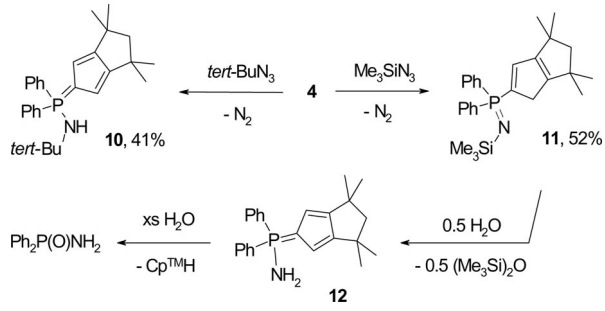


Figure 2. Molecular structure of $Ph_2P(Cp^{TM})Me$ (**9**). All hydrogen atoms have been omitted for clarity. Only one independent molecule is drawn. Selected bond lengths [Å] and angles [°]: P1–C1 1.714(2), P1–C13 1.803(2), P1–C19 1.802(3), P1–C25 1.795(3), C1–C2 1.425(3), C2–C3 1.373(3), C3–C7 1.404(3), C7–C8 1.385(3), C1–C8 1.441(3), C1–P1–C13 107.37(12), C13–P1–C19 106.62(11), C19–P–C1, 113.98(13), C1–P1–C25 113.72(13), C13–P1–C25 109.15(13), C19–P1–C25 105.74(13).

the *CpPN* derivatives has been confirmed also for the entitled ligand **4** (Scheme 5). Thus reaction of **4** with $tBuN_3$ proceeds at ambient temperature yielding a yellow, microcrystalline solid as the single *P*-amino-cyclopentadienylidenephosphorane tautomer $Ph_2P(Cp^{TM})NH(tBu)$ (**10**). The position of the NH-proton at δ = 2.04 ppm in **10** was also established by the HMQC spectroscopy. The ^{31}P NMR resonance of **10** (δ =17.1 ppm) appears essentially at the same δ_P as those ones of *CpPN*-ligands $R_2P(C_5Me_4)NHAd$ (R = Me: 17.6 ppm,[8] and R = Ph: 17.8 ppm[16]). The reaction of **4** with the less reactive Me_3SiN_3 was found to be extremely slow and gave the desired product only if Me_3SiN_3 was used as a solvent at the reflux temperature (5 d, ca. 100 °C). The ^{31}P NMR monitoring the reaction mixture after 14 h of heating reveals absence of both starting material **4** and its Staudinger phosphazide adduct (δ = –27 ppm) and two new resonances at ca. –5 (major) and 23 ppm (minor). The major signal appears in the characteristic *P*-iminophosphane region and belongs to the target **11**, whereas the minor signal is attributed to its tautomeric *P*-aminophosphorane form similar to **10**.[9] **11**, the better soluble tautomer was extracted from the reaction mixture into hexane. It comprises a highly air-sensitive, crystalline solid, that easily hydrolyzes, when in solution: first, by water traces with release of $(Me_3Si)_2O$ to *P*-amino-cyclopentadienylidenephosphorane **12**, and further by excess of water with release of free $Cp^{TM}H$ and precipitation of a colorless, crystalline solid, identified as diphenylphosphinic



Scheme 5. Reactions of **4** with organic azides.

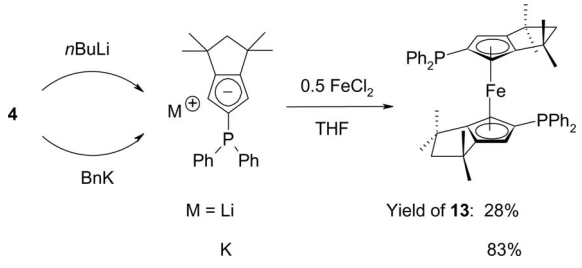
acid amide $Ph_2P(O)NH_2$ [δ_P(THF) = 25.0 ppm, m.p. 161–162 °C].[17]

Further studies of thus obtained organophosphorus(V) derivatives **5**–**12** of the title phopsphane Ph_2P-$Cp^{TM}H$ (**4**) as chelating ligands in organometallic chemistry are the focus of our current investigations.

Reactivity of Ph_2P-$Cp^{TM}H$ as Bifunctional Ligand

We have studied a possibility to use **4** as a bifunctional ligand in the synthesis of a bis-phosphanyl-substituted ferrocene and its further use as chelating, electron-rich and sterically demanding ligand towards $PdCl_2$.

Direct transmetallation of lithiated **4** by ferrous chloride [$FeCl_2(THF)_n$] gave the desired ferrocene **13** in 28% isolated yield (Scheme 6). A possible explanation for such a poor yield might be a partial deprotonation of Ph_2P-$Cp^{TM}H$ due to its low kinetic CH-acidity compared to unsubstituted Ph_2P-C_5H_5 (**1**) or the low nucleophilicity of the lithium salt. Benzylpotassium [$PhCH_2K$] is known as superior deprotonating reagent and its use instead of *n*BuLi gave rise to **13** in 83% isolated yield as a bright-orange, air-stable, non-volatile solid. Being analogous to the prominent chelate ligand [{Ph_2P-C_5H_4}$_2$Fe] (dppf),[18] we call this derivative **13** $dppf^{TM}$.



Scheme 6. Yield dependence of **13** on deprotonation agent.

The ^{31}P NMR spectroscopy reveals a single up-field shifted resonance at –15.8 ppm. In the ^1H NMR spectrum, the geminal protons of the CH_2-group and the methyl groups are, as expected, diastereotopic. The high conformational rigidity in solution is presented in the ^{13}C NMR spectroscopy – the resonances to *ortho*- and *ipso*-Ph carbons, observed at δ = 134.6 and 141.2 ppm, resp., show *pseudo*-triplet pattern ($|^2J_{CP} + {}^6J_{CP'}|$ = 10.5 Hz, $|^1J_{CP} + {}^5J_{CP'}|$ = 6.8 Hz, resp.). This coupling pattern is in contrast to those reported for the unsubstituted ferrocene (dppf),[19] which shows for these resonances solely two doublets.

Orange crystals of **13**, suitable for X-ray structure determination, were grown by slow cooling of its concentrated alcohol solution. The molecular structure of ferrocene with ellipsoids of 50% of probability is presented in Figure 3.

Complex **13** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The iron atom lies on the crystallographic inversion center, the molecule as a whole is centrosymmetric. The molecule has a strictly *anti*-conformation of substituents at both C5-rings. The distance between the iron atom and centroid (Z) of the C5-ring

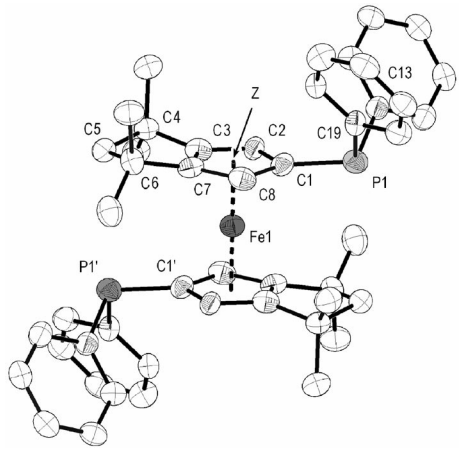
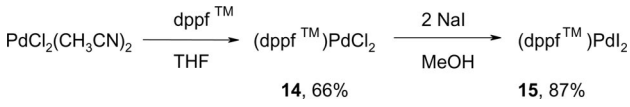


Figure 3. The molecular structure of [($Cp^{TM}PPh_2$)$_2$Fe] (**13**). Hydrogen atoms have been omitted for clarity (Z = centroid of C5-ring). Selected bond lengths [Å] and angles [°]: P1–C1 1.832(1), P1–C13 1.833(1), P1–C19 1.853(1), C1–C2 1.441(1), C2–C3 1.406(1), C3–C7 1.400(1), C7–C8 1.427(1), C8–C1 1.437(1), Z···Fe1 1.682(1), Fe1–C1 2.084(1), C1–P1–C13 101.2(2), C13–P1–C19 99.7(2), C19–P1–C1 100.1(1), C8–C1–P1–C19 46.6(1), C2–C1–P1–C13 24.5(1), P1–Z–Z′–P1′ 180.00(2).

[1.682(1) Å] is slightly longer than those in [($C_5H_4PPh_2$)$_2$Fe] [1.646(5) Å],[20] [($Me_4C_5PPh_2$)$_2$Fe] [1.653(1) Å].[21] Bond lengths and angles involving the phosphorus atoms compare well with the values in triphenylphosphane, [($C_5H_4PPh_2$)$_2$Fe] and **4** (vide supra). All Fe1–C_{C5} distances lie in a narrow range varying from 2.064(1)–2.088(1) Å.

Reaction of **13** with [$PdCl_2(CH_3CN)_2$] gives an light purple microcrystalline solid of composition [($dppf^{TM}$)$PdCl_2$] (**14**) in 66% yield. Further halogen exchange was achieved by reaction of **14** with an excess of NaI in MeOH (Scheme 7). Thus, [($dppf^{TM}$)PdI_2] (**15**) was isolated as a deep purple microcrystalline solid in 87% yield, higher than in the analogous synthesis of the [(dppp)PdI_2] reported recently.[22] Identification of both compounds was completed by microanalysis and multinuclear NMR spectroscopy.



Scheme 7.

NMR spectra of **14** and **15** are rather similar and spectroscopic characteristics will be discussed for **14** as representative. In its ^1H NMR spectrum four resonances for methyl groups were observed whereas two diastereotopic methyl groups are observed in $dppf^{TM}$. Moreover, the protons at the C_5 ring appear as *two* resonances at 3.64 (s) and 4.11 (d, $^3J_{HP}$ = 2.5 Hz) ppm. In the ^{13}C NMR spectrum two diastereotopic *para*- and *ipso*-Ph carbon resonances were observed. These findings confirm the molecular rigidity in solution and a helical structure with low degree or absence of Δ-/Λ interconversion.

Single crystals of palladium complex **15**, suitable for X-ray diffraction analysis, were obtained by a slow evapora-

tion of its chloroform solution. The compound crystallizes in the orthorhombic space group $Pca2_1$ with four molecules per unit cell (Figure 4).

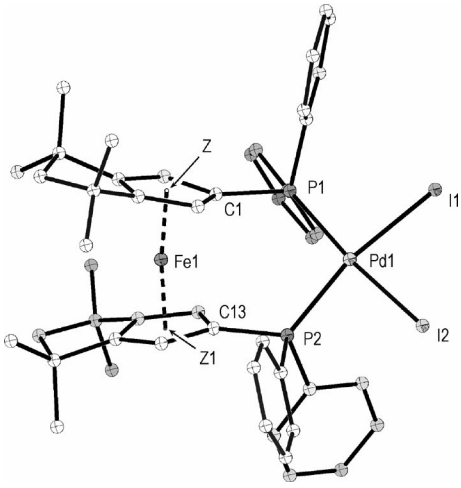


Figure 4. The molecular structure of [(dppf^{TM})PdI$_2$] (**15**). All H-atoms have been omitted for clarity (Z = centroid of C5-ring). Selected bond lengths [Å] and angles [°]: Pd1–I1 2.639(2), Pd1–I2 2.652(2), Pd1–P1 2.293(1), Pd1–P2 2.298(1), P1–C1 1.808(2), P2–C13 1.801(2), Fe–Z 1.683(1), Fe–Z1 1.675(1), I1–Pd1–I2 90.2(1), P1–Pd1–I1 86.3(1), P2–Pd1–I2 86.3(1), P1–Pd1–P2 99.3(1), Z–Pd1–Z1 172.0(1).

The palladium atom has a distorted square-planar geometry. The similar distortion was reported for complexes [(dppf)PdI$_2$] (Hal = Br, I).[23]

The P1–Pd1–P2 bite angle is of 99.3(1)° and comparable with those of in series [(dppf)PdHal$_2$] (Hal = Cl – I: 98.9–99.9°). The I1–Pd1–I2 angle is of 90.2(1)° and slightly larger than those in dppf complexes (Hal = Cl – I: 87.2–87.8°).[22,24] The most interesting feature is the dramatic distortion of both C_5 rings in the molecule. The Z–Fe–Z1 angle of 172.0(1)° is the lowest value in the whole series of the [(dppf)PdHal$_2$] [Hal = Cl: 179.5(1)°, Br 177.8(1), I: 178.3(1)°].[22,23]

Conclusions

Simple pyrrolidine catalyzed condensation of the known phosphane Ph$_2$P-C$_5$H$_5$ (**1**) with acetone leads to the formation of two different condensation products: either with 1 equiv. of acetone to yield diphenyl(6,6-dimethylfulven-2-yl)phosphane (**2**) or with two equiv. of acetone when reacted in acetone as a solvent to yield diphenyl(4,4,6-trimethyl-4,5-dihydropentalen-2-yl)-phosphane (**3**). Subsequent carbometallation of **3** with MeLi resulted in the first air-stable, sterically highly crowded tetramethypentalenylphosphane **4**. This cyclopentadienylphosphane (Ph$_2$P-Cp^{TM}H) appeared to be thermodynamically stable with respect to its dimerisation and it is the first compound of this class that has been crystallographically characterized. The oxidation reactions of Ph$_2$P-Cp^{TM}H with H_2O_2, S_8 and Se yield exclusively the corresponding chalcogenides Ph$_2$P-(X)Cp^{TM}H, X = O (**5**), X = S (**6**), X = Se (**7**). Quaternization of **4** with MeI proceeds smoothly to [Ph$_2$P(Cp^{TM}H)-Me]$^+$ I$^-$ (**8**), its dehydrohalogenation by reaction with *n*BuLi gives *P*-methyl-cyclopentadienylidenephosphorane Ph$_2$P-(Cp^{TM})Me (**9**). An alternative protocol towards **9**, the deprotonation of **8** with benzyl potassium followed by *P*-alkylation is superior and gives **9** in more than 95% yield. The NMR spectroscopy of the phosphane **4**, its chalcogenides **5**–**7** as well as the phosphonium salt **8** shows the presence of a single vinylic isomer in all cases. Compounds **4** and **9** have been structurally characterized by X-ray diffraction analyses.

The Staudinger reaction of **4** with *t*BuN$_3$ gives tautomer Ph$_2$P(Cp^{TM})NH*t*Bu (**10**) that exists exclusively in *P*-amino-cyclopentadienylidenephosphorane form, whereas with Me$_3$SiN$_3$ the major tautomer has the form of *P*-imino-cyclopentadienylphosphane Ph$_2$P(NSiMe$_3$)Cp^{TM}H (**11**). Hydrolysis of **11** with wet MeCN leads after tautomerization to the novel *P*-amino-cyclopentadienylidenephosphorane Ph$_2$P(Cp^{TM})NH$_2$ (**12**).

Finally, ferrocene [(η^5-Cp^{TM}PPh$_2$)$_2$Fe] (**13**) was synthesized by metallation of Ph$_2$P-Cp^{TM}H with [PhCH$_2$K] and transmetallation with FeCl$_2$. In analogy to its known predecessor dppf it is named dppf^{TM}. Despite of its extreme steric bulk and stereochemical rigidity, ferrocene **13** has been applied as a bidentate phosphane ligand for the synthesis of palladium complexes [(dppf^{TM})PdCl$_2$] (**14**) and [(dppf^{TM})-PdI$_2$] (**15**). Both **13** and **15** have also been characterized by X-ray diffraction analysis. The reported high-yield chemical transformation from cheap starting materials as well as proof of ligand properties will stimulate further development with respect to introducing other substituents at the phosphorus atom or via carbometallation at the reactive fulvene functionality.

Experimental Section

General Considerations: All manipulations were performed under purified argon or nitrogen using standard high vacuum or Schlenk or glovebox techniques. Solvent grade acetone, acetonitrile and MeOH were used without purification. Hexane and THF were distilled under argon employing standard drying agents.[25] Ph$_2$P-C$_5$H$_5$ (**1**)[2] and anhydrous metal salts FeCl$_2$,[26] [PdCl$_2$(MeCN)$_2$][27] were prepared according to the literature procedures. Ph$_2$PCl (95%, techn.) was used as supplied from Acros. NMR spectra were recorded at +25 °C on a Bruker ARX200 and Bruker AMX300. Elemental analyses were performed at the Analytical Laboratory of the Chemistry Department/Philipps-University of Marburg. EI mass spectra were obtained on a Varian MAT CH7A (70 eV), ESI mass spectra on a FINNIGAN TSQ 700 spectrometer. Melting points were determined with a Büchi melting point B-540 apparatus.

Fulvenylphosphane 2 (Ph$_2$P-C$_8$H$_9$): To a stirred solution of phosphane **1** (745 mg, 2.98 mmol) in methanol (10 mL), acetone (0.24 mL, 3.72 mmol, 1.1 equiv.) and pyrrolidine (0.1 mL, ca. 1.3 mmol, ca. 5 mol-%) were added at ambient temperature. The reaction mixture progressively turns deep yellow. The solution was stirred for 4 h whereupon a bright yellow, microcrystalline solid forms. It was filtered off and dried in vacuo for 4 h; yield 59% (510 mg); m.p. 83.0–83.5 °C. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 25 °C):

δ = 1.59, 1.67 (2× s, 2× 3 H, 2× *Me*), 6.52 (m, 1 H, C*H*), 6.56 (m, 1 H, C*H*), 6.71 (m, 1 H, C*H*), 7.07 (m, 6 H, *Ph*), 7.55–7.64 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 22.6 (s, *Me*), 122.4 (d, $J_{C,P}$ = 4.1 Hz, C_{C5}), 128.7 (d, $^3J_{C,P}$ = 7.0 Hz, *m-Ph*), 128.7 (s, *p-Ph*), 129.0 (d, $J_{C,P}$ = 22 Hz, P-C_{C5}), 133.6 (d, $J_{C,P}$ = 12.8 Hz, *ipso-Ph*), 134.0 (d, $^2J_{P,C}$ = 19.4 Hz, *o-Ph*), 138.5 (d, $^1J_{C,P}$ = 11.1 Hz, C_{C5}), 140.9 (d, $J_{P,C}$ = 10.3 Hz, C_{C5}), 143.8, 149.6 (2× d, $J_{C,P}$ = 7.8, $J_{C,P}$ = 2.5 Hz, *C*=*C*Me$_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = –16.8 ppm. EI-MS: *m*/*z* (%) = 290 (100) [M$^+$], 275 (1) [M$^+$ – Me], 213 (1) [M$^+$ – Ph]. $C_{20}H_{19}P$ (290.35): calcd. C 82.73, H 6.60; found C 82.91, H 6.63.

Fulvenylphosphane 3 (Ph_2P-$C_{11}H_{13}$): To a stirred solution of phosphane **1** (6.20 g, 24.8 mmol) in acetone (40 mL), pyrrolidine (0.5 mL, 6.4 mmol, 25 mol-%) was added at ambient temperature. The reaction mixture turns gradually deep orange. The proceeding of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixture sample. After the reaction completed (ca. 4 h), all volatiles were removed in vacuo and resulting orange, viscous oil was dried for 4 h at 60 °C under high vacuum. The obtained crude product was crystallized twice from hexane (2 × 20 mL) at –30 °C to give a bright yellow, microcrystalline solid in 44% yield (4.0 g); m.p. 93–94 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 1.12 (s, 6 H, *Me*$_2$C), 1.59 (q, $^4J_{H,H}$ = 1.2 Hz, 3 H, *Me*C=C), 2.44 (s, 2 H, CH_2), 5.97 (s, 1 H, C*H*), 6.27 (dd, $^3J_{H,P}$ = 3.0, $^4J_{H,H}$ = 1.2 Hz, 1 H, C*H*), 7.09 (m, 6 H, *m-*/*p-Ph*), 7.65 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 16.4 (s, *Me*C=C), 29.2 (s, *Me*$_2$C), 37.7 (Me$_2$*C*), 61.3 (s, *C*H$_2$), 115.7 (d, $^2J_{C,P}$ = 17.6 Hz, H*C*), 117.3 (d, $^2J_{C,P}$ = 17.1 Hz, H*C*), 128.6 (s, *Ph*), 128.7 (s, *Ph*), 134.3 (d, $^2J_{C,P}$ = 19.8 Hz, *o-Ph*), 138.4 (d, $^1J_{C,P}$ = 11.3 Hz, *ipso-Ph*), 148.7 (d, $J_{C,P}$ = 8.1 Hz, *Flv*), 151.3 (d, $J_{C,P}$ = 13.6 Hz, *Flv*), 153.2 (d, $J_{C,P}$ = 3.0 Hz, *Flv*), 161.6 (d, $J_{C,P}$ = 5.8 Hz, *Flv*) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = –13.9 ppm. EI-MS: *m*/*z* (%) = 331 (22.5) [M$^+$ + H], 330 (100) [M$^+$], 315 (18.6) [M$^+$ – CH$_3$], 253 (8.3) [M$^+$ – Ph]. $C_{23}H_{23}P$ (330.41): calcd. C 83.61, H 7.02; found C 83.31, H 6.64.

Phosphane 4 (Ph_2P-Cp^{TM}H): To a solution of fulvenylphosphane **3** (5.28 g, 16.0 mmol) in diethyl ether (50 mL), MeLi solution (1.6 M in ether, 15 mL, 24 mmol) was added at 0 °C during 15 min followed by stirring at ambient temperature for 1 h. The reaction mixture was quenched with methanol (3.5 mL). The clear, supernatant solution was decanted from the sticky residue and all volatiles were removed in vacuo. The residue was extracted into hexane (100 mL) and the solution was filtered through a Celite® pad. Cooling the solution to –80 °C overnight gives a pale yellow, crystalline material, which was isolated by low temperature filtration and dried in vacuo for 1 h. A pale yellow, crystalline solid was obtained in yield of 91% (5.04 g); m.p. 108–109 °C. An almost colorless sample was obtained by crystallization from $SiMe_4$ at –30 °C; m.p. 109.0–109.3 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 1.02 (s, 6 H, *Me*$_2$C), 1.11 (s, 6 H, *Me*$_2$C), 1.94 [s, 2 H, CH_2(CMe$_2$)$_2$], 2.89 (t, $^4J_{H,H}$ = 1.5 Hz, 1 H, H_2C_{C5}), 7.76 (dt, $^3J_{H,P}$ = 5.4, $^4J_{H,H}$ = 1.5 Hz, 1 H, HC_{C5}), 7.05 (m, 6 H, *m-*/*p-Ph*), 7.53 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 30.0, 30.4 (2× s, 2× C*Me*$_2$) 37.6 (d, $^2J_{C,P}$ = 9.8 Hz, H_2C_{C5}), 40.2, 41.8 (2× s, 2× *C*Me$_2$), 61.6 [s, *C*H$_2$(CMe$_2$)$_2$], 128.6, 128.7 (2× s, *m-*/*p-Ph*), 133.7 (d, $^1J_{C,P}$ = 19.7 Hz, *ipso-Ph*), 139.0 (d, $^2J_{C,P}$ = 24.1 Hz, *o-Ph*), 139.4 (d, $J_{C,P}$ = 10.9 Hz, C_{C5}), 145.8 (d, $J_{C,P}$ = 14.8 Hz, C_{C5}), 155.8 (d, $J_{C,P}$ = 8.2 Hz, C_{C5}), 160.6 (s, C_{C5}) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = –14.5 ppm. EI-MS: *m*/*z* (%) = 347 (1.4) [M$^+$ + H], 346 (34.5) [M$^+$], 331 (100) [M$^+$ – Me], 269 (1) [M$^+$ – Ph]. $C_{24}H_{27}P$ (346.45): calcd. C 83.21, H 7.86; found C 83.38, H 7.79.

Phosphane Oxide 5 [Ph_2P(O)Cp^{TM}H]: To a stirred solution of phosphane **4** (490 mg, 1.42 mmol) in THF (10 mL), aq. H_2O_2 (ca. 30%, ca. 1.6 mmol) was added in one portion at ambient temperature. An exothermic reaction takes place. The stirring was continued for 0.5 h after that the volatiles were completely removed in high vacuum. The traces of water were removed by azeotropic drying with toluene (50 mL). The solid residue was washed with cold hexane (2 × 5 mL), crystallized from hot heptane and dried in vacuo; yield 71% (365 mg) of a colorless, microcrystalline solid; m.p. 162.9–163.3 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.97, 1.02 (2× s, 2× 6 H, 2× *Me*$_2$C), 1.90 [s, 2 H, CH_2(CMe$_2$)$_2$], 3.10 (s, 2 H, H_2C_{C5}), 6.95 (d, $^3J_{C,P}$ = 8.7 Hz, 1 H, HC_{C5}), 7.05 (m, 6 H, *m-*/*p-Ph*), 7.89 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 29.8, 30.1 (2× s, 2× *Me*$_2$C), 36.8 (d, $^2J_{C,P}$ = 12.6 Hz, H_2C_{C5}), 40.1, 41.8 (2× s, 2× Me$_2$*C*), 61.4 [s, *C*H$_2$-(CMe$_2$)$_2$], 128.5, 128.7 (2× s, *m-*/*p-Ph*), 131.1 (d, $J_{C,P}$ = 2.7 Hz, C_{C5}), 132.2 (d, J = 10.9 Hz, *o-Ph*), 141.6 (d, J = 9.8 Hz, HC_{C5}), 155.0 (d, $^3J_{C,P}$ = 14.8 Hz, C_{C5}CMe$_2$), 164.2 (s, C_{C5}, C_{C5}CMe$_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = +18.1 ppm. EI-MS: *m*/*z* (%) = 362 (19) [M$^+$], 347 (87) [M$^+$ – Me]. $C_{24}H_{27}OP$ (362.4): calcd. C 79.53, H 7.51; found C 79.78, H 6.98.

Phosphane Sulfide 6 [Ph_2P(*S*)Cp^{TM}H]: Sulfur powder (340 mg, 1.33 mmol, 1 equiv.) was added to a stirred solution of phosphane **4** (460 mg, 1.33 mmol) in toluene (12 mL) at ambient temperature. A slightly exothermic reaction with dissolution of sulfur was observed. The reaction mixture was stirred for additional 2 h. The solvent was removed in vacuo and the solid residue obtained was triturated with hexane. The formed precipitate was filtered off and washed with small amount of hexane. Yield 72% (360 mg) of yellow powder with the melting point of 133–134 °C. The sample of analytical purity was obtained by crystallization from hot heptane solution: yellow, crystalline solid; m.p. 134.4–134.7 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.96, 1.00 (2× s, 2× 6 H, *Me*$_2$C), 1.87 [s, 2 H, CH_2(CMe$_2$)$_2$], 3.20 (s, 2 H, H_2C_{C5}), 6.94 (d, $^3J_{C,P}$ = 9.5 Hz, 1 H, HC_{C5}), 7.01 (m, 6 H, *m-*/*p-Ph*), 7.97 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 29.8, 30.1 (2× s, 2× *Me*$_2$C), 36.8 (d, $^2J_{CP}$ = 12.6 Hz, H_2C_{C5}), 40.1, 41.8 (2× s, 2× Me$_2$*C*), 61.4 [s, *C*H$_2$(CMe$_2$)$_2$], 128.5 (m, *m-*/*p-Ph*), 131.1 (d, $J_{C,P}$ = 2.7 Hz, C_{C5}), 132.2 (d, J = 10.9 Hz, *o-Ph*), 141.6 (d, J = 9.8 Hz, HC_{C5}), 155.0 (d, $^3J_{C,P}$ = 14.8 Hz, C_{C5}CMe$_2$), 164.2 (s, C_{C5}CMe$_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = +31.4 ppm. EI-MS: *m*/*z* (%) = 378 (55) [M$^+$], 363 (65) [M$^+$ – Me]. $C_{24}H_{27}PS$ (378.5): calcd. C 76.16, H 7.19; found C 76.46, H 7.13.

Phosphane Selenide 7 [Ph_2P(Se)Cp^{TM}H]: Red selenium powder (119 mg, 1.55 mol, 1.07 equiv.) was added to a solution of phosphane **4** (498 mg, 1.44 mmol) in chloroform (5 mL). The heterogenic reaction mixture was heated under reflux for 5 h. The excess of red selenium was removed by filtration through a Celite® pad. Removal of the solvent from the filtrate gives a brown, foamy solid; yield 96% (588 mg) of brown solid. The sample of analytical purity with the melting point of 143–144 °C was obtained by slow crystallization from hot heptane. Colorless, crystalline solid; m.p. 147.7–148.0 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.95, 1.00 (2× s, 2× 6 H, 2× *Me*$_2$C), 1.86 [s, 2 H, CH_2(CMe$_2$)$_2$], 3.25 (s, 2 H, H_2C_{C5}), 6.94 (d, $^3J_{C,P}$ = 9.8 Hz, 1 H, HC_{C5}), 6.99 (m, 6 H, *m-*/*p-Ph*), 7.97 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 30.0, 30.5 (2× s, 2× *Me*$_2$C), 36.8 (d, $^2J_{C,P}$ = 12.7 Hz, H_2C_{C5}), 40.2, 42.1 (2× s, 2× Me$_2$*C*), 61.3 [s, *C*H$_2$(CMe$_2$)$_2$], 128.6 (d, $^3J_{C,P}$ = 12.1 Hz, *m-Ph*), 131.5 (d, $^4J_{C,P}$ = 3.3 Hz, *p-Ph*), 132.4 (d, $^2J_{C,P}$ = 11.0 Hz, *o-Ph*), 132.5 (d, $^1J_{C,P}$ = 78 Hz, *ipso-Ph*), 138.3 (d, $^1J_{C,P}$ = 83 Hz, P-C_{C5}), 143.2 (d, $^2J_{C,P}$ = 9.9 Hz, HC_{C5}), 154.9 (d, $^3J_{C,P}$ = 15.4 Hz, C_{C5}CMe$_2$), 165.0 (d, $^3J_{C,P}$ = 7.2 Hz, C_{C5}CMe$_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = 22.3 ($^1J_{P,Se}$ = 710 Hz) ppm. $^{77}Se\{^1H\}$ NMR (76 MHz, C_6D_6, 25 °C): δ = –260.8 (d, $^1J_{Se,P}$ = 741 Hz) ppm. EI-MS: *m*/*z* (%): 426 (32.8) [M$^+$], 265

(84.5) [M^+ – Cp^{TM}]. $C_{24}H_{27}PSe$ (425.41): calcd. C 67.76, H 6.40; found C 68.06, H 6.87.

Phosphonium Salt 8 [$Ph_2P(Cp^{TM}H)Me]^+I^-$: To a solution of phosphane **4** (350 mg, 1.00 mmol) in CH_2Cl_2 (5 mL), MeI (0.15 mL, ca. 2.4 mmol) was added and resulting solution was stirred for 48 h. Progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After that all volatiles were removed in vacuo, ether (10 mL) was added. Vigorous stirring results in formation of a pale yellow, powdery solid that was filtered off and dried in high vacuum; yield 81% (395 mg); m.p. 195–200 °C ^1H NMR (200.1 MHz, $CDCl_3$, 25 °C): δ = 1.23, 1.26 (2× s, 2×6 H, 2× Me_2C), 2.12 [s, 2 H, $H_2C(CMe_2)_2$], 3.00 (d, $^2J_{H,P}$ = 13.5 Hz, *Me*P), 3.32 (br. d, $^4J_{H,H}$ = 2.0 Hz, 2 H, H_2C_{C5}), 7.29 (dt, $^3J_{H,P}$ = 9.6, $^4J_{H,H}$ = 2.0 Hz, 1 H, HC_{C5}), 7.69–7.83 (m, 10 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (50.1 MHz, $CDCl_3$, 25 °C): δ = 12.2 (d, $^2J_{C,P}$ = 58 Hz, Me_2P), 29.9, 30.3 (2× s, 2× Me_2C), 38.0 (d, $^2J_{C,P}$ = 13 Hz, H_2C_{C5}), 40.2, 42.5 (2× s, 2× Me_2C), 61.1 [s, $H_2C(CMe_2)_2$], 120.5 (d, $^1J_{C,P}$ = 91 Hz, *ipso-Ph*), 122.2 (d, $^1J_{C,P}$ = 96 Hz, P-C_{C5}), 130.5 (d, $^3J_{C,P}$ = 12.7 Hz, *m-Ph*), 132.8 (d, $^2J_{C,P}$ = 10.5 Hz, *o-Ph*), 134.9 (d, $^4J_{C,P}$ = 2.8 Hz, *p-Ph*), 151.5 (d, $^2J_{C,P}$ = 10.7 Hz, HC_{C5}), 156.3 (d, $^3J_{C,P}$ = 16.5 Hz, P-C=CH-$C_{C5}CMe_2$), 171.0 (d, $^3J_{C,P}$ = 7.3 Hz, CH_2-$C_{C5}CMe_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 25 °C): δ = +12.2 ppm. ESI-MS: *m*/*z* (%) = 361 [$Ph_2P(Cp^{TM}H)Me]^+$. $C_{25}H_{30}IP$ (488.39): calcd. C 61.48, H 6.19; found C 61.31, H 6.35.

Methylenephosphorane 9 [$Ph_2P(Cp^{TM})Me$]. a) By Deprotonation of 8: To a suspension of phosphonium salt **8** (320 mg, 0.66 mmol) in THF (20 mL), *n*BuLi (1.6 M, 0.4 mL, 0.64 mmol) was added at 0 °C. The reaction mixture was stirred at same temperature for 1 h and for further 14 h at ambient temperature. The pale yellow suspension formed was filtered thought a Celite® pad and the filtrate was concentrated in high vacuum to yield a waxy residue. Crystallization from ether gives a pale yellow microcrystalline solid; yield 67% (155 mg).

b) By Successive Reactions with [BnK] and MeI: To a solution of **4** (1.04 g, 3.00 mmol) in 20 mL of THF, solution of [BnK] (400 mg, 3.08 mmol) in THF (5 mL) was added drop-by-drop at 0 °C. After addition was completed the orange reaction mixture was stirred for 15 min and MeI (0.3 mL, 1.6 equiv.) was added within 5 min at room temp. After an exothermic reaction ceased, the pale yellow suspension was filtered thought a Celite® pad, washed with THF (5 mL) and the filtrate was completely evaporated under vacuum yielding a yellow viscous oil. Addition of ether (20 mL) results in crystallization with deposition of a pale yellow, microcrystalline solid. An additional crop of product can be obtained by storing the mother liquor at –30 °C; yield 95% (1.02 g); m.p. 203–204 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 1.56 (d, $^2J_{C,H}$ = 13.0 Hz, 3 H, *Me*P), 1.72 (s, 12 H, 2× Me_2C), [d, $^6J_{C,H}$ = 0.6 Hz, 2 H, $CH_2(CMe_2)_2$], 6.02 (d, $^3J_{C,H}$ = 3.6 Hz, 2 H, HC_{C5}), 6.86 (m, 4 H, *m-Ph*), 6.96 (m, 2 H, *p-Ph*), 7.24–7.31 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (50.1 MHz, C_6D_6 25 °C): δ = 12.2 (d, $^1J_{C,P}$ = 62 Hz, *Me*P), 33.3 (s, 2× Me_2C), 39.6 (d, $^4J_{C,P}$ = 1.7 Hz, Me_2C) 64.9 [s, $CH_2(CMe_2)_2$], 78.6 (d, $^1J_{C,P}$ = 108 Hz, P-C_{C5}), 103.5 (d, $^2J_{C,P}$ = 16.5 Hz, HC_{C5}), 128.6 (d, $^3J_{C,P}$ = 12.1 Hz, *m-Ph*), 129.5 (d, $^1J_{C,P}$ = 86 Hz, *ipso-Ph*), 131.8 (d, $^4J_{C,P}$ = 2.8 Hz, *p-Ph*), 132.5 (d, $^2J_{C,P}$ = 10.5 Hz, *o-Ph*), 145.7 (d, $^3J_{C,P}$ = 18.2 Hz, Me_2CC_{C5}) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = +4.2 ppm. ESI-MS: *m*/*z* (%) = 361 [M^+ + H]. $C_{25}H_{29}P$ (360.48): calcd. C 83.30, H 7.98; found C 82.97, H 8.21.

***P*-Aminophosphorane 10 [$Ph_2P(Cp^{TM})NHtBu$]:** To a solution of phosphane **4** (360 mg, 1.04 mmol) in THF (10 mL), *t*BuN_3 (500 mg, 5.0 mmol, 5.0 equiv.) was added at ambient temperature. The reaction mixture was stirred for 5 h. The proceeding of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After the reaction completed, all volatiles were removed in vacuo and the solid residue was triturated with acetonitrile, whereupon a yellow solid forms. The latter was filtered off and dried at high vacuum; yield 41% (170 mg) of a yellow, microcrystalline solid; m.p. 165.5–166.5 °C. The sample of the analytical purity was obtained by crystallization from concd. hot acetonitrile solution (m.p. 166.3–166.7 °C). The compound has high solubility in aromatic solvents, THF; it is weakly soluble in acetonitrile, ether and aliphatic solvents. ^1H NMR (300.1 MHz, C_6D_6 25 °C): δ = 0.90 (s, 9 H, *t*Bu), 1.69 (s, 12 H, 2× CMe_2), 2.07 (d, $^2J_{H,P}$ = 5.1 Hz, 1 H, N*H*), 2.47 [s, 2 H, $CH_2(CMe_2)_2$], 6.16 (d, $^3J_{C,P}$ = 4.0 Hz, 2 H, HC_{C5}), 7.03 (m, 6 H, *m-*/*p-Ph*), 7.83–7.90 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 31.4 (d, $^3J_{C,P}$ = 3.9 Hz, $NCMe_3$), 33.3 (s, 2× CMe_2), 39.6 (d, $^4J_{C,P}$ = 1.7 Hz, 2× CMe_2), 53.1 (d, $^2J_{C,P}$ = 2.2 Hz, CMe_3), 64.9 [s, $CH_2(CMe_2)_2$], 80.5 (d, $^1J_{C,P}$ = 118 Hz, P-C_{C5}), 106.1 (d, $^2J_{C,P}$ = 16 Hz, HC_{C5}) 128.5 (d, $^3J_{C,P}$ = 12 Hz, *m-Ph*), 131.5 (d, $^1J_{C,P}$ = 105 Hz, *ipso-Ph*), 131.7 (d, $^4J_{C,P}$ = 2.8 Hz, *p-Ph*), 133.9 (d, $^2J_{C,P}$ = 9.9 Hz, *o-Ph*), 146 ($^3J_{C,P}$ = 18.7 Hz, Me_2CC_{C5}) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = +17.0 ppm. EI-MS: *m*/*z* (%): 417 (100) [M^+], 340 (70) [M^+ – Ph], 412 (25) [M^+ – Me]. $C_{28}H_{36}NP$ (417.56): calcd. C 80.54, H 8.69, N 3.35; found C 80.25, H 8.57, N 3.38.

***P*-Iminophosphane 11 [$Ph_2P(NSiMe_3)Cp^{TM}H$]:** A suspension of phosphane **4** (334 mg, 0.96 mmol) in Me_3SiN_3 (1.0 mL, ca. 7.5 mmol) was stirred at 100 °C for 18 h, whereupon slow N_2 evolution takes place. The color of reaction mixture turns progressively brown. The proceeding of the reaction was performed by ^{31}P NMR spectroscopy of the crude reaction mixture. After the reaction proceeded to 87%, it was terminated. Removal of all volatiles in vacuo yields a light brown semisolid mass, which was extracted into hexane (10 mL). Filtration from a small amount of amorphous, brown solid followed by removal of the solvent results in the formation of the light brown crystalline product (m.p. 94.0–94.5 °C) The moisture and air-sensitive compound **11** shows very high solubility in all common aprotic solvents at room temp. A sample of analytical purity was obtained by crystallization from acetonitrile; m.p. 94.5–94.7 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.39 (s, 9 H, $SiMe_3$), 1.00, 1.04 (2× s, 2× 6 H, 2× Me_2C), 1.91 [s, 2 H, $CH_2(CMe_2)_2$], 3.03 (dd, $^3J_{H,P}$ = 1.0, $^4J_{H,H}$ = 1.7 Hz, 2 H, H_2C_{C5}), 6.95 (dt, $^4J_{H,H}$ = 1.7, $^3J_{H,P}$ = 9.0 Hz, HC_{C5}), 7.05 (m, 6 H, *m-*/*p-Ph*), 7.80–7.90 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6 25 °C): δ = 4.5 (d, $^2J_{C,P}$ = 3.3 Hz, $SiMe_3$), 29.9, 30.3 (2× s, 2× CMe_2), 36.6 (d, $^2J_{C,P}$ = 12.7 Hz, H_2C_{C5}), 40.0, 41.7 (2× s, 2× CMe_2), 61.6 [s, $CH_2(CMe_2)_2$], 128.2 (d, $^3J_{C,P}$ = 10.6 Hz, *m-Ph*), 130.7 (d, $^4J_{C,P}$ = 2.8 Hz, *p-Ph*), 131.9 (d, $^2J_{C,P}$ = 10.5 Hz, *o-Ph*), 136.8 (d, $^1J_{C,P}$ = 104 Hz, *ipso-Ph*), 140.3 (d, $^2J_{C,P}$ = 11 Hz, HC_{C5}), 144.6 (d, $^1J_{C,P}$ = 108 Hz, P-C_{C5}) ppm. 155.5 (d, $^3J_{C,P}$ = 14.9 Hz, $C_{C5}CMe_2$), 162.7 (d, $^3J_{CP}$ = 6.6 Hz, $C_{C5}CMe_2$) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ = –7.8 ppm. EI-MS: *m*/*z* (%): 433 (34) [M^+], 360 (100) [M^+ – $SiMe_3$]. $C_{27}H_{36}NPSi$ (433.65): calcd. C 74.78, H 8.37, N 3.23; found C 73.71, H 8.36, N 3.16.

***P*-Aminophosphorane 12 [$Ph_2P(Cp^{TM})NH_2$]:** This compound was isolated accidentally as a small amount of colorless precipitate by crystallization attempt from solvent-grade acetonitrile. Therefore, the synthesis of compound **12** was not optimized; m.p. 172.0–173.0 °C. ^1H NMR (300.1 MHz, C_6D_6 25 °C): δ = 1.66 (s, 12 H, 2× Me_2C), 2.10 (br. s, 2 H, NH_2), 2.42 [s, 2 H, $CH_2(CCMe_2)_2$], 5.68 (d, $^3J_{CP}$ = 3.4 Hz, 2 H, HC_{C5}), 6.87–7.03 (m, 6 H, *m-*/*p-Ph*), 7.48–7.56 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (50.1 MHz, C_6D_6, 25 °C): δ = 33.2 (s, 2× Me_2C), 39.5 (s, 2× CMe_2), 64.8 [s, $CH_2(CMe_2)_2$], 82.0 (d, $^1J_{C,P}$ = 110 Hz, P-C_{C5}), 104.8 (d, $^2J_{C,P}$ = 17.8 Hz, HC_{C5}), 128.3 (d, $^3J_{C,P}$ = 12.6 Hz, *m-Ph*), 131.1 (d, $^1J_{C,P}$ =

102 Hz, *ipso-Ph*), 131.7 (d, $^4J_{C,P}$ = 2.5 Hz, *p-Ph*), 132.4 (d, $^2J_{C,P}$ = 10.7 Hz, *o-Ph*), 146.0 (d, $^3J_{C,P}$ = 19.3 Hz, Me_2CC_{C5}) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = +22.1 ppm. EI-MS: *m/z* (%): 361 (100) [M^+], 284 (32) [M^+ – Ph]. $C_{24}H_{28}NP$ (361.47): calcd. C 79.75, H 7.81, N 3.88; found C 80.30, H 8.18, N 3.98.

Ferrocene Derivative 13 [(η^5-Cp^{TM}PPh$_2$)$_2$Fe], (dppf^{TM}): To a solution of phosphane **4** (690 mg, 2.05 mmol) in THF (25 mL), a solution of [$PhCH_2K$] (255 mg, 1.98 mmol) in THF (10 mL) at 0 °C was added followed by addition of solid $FeCl_2$ (64 mg, 0.50 mmol). A dark brown suspension forms. The reaction mixture was stirred for 2 h at room temp., after that all volatiles were removed in vacuo and residue was extracted with hexane; solvent was stripped off yielding a brown-orange, foamy residue. This was dissolved in acetonitrile, treated with ultrasound whereupon an orange-pink solid forms. It was filtered off and dried in high vacuum; yield 83% (620 mg). Ferrocene **13** is highly soluble in hydrocarbons, aromatic solvents, ethers, ethanol and virtually insoluble in methanol and acetonitrile; m.p. 180.5 °C (dec. > 188 °C). ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 1.16 (s, 6 H, 2× *Me*), 1.25 (s, 6 H, 2× *Me*), 1.68, 2.42 [2× d of AB system, $^2J_{H,H}$ = 12.8 Hz, 2× 1 H, diastereotopic $H_2C(CMe_2)$], 4.00 (s, 2 H, HC_{C5}), 7.06 (m, 6 H, *p-/m-Ph*), 7.60 (m, 4 H, *o-Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 31.3 (s, *Me*), 32.7 (s, *Me*), 37.9 (s, CMe_2), 59.2 (s, CH_2), 63.7 (pst, $|^2J_{C,P} + {}^3J_{C,P}|$ = 7.6 Hz, HC_{C5}), 109.6 (s, $C_{C5}CMe_2$), 128.4, 128.7 (2× s, *m-/p-Ph*), 134.6 (pst, $|^2J_{C,P} + {}^6J_{C,P}|$ = 10.5 Hz, *o-Ph*), 141.2 (pst, $|^1J_{C,P} + {}^5J_{C,P}|$ = 6.8 Hz, *ipso-Ph*) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): δ = –16.7 ppm. ESI-MS: *m/z* (%) = 747.2 [M^+ + H]. $C_{48}H_{52}FeP_2$ (746.7): calcd. C 77.21, H 7.02; found C 76.62, H 7.13.

Palladium Complex 14 [(dppf^{TM})PdCl$_2$]: To a solution of ferrocene **13** (500 mg, 0.67 mmol, 1.07 equiv.) in THF (10 mL), [$PdCl_2(MeCN)_2$] (160 mg, 0.63 mmol) was added and reaction mixture was stirred for 24 h. During that period a lustrous, purple-orange, microcrystalline precipitate forms. It was filtered off and dried in high vacuum; yield 66% (395 mg). The compound is air-stable and shows high solubility in CH_2Cl_2 and low solubility in THF; not soluble in aromatic solvents, hexane, ether, acetone, lower alcohols; m.p. > 250 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 1.00, 1.03, 1.08, 1.39 (4× s, 4×3 H, 4× *Me*), 1.76, 2.30 (2× d of AB system, $^2J_{H,H}$ = 13.4 Hz, 2× 1 H, *exo-/endo-*CH_2), 3.64 (s, 1 H, HC_{C5}), 4.11 (d, $^3J_{H,P}$ = 2.5 Hz, 1 H, HC_{C5}), 7.33–7.65 (m, 8 H, *Ph*), 8.11 (m, 2 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 29.4, 30.4, 31.7, 32.7 (4× s, 4× *Me*), 36.3, 38.1 (2× s, 2× CMe_2), 58.1 [s, $CH_2(CMe_2)_2$], 62.2 (s, HC_{C5}), 66.5 (pst, $|^2J_{C,P} + {}^4J_{C,P}|$ = 20.2 Hz, HC_{C5}), 71.1 (dd, $^1J_{C,P}$ = 56, $^3J_{C,P}$ = 4 Hz, P-C_{C5}), 112.6 (pst, $|^3J_{C,P} + {}^5J_{C,P}|$ = 5.4 Hz, $C_{C5}CMe_2$), 127.2, 128.1 (2× pst, $|^3J_{C,P} + {}^5J_{C,P}|$ = 11.0, $|^3J_{C,P} + {}^5J_{C,P}|$ = 11.6 Hz, 2× *m-Ph*), 130.0, 131.6 (2× s, 2× *p-Ph*), 133.7 (pst, $|^2J_{C,P} + {}^4J_{C,P}|$ = 9.2 Hz, *o-Ph*), 134.6 (d, $^1J_{C,P}$ = 60 Hz, *ipso-Ph*), 135.6 (pst, $|^2J_{C,P} + {}^4J_{C,P}|$ = 12.4 Hz, *o-Ph*) ppm. $^{31}P\{^1H\}$ NMR (121.0 MHz, CD_2Cl_2, 25 °C): δ = +30.3 ppm. ESI-MS: *m/z* (%): 924.2 [M^+]. $C_{48}H_{52}Cl_2FeP_2Pd$ (924.07): calcd. C 62.39, H 5.67; found C 62.05, H 5.81.

Palladium Complex 15 [(dppf^{TM})PdI$_2$]: A stirred suspension of complex **14** (166 mg, 0.18 mmol) and NaI (660 mg, 4.4 mmol, ca. 24 equiv.) in MeOH (30 mL) was refluxed for 10 min. After that the reaction mixture was cooled to room temperature and major amount of inorganic salts was removed by centrifugation. The filtrate was collected by decantation and the solid was extracted in the same way three times. The solvent from combined organic phases was removed in vacuo and the brown residue was extracted with CH_2Cl_2. The subsequent filtration and removal of the solvent yield a deep purple, microcrystalline solid; yield 87% (173 mg). The compound shows very high solubility in CH_2Cl_2; marginally soluble in THF and insoluble in MeCN and Et_2O; m.p. > 250 °C. ^1H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 1.01, 1.06, 1.039 (3× s,

Table 1. Details of the crystal data, structural resolution and refinement procedure for compounds **4**, **9**, **13** and **15**.

	4	**9**	**13**	**15**
Empirical formula	$C_{24}H_{27}P$	$C_{25}H_{29}P$	$C_{48}H_{52}FeP_2$	$C_{48}H_{52}FeI_2P_2Pd$
Fw /g mol^{-1}	346.43	360.45	746.69	1106.89
Crystal color, habit	colorless, prism	colorless, needle	dark red, prism	light red, plate
Crystal size /mm	0.30×0.18×0.12	0.36×0.08×0.04	0.08×0.05×0.03	0.21×0.06×0.03
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	$P\,2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
Z	4	4	1	4
a /Å	6.4001(3)	10.5140(11)	8.8276(18)	26.3109(17)
b /Å	37.8489(13)	13.1131(13)	11.002(3)	11.4236(7)
c /Å	8.4024(4)	15.7793(17)	11.123(3)	14.8667(7)
α /°	90	89.722(8)	80.50(2)	90
β /°	96.017(6)	72.761(8)	71.261(17)	90
γ /°	90	86.898(8)	84.658(19)	90
Volume /Å^3	2024.16(15)	2074.6(4)	1008.0(4)	4468.4(5)
$d_{calcd.}$ /g cm^{-3}	1.137	1.154	1.230	1.645
μ /mm^{-1}	0.139	0.138	0.486	2.212
F(000)	744	776	396	2192
Diffractometer type	IPDS1	IPDS2	IPDS2	IPDS2
Temperature /K	173(2)	100(2)	130(2)	100(2)
Number of reflections collected	12322	23974	8283	20064
Number of independent reflections	3874	23794	3532	7797
Absorption correction	semi-empirical	none	integration	semi-empirical
R(int)	0.0510	"HKLF 5" refinement, no merging, BASF = 0.157	0.1276	0.0745
GOF	0.956	0.690	0.763	0.898
*R*1 [$I > 2\sigma(I)$]	0.0379	0.00583	0.0551	0.0439
wR_2 (all data)	0.0953	0.1313	0.0980	0.0767

3 H, 6 H, 3 H, 4× *Me*), 1.75, 2.30 (2× d of AB system, $^2J_{H,H}$ = 12.6 Hz, 2× 1 H, *exo*-/*endo*-CH_2), 3.55 (s, 1 H, *H*C$_{C5}$), 3.94 (d, $^2J_{H,P}$ = 3.3 Hz, 1 H, *H*C$_{C5}$), 7.30–7.44 (m, 5 H, *Ph*), 7.51–7.63 (m, 3 H, *Ph*), 8.00–8.06 (m, 2 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 30.0, 31.2, 32.4, 33.5 (4× s, 4× *Me*), 36.8, 38.5 (2× s, 2× *C*Me$_2$), 58.7 [s, *C*H$_2$(CMe$_2$)$_2$], 62.7 (s, H*C*$_{C5}$), 67.0 (pst, $|^2J_{C,P} + {}^4J_{C,P}|$ = 21 Hz, H*C*$_{C5}$), 73.9 (dd, $^1J_{C,P}$ = 47, $^3J_{C,P}$ = 6 Hz, P-*C*$_{C5}$), 112.4 (d, $^3J_{C,P}$ = 6.6 Hz, *C*$_{C5}$CMe$_2$), 112.5 (pst, $|^3J_{C,P} + {}^5J_{C,P}|$ = 2.2 Hz, *C*$_{C5}$CMe$_2$), 127.4, 128.2 (2× pst, 2× $|^3J_{C,P} + {}^5J_{C,P}|$ = 11.6 Hz, *m*-*Ph*), 130.3, 131.6 (2× s, 2× *p*-*Ph*), 132.2 (d, $^1J_{C,P}$ = 54 Hz, *ipso*-*Ph*), 134.8, 135.9 (2× pst, $|^2J_{C,P} + {}^4J_{C,P}|$ = 9.4 Hz, $|^2J_{C,P} + {}^4J_{C,P}|$ = 12.5 Hz, 2× *o*-*Ph*), 136.6 (d, $^1J_{C,P}$ = 55 Hz, *ipso*-*Ph*) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 25 °C): δ = +19.9 ppm. ESI-MS: *m*/*z* (%): 1106.4 [M$^+$]. $C_{48}H_{52}FeI_2P_2Pd$ (1106.97): calcd. C 52.08, H 4.74; found C 52.53, H 4.65.

X-ray Crystallographic Studies: The crystals of compounds were grown by cooling of their concentrated solutions: 4, 13 (EtOH, +25 °C), 9 (Et_2O, 0 °C) and 15 (CH_2Cl_2, 0 °C). Diffraction data were collected with STOE IPDS1 (for 4, 9) and IPDS2 (for 13, 15) diffractometers using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data and structure refinement details are collected in Table 1. All structures were solved by direct methods and expanded by difference-Fourier synthesis using SIR2004 (Giacovazzo, 2004) and refined by the full-matrix least-squares procedure based on *F*2, using the SHELXL-97 (Sheldrick, 1997) computer program. ORTEP plots of all molecular structures were generated with Diamond 3.1, Crystal Impact software.

CCDC-746654 (for **4**), -746655 (for **9**), -746656 (for **13**), -746657 (for **15**) 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.

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