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High Structural Control in Metal-Mediated Synthesis of New Functionalized Diphosphines Using Diphosphinoketenimines as Precursors

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Dedicated to Professor Víctor Riera on the occasion of his 70th birthday

Abstract: The diphosphinoketenimine ligand in the neutral complexes *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NR}] (**1a**: R = Ph; **1b**: R = *p*-tolyl) undergoes nucleophilic attack by MeLi and *n*BuMgCl yielding, after hydrolysis, the diphosphinoenamine-containing complexes *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C(R′)-NHR}] (**3a**,**b**: R′ = Me; **4a**,**b**: R′ = *n*Bu). Complex **1a** reacts under the same conditions with H$_2$C=C=CH-MgBr to afford *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$-C=C(CH$_2$CC≡CH)NHR}] (**5a**), which contains a terminal alkyne group on the α-carbon atom of the diphosphinoenamine ligand. The cationic complexes *fac*-[Mn(CO)$_4${(PPh$_2$)$_2$C=C=NR}]$^+$ (**6**) react with H$_2$C=C=CHMgBr to afford diphosphinomethanide derivatives bearing three different types of functional groups, depending upon the substituent on the nitrogen atom of the ketenimine: cumulene in *fac*-[Mn(CO)$_4${(PPh$_2$)$_2$C−C(CH=C=CH$_2$)=N-xylyl}] (**7d**), internal alkyne in *fac*-[Mn(CO)$_4${(PPh$_2$)$_2$C−C(C≡CCH$_3$)=N*t*Bu}] (**8**), and quinoline in **9** (R = Ph), whose formation implies an unusual cyclization process. Protonation of **7d**, **8**, and **9** with HBF$_4$ occurs at the nitrogen atom to give the cationic derivatives **10d**, **11**, and **12**, respectively, which contain the corresponding functionalized diphosphine ligands. Irradiation of **3a**,**b** and **4a**,**b** with Vis/UV light makes it possible to isolate the free ligands (PPh$_2$)$_2$C=C(R′)NHR (**13a**,**b** and **14a**,**b**), completing the metal-assisted synthesis of these novel functionalized diphosphines. Irradiation of **12** with Vis/UV light generates free phosphinoquinoline ligand **15**, which readily affords a complex **16** containing **15** as a P,N-chelating ligand when treated with [PdCl$_2$(NCMe)$_2$], thus demonstrating its coordination capability.

Keywords: ketenimines · manganese · nucleophilic addition · phosphanes · synthesis design

Introduction

Functionalized phosphines, especially with nitrogen-containing functional groups, have aroused great interest in recent years due to their increasing application in homogeneous catalysis.[1] Diphosphines bearing additional functionalities have also attracted considerable attention, owing to their versatility and to the improvement that the new functional groups confer on these ligands with respect to normal diphosphines. Thus, functionalized diphosphines show a wider variety of coordination modes in mononuclear and polynuclear complexes due to the participation of the new donor centers in the metal–ligand bonds, in addition to the two phosphorus atoms of the diphosphine.[2] The physical properties of the diphosphines, such as solubility in water, can be conveniently modified by the presence of the appropriate functionality.[3] Functionalized diphosphines improve the selectivity of some catalytic processes,[4] and the extra functional group can allow the anchoring of the diphosphine to solid matrices.[5]

Our group has synthesized new functionalized diphosphines via diphosphinomethanide complexes from a readily available diphosphine such as diphenylphosphinomethane (dppm).[6] We have reported the synthesis in this way of diphosphinoketenimines of general formula (PPh$_2$)$_2$C=C=NR, involving the formal coupling of a diphosphinocarbene fragment and an isocyanide through the mediation of a metal center.[7] Diphosphinoketenimes possess high synthetic potential as they combine the properties of the diphosphines with the rich chemistry of the ketenimines, being suitable

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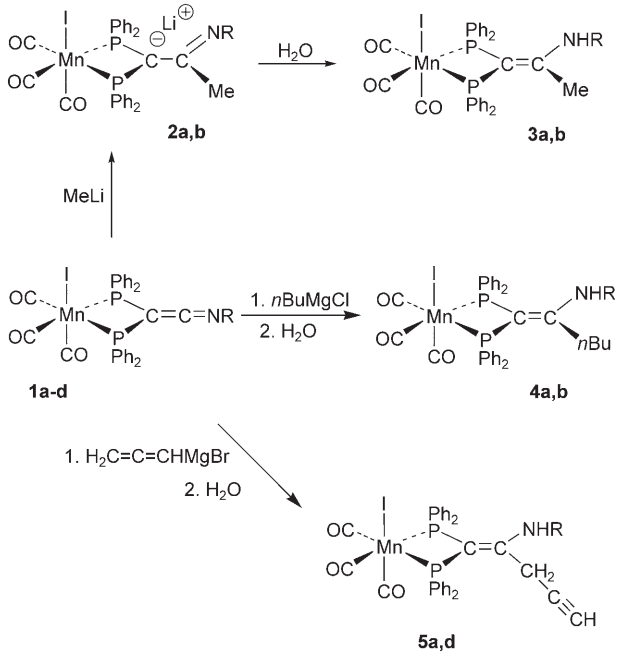
substrates for the preparation of a number of phosphaheterocycles.[8] Previously our group has also shown that coordinated diphosphinoketenimines react with propargylamine and propargylic alcohol leading to the formation of imidazoline- and oxazoline-functionalized diphosphines, through an unprecedented cyclization process.[9]

Herein we report a detailed study of the reactivity of neutral and cationic complexes bearing diphosphinoketenimine ligands toward lithiated and Grignard reagents. In these reactions the final result of the nucleophilic attack on the ketenimine group depends strongly on the nature of the ligands bonded to the metal center and on the substituent of the nitrogen atom of the ketenimine. This behavior allows the controlled formation of a variety of functionalized diphosphines tuned by the metal center, the ancillary ligands, and the substituent at the nitrogen atom of the ketenimine residue.

Results and Discussion

Reactions of *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NR}] (1) with MeLi and Grignard reagents: The diphosphinoketenimine metal complexes *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NR}] (**1a**: R = Ph, **1b**: R = *p*-tolyl) react cleanly with MeLi at 0 °C. The reaction is regiospecific and the nucleophilic attack happens selectively on the α-carbon atom of the ketenimine moiety, leading to the formation of the anionic intermediates *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C−C(Me)=NR}]$^-$(**2a**,**b**; see Scheme 1).



Scheme 1. Reaction of diphosphinoketenimine complexes *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NR}] (**1a**: R = Ph; **1b**: R = *p*-tolyl; **1c**: R = *t*Bu; **1d**: R = xylyl) with MeLi and Grignard reagents to yield diphosphinoenamine complexes **3a**,**b**, **4a**,**b**, and **5a**,**d**.

These species were not isolated but could be detected by IR spectroscopy, showing bands at lower frequencies than the neutral complexes **1a**,**b** (see Table 1). In the ^{31}P{^{1}H} NMR spectra, only one broad signal was observed (δ = 7.5 and 7.9 ppm for **2a** and **2b**, respectively) even at low temperature. These data would agree with the existence of free rotation around the P$_2$C−C bond, which indicates that a resonance form with the negative charge placed on the P$_2$C carbon atom (**a** in Scheme 2) has a high contribution to the bond description of **2**.

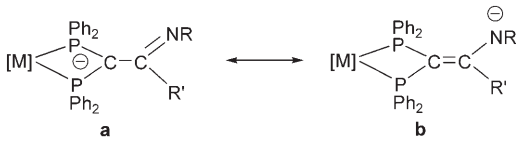
The anionic intermediates **2a**,**b** evolve cleanly to the neutral derivatives **3a**,**b** (Scheme 1) after addition of water to the reaction medium. The structure of the new complexes was determined by spectroscopic methods. Thus, the appearance of two signals in the ^{31}P{^{1}H} NMR spectra revealing the existence of two nonequivalent phosphorus atoms, together with the presence of an N−H signal at δ = 6.62 ppm in the ^{1}H NMR spectra, indicate that the species formed have an enamine structure. Additionally, a singlet signal at δ = 1.82 and 1.73 ppm for **3a** and **3b**, respectively, confirms the presence of the new methyl group in the ligand. The structures of **3a**,**b** suggest that, in the hydrolysis, protonation occurs on the nitrogen atom; however, protonation could have happened initially on the methanide carbon atom, gen-

Abstract in Spanish: *El ligando difosfinocetenimina en los complejos neutros* fac-*[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NR}] (**1a**: R = Ph, **1b**: R = p-tolyl) experimenta un ataque nucleofílico con MeLi y* n*BuMgCl generando, después de la hidrólisis, los complejos* fac-*[MnI(CO)$_3${(PPh$_2$)$_2$C=C(R′)NHR}] (**3a**,**b**: R′ = Me; **4a**,**b**: R′ = n*Bu), que contienen un ligando difosfinoenamina. **1a** reacciona en las mismas condiciones con H$_2$C=C=CHMgBr para dar* fac-*[MnI(CO)$_3${(PPh$_2$)$_2$C=C-(CH$_2$C≡CH)NHR}] (**5a**), que contiene un grupo alquino terminal sobre el átomo de carbono α del ligando difosfinoenamina. Los complejos catiónicos fac-[Mn(CO)$_4${(PPh$_2$)$_2$C=C=NR}]$^+$ (**6**) reaccionan con H$_2$C=C=CHMgBr formando derivados difosfinometanuro que presentan tres tipos diferentes de grupos funcionales, dependiendo del sustituyente sobre el átomo de nitrógeno de la cetenimina: cumuleno en* fac-*[Mn(CO)$_4${(PPh$_2$)$_2$C−C(CH=C=CH$_2$)=N-xylyl}] (**7d**), alquino interno en* fac-*[Mn(CO)$_4${(PPh$_2$)$_2$C−C(C≡CCH$_3$)=NtBu}] (**8**), y quinolina en **9** (R = Ph), cuya formación implica un proceso de ciclación inusual. La protonación de **7d**, **8**, y **9** con HBF$_4$ tiene lugar sobre el átomo de nitrógeno para formar **10d**, **11**, y **12**, respectivamente, que contienen los correspondientes ligandos difosfina funcionalizados. La irradiación de **3a**,**b** y **4a**,**b** con luz Vis/UV permite el aislamiento de los ligandos libres (PPh$_2$)$_2$C=C(R′)NHR (**13a**,**b** y **14a**,**b**), completando la síntesis asistida por metal de estas nuevas difosfinas funcionalizadas. La irradiación de **12** con luz Vis/UV genera el ligando libre fosfino-quinolina **15**, cuya capacidad coordinativa ha sido chequeada con [PdCl$_2$(NCMe)$_2$], formando fácilmente el complejo **16** que contiene **15** como un ligando quelato-P,N.*

Table 1. Selected spectroscopic data for **2**–**5**.

Compd.	ν(CO)[a] [cm^{-1}]	^{31}P{^{1}H} NMR: δ[c] [ppm]	^{1}H NMR: δ [ppm]; J(H,H) [Hz][d]
1a	2014 (s)		
	1953 (m)		
	1920 (m)		
1b	2014 (s)		
	1952 (m)		
	1918 (m)		
2a	1988 (s)	7.5(br)	
	1909 (m)		
	1894 (m)		
2b	1988 (s)	7.9(br)	
	1909 (m)		
	1894 (m)		
3a	2012 (s)	20.7 (br)[d]	6.62 (s, N−H)
	1949 (m)	13.0 (br)	1.81 (s, CH_3−C=C)
	1915 (m)		
3b	2011 (s)[b]	20.2 (br)[d]	6.62 (s, N−H)
	1943 (m)	13.0 (br)	1.76 (s, CH_3−C=C)
	1912 (m)		
4a	2009 (s)	20.8 (br)[d]	6.45 (s, N−H)
	1943 (m)	14.2 (br)	2.22 (m, −CH_2−C=)
	1917 (m)		0.61 (m, −CH_2−CH_2C=)
			0.43 (m, −CH_2−CH_3)
			0.32 (m, CH_3−CH_2)
4b	2008 (s)	20.4 (br)[d]	6.45 (s, N−H)
	1944 (m)	13.4 (br)	2.23 (m, CH_2−C=)
	1918 (m)		0.76 (m, −CH_2−CH_2C=)
			0.53 (m, −CH_2−CH_3)
			0.32 (m, CH_3−CH_2)
5a	2010 (s)	23.1 (s)	6.59 (s, N−H)[c]
	1944 (m)	15.3 (s)	1.83 (t, ^4J(H,H) = 2, CH)
	1913 (m)		3.15 (dd, ^4J(H,H) = 2, ^2J(H,H) = 17, CH_2)
			3.06 (dd, ^4J(H,H) = 2, ^2J(H,H) = 17, CH_2)
5d	2009 (s)	23.0 (s)	6.09 (s, N−H)[c]
	1945 (m)	14.8 (s)	1.76 (t, ^4J(H,H) = 3, CH)
	1909 (m)		2.78 (t, ^4J(H,H) = 3, CH_2)

[a] In THF. Abbreviations: m = medium, s = strong. [b] In CH_2Cl_2. [c] In CD_2Cl_2. Abbreviations: br = broad, dd = doublet of doublets, s = singlet, t = triplet. [d] In $CDCl_3$.



Scheme 2. Resonance forms of the functional group in the diphosphinomethanide complexes **2a**,**b**.

erating an imine-functionalized diphosphine ligand, which quickly isomerized to the diphosphinoenamine form as a final product.

The reaction of **1a**,**b** with *n*BuMgCl proceeds similarly to that with MeLi, yielding the complexes **4a**,**b** (Scheme 1). In this case, however, the hydride complexes *fac*-[$MnH(CO)_3${$(PPh_2)_2C$=C=NR}] appeared as by-products and were separated by column chromatography. The generation of such complexes could be due to the initial substitution of the iodine ligand by the butyl group followed by a β-elimination. The spectroscopic data of **4a**,**b** are comparable with those of **3a**,**b**, and are in agreement with the proposed formulation (see Table 1 and Experimental Section).

The formation of the enamine-functionalized diphosphine complexes **3a**,**b** and **4a**,**b** proves that, in these reactions, the diphosphinoketenimines behave similarly to conventional organic ketenimines, which react with organolithium reagents to afford enamine derivatives.[10]

We extended the reaction described above to the Grignard reagent H_2C=C=CHMgBr, in which the unsaturated organic residue could lead to further transformations of the diphosphine ligand formed initially. Complexes **1a**,**d** reacted with H_2C=C=CHMgBr at −70 °C, leading immediately to derivatives **5a**,**d** (Scheme 1) upon quenching the reaction mixture with water. The spectroscopic data for these complexes are in accordance with the presence of an enamine-functionalized diphosphine ligand (Table 1), as in **3** and **4**. The ^{1}H NMR spectra reveal the structure of the new organic residue bonded to the central carbon atom of the enamine skeleton. Thus a triplet for a CH group and two doublets of doublets for the inequivalent protons of a CH_2 group are observed for **5a** (Table 1), indicating the presence of a −CH_2C≡CH moiety (in the case of **5d** a deceptively simple pseudo-triplet appears for the second-order CH_2 spin system), which should result from a 1,3 proton transfer within the cumulene fragment of the initial addition product.

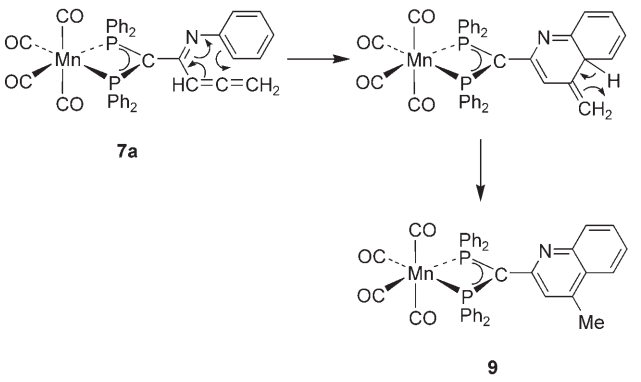
No reaction was observed in the treatment of *fac*-[$MnI(CO)_3${$(PPh_2)_2C$=C=N*t*Bu}] (**1c**) with organolithium and organomagnesium reagents, showing that *N*-alkyl diphosphinoketenimines are clearly less sensitive to nucleophilic attack than *N*-aryl ones.

Reactions of [$Mn(CO)_4${$(PPh_2)_2C$=C=NR}]ClO_4 (6) with H_2C=C=CHMgBr: To obtain further insight into the influence of the chemical environment of the diphosphine on the ketenimine reactivity, we modified the metallic fragment by varying the ligands bonded to the metal. We prepared the cationic derivatives [$Mn(CO)_4${$(PPh_2)_2C$=C=NR}]ClO_4 (**6a**: R = Ph; **6c**: R = *t*Bu; **6d**: R = xylyl), where the iodide ligand has been substituted for a carbonyl group. This alteration modified the electropositive character of the ketenimine fragment, enhancing the reactivity of this functional

group toward nucleophiles, and allowing even *N*-alkyl ketenimines to react with organomagnesium reagents.

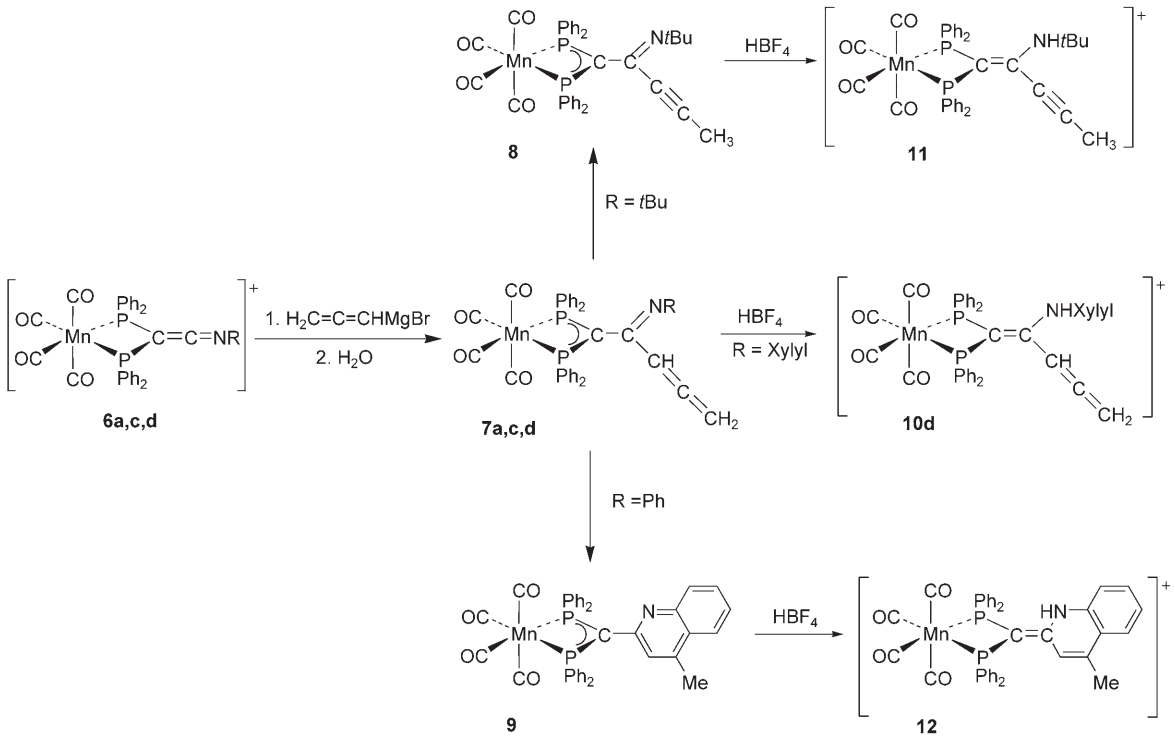
The reaction of the cationic complexes **6** with $H_2C{=}C{=}CHMgBr$ is instantaneous at room temperature, leading to selective nucleophilic attack of the central carbon atom of the ketenimine functionality by the carbanion to yield three different types of neutral diphosphinomethanide complexes (Scheme 3). IR spectroscopic monitoring of the reaction showed the shift to lower frequencies of the bands when passing from the cationic starting complexes to the neutral products. When the reaction was complete water was added to quench the excess of Grignard reagent.

The final output of the reaction depends heavily on the substituent at the ketenimine nitrogen atom. For R = xylyl, the product resulting from direct addition of the cumulenic carbanion to the ketenimine residue was formed and isolated as a yellow solid (**7d**). However, for R = *t*Bu and Ph the initial product of the addition evolved rapidly. For R = *t*Bu a prototropic rearrangement afforded **8**, containing a $-C{\equiv}CCH_3$ residue bonded to the iminic carbon atom. For R = Ph, a subsequent cyclization process led to the formation of a new diphosphinomethanide ligand with a quinoline substituent on the methanide carbon atom (**9** in Scheme 3). The proposed mechanism for this reaction (Scheme 4) implies a pericyclic rearrangement among the phenyl group, the imine residue, and the internal double bond of the cumulene, leading to the formation of a six-membered ring. In a final step a proton shift to the exocyclic methylene group generates the aromatic quinoline ring. In agreement with this mechanism, no cyclization occurs for the xylyl derivative **7d**, because of the two methyl groups blocking positions 2 and 6 in the phenyl ring. *N*-Aryl ketenimines have been used occasionally in the synthesis of quinolines by either intermolecular[11] or intramolecular[12] cyclization processes, but, to our knowledge, this is the first time that a cumulene residue has been involved in such a process.



Scheme 4. Proposed mechanism for the formation of the quinoline functionality in complex **9**.

The new compounds were characterized spectroscopically, and **7d** and **9** by an X-ray diffraction study. In the $^{31}P\{^1H\}$ NMR spectra of the three compounds, only one signal appears within the range observed for diphosphinomethanides,[6a] indicating free rotation about the $P_2C{-}C$ bond, although some degree of carbon–carbon multiple



Scheme 3. Reaction of $[Mn(CO)_4\{(PPh_2)_2C{=}C{=}NR\}]^+$ (**6a**: R = Ph; **6c**: R = *t*Bu; **6d**: R = xylyl) with $H_2C{=}C{=}CHMgBr$ to afford compounds **7d**, **8**, and **9**, and subsequent formation of the corresponding functionalized diphosphine complexes **10d**, **11**, and **12**.

bonding should exist owing to charge delocalization from the methanide carbon atom to the imine moiety. In the ^{1}H NMR spectra (Table 2) of **7d** the resonances corresponding to the cumulene group appear at $\delta = 3.82$ (d, CH_2) and 5.23 ppm (t, CH), whereas for complex **8** those signals are absent and a singlet in the methyl range ($\delta = 1.07$ ppm) is observed. For **9**, the quinoline ring signals appear in the range $\delta = 7.70$–6.45 ppm and the methyl group is revealed as a singlet at $\delta = 2.24$ ppm.

X-ray diffraction studies confirmed the structure of **7d** (Figure 1) and **9** (Figure 2). In both cases the manganese atom shows a pseudo-octahedral coordination. The P–C distances (**7d**: 1.749(3), 1.756(3) Å; **9**: 1.738(5), 1.735(5) Å), as well as the angles P(1)-C(1)-P(2) (**7d**: 99.16(17)°; **9**: 100.9(3)°) are within the range observed for diphosphinomethanide complexes.[6] The cumulene group and the quinoline fragment are nearly coplanar with the metalladiphosphino ring MnP_2C. In **7d** the C(1)–C(2) distance (1.447(5) Å) is slightly shorter that expected for a single bond, whereas C(2)–N(1) (1.306(4) Å) is slightly longer than the distance corresponding to a double bond, indicating some electron charge sharing among these atoms. Bond lengths within the cumulene fragment correspond to a double bond (1.294(5) and 1.306(6) Å), and the geometry around the central carbon atom C(3) is nearly linear (C(3)-C(4)-C(5) 176.8(4)°).

The diphosphinomethanide complexes **7d**, **8**, and **9** are protonated easily with acids (HBF_4) to afford the cationic derivatives **10d**, **11**, and **12**, respectively (Scheme 3), containing the corresponding new functionalized diphosphine ligands. In all cases the proton-receptor atom was nitrogen. In the proton spectra a singlet at $\delta = 6.32$ (**10d**), 5.20 (**11**), and 8.6 ppm (**12**) confirmed the presence of the NH group.

It is noteworthy that fine control of the final product of the addition of $H_2C{=}C{=}CHMgBr$ to the ketenimine functionality can be exercised, depending on the ancillary ligands of the metal complex as well as on the substituents at the nitrogen atom of the diphosphinoketemine. In this way, the three tautomeric forms of the addition product (cumulene **7d**, terminal alkyne **5a**,**d**, and internal alkyne **8**), and even the quinoline cyclization product **9**, can be obtained.

This behavior prompted us to study further the influence of the ancillary ligands by using a ligand such as ClO_4^- with intermediate donor properties between those of I^- (in **1**) and CO (in **6**). Thus, when **5a** was treated with $AgClO_4$, a precipitate of AgI appeared readily, and a new perchlorate derivative was

Table 2. Selected spectroscopic data for **7**–**17**.

Compd.	ν(CO)[a] [cm^{-1}]	^{31}P{^{1}H} NMR: δ[b] [ppm]	^{1}H NMR: δ [ppm]; J(H,H) [Hz][c]
7d	2073 (s)	2.36 (br)	5.23 (t, ^4J(H,H) = 7, CH=C=)[d]
	1997 (s)		3.82 (d, ^4J(H,H) = 7, =CH_2)
	1989 (vs)		
	1963 (s)		
8	2071 (s)	−1.30(br)	1.07 (s, CH_3)[d]
	1991 (vs)		
	1958 (s)		
9	2073 (s)	−2.4 (br)	2.24 (s, CH_3)[d]
	1993 (vs)		
	1963 (s)		
10a	2088 (s)	15.0 (br)[c]	6.73 (s, NH)
	2023 (m)		5.51 (t, ^3J(H,H) = 6, CH=C=)
	2007 (vs)		4.39 (d, ^3J(H,H) = 6, =C=CH_2)
	1994 (sh)		
10d	2088 (s)	13.8 (br)	6.32 (s, N*H*-xylyl)
	2024 (m)		5.39 (t, ^4J(H,H) = 7, CH=C=)
	2006 (vs)		4.33 (d, ^4J(H,H) = 7, =C=CH_2)
	1994 (sh)		
11	2087 (s)	14.8 (br)	5.20 (s, NH)
	2022 (m)		1.38 (s, CH_3)
	2006 (vs)		
	1992 (sh)		
12	2087 (s)	6.9 (br)[c]	8.60 (s, NH)
	2021 (m)		2.30 (s, CH_3)
	2005 (vs)		
	1991 (sh)		
13a	3366[e]	−0.6 (d)	6.99 (s, NH)
		−21.1 (d)	2.46 (s, CH_3–C=C)
		^2J(P,P) = 7	
13b	3357[e]	−0.5 (d)	6.91 (s, NH)
		−21.4 (d)	2.43 (s, CH_3–C=C)
		^2J(P,P) = 7	
14a	3362[e]	0.3 (br)	6.63 (s, NH)
		−22.7 (br)	3.11 (t, ^3J(H,H) = 8, −CH_2–C=)
			1.51 (m, −CH_2–CH_2C=)
			1.20 (m, −CH_2–CH_3)
			0.70 (t, ^3J(H,H) = 7, −CH_2–CH_3)
14b	3392[e] (NH)	3.5 (br)	6.56 (s, NH)
		−19.8 (br)	3.00 (t, ^3J(H,H) = 8, −CH_2–C=)
			1.52 (m, −CH_2–CH_2C=)
			1.21 (m, −CH_2–CH_3)
			0.71 (t, ^3J(H,H) = 7, −CH_2–CH_3)
15		−11.5 (s)	3.77 (br, PCH_2)
			2.57 (s, CH_3)
16		49.7 (s)	4.48 (d, ^2J(P,H) = 12, PCH_2)[d]
			2.67 (s, CH_3)
17		51.9 (s)	4.48 (d, ^2J(P,H) = 13, PCH_2)[d]
			2.69 (s, CH_3)

[a] In CH_2Cl_2. Abbreviations: m = medium, s = strong, sh = shoulder, vs = very strong. [b] In CH_2Cl_2 with a D_2O capillary. Abbreviations: br = broad, d = doublet. [c] In $CDCl_3$. [d] In CD_2Cl_2. [e] ν(NH) in Nujol.

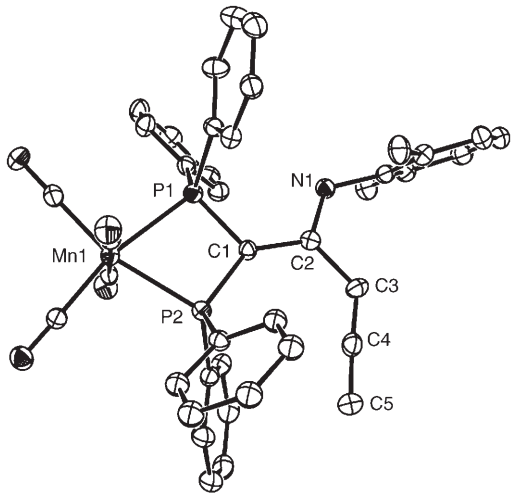


Figure 1. Molecular structure of **7d** (thermal ellipsoids at 30% probability level). Selected bond lengths [Å] and angles [°]: Mn1–P1 2.3376(10), Mn1–P2 2.3448(10), P1–C1 1.749(3), P2–C1 1.756(3), C1–C2 1.447(5), N1–C2 1.306(4), C2–C3 1.484(5), C3–C4 1.294(5), C4–C5 1.306(6); P2-Mn1-P1 69.48(3), C2-C1-P2 137.2(3), C2-C1-P1 123.5(2), P1-C1-P2 99.16(17), C1-C2-C3 122.2(3), C1-C2-N1 117.6(3), N1-C2-C3 120.2(3), C2-C3-C4 130.9(4), C3-C4-C5 176.8(4), C2-N1-C11 120.8(3).

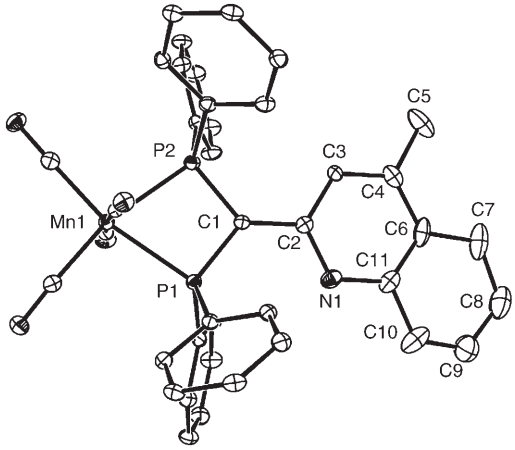
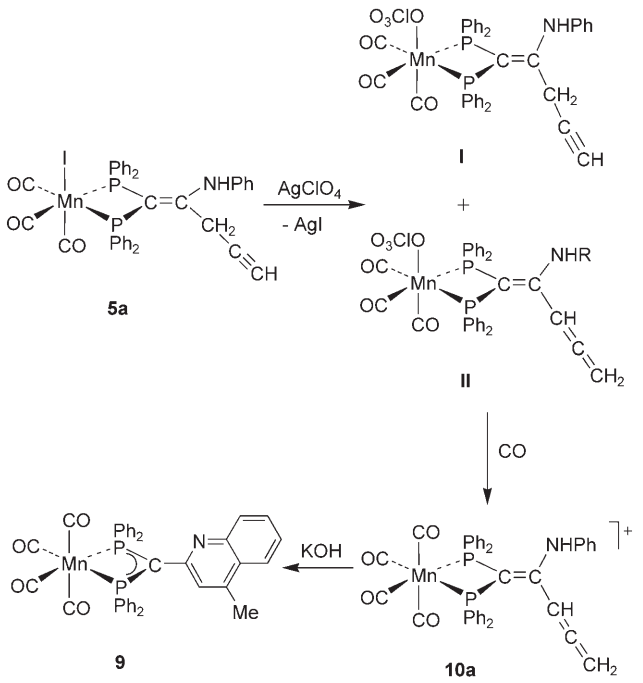


Figure 2. Molecular structure of **9** (thermal ellipsoids at 20% probability level). Selected bond lengths [Å] and angles [°]: Mn–P1 2.3398(14), Mn1–P2 2.3390(15), P1–C1 1.738(5), P2–C1 1.735(5), C1–C2 1.444(7), N1–C2 1.361(6), C2–C3 1.402(7); P2-Mn1-P1 69.91(5), C2-C1-P1 130.9(4), C2-C1-P1 128.0(4), P2-C1-P1 101.0(2), C1-C2-C3 120.8(4), C1-C2-N1 117.0(4), N1C2-C3 122.2(5), C2-C3-C4 120.6(5).



Scheme 5. Conversion of complex **5a** into complex **9** by ligand substitution and treatment with base.

generated as two tautomers: terminal alkyne **I** and cumulene **II** (Scheme 5); the cumulene isomer predominated in the equilibrium. These tautomers could be distinguished only by their proton NMR spectra (see Experimental Section). Interestingly, when the perchlorate ligand was substituted by CO only the tautomer with a cumulene group appeared (**10a**). Unlike the neutral derivative **7a** this cationic compound was isolable and it could be characterized spectroscopically. In the proton spectrum a singlet at δ = 6.73 ppm confirmed the presence of an NH group and the signals corresponding to the $-CH{=}C{=}CH_2$ residue appeared at δ = 5.51 (t, CH) and 4.39 ppm (d, CH_2).

In agreement with the proposed mechanism, the enamine derivative **10a** does not suffer a cyclization process. However, when **10a** was treated with KOH the N–H group was deprotonated, generating a transient imine form which quickly evolved to the derivative **9** through the cyclization process described above (Scheme 4).

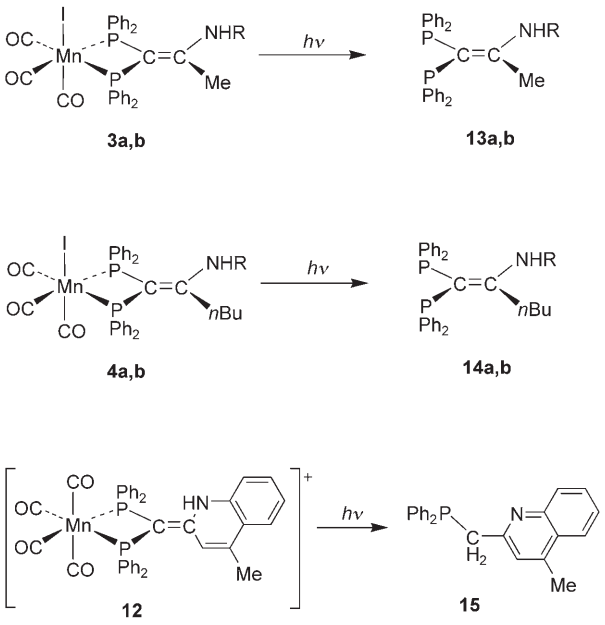
All the reactions carried out on the *N*-phenyl diphosphinoketenimine ligand exemplify the modification of the functional group on the diphosphine (terminal alkyne, cumulene or quinoline) by subtle changes in the electronic features of the metal center as well as by simple acid–base processes.

Free diphosphine and phosphine ligands: In complexes **3**, **4**, and **12** the new functionalized diphosphines could be removed from the metal by irradiation of a toluene or THF solution of the compounds with UV/Vis light. The final point of the reaction was determined by IR spectroscopy (disappearance of the ν(CO) bands owing to complex degradation) and the new diphosphines were isolated as white solids after purification by column chromatography and characterized spectroscopically.

For derivatives **3a**,**b** and **4a**,**b** the diphosphines (**13a**,**b** and **14a**,**b**, respectively) decoordinate from the metal center without suffering any further transformation, as shown in the NMR spectra (see Table 3 and Experimental Section). However irradiation of **12** leads to further changes implying the loss of a diphenylphosphino moiety from the original diphosphine, and affording the new monophosphine **15** as the final product (Scheme 6). As a consequence, a single signal

Table 3. Crystal and refinement data for **7d**, **9**, and **17**.

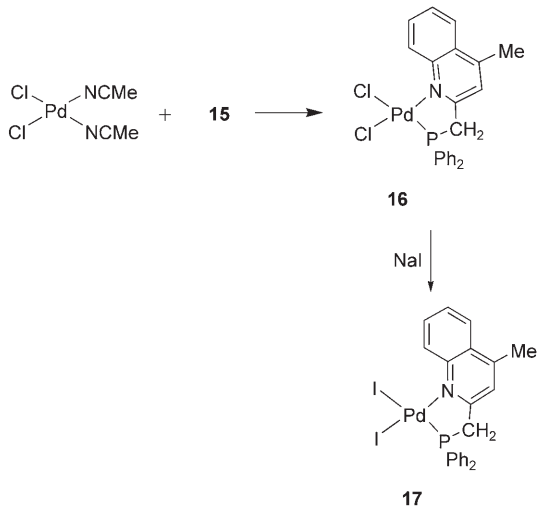
	7d	**9**	**17**
empirical formula	$C_{41}H_{32}NO_4P_2Mn$	$C_{39}H_{30}NO_5P_2Mn$	$C_{30}H_{28}I_2NPPd$
formula weight	719.56	709.52	793.70
temperature [K]	150(2)	120(2)	293(2)
wavelength [Å]	1.54184	1.54184	0.71069
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a [Å]	10.5490(3)	20.5973(6)	9.9120(6)
b [Å]	24.2270(9)	8.3211(3)	11.1940(10)
c [Å]	13.5051(4)	40.1083(12)	14.1730(17)
α [°]	90	90	73.715(9)
β [°]	94.098(2)	101.873(17)	88.573(7)
γ [°]	90	90	75.467(6)
volume [Å^3]	3442.68(19)	6727.2(4)	1459.4(2)
Z	4	8	2
ρ_{calcd} [g cm^{-3}]	1.388	1.401	1.806
μ [mm^{-1}]	4.352	4.469	2.825
F(000)	1488	2928	764
crystal size [mm^3]	0.27×0.12×0.10	0.20×0.15×0.02	0.23×0.21×0.11
θ range [°] for data collection	3.65 to 68.27	2.25 to 68.94	3.08 to 27.49
reflections collected	30023	17711	11748
unique reflections	6306	5963	6641
R_{int}	0.071	0.1038	0.0614
parameters	456	433	316
goodness-of-fit on F^2	0.969	0.994	1.016
final R indices [$I>2\sigma(I)$]	$R_1 = 0.0514$	$R_1 = 0.0641$	$R_1 = 0.0489$
	$wR_2 = 0.1583$	$wR_2 = 0.1606$	$wR_2 = 0.0750$
R indices (all data)	$R_1 = 0.0726$	$R_1 = 0.1151$	$R_1 = 0.1052$
	$wR_2 = 0.1934$	$wR_2 = 0.1894$	$wR_2 = 0.0875$
largest diff. peak/hole [e Å^{-3}]	0.625/−0.520	0.710/−0.404	0.688/−0.790



Scheme 6. Generation of free diphosphinoenamines **13a**,**b** and **14a**,**b**, and phosphinoquinoline **15**.

was observed in the $^{31}P\{^1H\}$ NMR spectrum of **15** (δ = −11.5 ppm), and in the proton spectrum a resonance at δ = 3.77 ppm appeared corresponding to the new CH_2 group, whereas a signal at δ = 2.57 ppm confirmed the presence of the methyl group of the quinoline residue. Naturally, resonances for both methylene and methyl carbon atoms, as well as for the rest of the carbon atoms in the phosphine ligand, are present in the $^{13}C\{^1H\}$ NMR spectrum of **15** (see Experimental Section). The cleavage of the P–C bond in the diphosphine ligand of **12** could be due to the presence of traces of water in the reaction mixture, so that, in addition to **15**, diphenylphosphine oxide should be formed, although it was not detected spectroscopically, perhaps owing to further evolution of this species. Phosphine ligands containing quinoline functionalities are usually made by coupling phosphine and quinoline fragments in various ways,[13] unlike the synthetic procedure described herein which involves generation of the quinoline residue by metal-assisted transformation of functionalized diphosphines.

The coordination chemistry of the new functionalized diphosphines **3a**,**b** and **4a**,**b**, and the monophosphine **15**, is a promising candidate for study, as they should behave as ambivalent ligands through soft phosphorus and hard nitrogen donor atoms. In particular, phosphines with aromatic nitrogenated substituents show a very interesting behavior in transition metal catalyzed reactions such as hydrogenation and allylic alkylation.[13a,b,14] As a preliminary study we checked the reactivity of **15** toward the complex $[PdCl_2(NCMe)_2]$; this reaction leads readily to **16**, containing the new functionalized phosphine acting as a P,N-chelating ligand (Scheme 7). As expected, in the phosphorus spectra of **16** only one signal appears shifted to low field (δ = 49.7 ppm) in comparison with the free phosphine. To obtain suitable crystals for X-ray analysis, complex **16** was convert-



Scheme 7. Formation of the palladium(II) phosphinoquinoline complexes **16** and **17**.

ed to **17**, the corresponding di-iodide analogue (Scheme 7), by treatment of a dichloromethane solution of **16** with an excess of NaI. In **17** (Figure 3), the Pd atom has a distorted square-planar geometry in which two iodide ligands are mutually *cis* and the two other coordination sites are occupied by the monophosphine, which is bonded to the metal through the phosphorus and the nitrogen atoms. The P(1)-Pd(1)-N(1) angle (79.55(12)°) is noticeably smaller than the I(1)-Pd(1)-I(2) angle (91.91(2)°) due to the constraints imposed by the five-membered Pd(1)-P(1)-C(1)-C(2)-N(1) ring formed. Within this nonplanar ring, the P(1)–C(1) and C(1)–C(2) distances are in the range for a single bond

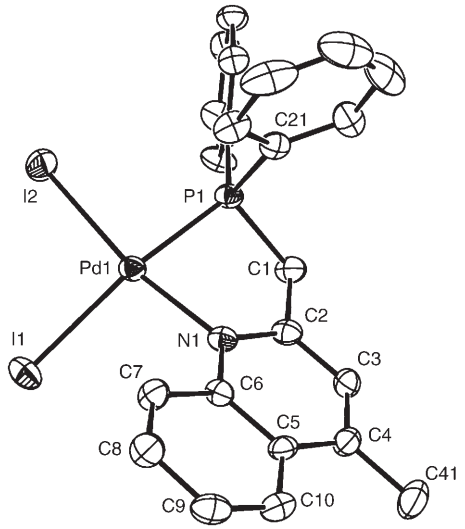


Figure 3. Molecular structure of **17** (thermal ellipsoids at 30% probability level). Pd1–P1 2.2348(14), Pd1–N1 2.144(4), Pd1–I1 2.6987(6), Pd1–I2 2.5921(6), P1–C1 1.853(5), C1–C2 1.514(7), N1–C2 1.352(6), N1–C6 1.397(6), C2–C3 1.416(7); P1-Pd1-N1 79.55(12), N1-Pd1-I1 98.63(11), I1-Pd1-I2 91.91(2), I2-Pd1-P1 91.58(4), C1-P1-Pd1 96.89(18), C2-C1-P1 106.6(4), C1-C2-C3 121.0(5), C1-C2-N1 117.1(5), N1-C2-C3 121.9(5), C6-N1-C2 118.4(4), C2-N1-Pd1 116.7(3), C6-N1-Pd1 124.9(3).

(1.853(5) Å and 1.514(7) Å respectively). No changes in the structural parameters of the quinoline ring are observed. The two Pd–I distances differ markedly from each other (Pd(1)–I(1) 2.6987(6) Å; Pd(1)–I(2) 2.5921(6) Å), which is clearly due to the difference in nature of the atoms located trans to the iodide ligands.[15]

Conclusion

The simple diphosphine DPPM can be converted to highly functionalized diphosphines by means of metal-mediated transformations of previously prepared diphosphinoketenimine ligands. The reactions of the ketenimine functional group in these ligands with various organolithium and organomagnesium reagents yields new functionalized diphosphines whose final structure can be modulated by controlling the electronic and steric features of the complexes, namely the nature of the ancillary ligands and of the substituents at the nitrogen atom of the ketenimine group. In some cases, the new diphosphine ligands can be liberated from the metal center by irradiation with UV/Vis light, allowing further coordination of the ligand to a different metallic center.

Experimental Section

General: All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk and glove-box techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer FT 1720-X and Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. Chemical shifts of the NMR spectra were referenced to internal $SiMe_4$ (^1H and ^{13}C) or external H_3PO_4 (^{31}P). $H_2C{=}C{=}CHMgBr$,[16] $[PdCl_2(CNCH_3)_2]$,[17] $[MnI(CO)_3\{(PPh_2)_2C{=}C{=}NR\}]$ (**1**),[7] and $[Mn(CO)_4\{(PPh_2)_2C{=}C{=}NR\}]ClO_4$ (**6**)[9,18] were prepared as described elsewhere. All other reagents were obtained commercially and used without further purification.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of such materials should be prepared, and these should be handled with great caution.

Compound 3a: A solution of MeLi in diethyl ether (1.6 M, 1 mL, 1.6 mmol) was added dropwise to a solution of **1a** (0.10 g, 0.13 mmol) in THF (20 mL) at 0°C. The mixture was stirred for 40 min. Distilled water (1 mL) was added and the mixture was filtered off. The solvent was evaporated to dryness and the solid residue recrystallized in a mixture of CH_2Cl_2/hexane to afford a yellow product (80 mg, 80%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2012 (ν(CO)) (s), 1944 (ν(CO)) (m), 1912 (ν(CO)) cm^{-1} (m); FTIR (THF): $\tilde{\nu}$ = 2012 (ν(CO)) (s), 1949 (ν(CO)) (m), 1915 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.3 (21H, Ph), 7.21 (m, 2H, *m*-N-Ph), 6.70 (d, ^3J(H,H) = 8 Hz, 2H, *o*-N-Ph), 6.62 (s, NH), 1.81 ppm (s, 3H, CH_3–C=C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 20.7 (br, PPh_2), 13.0 ppm (br, PPh_2); elemental analysis calcd (%) for $C_{36}H_{29}NIMnO_3P_2$ (767.43): C 56.34, H 3.81, N 1.82; found: C 56.15, H 4.02, N 1.77.

Compound 3b: This compound was prepared similarly to **3a** by adding MeLi 1.6 M (1 mL, 1.6 mmol) to **1b** (0.10 g, 0.13 mmol) in THF. Yield 85 mg, 20 mL (79%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2011 (ν(CO)) (s), 1943 (ν(CO)) (m), 1912 (ν(CO)) cm^{-1} (m); FTIR (toluene): $\tilde{\nu}$ = 2009 (ν(CO)) (s), 1942 (ν(CO)) (m), 1914 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.1 (20H, Ph), 7.0 (d, ^3J(H,H) = 7 Hz, 2H, *m*-(*p*-

tolyl)), 6.62 (s, NH), 6.61 (d, ^3J(H,H) = 7 Hz, 2H, *o*-(*p*-tolyl)), 2.31 (s, 3H, CH_3–Ph), 1.76 ppm (s, 3H, CH_3–C=C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 20.2 (br, PPh_2), 13.0 ppm (br, PPh_2); elemental analysis calcd (%) for $C_{37}H_{31}NIMnO_3P_2$ (781.45): C 56.87, H 4.00, N 1.79; found: C 56.90, H 3.68, N 1.79.

Compound 4a: *n*BuMgCl solution was prepared by refluxing Mg (0.24 g) and 1-chlorobutane (1.05 mL) in THF for 10 min, and a portion of it (1 mL, 1 mmol, 1 M) was added dropwise at 0 °C to a solution of **1a** (80 mg, 0.12 mmol) in THF (15 mL). The reaction was monitored by IR spectroscopy until it was finished after 2 h. The mixture was hydrolyzed at 0 °C by adding distilled water (1 mL), the solution was filtered off and the solvent was removed under vacuum. The remaining solid was chromatographed through an alumina column (activity III) prepared in hexane. Elution with CH_2Cl_2/hexane (3:4, v/v) produced a yellow fraction, which was evaporated to dryness, giving **4a** as a yellow solid. Yield 52 mg (60 %). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2012 (ν(CO)) (s), 1945 (ν(CO)) (m), 1914 (ν(CO)) cm^{-1} (m); FTIR (THF): $\tilde{\nu}$ = 2009 (ν(CO)) (s), 1943 (ν(CO)) (m), 1917 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.3 (21H, Ph), 7.22 (m, 2H, *m*-N–Ph), 6.71 (d, 2H, ^3J(H,H) = 8 Hz, *o*-N–Ph), 6.45 (s, NH), 2.22 (m, 2H, CH_2–C=C), 0.61 (m, 2H, CH_2–CH_2C=C), 0.43 (m, 2H, CH_2–CH_3), 0.32 ppm (m, 3H, CH_3–CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 20.8 (br, PPh_2), 14.2 ppm (br, PPh_2); elemental analysis calcd (%) for $C_{39}H_{35}NIMnO_3P_2$ (809.49): C 57.87, H 4.36, N 1.73; found: C 57.51, H 4.60, N 1.52.

Compound 4b: *n*BuMgCl (1 mL, 1 M) was added to a solution of **1b** (90 mg, 0.12 mmol) in THF (20 mL). After a procedure analogous to that for **4a**, **4b** was isolated as a yellow solid (66 mg, 68 %). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2011 (ν(CO)) (s), 1944 (ν(CO)) (m), 1912 (ν(CO)) cm^{-1} (m); FTIR (THF): $\tilde{\nu}$ = 2008 (ν(CO)) (s), 1944 (ν(CO)) (m), 1918 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.3 (20H, Ph), 7.01 (d, 2H, ^3J-(H,H) = 7 Hz, 2H, *m*-(*p*-tolyl)), 6.72 (d, ^3J(H,H) = 8 Hz, 2H, *o*-(*p*-tolyl)), 6.45 (s, N*H*), 2.28 (s, CH_3–Ph), 2.23 (m, 2H, CH_2–C=C); 0.76 (m, 2H, CH_2–CH_2C=C), 0.53 (m, 2H, CH_2–CH_3), 0.32 ppm (m, 3H, CH_3–CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 20.4 (br, PPh_2), 13.4 ppm (br, PPh_2); elemental analysis calcd (%) for $C_{40}H_{37}NIMnO_3P_2$ (823.52): C 58.34, H 4.53, N 1.70; found: C 58.42, H 4.61, N 1.61.

Compound 5a: Reaction occurred immediately when a THF solution of H_2C=C=CHMgBr (0.5 mL, 1 M, 0.5 mmol) was added dropwise at −70 °C to a solution of **1a** (0.18 g, 0.25 mmol) in THF (30 mL). Distilled water (1 mL) was added and the solution was filtered off. The solvent was reduced under vacuum to 5 mL and the compound precipitated by addition of hexane (15 mL). The yellow solid was washed with hexane (2×5 mL) and dried under vacuum. Yield 200 mg (95 %). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2014 (ν(CO)) (s), 1947 (ν(CO)) (m), 1914 (ν(CO)) cm^{-1} (m); FTIR (THF): $\tilde{\nu}$ = 2010 (ν(CO)) (s), 1944 (ν(CO)) (m), 1913 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.91–7.50 (20H, Ph), 7.29–7.19 (3H, NPh), 6.82 (d, ^3J(H,H) = 7 Hz, 2H, *o*-NPh), 6.59 (br, 1H, N*H*Ph), 3.15 (dd, ^4J(H,H) = 2 Hz, ^2J(H,H) = 17 Hz, 1H, CH_2), 3.06 (dd, ^4J(H,H) = 2 Hz, ^2J(H,H) = 17 Hz, 1H, CH_2), 1.83 ppm (t, ^4J(H,H) = 2 Hz, 1H, C≡CH); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 23.1 (s, PPh_2), 15.3 ppm (s, PPh_2); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 223.6 (br, CO), 221.6 (br, 2CO), 157.0 (s, *C*–NPh), 137.8 (s, C_{ipso}-NPh), 133.6 (d, ^1J(P,C) = 9 Hz, C_{ipso}-Ph), 133.4 (d, ^1J(P,C) = 9 Hz, C_{ipso}-Ph), 132.2 (d, ^1J(P,C) = 5 Hz, C_{ipso}-Ph), 131.9 (d, ^1J(P,C) = 5 Hz, C_{ipso}-Ph), 130.7–128.1 (Ph), 90.6 (dd, ^1J(P,C) = 24 Hz, ^1J(P,C) = 32 Hz, P_2C=C), 76.8 (s, *C*≡CH), 73.1 (s, C≡*C*H), 30.4 ppm (s, CH_2); elemental analysis calcd (%) for $C_{38}H_{29}NIMnO_3P_2$ (791.43): C 57.67, H 3.69, N 1.77; found: C 57.47, H 3.85, N 1.82.

Compound 5d: An excess of a THF solution of H_2C=C=CHMgBr (0.2 mL, 1 M, 0.2 mmol) was added to **1d** (60 mg, 0.08 mmol) dissolved in THF (15 mL). By a similar procedure to that for **5a**, **5d** was isolated as a yellow solid (50 mg, 79 %). FTIR (THF): $\tilde{\nu}$ = 2009 (ν(CO)) (s), 1945 (ν(CO)) (m), 1909 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.96–7.49 (20H, Ph), 7.13–6.95 (3H, N-xylyl), 6.09 (s, 1H, NH), 2.78 (t, ^4J(H,H) = 3 Hz, 2H, CH_2), 2.14 (s, 3H, xylyl CH_3), 1.96 (s, 3H, xylyl CH_3), 1.76 ppm (t, 1H, ^4J(H,H) = 3 Hz, C≡C*H*); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 23.0 (s), 14.8 ppm (s); elemental analysis calcd (%) for $C_{40}H_{33}NIMnO_3P_2$ (819.48): C 58.63, H 4.06, N 1.71; found: C 58.40, H 4.17, N 1.68.

Compound 7d: An excess of a THF solution of H_2C=C=CHMgBr (1 mL, 1 M, 1 mmol) was added dropwise to a solution of **6d** (101.4 mg, 0.13 mmol) in toluene (20 mL). The reaction took place very quickly. Distilled water (1 mL) was added and the solution was filtered. Yellow crystals were obtained by evaporation of the solvent in an open flask. Yield 84 mg (80 %). FTIR (CH_2Cl_2): $\tilde{\nu}$= 2073 (ν(CO)) (s), 1997 (ν(CO)) (s), 1989 (ν(CO)) (vs), 1963 (ν(CO)) (s); FTIR (toluene): $\tilde{\nu}$= 2071 (ν(CO)) (s), 1997 (ν(CO)) (s), 1990 (ν(CO)) (vs), 1961 (ν(CO)) cm^{-1} (s); ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.9–7.4 (20H, Ph), 6.85–6.61 (3H, xylyl), 5.23 (t, ^4J(H,H) = 7 Hz, 1H, −C*H*=C=CH_2), 3.82 (d, ^4J(H,H) = 7 Hz, 2H, =CH_2), 1.96 ppm (s, 6H, 2×CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 2.36 ppm (br); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 213.0 (br, *C*O), 210.5 (s, CH=*C*=CH_2), 157.5 (s, *C*=N), 79.5 (s, *C*H=C=CH_2), 75.8 (s, CH=C=*C*H_2), 58.0 (t, ^1J(P,C) = 53 Hz, P_2C), 19.9 ppm (s, 2×*C*H_3); elemental analysis calcd (%) for $C_{41}H_{32}NMnO_4P_2$ (719.60): C 68.43, H 4.48, N 1.95; found: C 68.01, H 4.98, N 1.84.

Compound 8: A THF solution of H_2C=C=CHMgBr (1 mL, 1 M, 1 mmol) was added at room temperature to a solution of **6c** (30 mg, 0.04 mmol) in toluene (10 mL). By a similar procedure to that for **7d**, yellow crystals were obtained for **8** (15 mg, 56 %). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2071 (ν(CO)) (s), 1991 (ν(CO)) (vs), 1958.1 (ν(CO)) cm^{-1} (s); FTIR (toluene): $\tilde{\nu}$ = 2070 (ν(CO)) (s), 1994 (ν(CO)) (vs), 1990 (ν(CO)) (vs), 1956 (ν(CO)) cm^{-1} (s); FTIR (Nujol): $\tilde{\nu}$ = 2070 (ν(CO)) (s), 2186 (ν(CO)) (vs), 2152 (ν(CO)) cm^{-1} (s); ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.95–7.15 (20H, Ph), 1.17 (s, 9H, *t*Bu), 1.07 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = −1.30 ppm (br); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 213.4 (br, CO), 144.0 (s, C=N), 96.2 (s, −*C*≡C−CH_3), 78.9 (s, −C≡*C*−CH_3), 56.6 (t, ^1J(P,C) = 57 Hz, P_2C), 30.7 (s, C-(*C*H_3)$_3$), 30.0 ppm (s, *C*H_3); elemental analysis calcd (%) for $C_{37}H_{32}NMnO_4P_2$ (671.56): C 66.18, H 4.80, N 2.09; found: C 65.91, H 4.64, N 1.84.

Compound 9: An excess of a THF solution of H_2C=C=CHMgBr (1 mL, 1 M, 1 mmol) was added to a solution of **6a** (75 mg, 0.1 mmol) in toluene (20 mL). By a similar procedure to that for **7d**, **9** was isolated. Suitable crystals for X-ray diffraction were obtained from slow evaporation of a toluene solution in an open flask. Yield 92 mg (95 %). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2073 (ν(CO)) (s), 1993 (ν(CO)) (vs), 1963 (ν(CO)) cm^{-1} (s); FTIR (toluene): $\tilde{\nu}$ = 2072 (ν(CO)) (s), 1996 (ν(CO)) (vs), 1991 (ν(CO)) (vs), 1959 (ν(CO)) cm^{-1} (s); FTIR (Nujol): $\tilde{\nu}$ = 2072 (ν(CO)) (m), 1988 (ν(CO)) (s), 1952 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.04–7.98 (Ph), 7.43 ppm (Ph); ^1H NMR (300 MHz, quinoline): δ = 7.70 (d, ^3J(H,H) = 7 Hz, 1H), 7.37 (d, ^3J(H,H) = 7 Hz, 1H), 7.31 (t, ^3J(H,H) = 7 Hz, 1H), 7.14 (t, ^3J(H,H) = 7 Hz, 1H), 6.45 (s, 1H), 2.24 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = −2.4 (br) (room temperature), −1.4 (br), −4.53 ppm (br) (−80 °C); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 219.3 (br, CO), 158.2 (s, C−N), 149.2 (s, C−N), 53.1 (t, ^1J(P,C) = 58 Hz, P_2C), 19.2 ppm (s, CH_3); elemental analysis calcd (%) for $C_{39}H_{28}NMnO_4P_2$ (691.53): C 67.74, H 4.08, N 2.03; found: C 67.52, H 4.28, N 1.95.

Compounds I and II: Mixtures of these tautomers were obtained by stirring a CH_2Cl_2 solution (15 mL) of **5a** (50 mg, 0.063 mmol) with $AgClO_4$ (16 mg, 0.076 mmol) for 10 min. The solution was filtered off and hexane added to obtain a solid for spectroscopic analysis. The IR spectrum was identical for the two compounds and only by ^1H NMR was it possible to distinguish them. A major proportion was **I**. FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2033 (ν(CO)) (s), 1964 (ν(CO)) (m), 1928 (ν(CO)) cm^{-1} (m); FTIR (THF): $\tilde{\nu}$ = 2030 (ν(CO)) (s), 1962 (ν(CO)) (m), 1928 (ν(CO)) cm^{-1} (m); ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.90–7.52 (20H, Ph), 7.28–7.24 (3H, NPh); **I**: δ = 6.80 (d, ^3J(H,H) = 8 Hz, 2H, *o*-NHPh), 6.76 (s, 1H, NH), 3.14 (dd, ^4J-(H,H) = 3 Hz, ^3J(H,H) = 17 Hz, 1H, CH_2), 2.98 (dd, ^4J(H,H) = 3 Hz, ^3J(H,H) = 17 Hz, 1H, CH_2), 1.86 ppm (t, ^4J(H,H) = 3 Hz, 1H, C≡CH); **II**: δ = 6.70 (d, ^3J(H,H) = 8 Hz, 2H, *o*-NHPh), 6.56 (s, 1H, NH), 5.51 (t, ^4J(H,H) = 8 Hz, 1H, CH=C), 4.30 ppm (d, ^4J(H,H) = 8 Hz, 2H, =CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 24.7 (br), 18.0 ppm (br).

Compound 10a: A solution of a mixture of **I** and **II** in CH_2Cl_2 (15 mL), prepared as described above, was stirred in a CO atmosphere for 3 h.

The end of the reaction was detected by IR spectroscopy. When the reaction had finished the mixture was filtered off. Then the solvent was reduced to approximately 5 mL under vacuum and a yellow solid was precipitated by the addition of hexane (15 mL). Yield 42 mg (84%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2088 (ν(CO)) (s), 2023 (ν(CO)) (m), 2007 (ν(CO)) (vs), 1994 (ν(CO)) cm^{-1} (sh); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.68 (20H, Ph), 7.29–7.18 (3H, NPh), 7.04 (d, ^3J(H,H) = 8 Hz, 2H, *o*-NHPh), 6.73 (s, 1H, NH), 5.51 (t, ^3J(H,H) = 6 Hz, 1H, C*H*=C=CH$_2$), 4.39 ppm (d, ^3J(H,H) = 6 Hz, 2H, CH=C=C*H*$_2$); $^{31}P\{^1H\}$ NMR: (121.5 MHz, $CDCl_3$): δ = 15.0 (br); elemental analysis calcd for $C_{39}H_{29}NClMnO_8P_2$ (792.00): C 59.15, H 3.69, N 1.77; found: C 59.27, H 3.73, N 1.89.

Compound 11: HBF_4 (33 μL, 0.24 mmol, 54% v/v, d = 1.18) was added to a solution of **8** (150 mg, 0.22 mmol) in CH_2Cl_2 (20 mL). After 5 min of stirring, the solvent was reduced under vacuum to approximately 5 mL and the product was precipitated as a beige solid by addition of hexane (15 mL, 115 mg, 74%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2087 (ν(CO)) (s), 2022 (ν(CO)) (m), 2006 (ν(CO)) (vs), 1992 (ν(CO)) cm^{-1} (sh); FTIR (Nujol): $\tilde{\nu}$ = 3376 (ν(NH)), 2083 (ν(CO)), 2017 (ν(CO)), 1989 (ν(CO)), = 1092 (ν(BF_4)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.16 (20H, Ph); 5.20 (s, 1H, NH), 1.38 (s, 3H, CH_3), 1.15 ppm (s, 9H, *t*Bu); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 14.8 ppm (br); elemental analysis calcd (%) for $C_{37}H_{33}NBF_4MnO_4P_2$ (759.35): C 58.52, H 4.38, N 1.84; found: C 58.19, H 4.41, N 1.78.

Compound 10d: A similar procedure was followed to that for **11**, by adding HBF_4 (21 μL, 0.154 mmol, 54% v/v, d = 1.18) to a solution of **7d** (100 mg, 0.14 mmol) in CH_2Cl_2 (20 mL). Orange solid, yield 105 mg (93%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2088 (ν(CO)) (s), 2024 (ν(CO)) (m), 2006 (ν(CO)) (vs), 1994 (ν(CO)) cm^{-1} (sh); FTIR (Nujol): $\tilde{\nu}$ = 3352 (ν(NH)), 2083 (ν(CO)), 1990 (ν(CO)), 1050 (ν(BF_4)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.66 (20H, Ph); 7.05 (t, ^3J(H,H) = 7 Hz, 1H, *p*-xyl*yl*), 6.95 (d, ^3J(H,H) = 7 Hz, 2H, *m*-xylyl), 6.32 (s, 1H, NH-xylyl), 5.39 (t, ^4J(H,H) = 7 Hz, 1H, C*H*=C=CH$_2$), 4.33 (d, ^4J(H,H) = 7 Hz, 2H, CH=C=C*H*$_2$), 2.01 ppm (s, 6H, 2 CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 13.8 ppm (br); elemental analysis calcd (%) for $C_{41}H_{33}NBF_4MnO_4P_2$ (807.39): C 60.99, H 4.12, N 1.73; found: C 60.66, H 4.32, N 1.63.

Compound 12: A procedure similar to that for **11** was followed. HBF_4 (33 μL, 0.24 mmol, 54% v/v, d = 1.18) was added to a solution of **9** (150 mg, 0.22 mmol) in CH_2Cl_2 (20 mL). Yellow solid; yield 127 mg (81%). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2087 (ν(CO)) (s), 2021 (ν(CO)) (m), 2005 (ν(CO)) (vs), 1991 (ν(CO)) cm^{-1} (sh); FTIR (Nujol): $\tilde{\nu}$ = 3355 (ν(NH)), 2082 (ν(CO)), 1990 (ν(CO)), 1050 (ν(BF_4)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.6 (s, 1H, NH), 7.83–7.37 (23H, Ph+quinoline); 6.79 (d, ^3J(H,H) = 7 Hz, 1H, quinoline), 6.34 (s, 1H, quinoline), 2.30 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 6.9 ppm (br); $^{13}C\{^1H\}$ NMR (75.5 MHz, D_2O): δ = 210.0 (br, CO), 134.2–130.2 (Ph); quinoline: 149.7 (s), 149.6 (s), 136.2 (s), 133.0 (s), 125.8 (s), 125.4 (s), 122.3 (s), 118.6 (t, ^3J(P,C) = 8 Hz), 116.5 (s), 65.5 (t, ^1J(P,C) = 45 Hz, P_2C), 19.4 ppm (s, CH_3); elemental analysis calcd (%) for $C_{39}H_{29}NBF_4MnO_4P_2$ (779.36): C 60.10, H 3.75, N 1.80; found: C 60.31, H 4.01, N 1.62.

Synthesis of free diphosphinoenamines and phosphinoquinoline: In a typical procedure, a solution of the metallic complex was irradiated with UV/Vis light at 10°C. The reaction was followed by IR spectroscopy. When the reaction was finished (after about 4 h) the solvent was eliminated under vacuum and the remaining solid chromatographed through an alumina column (activity III) prepared in hexane. Elution with CH_2Cl_2/hexane (2:5) gave a colorless fraction, which was evaporated to dryness, depositing a white solid. The solid was recrystallized in CH_2Cl_2/hexane for the diphosphinoenamines and CH_2Cl_2 for the phosphinoquinoline.

Compound 13a: Prepared from **3a** (70 mg, 0.14 mmol) in toluene (20 mL). Yield 27 mg (60%). FTIR (Nujol): $\tilde{\nu}$ = 3366 (ν(NH)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.1 (21H, Ph), 7.0 (m, 2H, *m*-NPh), 6.99 (s, NH), 6.47 (d, ^3J(H,H) = 8 Hz, *o*-NPh), 2.46 ppm (s, 3H, CH_3–C=C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −0.6 (d, ^2J(P,P) = 7 Hz), −21.1 ppm (d, ^2J(P,P) = 7 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, D_2O): δ = 162.4 (d, ^2J(P,C) = 40 Hz, P_2C=*C*), 89.1 (dd, ^1J(P,C) = 41 Hz, ^1J(P,C) = 20 Hz, P_2C=C), 20.4 ppm (d, ^3J(P,C) = 34 Hz, C=C−*C*H$_3$); elemental analysis calcd (%) for $C_{33}H_{29}NP_2$ (501.55): C 79.03, H 5.83, N 2.79; found: C 78.71, H 5.67, N 2.58.

Compound 13b: Prepared from **3b** (70 mg, 0.135 mmol) in toluene (20 mL). Yield 27 mg (60%). FTIR (Nujol): $\tilde{\nu}$ = 3357 (ν(NH)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.0 (20H, Ph), 6.96 (d, ^3J(H,H) = 8 Hz, 2H, *m*-(*p*-tolyl)), 6.91 (s, NH), 6.39 (d, ^3J(H,H) = 8 Hz, 2H, *o*-(*p*-tolyl)), 2.43 (s, 3H, CH_3–C=C), 2.23 ppm (s, 3H, CH_3–Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −0.5 (d, ^2J(P,P) = 9 Hz), −21.4 ppm (d, ^2J(P,P) = 7 Hz); elemental analysis calcd (%) for $C_{34}H_{31}NP_2$ (515.56): C 79.21, H 6.06, N 2.72; found: C 79.54, H 6.01, N 2.64.

Compound 14a: Prepared from **4a** (60 mg, 0.11 mmol) in toluene (20 mL). Yield 24 mg (60%). FTIR (Nujol): $\tilde{\nu}$ = 3362 (ν(NH)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.1 (21H, Ph), 7.0 (m, 2H, *m*-NPh), 6.63 (s, NH), 6.44 (d, ^3J(H,H) = 7 Hz, 2H, *o*-NPh), 3.11 (t, ^3J(H,H) = 8 Hz, 2H, CH_2–C=C), 1.51 (m, 2H, CH_2–CH$_2$–C=C), 1.20 (m, 2H, CH_2–CH$_3$), 0.70 ppm (t, 3H, ^3J(H,H) = 7 Hz, CH$_2$–CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 0.3 (br), −22.7 ppm (br); elemental analysis calcd (%) for $C_{36}H_{35}NP_2$ (543.62): C 79.54, H 6.49, N 2.58; found: C 79.99, H 6.60, N 2.54.

Compound 14b: Prepared from **4b** (60 mg, 0.10 mmol) in toluene (20 mL). Yield 20 mg (50%). FTIR (Nujol): $\tilde{\nu}$ = 3392 (ν(NH)) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.0 (20H, Ph), 6.95 (d, ^3J(H,H) = 8 Hz, 2H, *m*-(*p*-tolyl)), 6.56 (s, N−*H*), 6.36 (d, ^3J(H,H) = 8 Hz, 2H, *o*-(*p*-tolyl)), 3.00 (t, ^3J(H,H) = 8 Hz, 2H, −CH_2–C=C), 2.23 (s, 3H, CH_3–Ph), 1.52 (m, 2H, −CH_2–CH$_2$C=C), 1.21 (m, 2H, −CH_2–CH$_3$), 0.71 ppm (t, 3H, ^3J(H,H) = 7 Hz, CH_3–CH$_2$−); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 3.5 (br), −19.8 ppm (br); elemental analysis calcd (%) for $C_{37}H_{37}NP_2$ (557.64): C 79.69, H 6.69, N 2.51; found: C 79.66, H 6.62, N 2.48.

Compound 15: Prepared from **12** (200 mg, 0.26 mmol) in an acidified THF solution. Yield 37 mg (40%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.31 (Ph); quinoline: 8.0 (d, ^3J(H,H) = 8 Hz, 1H), 7.91 (d, ^3J(H,H) = 8 Hz, 1H), 7.82 (br, 1H), 7.65 (t, ^3J(H,H) = 8 Hz, 1H), 7.00 (s, 1H); 3.77 (br, 2H, PCH_2), 2.57 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, D_2O): δ = −11.5 (br); $^{13}C\{^1H\}$ NMR (75.5 MHz, D_2O): δ = 128.7–128.2 (Ph), 139.1 (d, ^1J(P,C) = 16 Hz, C_{ipso}-Ph), 132.9 (d, ^2J(P,C) = 20 Hz, C_{ortho}-Ph); quinoline: 158.5 (d, ^2J(P,C) = 8 Hz), 148.1 (s), 143.5 (s), 131.1 (s), 129.7 (s), 126.7 (s), 125.3 (s), 123.5 (s), 122.5 (d, ^3J(P,C) = 6 Hz), 39.4 (d, ^1J(P,C) = 18 Hz, PCH_2), 17.6 ppm (s, CH_3); elemental analysis calcd (%) for $C_{23}H_{20}NP$ (341.40): C 80.92, H 5.90, N 4.11; found: C 80.40, H 5.80, N 3.80.

Compound 16: To a solution of $[PdCl_2(NCCH_3)_2]$ (7 mg, 0.026 mmol) in CH_2Cl_2 (10 mL), **15** was added and the mixture was stirred for 10 min. The solvent was evaporated to dryness under vacuum and the yellow solid obtained was recrystallized by slow evaporation of a CH_2Cl_2 solution. Yield 12 mg (86%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.82–7.75 (5H, Ph), 7.45 (5H, Ph); quinoline: 9.49 (d, ^3J(H,H) = 8 Hz, 1H), 7.94 (d, ^3J(H,H) = 8 Hz, 1H), 7.65 (t, ^3J(H,H) = 8 Hz, 1H), 7.56–7.53 (2H); 4.48 (d, ^2J(P,H) = 12 Hz, 2H, PCH_2), 2.67 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, D_2O): δ = 49.7 (s); elemental analysis calcd (%) for $C_{23}H_{20}NCl_2PPd$ (518.70): C 53.26, H 3.89, N 2.70; found: C 53.16, H 3.73, N 2.64.

Compound 17: An excess of NaI (30 mg, 0.19 mmol) was added to a solution of **16** (10 mg, 0.019 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 10 min. The solution was filtered and the solvent evaporated to dryness under vacuum. Suitable crystals for X-ray diffraction were obtained by slow evaporation of a $CHCl_3$ solution in an open vessel. Yield 11 mg (85%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.83–7.69 (5H, Ph), 7.29–7.14 (5H, Ph); quinoline: 9.37(d, ^3J(H,H) = 8 Hz, 1H), 7.97 (d, ^3J(H,H) = 8 Hz, 1H), 7.65 (t, ^3J(H,H) = 8 Hz, 1H), 7.55–7.45 (2H); 4.48 (d, ^2J(P,H) = 13 Hz, 2H, PCH_2), 2.69 ppm (s, 3H, CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 51.9 ppm (s); elemental analysis calcd (%) for $C_{23}H_{20}NI_2PPd$ (701.60): C 39.37, H 2.87, N 1.99; found: C 39.43, H 2.98, N 1.84.

X-ray crystallographic study: Selected crystals of **7d** and **9** were manipulated under perfluoropolyether and mounted on a glass fiber, and data were collected on an Enraf-Nonius Kappa CCD diffractometer at 100 K and 150 K respectively. Data for crystals of **17** were collected at room

temperature on a Nonius Kappa CCD diffractometer. Crystal structures were solved by direct methods and refined using full-matrix least squares on F^2.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and left riding on their parent atoms. For **9** a residual peak of electronic density was modeled satisfactorily as a disordered water molecule. Relevant crystallographic data and details of the refinements for the three structures are given in Table 3. CCDC-600482 (**7d**), CCDC-600483 (**9**), and CCDC-600484 (**17**) 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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