Synthesis and reactivity of diphosphine metal complexes bearing peripheral ketenimine functionalities†

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Diphosphinoketenimine ligands $(PPh_2)_2C{=}C{=}NR$ (**1a** R = ^{t}Bu, **1b** R = Ph) were reacted with different Cu(I), Ag(I), Au(I), Pd(II), Ru(II) and Mo(0) metal complexes bearing weakly coordinating ligands yielding a number of mono-, di-, and trimetallic species with the diphosphine acting as either chelate or bridging ligand. The reactivity of some of the new complexes toward water and MeLi was investigated. The mononuclear Pd(II) complex $[PdCl_2\{(PPh_2)_2C{=}C{=}NPh\}]$ (**6b**) is transformed into the diphosphinoamide complex $[PdCl_2\{(PPh_2)_2CHC(=O)(NHPh)\}]$ (**12**) by nucleophilic addition of water. Similarly, treatment of **6b** with MeLi yields the diphosphinoenamine complex $[PdCl_2\{(PPh_2)_2C{=}C(Me)(NHPh)\}]$ (**14**). A different behaviour is observed in the treatment of diphosphinoketexnimine with water in the presence of Cu(I) ion, which leads to hydrolysis of the ligand involving P–C bond cleavage, underscoring the influence of the coordination environment in the reactivity showed by the coordinated ligand. The liberation of the metal assisted synthesized diphosphines from the Pd(II) metal center can be achieved easily and in quantitative yields by treatment with aqueous KCN solution.

Introduction

Development of new ligands for their use in homogeneous catalysis is an area of intense research, and functionalized phosphines, especially those with nitrogen-containing functional groups, have found increasing applications in this field.[1] Indeed, functionalized diphosphines have been shown to improve the selectivity of some catalytic processes.[2] The presence of additional functional groups in the diphosphine provides interesting properties to these ligands such as water solubility[3] or the ability for anchoring to solid matrices.[4] Additionally, the new donor atoms in the functional groups enhance the coordination versatility of these ligands.[5]

We have extensively studied the usefulness of simple bis(diphenylphosphino)methane complexes in the synthesis of functionalized diphosphine ligands.[6] In this regard, we have reported the formation of diphosphinoketenimines of formula $(PPh_2)_2C{=}C{=}NR$ (R = ^{t}Bu, Ph) coordinated in the Mn(I) complex *fac*-$[MnI(CO)_3\{(PPh_2)_2C{=}C{=}NR\}]$ *via* metal-assisted coupling of a transient diphosphinocarbene and isocyanides.[7] The ketenimine moiety of the new coordinated diphosphines display a rich reactivity, which further increases the synthetic potential of these ligands for the generation of sophisticated diphosphines. Reaction with isocyanides,[7] and nucleophilic additions of propargylic amines and alcohols,[8a] or Grignard reagents[8b] allow the controlled transformation of the diphosphinoketenimine, affording indole, imidazoline, oxazoline, and quinoline functionalized diphosphine ligands, respectively. We have also succeeded in obtaining the diphosphinoketenimine as free ligands by photochemical degradation of the metal complexes,[7] and shown their unique reactivity in cycloaddition reactions with alkynes and heterocumulenes.[9]

On the other hand, apart from the above mentioned parent complex *fac*-$[MnI(CO)_3\{(PPh_2)_2C{=}C{=}NR\}]$ the coordination chemistry of the new diphosphinoketenimine ligands remains unexplored. It is expected that the reactivity of the ketenimine fragment may be modulated by coordination to different metals. In this paper we describe the synthesis of different copper(I), silver(I), gold(I), palladium(II), ruthenium(II) and molybdenum(0) complexes containing diphosphinoketenimines ligands, defining mono-, di- and trimetallic cores surrounded by organic peripheral functionalities. The results show that the new complexes are structurally comparable to those of the parent ligand dppm, but present notable differences arising from the electronic and structural singularities of the diphosphinoketenimine ligand, as well as from the possibility of the ketenimine residue to undergo further transformations on coordination. The reactivity of the ketenimine moiety is dependent on the coordination environment and some of the new functionalized ligands synthesized can be liberated from the metal center effectively when using palladium(II) complexes.

Results and discussion

Complexes of group 11 metals

The treatment of $[Cu(NCMe)_4]BF_4$, $AgClO_4$ or [AuCl(THT)] (THT = tetrahydrothiophene) with stoichiometric amounts of $(PPh_2)_2C{=}C{=}NR$ (**1a** R = ^{t}Bu, **1b** R = Ph) readily affords the dinuclear diphosphine complexes $[Cu_2\{(Ph_2P)_2C{=}C{=}NR\}_2(NCMe)_2][BF_4]_2$ (**2a-b**), $[Ag_2(OClO_3)_2\{(Ph_2P)_2C{=}C{=}NR\}_2]$ (**3a-b**), and $[Au_2\{(Ph_2P)_2C{=}C{=}NR\}_2][Cl]_2$ (**4a-b**), respectively

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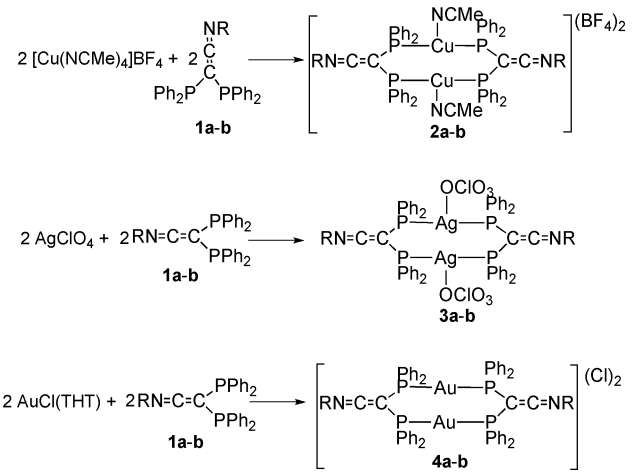
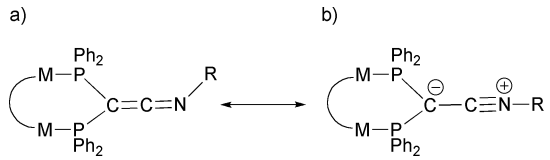
in high yield (Scheme 1). The use of the coordinatively unsaturated metallic fragment ($AgClO_4$) or the presence of weakly coordinating ligands such as acetonitrile or THT, allows the reaction to take place under very mild conditions (5–15 min of stirring at room temperature). The new compounds were characterized spectroscopically, by elemental analysis, and single crystal X-ray diffraction (in the case of **3a**). The frequency of the ν(C=C=N) band in the free diphosphinoketenimine ligand (2030 and 2002 cm^{-1} for **1a** and 1997 cm^{-1} for **1b**) undergoes an appreciable increase upon coordination (between 15 and 66 cm^{-1}),



Scheme 1 Synthesis of dinuclear compounds **2–4a-b** (a: R = ^{t}Bu, b: R = Ph).

more apparent in the case of **1a**, as a result of the stabilization of the zwitterionic form of the ketenimine group (form b) Scheme 2). These data suggest that the peripheral ketenimine functionalities become activated toward further reactivity compared to the free ligand. As expected, the $^{31}P\{^1H\}$ NMR spectra show signals at higher chemical shifts than those of the free ligand (Table 1). For **2a-b** and **4a-b** singlet signals were observed corresponding to the two equivalent phosphorus atoms; however the spectra of **3a** displays a complex multiplet signal arising from the coupling of the phosphorus atoms with the silver nuclei in the three possible combinations of isotopes ^{107}Ag (I = 1/2; natural abundance 51.82%) and ^{109}Ag (I = 1/2; natural abundance 48.18%). By contrast, the $^{31}P\{^1H\}$ NMR spectrum of **3b** consists of a broad singlet, indicating dissociation of the diphosphine ligand in solution,[10] which can be due to the lower donor ability of the N-aryl ketenimine compared to the N-alkyl one. Coordination of two acetonitrile molecules in complexes **2a** and **2b** is evidenced by the presence of singlet signals for the methyl groups at 1.85 and 2.13 ppm, respectively, in the ^1H NMR spectra. For complexes **4a-b**, conductivity measurements indicate that the chloride anions



Scheme 2 Possible resonance forms of the coordinated diphosphinoketenimine ligands

Table 1 Selected spectroscopic data for compounds **1–17**

Compound	IR[a] cm^{-1}	$^{31}P\{^1H\}$ NMR: δ (ppm)[b]	^1H NMR: δ (ppm)[a]
1a	2030 (m), 2002 (s)	−10.5	
1b	1997 (s)	−9.8	
2a	2064 (s), 2022 (m)	4.3 (s)	01.85 (s, 6 H, NCCH_3)
2b	2012 (s)	4.8 (s)[c]	2.13 (s, 6 H, NCCH_3)
3a	2067 (s)	20.6 (m)[c]	
3b	2017 (s)	23.0 (br)[c]	
4a	2071 (s)	37.4 (s)	
4b	2034 (s)	38.7 (s)	
5a	2051 (s)	0.7 (m)[c]	
5b	2018 (s)	2.4 (m)[c]	
6a	2078 (s), 2054 (m)	−36.7 (s)	
6b	2042 (s)	−33.6 (s)[e]	
7a	2069 (m), 2046 (s)[d]	9.4 (s, PPh_2), −143.2 (hp, $^1J_{PF}$ = 711 Hz, PF_6)[d]	
7b	2023 (m), 2009 (s)[d]	13.3 (s, PPh_2), −143.6 (hp, $^1J_{PF}$ = 711 Hz, PF_6)[d]	
8a	2045 (w), 2023 (w)[f] ν(CO) 1928 (s), 1833 (m), 1815 (m)[f]	13.4 (s)	1.01 (s, 3 H, CH_3), 0.77 (s, 9 H, C(CH_3)$_3$),
9a	2068 (s)	34.1 (s)	
9b	2036 (s)	35.2 (s)[c]	
11	ν(C=C=N) 2102 (s);[g]ν(P=O) 1177 (s)[g]		δ 0.91 (br, 18 H, C(CH_3)$_3$)
12	ν(N–H) 3406, ν(C=O) 1629[g]	−43.1 (s)[e]	4.69 (br, 1H, P_2CH), 6.12 (s, 1H, NH)[e]
13	ν(N–H) 3335, ν(C=C=N) 2074, ν(C=O) 1615[g]	−14.4 (q, $^2J_{PP}$ = 51 Hz, 1 P), 7.6 (d,$^2J_{PP}$ = 51 Hz, 4 P)	0.83 (s, 18 H, 2 C(CH_3)$_3$), 1.12 (s, 9 H, C(CH_3)$_3$), 3.50 (d, 2 H, $^2J_{HP}$ = 8 Hz, CH_2), 7.82 (s, 1H, NH)
14	ν(N–H) 3347[g]	−38.9 (d), −31.1 6 (d),$^2J_{PP}$ = 22 Hz[e]	1.81 (s, 3H, CH_3)[e]
15a	2050 (s)[d]	45.5 (s)	0.32 (t, 6 H, $^3J_{HP}$ = 4 Hz, AuCH_3),
15b	2027 (s)[d]	47.1 (s)	0.41 (t, 6 H, $^3J_{HP}$ = 4 Hz, AuCH_3)
16	ν(N–H) 3374 ν(C=O) 1660	−11.6 (s)	4.21 (br, 1 H, P_2CH)
17	ν(N–H) 3366	−21.1 (d), −0.6 (d), $^2J_{PP}$ = 7 Hz	

[a] CH_2Cl_2, ν(C=C=N) unless otherwise stated; [b] CD_2Cl_2; [c] D_2O capillary/CH_2Cl_2; [d] THF; [e] $CHCl_3$; [f] MeCN; [g] nujol.

Table 2 Selected bond lengths (Å) and angles (°) for compound **3a**

Ag(1)–Ag(2)	3.0170(11)	P(1)–Ag(1)–P(2)	151.25(7)
Ag(1)–O(1)	2.559(5)	P(1)–Ag(1)–O(1)	115.67(16)
P(2)–Ag(1)	2.447(2)	P(2)–Ag(1)–O(1)	93.06(16)
P(1)–Ag(1)	2.440(2)	O(1)–Ag(1)–Ag(2)	97.60(14)
C(1)–C(2)	1.328(11)	P(1)–Ag(1)–Ag(2)	93.95(5)
C(2)–N(1)	1.195(10)	P(2)–Ag(1)–Ag(2)	82.60(5)
P(1)–C(1)	1.806(7)	P(1)–C(1)–P(3)	119.2(4)
		C(2)–N(1)–C(4)	133.0(7)

are dissociated in solution, though weak Au···Cl contacts could exist in the solid state.[11]

Complex **3a** was further characterized by X-ray diffraction. Colorless single crystals suitable for an X-ray analysis were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. A view of the structure is shown in Fig. 1, and a selection of bond distances and angles is included in Table 2. As the analogous dppm derivative $[Ag_2(OClO_3)_2(dppm)_2]$ (**3a′**),[12] **3a** is centrosymmetric, with the inversion center located in the middle of the Ag–Ag segment. However other structural features of **3a** are different from those of the dppm complex. Thus, the Ag–O distance is much shorter in **3a** (2.559(5) Å) than in **3a′** (2.878(9) Å), implying a stronger interaction of the perchlorate anion with the metal in the first case. The P–Ag–P arrangement, which is almost linear in **3a′** (173.49(3)°) and other similar diphosphine Ag(I) complexes, appears considerably bent in **3a** (151.25(7)°), so that the structure may no longer be viewed as an elongated chair form of an eight-membered ring. The coordination geometry around the silver atoms in **3a** can be considered as very distorted trigonal or almost T-shaped, and is completed with a silver–silver contact of 3.017 Å, which is slightly longer than that found in **3a′**. The Ag–P bond lengths in **3a** (mean value 2.44 Å) are similar to those displayed by **3a′** (mean value 2.40 Å), and the P–C–P angle in **3a** (119.2(4)°) is in the expected range considering the sp^2 hybridization of the carbon atom, being clearly larger than that found in **3a′** (111.36(9)°). It should be noted that conductivity experiments carried out on dichloromethane solutions show that **3a** behaves as a 1:2 electrolyte, indicating that the perchlorate anion is dissociated from the metal center in solution.

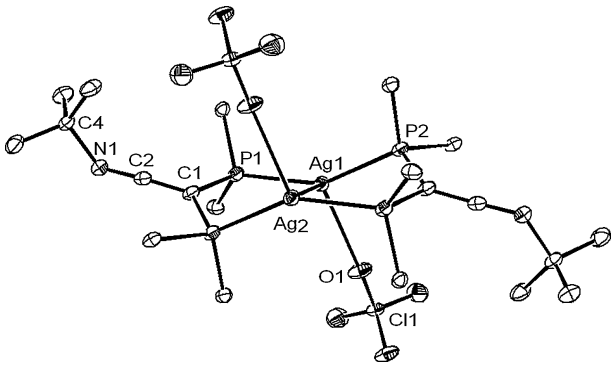
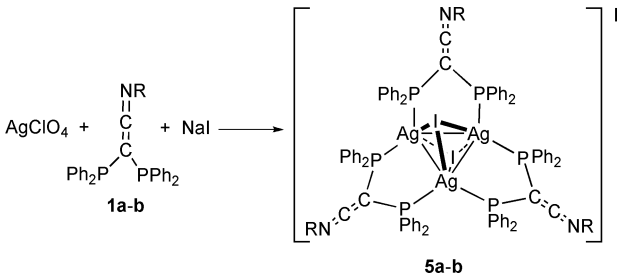


Fig. 1 Crystal structure of complex **3a** (thermal ellipsoids at 30% probability level) with the atomic numbering scheme. Phenyl groups omitted for clarity.

When the reaction of $AgClO_4$ with a stoichiometric amount of $(PPh_2)_2C{=}C{=}NR$ (**1a** R = ^{t}Bu, **1b** R = Ph) was carried out in the presence of NaI, cationic trinuclear silver(I) complexes of formula $[Ag_3I_2\{(PPh_2)_2C{=}C{=}NR\}_3]I$ (**5a–b**) were obtained (Scheme 3).



Scheme 3 Synthesis of trinuclear silver (I) cluster **5a-b** (a: R = ^{t}Bu, b: R = Ph).

This type of $[Ag_3X_2(PP)_3]X$ clusters is well known when PP is a simple diphosphine ligand and X an anion such as halides, pseudohalides or acetylides.[13] The IR spectra of these compounds show an increase of the frequency of the ν(C=C=N) band, similarly to that discussed in the case of the dinuclear derivatives **2–4** (Table 1). The $^{31}P\{^1H\}$ NMR spectra displayed a complex signal centered at 0.6 and 2.4 ppm for **5a** and **5b**, respectively. Conductivity experiments in acetone suggest a 1:1 electrolyte, showing that the bridging iodide ligands do not dissociate in solution. In order to obtain suitable crystals for X-ray analysis, the external iodide anion in **5b** was replaced by ClO_4^-, by treatment of this compound with $AgClO_4$. The structure of the complex cation of **5b-ClO$_4$** (Fig. 2) is very similar to that of $[Ag_3I_2(dppm)_3]^+$ (**5b′**),[12c] featuring a trigonal bipyramidal Ag_3I_2 core and three bridging diphosphine ligands defining an almost planar Ag_3P_6 skeleton, but additionally containing three peripheral ketenimine groups, two of them being slightly laid out toward one side of that Ag_3P_6 plane and the remaining one toward the opposite side. The Ag–Ag distances (average 3.135 Å) are slightly shorter than those in **5b′** (average 3.236 Å) (Table 3). The Ag–P and Ag–I distances in **5b** (2.47 and 2.95 Å, respectively) are almost identical to those found in **5b′** (2.47 and 2.97 Å, respectively), and the P–C–P angle in **5b** is 114°.

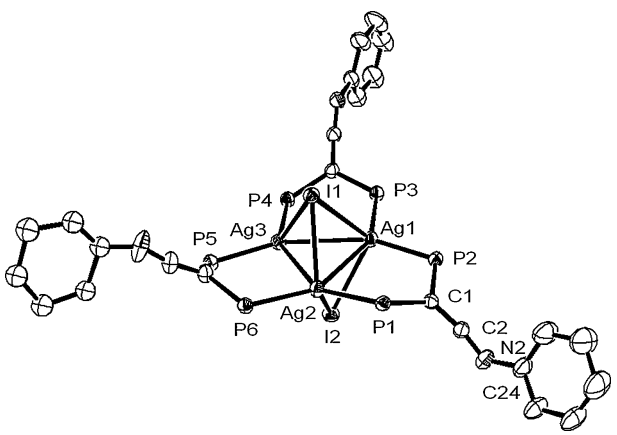


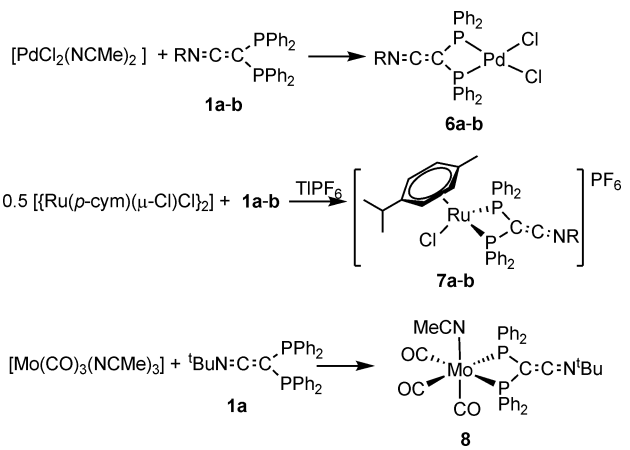
Fig. 2 Crystal structure of cation complex **5b** with atomic numbering scheme (thermal ellipsoids at 30% probability level). For clarity, phenyl groups have been omitted.

Table 3 Selected bond lengths (Å) and angles (°) for compound **5b**

Ag(1)–Ag(2)	3.0797(7)	Ag(2)–Ag(1)–Ag(3)	62.912(15)
Ag(2)–Ag(3)	3.2259(7)	Ag(1)–Ag(2)–Ag(3)	58.881(15)
Ag(1)–Ag(3)	3.1019(6)	Ag(1)–Ag(3)–Ag(2)	58.208(15)
Ag(1)–I(1)	2.9431(6)	I(2)–Ag(2)–I(1)	103.863(19)
Ag(2)–I(1)	3.0167(6)	P(3)–Ag(1)–Ag(2)	151.14(4)
Ag(3)–I(1)	2.9550(6)	P(1)–Ag(2)–Ag(3)	145.96(4)
P(1)–C(1)	1.821(7)	P(5)–Ag(3)–Ag(1)	145.87(4)
P(2)–C(1)	1.814(7)	P(1)–C(1)–P(2)	117.2(3)
C(1)–C(2)	1.332(9)	C(24)–N(2)–C(2)	131.3(7)
C(2)–N(2)	1.195(9)		

Mononuclear Pd(II), Ru(II) and Mo(0) complexes

We decided to prepare mononuclear complexes with chelating diphosphino ligands, more similar to our previously reported manganese(I) complexes.[7] Following conventional procedures for the synthesis of diphosphine complexes we reacted $[PdCl_2(NCMe)_2]$, $[\{Ru(p\text{-cymene})(\mu\text{-}Cl)Cl\}_2]$ and *fac*-$[Mo(CO)_3(NCMe)_3]$ with **1a-b** to readily obtain $[PdCl_2\{(PPh_2)_2C{=}C{=}NR\}]$ (**6a-b**), $[\{Ru(p\text{-cymene})Cl\{(PPh_2)_2C{=}C{=}NR\}]PF_6$ (**7a-b**) and *fac*-$[Mo(CO)_3(NCMe)\{(PPh_2)_2C{=}C{=}N^tBu\}]$ (**8**) respectively in very high yields (Scheme 4). All the compounds were characterized spectroscopically and by elemental analysis (Table 1). The treatment of the dinuclear ruthenium complex with **1a-b** is carried out in the presence of $TlPF_6$ as halide extractor in order to facilitate the reaction. If the reaction is carried out in the absence of $TlPF_6$, an intermediate complex is spectroscopically detected, corresponding to a neutral derivative in which the diphosphine is coordinated in a monodentate fashion $[\{Ru(p\text{-cymene})(Cl)_2\{\eta1\text{-}(PPh_2)_2C{=}C{=}N^tBu\}]$ ($^{31}P\{^1H\}$ NMR spectra shows two doublets at δ −11.8 and 28.7, $^2J_{PP}$ = 73 Hz). This compound slowly evolved to $[\{Ru(p\text{-cymene})Cl\{(PPh_2)_2C{=}C{=}N^tBu\}]Cl$ (**7a-I**) by displacement of one of the chloride ligands from the coordination sphere by the free phosphorus atom albeit in a lower yield.

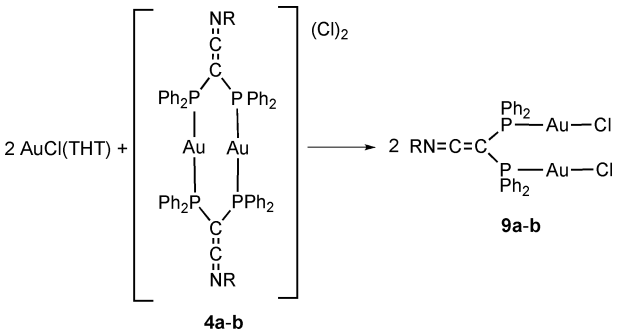


Scheme 4 Synthesis of mononuclear complexes **6a-b**, **7a-b** and **8** (a: R = ^{t}Bu, b: R = Ph).

The molybdenum compound **8** is not stable in solution and decomposes to the corresponding tetracarbonyl derivative $[Mo(CO)_4\{(PPh_2)_2C{=}C{=}N^tBu\}]$ (**8-I**). This compound is also quantitatively obtained by treatment of **8** with CO.

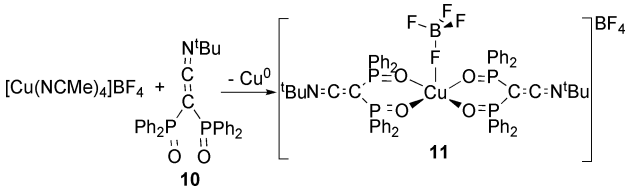
Attempts to coordinate the ketenimine residue

In all the examples discussed so far the coordination of the diphosphinoketenimine occurs exclusively through the phosphorus atoms either as a bridging or chelating ligand. This prompted us to explore the possibility of coordinating the ketenimine group to metal centers.[14] Treatment of the dinuclear gold(I) complexes **4a-b** with two equivalents of [AuCl(THT)] yielded the neutral dinuclear complexes $[Au_2(Cl)_2\{(Ph_2P)_2C{=}C{=}NR\}]$ (**9a-b**) in which the diphosphinoketenimine is bridging two AuCl fragments (Scheme 5), instead of the target coordination of the new Au(I) fragment through the ketenimine residue. This compound can also be prepared by direct treatment of **1a-b** with two equivalents of [AuCl(THT)]. Reaction of the parent diphosphinoketenimine complex *fac*-$[MnI(CO)_3\{(PPh_2)_2C{=}C{=}N^tBu\}]$ with metallic fragments containing labile ligands such as the above [AuCl(THT)] or $[PdCl_2(NCMe)_2]$ also led to transmetalation of the diphosphine ligand giving **9a** and **6a**, respectively. A different strategy would be to use the oxidized form of the diphosphinoketenimine $\{(O{=}PPh_2)_2C{=}C{=}N^tBu\}$ (**10**).[15]



Scheme 5 Synthesis of gold(I) complexes **9a-b** (a: R = ^{t}Bu, b: R = Ph).

The donor nature of the O=P groups does not favor the coordination with soft metal ions, thus coordination of the ketenimine group may result. Surprisingly, reaction of $[Cu(NCMe)_4]BF_4$ with **10** yielded a green solution which displayed no signals in the $^{31}P\{^1H\}$ NMR spectrum, suggesting the presence of a paramagnetic Cu(II) complex. From this solution, the complex $[Cu\{(Ph_2P{=}O)_2C{=}C{=}N^tBu\}_2(BF_4)][BF_4]$ (**11**) was isolated (Scheme 6). Disproportionation of Cu(I) to Cu(II) and Cu(0) seems to be favored by the coordination of the P=O group. The frequency of the ν(C=C=N) band in the IR spectra (2102 cm^{-1}) indicates the non-participation of this group in the coordination to the metal center. The structure of the complex **11** was elucidated by X-ray diffraction (Fig. 3). The metal center is found in a square pyramid coordination environment, interacting with two dioxidized diphosphinoketenimine ligands and a fluorine atom of the tetrafluoroborate group in an apical position. Cu–O distances are 1.927(2)–1.950(2) Å, similar to other copper(II) complexes



Scheme 6 Synthesis of Cu(II) derivative **11**.

Table 4 Selected bond lengths (Å) and angles (°) for compound **11**

Cu(1)–O(2)	1.928(2)	P(2)–C(2)	1.775(3)
Cu(1)–O(1)	1.935(2)	P(4)–C(2)	1.772(3)
Cu(1)–O(4)	1.938(2)	O(1)–Cu(1)–O(3)	92.46(9)
Cu(1)–O(3)	1.951(2)	O(1)–Cu(1)–O(4)	174.64(10)
Cu(1)–F(11)	2.2719(19)	O(2)–Cu(1)–O(3)	166.42(9)
C(3)–N(3)	1.175(4)	O(2)–Cu(1)–O(4)	92.91(9)
C(4)–N(4)	1.177(4)	C(3)–N(3)–C(30)	147.2(3)
C(1)–C(3)	1.346(4)	C(4)–N(4)–C(40)	143.5(3)
C(2)–C(4)	1.343(4)	P(1)–C(1)–P(3)	119.36(17)
P(1)–C(1)	1.774(3)	P(2)–C(2)–P(4)	118.08(16)
P(3)–C(1)	1.765(3)		

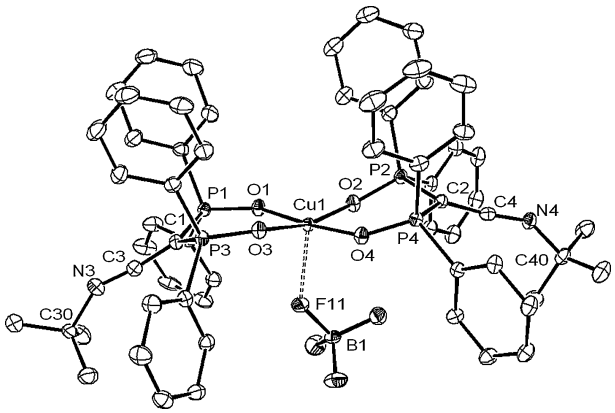


Fig. 3 Crystal structure of cation complex **11** with atomic numbering scheme (thermal ellipsoids at 30% probability level).

with O-donor ligands.[15] The copper site is displaced slightly above the plane containing the four oxygen atoms and the Cu–F distance of 2.272(2) Å is short compared to other complexes with coordinated BF_4^- indicating a strong interaction with the metal center.[16,17] The structural parameters of the ketenimine fragment are in agreement with an important contribution of a charge-separated form of the ligand (form b) in scheme 1), which is also in consonance with the high frequency of the ν(C=C=N) band (2102 cm^{-1}) found in the IR spectrum of this complex. Thus, C3–N3 and C4–N4 bond distances, 1.173(5) Å and 1.175(5) Å respectively are shorter than a double bond, and the bond angles C3–N3–C30 (147.3(4)°) and C4–N4–C40 (143.6(4)°) are significantly wider than 120° (Table 4).

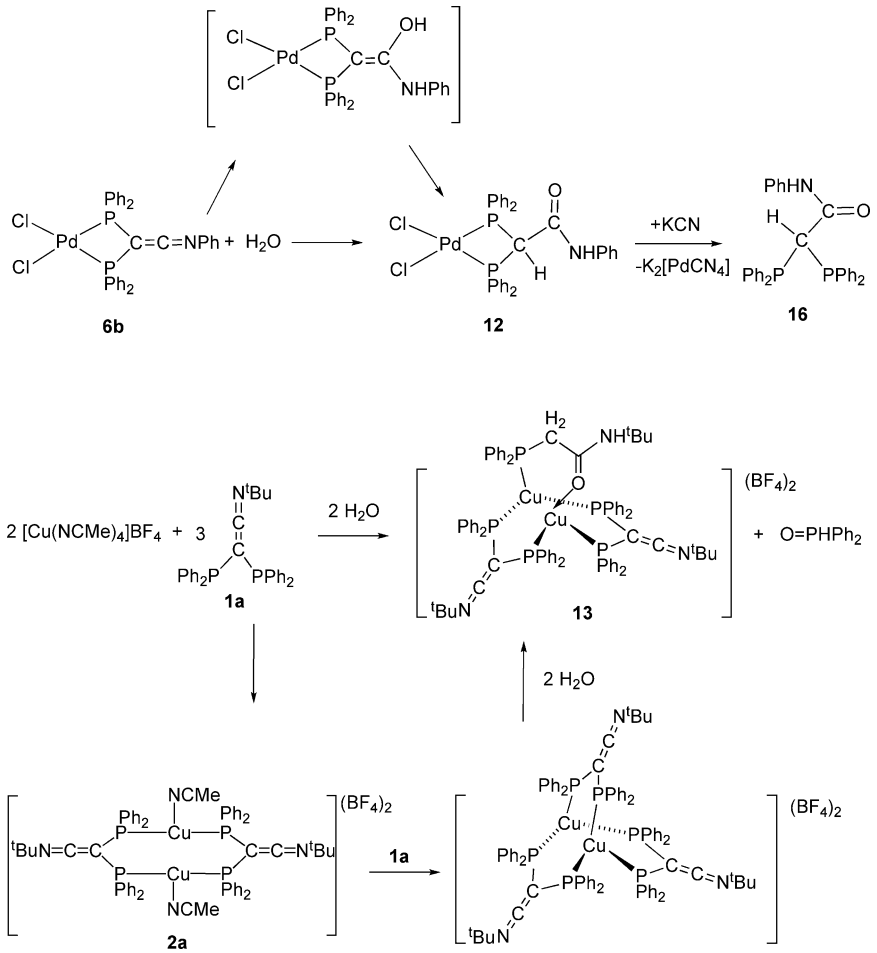
Reactivity of coordinated diphosphinoketenimine ligands

We set out to study the reactivity of the coordinated diphosphinoketenimine ligands with nucleophiles such as water and MeLi. We have previously examined the reactivity of the carbonyl Mn(I) complex *fac*-[MnI(CO)$_3${(PPh$_2$)$_2$C=C=NPh}] with these reagents, and found no reaction with water and formation of a diphosphinoenamine ligand on treatment with MeLi.[8b] Liberation of the diphosphinoenamine ligand from the metal center proved to be difficult and only moderate to low yields could be obtained after photodegradation of the complex. In this regard, we envisioned that palladium(II) complexes would be more appropriate in order to enhance the reactivity of the ketenimine functionality and to achieve the demetalation of the newly obtained diphosphine ligands.

The reaction of [PdCl$_2${(PPh$_2$)$_2$C=C=NPh}] (**6b**) with an excess of distilled water in THF led to the diphosphinoamide complex [PdCl$_2${(PPh$_2$)$_2$CHC(=O)(NHPh)}] (**12**) as a result of the nucleophilic addition of H_2O to the C=N ketenimine double bond (Scheme 7). Presumably the reaction takes place through an enol intermediate, which spontaneously tautomerizes giving the observed product. The spectroscopic data of this compound are in agreement with this proposed formulation. The IR spectrum displays bands at 1629 cm^{-1} and 3406 cm^{-1} assignable to the C=O and N–H stretchings respectively. The ^{1}H NMR spectrum showed signals corresponding to the N–H and P$_2$C–H groups and the ^{31}P{^{1}H} NMR spectrum displayed one signal corresponding to the two equivalent phosphorus atoms (Table 1). No reaction occurred in the treatment of **6a** with water showing the minor ability of N-alkyl diphosphinoketenimine to undergo nucleophilic addition compared to the N-aryl ones.

Group 11 dimetallic compounds of the type **2**, **3** and **4** did not react with water under these conditions, which reflect the distinct reactivity of the ligand depending on the metal complex examined. In this case we observed the hydrolysis of the tert-butyl diphosphinoketenimine **1a** when an excess of the diphosphine is reacted with [Cu(NCMe)$_4$]BF$_4$. Under these conditions a new derivative **13** was obtained (Scheme 7). This compound displays a bridging phosphinoamide ligand in addition to two diphosphinoketenimine ligands. The new ligand appears to be the result of the hydrolysis of a diphosphinoketenimine ligand by two molecules of water, involving P–C bond cleavage.[18] This mechanism is also supported by the formation of a stoichiometric amount of O=PHPh$_2$ (singlet signal at 22.4 ppm in the ^{31}P{^{1}H} NMR spectrum) together with **13**. In fact, the 1:1 adduct of **13** with O=PHPh$_2$ (compound **13-I**) can also be obtained by quick crystallization from the reaction mixture (see Experimental section). During the reaction, the immediate formation of **2a** was observed, followed soon afterwards by an intermediate which only displays one signal at 13 ppm in the ^{31}P{^{1}H} NMR spectrum was detected, being likely a dinuclear copper complex with three coordinated diphosphinoketenimine ligands.[19] This compound spontaneously evolved to give O=PHPh$_2$ and **13**. The spectroscopic data of **13** are in agreement with the proposed formulation (Table 1). The IR spectrum showed signals corresponding to the C=O (1615 cm^{-1}) and N–H (3335 cm^{-1}) stretching bands respectively. The ^{1}H NMR spectrum showed signals corresponding to two different tert-butyl groups in a 2:1 ratio, along with a doublet corresponding to the CH$_2$ group and a broad singlet at 7.82 ppm assignable to the N–H residue. The ^{31}P{^{1}H} NMR spectra displayed two signals as a quintuplet and doublet corresponding to the phosphinoamide and diphosphinoketenimine ligands respectively. The equivalence of the diphosphinoketenimine phosphorus atoms suggest the existence of a fluxional process interconverting the positions of the phosphinoamide ligand.[20] At low temperature (–60 °C) the ^{31}P{^{1}H} NMR spectra of this compound showed a triplet signal for the phosphinoamide ligand, suggesting that this fluxional process is frozen, although the signal corresponding to the phosphorus atoms of the diphosphinoketenimine ligands appeared as a poorly resolved multiplet. A preliminary X-ray diffraction study for **13-I** was carried out confirming the proposed structure for this complex (Fig. 4).[21,22]

Treatment of [PdCl$_2${(PPh$_2$)$_2$C=C=NPh}] (**6b**) with one equivalent of MeLi in THF at −78 °C resulted in the diphosphinoenamine complex [PdCl$_2${(PPh$_2$)$_2$C=C(Me)(NHPh)}] (**14**) after hydrolysis of the anionic intermediate obtained by nucleophilic addition of



Scheme 7 Reactivity of diphosphinoketenimine complexes with H_2O.

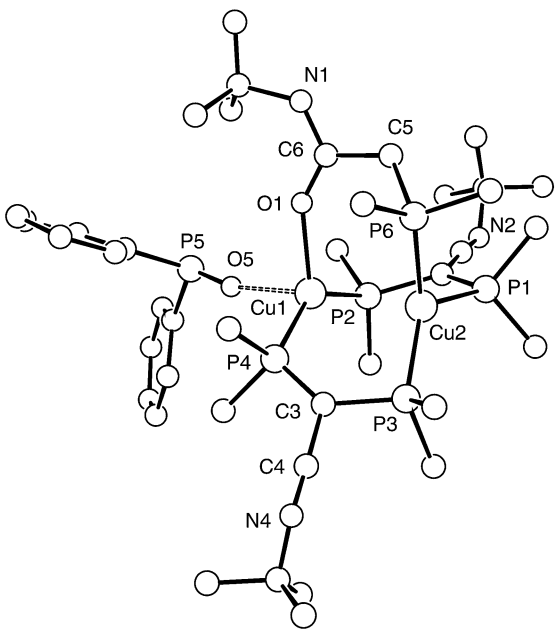


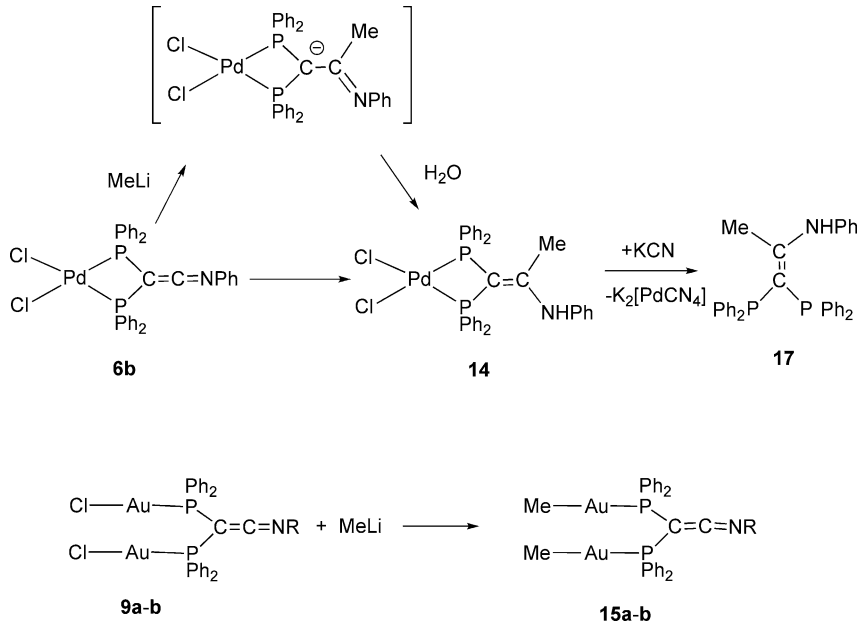
Fig. 4 Molecular structure of cation complex **13-I** with atomic numbering scheme. For clarity, only the ipso carbons of the diphosphinoketenimine groups are shown.

the carbanion (Scheme 8). The enamine form of the ligand is supported by the spectroscopic data of the compound (Table 1). Thus, the $^{31}P\{^1H\}$ NMR spectrum displayed two signals corresponding to the inequivalent phosphorus atoms and the IR spectrum showed a band at 3347 cm^{-1} assignable to the N–H stretching.

Similar to the results obtained in the reaction with water, the dinuclear complexes **2–4a-b** did not undergo nucleophilic attack by MeLi under these conditions. On the other hand, the neutral gold(I) complexes $[Au_2(Cl)_2\{(Ph_2P)_2C{=}C{=}NPR\}]$ (**9a-b**), reacted with MeLi to give the substitution products $[Au_2(Me)_2\{(Ph_2P)_2C{=}C{=}NPR\}]$ (**15a-b**), as a result of the replacement of the chloride ligands by methyl groups (Scheme 8), instead of nucleophilic addition to the ketenimine functionality.

Liberation of the diphosphines

Another target we wanted to address with this work was to develop an efficient method to liberate the functionalized diphosphines from the metal centers in a simple high yielding procedure. So far, our efforts involving ligands coordinated to manganese(I) complexes resulted in low yields of the free ligands.[8b] In this regard, the demetalation of diphosphine ligands coordinated to Pd(II) complexes by treatment with aqueous solutions of KCN has been reported.[23] We adapted this method to our system, and treatment of solutions of **12** or **14** in dichloromethane with a small



Scheme 8 Reactivity of diphosphinoketenimine complexes **6b** and **9a-b** (a: R = ^{t}Bu, b: R = Ph) with MeLi.

volume of an aqueous solution KCN with vigorous stirring yielded quantitatively free diphosphinoamide $(PPh_2)_2CHC(=O)(NHPh)$ (**16**) and diphosphinoenamine $(PPh_2)_2C=C(CH_3)(NHPh)$ (**17**) ligands, respectively (Schemes 7 and 8), which are purified by simple filtration over diatomaceous earth (see Table 1 and the Experimental section for the spectroscopic data of these compounds). This result bodes well for use of this type of complex in the metal-mediated synthesis of more sophisticated diphosphines.

Conclusions

We have synthesized different mononuclear complexes of Pd(II), Ru(II) and Mo(0), and polynuclear complexes of Cu(I), Ag(I) and Au(I) bearing the diphosphinoketenimines $(PPh_2)_2C=C=NR$ (**1a** R = ^{t}Bu, **1b** R = Ph) acting as either chelating or bridging ligands, respectively. The peripheral ketenimine functionalities in these complexes show no tendency to coordinate to other metallic fragments, and its reactivity in nucleophilic addition processes depends on the coordination environment of the diphosphine. Thus, reaction of the mononuclear complex $[PdCl_2\{(PPh_2)_2C=C=NPh\}]$ (**6b**) with water and MeLi affords $[PdCl_2\{(PPh_2)_2CHC(=O)(NHPh)\}]$ (**12**) and $[PdCl_2\{(PPh_2)_2C=C(Me)(NHPh)\}]$ (**14**), respectively, whereas no reaction occurred when using group 11 dinuclear complexes, except in the treatment of a Cu(I) derivative with water which leads to the hydrolysis of the diphosphine involving P–C bond cleavage. The new functionalized diphosphines of complexes **12** and **14** can be liberated from the Pd(II) center in quantitative yield using a straightforward procedure. It is expected that this result will allow the metal mediated synthesis of more sophisticated diphosphines, including asymmetric ones, by reaction with amines and alcohols. Work along these lines is currently in progress in our group.

Experimental

General

All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk 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. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants *J* are given in Hz. Chemical shifts of the NMR spectra were referenced to internal $SiMe_4$ (^{1}H and ^{13}C) or external H_3PO_4 (^{31}P). $[Cu(NCMe)_4]BF_4$,[24] AuCl(THT),[25] $[PdCl_2(NCMe)_2]$,[26] $[\{Ru(p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$,[27] $[Mo(CO)_3(NCMe)_3]$,[28] $[(PPh_2)_2C=C=NR]$,[7] and $[(O=PPh_2)_2C=C=N^tBu]$,[15] 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.

Syntheses

$[Cu_2\{(Ph_2P)_2C=C=N^tBu\}_2(NCMe)_2][BF_4]_2$ (2a). To a solution of $(Ph_2P)_2C=C=N^tBu$ **1a** (50 mg, 0.11 mmol) in 20 mL of CH_2Cl_2 was added $[Cu(NCMe)_4]BF_4$ (34 mg, 0.11 mmol) at room temperature with continuous stirring. The reaction occurs instantaneously, then, the solution was concentrated to 4 mL. Addition of hexane (15 mL) gave a white solid. Yield: 67 mg (95%). Anal. Calcd for $C_{64}H_{64}B_2Cu_2F_8N_4P_4$: C, 58.51; H, 4.91; N, 4.26. Found: C, 58.13; H, 5.03; N, 4.06. FTIR (CH_2Cl_2): ν(C=C=N) 2064 (s), 2022 (m) cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 4.3 (s); ^{1}H NMR (CD_2Cl_2): δ 0.73 (s, 18 H, C(CH_3)$_3$), 1.85 (s, 6 H,

NCCH_3), 7.3–7.6 (m, 40 H, Ph); $^{13}C\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 2.1 (s, N≡C–CH_3), 29.7 (s, C(CH_3)$_3$), 35.9 (br, P_2C=C=N), 61.7 (s, C(CH_3)$_3$), 123.0 (s, N≡C–CH_3), 148.3 (s, P_2C=C=N).

[Cu_2{(Ph_2P)$_2$C=C=NPh}$_2$(MeCN)$_2$][BF_4]$_2$ (2b). The procedure is analogous to that described above, using [Cu(NCMe)$_4$]BF_4 (32 mg, 0.10 mmol) and (Ph_2P)$_2$C=C=NPh **1b** (50 mg, 0.10 mmol). The product obtained is a white solid. Yield: 66 mg (95%). Anal. Calcd for $C_{68}H_{56}B_2Cu_2F_8N_4P_4$: C, 60.33; H, 4.17; N, 4.14. Found: C, 59.90; H, 4.28; N, 4.05. FTIR (CH_2Cl_2): ν(C=C=N) 2012 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 4.8 (s); ^{1}H NMR (CD_2Cl_2): δ 2.13 (s, 6 H, NCCH_3), 6.5–7.7 (m, 50 H, Ph).

[Ag_2(OClO$_3$)$_2${(Ph_2P)$_2$C=C=N^{t}Bu}$_2$] (3a). (Ph_2P)$_2$C=C=N^{t}Bu **1a** (40 mg, 0.09 mmol) was dissolved in a mixture of THF (10 mL) and CH_2Cl_2 (5 mL). $AgClO_4$ (18 mg, 0.09 mmol) was added to this solution in the dark and the resulting mixture was vigorously stirred for 15 min. After this time, the solvent was evaporated to dryness under reduced pressure. To the residue was added CH_2Cl_2 (10 mL) and the resulting solution was filtered off and concentrated to 5 mL. Addition of hexane (20 mL) gave a white solid. Slow diffusion of hexane into a CH_2Cl_2 solution of the compound afforded colourless crystals suitable for X-ray diffraction. Yield: 51 mg (89%). Anal. Calcd for $C_{60}H_{58}Ag_2Cl_2N_2O_8P_4$: C, 53.55; H, 4.34; N, 2.08. Found: C, 53.27; H, 4.21; N, 2.03. FTIR (CH_2Cl_2): ν(C=C=N) 2067 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 20.6 (m); ^{1}H NMR (CD_2Cl_2): δ 0.72 (s, 18 H, C(CH_3)$_3$), 7.3–7.6 (m, 40 H, Ph); $^{13}C\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 29.9 (s, C(CH_3)$_3$), 62.1 (s, C(CH_3)$_3$), 148.1 (s, P_2C=C=N). Conductivity (dichloromethane, 20 °C): 46 S cm^2 mol^{-1}.

[Ag_2(OClO$_3$)$_2${(Ph_2P)$_2$C=C=NPh}$_2$] (3b). The procedure was similar to that for **3a** except (Ph_2P)$_2$C=C=NPh **1b** (40 mg, 0.08 mmol) and $AgClO_4$ (17 mg, 0.08 mmol) were used instead to give a white solid. Yield: 48 mg (85%). Anal. Calcd for $C_{64}H_{50}Ag_2Cl_2N_2O_8P_4$: C, 55.48; H, 3.64; N, 2.02. Found: C, 55.61; H, 3.72; N, 1.96. FTIR (CH_2Cl_2): ν(C=C=N) 2017 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 23.0 (m);^{1}H NMR (CD_2Cl_2): δ 6.6–7.8 (m, 50 H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 44.0 (br, P_2C=C=N), 159.3 (s, P_2C=C=N).

[Au_2{(Ph_2P)$_2$C=C=N^{t}Bu}$_2$](Cl)$_2$ (4a). AuCl(THT) (28 mg, 0.08 mmol) was added to a solution of (Ph_2P)$_2$C=C=N^{t}Bu **1a** (40 mg, 0.08 mmol) in CH_2Cl_2 (15 mL) at room temperature with continuous stirring. After 5 min, most of the solvent was removed, and 20 mL of hexane was then added to produce a white solid. Yield: 51 mg (92%). Anal. Calcd for $C_{60}H_{58}Au_2Cl_2N_2P_4$: C, 51.64; H, 4.19; N, 2.01. Found: C, 51.93; H, 4.19; N, 1.96. FTIR (CH_2Cl_2): ν(C=C=N) 2071 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.4 (s); ^{1}H NMR (CD_2Cl_2): δ 0.69 (s, 18 H, C(CH_3)$_3$), 7.3–8.0 (m, 40 H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.2 (s, C(CH_3)$_3$), 43.4 (br, P_2C=C=N), 62.6 (s, C(CH_3)$_3$), 151.1 (s, P_2C=C=N); Conductivity (dichloromethane, 20 °C): 63 S cm^2 mol^{-1}.

[Au_2{(Ph_2P)$_2$C=C=NPh}$_2$](Cl)$_2$ (4b). This was prepared using an identical procedure to **9a**, starting from (Ph_2P)$_2$C=C=NPh **2b** (20 mg, 0.04 mmol) and AuCl(THT) (14 mg, 0.04 mmol). Yield: 25 mg (89%). Anal. Calcd for $C_{64}H_{50}Au_2Cl_2N_2P_4$: C, 53.54; H, 3.51; N, 1.95. Found: C, 53.87; H, 3.31; N, 2.04. FTIR (CH_2Cl_2): ν(C=C=N) 2034 (s), cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.7 (s); ^{1}H NMR (CD_2Cl_2): δ 6.4–7.9 (m, 50 H, Ph).

[Ag_3I_2{(Ph_2P)$_2$C=C=N^{t}Bu}$_3$]I (5a). To a mixture of NaI (66 mg, 0.44 mmol) and (Ph_2P)$_2$C=C=N^{t}Bu **1a** (50 mg, 0.11 mmol) in THF/CH_2Cl_2 (20 mL/10 mL) was added solid $AgClO_4$ (22 mg, 0.11 mmol) in the dark. The reaction mixture was stirred for 2 h, the solution was then removed *in vacuo* and the crude product was taken up in dichloromethane (15 mL) and filtered. The filtrate was concentrated to 5 mL and 20 mL of hexane was then added to produce a white solid. Yield: 65 mg (86%). Anal. Calcd for $C_{90}H_{87}Ag_3I_3N_3P_6$: C, 51.45; H, 4.17; N, 2.00. Found: C, 51.69; H, 4.35; N, 1.96. FTIR (CH_2Cl_2): ν(C=C=N) 2051 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 0.7 (m); ^{1}H NMR (CD_2Cl_2): δ 0.61 (s, 27 H, C(CH_3)$_3$), 7.1–7.6 (m, 60 H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.1 (s, C(CH_3)$_3$), 41.9 (br, P_2C=C=N), 60.6 (s, C(CH_3)$_3$), 154.7 (s, P_2C=C=N); Conductivity (acetone, 20 °C): 118 S cm^2 mol^{-1}.

[Ag_3I_2{(Ph_2P)$_2$C=C=NPh}$_3$]I (5b). The compound was prepared following the same method described for **5a**, with (Ph_2P)$_2$C=C=NPh (50 mg, 0.10 mmol) and $AgClO_4$ (21 mg, 0.10 mmol). Yield: 61 mg (82%). Anal. Calcd for $C_{96}H_{75}Ag_3I_3N_3P_6$: C, 53.36; H, 3.50; N, 1.94. Found: C, 53.25; H, 3.61; N, 2.01. FTIR (CH_2Cl_2): ν(C=C=N) 2018 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 2.4 (m);^{1}H NMR (CD_2Cl_2): δ 6.5–7.9 (m, 75 H, Ph); Conductivity (acetone, 20 °C): 126 S cm^2 mol^{-1}. In order to obtain suitable crystals for X-ray analysis, the external iodide anion in **5b** was replaced by ClO_4^- as follows: To a solution of **5b** (104 mg, 0.048 mmol) in CH_2Cl_2 (20 mL) $AgClO_4$ (10 mg, 0.048 mmol) was added in the dark. The mixture was stirred for 30 min. The solution was then filtered off and concentrated to 3 mL. Slow diffusion of hexane gave white crystals of [Ag_3I_2{(Ph_2P)$_2$C=C=NPh}$_3$]ClO_4 (**5b-ClO$_4$**) Yield 83 mg (81%). Anal. Calcd for $C_{96}H_{75}Ag_3ClI_2N_3O_4P_6$: C, 54.05; H, 3.54; N, 1.97. Found: C, 53.84; H, 3.41; N 1.85.

[$PdCl_2${(PPh_2)$_2$C=C=N^{t}Bu}] (6a). (Ph_2P)$_2$C=C=N^{t}Bu **1a** (40 mg, 0.09 mmol) was added to a solution of [$PdCl_2$(NCMe)$_2$] (22 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) at room temperature with continuous stirring. After 5 min, the solution turned dark yellow and the solvent was removed *in vacuo*. The solid obtained was washed with hexane (2 × 5 mL) and dried, yielding a yellow solid. Yield: 53 mg (97%). Anal. Calcd for $C_{30}H_{29}Cl_2NP_2Pd$: C, 56.05; H, 4.55; N, 2.18. Found: C, 55.83; H, 4.54; N, 2.15. FTIR (CH_2Cl_2): ν(C=C=N) 2078 (s), 2054 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –36.7 (s); ^{1}H NMR (CD_2Cl_2): δ 1.05 (s, 9 H, C(CH_3)$_3$), 7.4–8.0 (m, 20 H, Ph).

[$PdCl_2${(PPh_2)$_2$C=C=NPh}] (6b). The procedure was similar to that for **6a** using (Ph_2P)$_2$C=C=NPh **1b** (40 mg, 0.08 mmol) and [$PdCl_2$(NCMe)$_2$] (21 mg, 0.08 mmol). Yield: 50 mg (94%). Anal. Calcd for $C_{32}H_{25}Cl_2NP_2Pd$: C, 57.99; H, 3.80; N, 2.11. Found: C, 58.05; H, 3.94; N, 2.17. FTIR (CH_2Cl_2): ν(C=C=N) 2042 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –33.6 (s); ^{1}H NMR (CD_2Cl_2): δ 6.09–8.1 (m, 25 H, Ph);$^{13}C\{^1H\}$ NMR (CD_2Cl_2): 45.8 (br, P_2C=C=N), 151.5 (s, P_2C=C=N).

[{Ru(*p*-cymene)Cl}{(PPh_2)$_2$C=C=N^{t}Bu}]PF_6 (7a). (Ph_2P)$_2$-C=C=N^{t}Bu **1a** (36 mg, 0.07 mmol) and $TlPF_6$ (36 mg, 0.07 mmol) were added to a solution of [{Ru(*p*-cymene)(μ-Cl)Cl}$_2$] (16 mg, 0.03 mmol) in THF (15 mL) at room temperature with continuous stirring. After 20 min, the colour of the solution changed from red to yellow. The solution was filtered under an inert atmosphere and the filtrate was concentrated to 3 mL. 15 mL of hexane was

then added to produce a yellow solid. Yield: 48 mg (91%). Anal. Calcd for $C_{40}H_{43}ClF_6NP_3Ru$: C, 54.52; H, 4.92; N, 1.59. Found: C, 54.32; H, 4.92; N, 1.39. FTIR (THF): ν(C=C=N) 2069 (m), 2046 (s), cm^{-1}; $^{31}P\{^1H\}$ NMR (THF): δ 9.4 (s, PPh_2), −143.2 (hp, $^1J_{PF} = 711$ Hz, PF_6); ^1H NMR (CD_2Cl_2): δ 1.05 (d, 6 H, $^3J_{HH} = 7$, $CH(CH_3)_2$), 1.28 (s, 9H, $C(CH_3)_3$), 1.36 (s, 3H, CH_3), 2.32 (hp, 1H, $^3J_{HH} = 7$, $CH(CH_3)_2$), 5.61 (d, 2 H, $^3J_{HH} = 6$, *p*-cymene), 5.88 (d, 2 H, $^3J_{HH} = 6$, *p*-cymene), 7.3–7.7 (m, 20 H, Ph).

[{Ru(*p*-cymene)Cl{$(PPh_2)_2C$=C=NPh}]PF_6 (7b). The compound was prepared following the same method described for **7a**, with [{Ru(*p*-cymene)(μ-Cl)Cl}$_2$] (16 mg, 0.03 mmol), $(Ph_2P)_2C$=C=NPh **1b** (30 mg, 0.06 mmol) and $TlPF_6$ (36 mg, 0.07 mmol). Yield: 46 mg (86%). Anal. Calcd for $C_{42}H_{39}ClF_6NP_3Ru$: C, 55.98; H, 4.36; N, 1.55. Found: C, 55.64; H, 4.42; N, 1.66. FTIR (THF): ν(C=C=N) 2023 (m), 2009 (s), cm^{-1}; $^{31}P\{^1H\}$ NMR (THF): δ 13.3 (s, PPh_2), −143.6 (hp, $^1J_{PF} = 711$ Hz, PF_6); ^1H NMR (CD_2Cl_2): δ 1.05 (d, 6 H, $^3J_{HH} = 7$, $CH(CH_3)_2$), 1.38 (s, 3H, CH_3), 2.31 (hp, 1H, $^3J_{HH} = 7$, $CH(CH_3)_2$), 5.70 (d, 2 H, $^3J_{HH} = 6$, *p*-cymene), 5.97 (d, 2 H, $^3J_{HH} = 6$, *p*-cymene), 7.1-7.8 (m, 25 H, Ph);$^{13}C\{^1H\}$ NMR (CD_2Cl_2): 17.2 (s, CH_3), 22.0(s, $CH(CH_3)_2$), 31.0 (s, $CH(CH_3)_2$), 50.3 (t, $^1J_{CP} = 38$, P_2C=C=N), 68.1 (s, 2 ×C *p*-cymene), 89.9 (s, 2 × CH *p*-cymene), 91.2 (s, 2 ×CH *p*-cymene), 102.9 (s, 2 ×C *p*-cymene), 150.5 (t, $^2J_{CP} = 8$, P_2C=C=N).

***fac*-[Mo(CO)$_3$(NCMe){$(PPh_2)_2C$=C=N^{t}Bu}] (8).** $(Ph_2P)_2$-C=C=N^{t}Bu **1a** (23 mg, 0.05 mmol) was added to a solution of [$Mo(CO)_3(NCMe)_3$] (15 mg, 0.05 mmol) in acetonitrile (8 mL) at room temperature with continuous stirring. After 5 min, the solution was concentrated to 4 mL and 10 mL of hexane was then added to produce a green-yellow solid. Yield: 34 mg (65%). Anal. Calcd for $C_{35}H_{32}MoN_2O_3P_2$: C, 61.23; H, 4.70; N, 4.08. Found: C, 60.75; H, 4.43; N, 3.91. FTIR (NCMe): ν(C=C=N) 2045 (w), 2023 (w), ν(CO) 1928 (s), 1833 (m), 1815 (m), cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 13.4 (s); ^1H NMR (CD_2Cl_2): δ 1.01 (s, 3 H, CH_3), 0.77 (s, 9 H, $C(CH_3)_3$), 7.3–7.8 (m, 20 H, Ph).

[Au_2Cl_2{$(Ph_2P)_2C$=C=N^{t}Bu}] (9a). A solution of $(Ph_2P)_2C$=C=N^{t}Bu **1a** (40 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of AuCl(THT) (58 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) at room temperature with continuous stirring. After 10 min, most of the solvent was removed, and 20 mL of hexane was then added to produce a white solid. Yield: 70 mg (88%). Anal. Calcd for $C_{30}H_{29}Au_2Cl_2NP_2$: C, 38.73; H, 3.14; N, 1.51. Found: C, 38.94; H, 3.26; N, 1.49. FTIR (CH_2Cl_2): ν(C=C=N) 2068 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.1 (s); ^1H NMR (CD_2Cl_2): δ 0.76 (s, 9 H, $C(CH_3)_3$), 7.5–7.7 (m, 20 H, Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.3 (s, $C(CH_3)_3$), 62.8 (s, $C(CH_3)_3$), 148.9 (s, P_2C=C=N).

[Au_2Cl_2{$(Ph_2P)_2C$=C=NPh}] (9b). This was prepared similarly to **9a** starting from $(Ph_2P)_2C$=C=NPh (40 mg, 0.08 mmol) and AuCl(THT) (56 mg, 0.16 mmol). Yield: 66 mg (84%). Anal. Calcd for $C_{32}H_{25}Au_2Cl_2NP_2$: C, 40.44; H, 2.65; N, 1.47. Found: C, 40.76; H, 2.87; N, 1.48. FTIR (CH_2Cl_2): ν(C=C=N) 2036 (s), cm^{-1}; $^{31}P\{^1H\}$ NMR (D_2O/CH_2Cl_2): δ 35.2 (s);^1H NMR (CD_2Cl_2): δ 6.5–7.9 (m, 25 H, Ph).

[Cu(FBF$_3$){$(Ph_2P$=O$)_2C$=C=N^{t}Bu}$_2$][BF_4] (11). To a dichloromethane solution (10 mL) of $(Ph_2P$=O$)_2C$=C=N^{t}Bu **10** (50 mg, 0.10 mmol), 32 mg of [$Cu(NCMe)_4$]BF_4 (0.10 mmol) were added. The mixture was stirred at room temperature for 10 min giving a clear green solution which was then filtered to remove a small amount of Cu(0). Hexane (15 mL) was added and the dichloromethane was removed by slow evaporation to give a green precipitate. Suitable crystals of **5** for X-ray analysis were obtained from a CH_2Cl_2/hexane solution. Yield: 52 mg (87%). Anal. Calcd for $C_{60}H_{58}B_2CuF_8N_2O_4P_4$: C, 58.49; H, 4.74; N, 2.27. Found: C, 58.41; H, 4.61; N, 2.22. FTIR (Nujol): ν(C=C=N) 2102 (s), ν(P=O) 1177 (s) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 0.91 (br, 18 H, $C(CH_3)_3$), 7.2–9.1 (br, 40, Ph).

[$PdCl_2${$(PPh_2)_2$CHC(=O)(NHPh)}] (12). To a solution of **6b** (40 mg, 0.06 mmol) in THF (10 mL) an excess of distilled water (0.1 mL) was added and the mixture stirred vigorously for 1 h. Over this time, a yellow precipitate appeared. The solvent was then evaporated and the residue washed with diethyl ether (2 × 5 mL) to yield a yellow solid. Yield: 38 mg (93%). Anal. Calcd for $C_{32}H_{27}Cl_2NOP_2Pd$: C, 56.45; H, 4.00; N, 2.06. Found: C, 56.86; H, 4.12; N, 2.00. FTIR (nujol): ν(N–H) 3406, ν(C=O) 1629 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −43.1 (s); ^1H NMR ($CDCl_3$): δ 4.69 (br, 1H, P_2CH), 6.12 (s, 1H, NH) 6.7–8.1 (m, 25 H, Ph).

[Cu_2 { $(Ph_2P)_2$ C=C=N^{t}Bu}$_2$ {Ph_2PCH_2C (O) NH^{t}Bu}] [BF_4]$_2$ (13). To a stirred dichloromethane (15 mL) solution of $(Ph_2P)_2C$=C=N^{t}Bu (100 mg, 0.22 mmol) was added in one portion solid [$Cu(NCMe)_4$]BF_4 (30 mg, 0.09 mmol) and stirred for 20 min. Addition of hexane caused the formation of a very small amount of crystals corresponding to [Cu_2{$(Ph_2P)_2C$=C=N^{t}Bu}$_2${Ph_2PCH_2C(O)NH^{t}Bu}$(OPHPh_2)$]-[BF_4]$_2$ (**13-I**), as confirmed by X-ray diffraction. The mother liquor was left to stand at −10 °C for two days, affording colourless crystals of **13**. Yield: 50 mg (52%). Anal. Calcd for $C_{78}H_{80}B_2Cu_2F_8N_3OP_5$: C, 61.19; H, 5.27; N, 2.74. Found: C, 60.87; H, 5.39; N, 2.57. FTIR (Nujol): ν(N–H) 3335, ν(C=C=N) 2074, ν(C=O) 1615 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −14.4 (q, $^2J_{PP} = 51$ Hz, 1 P), 7.6 (d,$^2J_{PP} = 51$ Hz, 4 P); ^1H NMR (CD_2Cl_2): δ 0.83 (s, 18 H, 2 $C(CH_3)_3$), 1.12 (s, 9 H, $C(CH_3)_3$), 3.50 (d, 2 H, $^2J_{HP} = 8$ Hz, CH_2), 6.5–7.5 (m, 50 H, Ph), 7.82 (s, 1H, NH).

[$PdCl_2${$(PPh_2)_2C$=C(CH$_3$)(NHPh)}] (14). To a solution of **6b** (40 mg, 0.06 mmol) in THF (20 mL) at −78 °C, 0.043 mL of MeLi 1.4 M (0.06 mmol) were added. The mixture was then allowed to reach room temperature with stirring and then distilled water (0.03 mL) was added. The mixture was filtered over diatomaceous earth and the filtrate concentrated to 5 mL. Addition of hexane (15 mL) resulted in the precipitation of a yellow solid. Yield: 33 mg (83%). Anal. Calcd for $C_{33}H_{29}Cl_2NP_2Pd$: C, 58.39; H, 4.31; N, 2.06. Found: C, 58.39; H, 4.22; N, 2.13. FTIR (nujol): ν(N–H) 3347 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −38.9 (d,$^2J_{PP} = 22$, PPh_2), −31.1 (d,$^2J_{PP} = 22$, PPh_2); ^1H NMR ($CDCl_3$): δ 1.81 (s, 3H, CH_3), 6.7–8.1 (m, 26 H, NH, Ph).

[Au_2Me_2{$(Ph_2P)_2C$=C=N^{t}Bu}] (15a). To a suspension of the complex **4a** (40 mg, 0.04 mmol) in THF (10 mL) was added 54 μL (0.08 mmol) of MeLi (1.6 M) at −78° C. The reaction mixture was stirred until the solution reached room temperature and was then concentrated *in vacuo* until a precipitate started to appear; precipitation of the product was completed by addition of hexane to afford a white solid. Yield: 31 mg (81%). Anal. Calcd for $C_{32}H_{35}Au_2NP_2$: C, 43.21; H, 3.97; N, 1.57. Found: C, 43.07; H,

Table 5 Crystallographic data for **3a**, **5b** and **11**

Compound	**3a**	**5b**·C_6H_{14}	**11**·2$CHCl_3$
Empirical formula	$C_{60}H_{58}Ag_2Cl_2N_2O_8P_4$	$C_{102}H_{89}Ag_3ClI_2N_3O_4P_6\cdot C_6H_{14}$	$C_{62}H_{60}B_2Cl_6CuF_8N_2O_4P_4\cdot 2CHCl_3$
Formula weight	1345.60	2219.44	1470.86
cryst syst	Monoclinic	Triclinic	Orthorhombic
Crystal size (mm^3)	$0.20\times0.15\times0.12$	$0.22\times0.07\times0.02$	$0.25\times0.22\times0.20$
space group	$P2_1/n$	P-1	$Pbca$
a (Å)	9.6256(2)	12.8216(5)	19.6068(2)
b (Å)	13.3816(3)	19.2320(7)	17.5173(2)
c (Å)	22.2405(4)	20.9922(8)	39.3124(5)
α (°)	90	110.960(2)	90
β (°)	96.0440(10)	104.228(2)	90
γ (°)	90	92.629(3)	90
V ($Å^3$)	2848.78(10)	4634.1(3)	13502.2(3)
Z, density (Mg/m^3)	2, 1.569	2, 1.591	8, 1.455
T (K)	120(2)	200(2)	120(2)
wavelength (Å)	1.54178	1.54178	1.54178
μ (mm^{-1})	7.906	11.933	4.128
F (000)	1368	2216	6044
θ range for data collection (deg)	$3.86 < \theta < 65.00$	$2.35 < \theta < 65.00$	$3.57 < \theta < 69.99$
Reflections collected/unique	43690/4865 [R(int) = 0.044]	27111/15745 [R(int) = 0.0678]	71577/12679 [R(int) = 0.0250]
Data/restraints/parameters	4865/0/353	15745/953/1051	12679/342/839
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0803$	$R1 = 0.0536$	$R1 = 0.0480$
	$wR2 = 0.2146$	$wR2 = 0.1537$	$wR2 = 0.1293$
R indices (all data)	$R1 = 0.0892$	$R1 = 0.0660$	$R1 = 0.0692$
	$wR2 = 0.2210$	$wR2 = 0.1654$	$wR2 = 0.1405$
GOF	1.063	1.084	1.059

4.11; N, 1.45. FTIR (THF): ν(C=C=N) 2050 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.5 (s); ^1H NMR (CD_2Cl_2): δ 0.32 (t, 6 H, $^3J_{HP} = 4$ Hz, AuCH_3), 0.70 (s, 9 H, C(CH_3)$_3$), 7.4–7.8 (m, 20 H, Ph).

[Au_2Me_2{$(Ph_2P)_2C$=C=NPh}] (15b). The compound was prepared from **4b** (40 mg, 0.04 mmol) and 53 μL (0.08 mmol) of MeLi (1.6 M) by following the same method described for **15a**. Yield: 30 mg (79%). Anal. Calcd for $C_{34}H_{31}Au_2NP_2$: C, 44.90; H, 3.44; N, 1.54. Found: C, 44.55; H, 3.33; N, 1.45. FTIR (THF): ν(C=C=N) 2027 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.1 (s); ^1H NMR (CD_2Cl_2): δ 0.41 (t, 6 H, $^3J_{HP} = 4$ Hz, AuCH_3), 7.1–8.0 (m, 25 H, Ph).

(PPh_2)$_2$CHC(=O)(NHPh) (16). To a solution of [$PdCl_2$-{(PPh_2)$_2$CHC(=O)(NHPh)}] (**12**) (40 mg, 0.06 mmol) in dichloromethane (15 mL) a saturated aqueous solution of KCN (0.2 mL) was added, and the mixture vigorously stirred for 40 min. The solution was then filtered off through diatomaceous earth and concentrated to 2 mL. Addition of hexane (10 mL) afforded a white solid, which was filtered off and dried under vacuum. Yield: 28 mg, 95%. Anal. Calcd for $C_{32}H_{27}NOP_2$: C, 76.33; H, 5.40; N, 2.78. Found: C, 75.99; H, 5.32; N, 2.88. FTIR (nujol): ν(N–H) 3374, ν(C=O) 1660 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −11.6 (s); ^1H NMR ($CDCl_3$): δ 4.21 (br, 1H, P_2CH), 6.7–8.0 (26 H, Ph + NH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 46.6 (t, $^1J_{CP} = 31$ Hz, P_2CH) C(CH_3)$_3$), 166.9 (s, C=O).

(PPh_2)$_2$C=C(CH_3)(NHPh) (17). This compound was prepared from [$PdCl_2${(PPh_2)$_2$C=C(CH_3)(NHPh)}] (**14**) (40 mg, 0.06 mmol) by following the same method described for **16**. Yield: 28 mg, 92%. Anal. Calcd for $C_{33}H_{29}NP_2$: C, 79.03; H, 5.83; N, 2.79. Found: C, 78.70; H, 5.64; N, 2.81. FTIR (nujol): ν(N–H) 3366 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −21.1 (d, $^2J_{PP} = 7$ Hz, PPh_2), −0.6 (d, $^2J_{PP} = 7$ Hz, PPh_2); ^1H NMR ($CDCl_3$): δ 2.46 (s, 3H, CH_3), 6.47 (d, 2 H, $^3J_{HH} = 8$ Hz, *o*-NPh), 6.99 (s, NH), 7.1–8.0 (m, 23H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.4 (d, $^3J_{CP} = 34$ Hz, CH_3), 98.1 (dd, $^1J_{CP} = 41$ Hz, $^1J_{CP} = 20$ Hz, P_2C=C), 162.4 (d, $^2J_{CP} = 40$ Hz, P_2C=C).

X-Ray crystallography

Suitable single crystals of **3a**, **5b**·C_6H_{14} and **11**·2$CHCl_3$ for X-ray diffraction were selected (Table 5). Data collection was performed at 120(2) K for **3a** and **11**·2$CHCl_3$, and at 200(2) K for **5b**·C_6H_{14}. Crystals were covered with perfluorinated ether. The crystals were mounted on a Bruker-Nonius KappaCCD single crystal diffractometer. The structures were solved, using the WINGX package,[29] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against F^2 (SHELXL-97).[30] All non-hydrogen atoms were anisotropically refined and hydrogen atoms were geometrically placed and left riding on their parent atoms. For the three structures full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001.

In **3a** the refinement converges with a discrepancy index $R_1 = 8.03\%$ and the difference-Fourier map shows a prominent peak placed at 1.01 Å from the Ag atom. Many attempts to improve the resolution were made including using lower symmetry groups, however the resolutions led to a poorer agreement value, unrealistic geometry of the different rings present in the molecule and a high peak near each Ag atom was still appearing in the Fourier map. A twinning treatment was performed but no better solution was reached. Finally the peak was modelled as disordered but again the obtained solution did not make chemical sense. In **5b·C_6H_{14}** one phenyl group and the perchlorate anion were disordered in two positions, this disorder was modeled. The disordered phenyl group was fitted to a regular hexagon in each position using the AFIX 69 instruction and the carbon atoms

were left anisotropic. Geometrical restraints (DFIX) were applied to the perchlorate anion. Also, a molecule of hexane crystallized with every molecule of the compound; this solvent molecule was found in the difference Fourier map but was very disordered and it was not possible to get a chemically sensible model for it, so the Squeeze procedure[31] was used to remove its contribution to the structure factors. SIMU and DELU restraints were applied as well. For **11**·2$CHCl_3$ one of the chloroform molecules was disordered in two positions and was modeled. Some SIMU restraints were applied in this structure.

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