4,6-Bis(supermesitylphosphanylidenemethyl)dibenzofuran. Synthesis, X-ray structure and reactivity towards group 11 metals†

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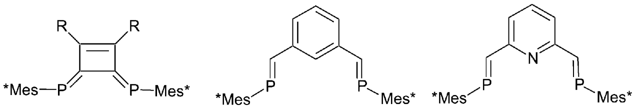
New kinetically stabilized mono- and bis-phosphaalkene ligands (**2** and **3**, respectively) were synthesized *via* the phospha-Wittig approach. Ligand **3** was characterized by X-ray diffraction. The coordinating behaviour of the bidentate ligand was investigated towards group 11 metal centers in order to test its capacity to bind two coordination sites located in a *trans*-fashion. The [Au(**3**)][BF_4], [Ag(**3**)(H_2O)][BF_4] and [Cu(**3**)(CH_3CN)][BF_4] complexes **4**, **5** and **6**, respectively, were characterized by X-ray diffraction. The peculiar geometries of **4** and **6** were rationalized by means of DFT calculations.

Introduction

Low-coordinate phosphorus molecules incorporating P=C double bonds are slowly emerging as a very important class of ligands with unique electronic properties that markedly differ from that of classical tertiary phosphines and sp^2-hybridized nitrogen ligands.[1] Over the last decade, a great deal of effort has been devoted to the understanding both of their electronic properties and their use in coordination chemistry of low valent and reduced transition metals. Thus, it was shown that ligands such as phosphinines and their functional derivatives can act as efficient ligands for the stabilization of various electron rich or electron excessive metal fragments.[2] Much more recently, due to their strong π-accepting capacity, these ligands were also employed in the stabilization of gold nanoparticles presenting unique optical properties.[3] On the other hand, some low-coordinate phosphorus ligands have found promising applications in homogeneous catalysis. Thus, phosphaferrocenes[4] and kinetically stabilized phosphaalkenes[5] were successfully employed as ligands in some catalytic processes of synthetic relevance such as C–X bond forming reactions, ethylene polymerization, nucleophilic allylic substitutions and hydrogenations. Concerning phosphalkenes, much effort have focused on the use of phosphorus equivalents of 1,4-diazabutadienes, namely 1,4-diphosphabutadienes such as 1,2-diaryl-3,4-diphosphinidene cyclobutene (DCPB) developed by the group of Yoshifuji.[5] Though some studies were devoted to the synthesis of tridentate pincer ligands featuring two phosphaalkene moieties as pendant ligands (Mes* = 2,4,6-tris(*tert*-butyl)phenyl) and a carbon[6] or nitrogen atom as central binding site (Scheme 1),[7] little information is available on the coordination chemistry of these ligands and the catalytic activity of their corresponding complexes.



Scheme 1

As part of a program aimed at developing the use of such polydentate ligands featuring sp^2-hybridized phosphorus atoms in coordination chemistry and catalysis,[8] we recently investigated the synthesis of bidentate structures featuring the dibenzofuran skeleton. Indeed, 4,6-bis(carbaldehyde)dibenzofuran proved to be a convenient precursor for the elaboration of bidentate ligands featuring imines[9] or oxazolines (DBFOX ligands) as pendant ligands which can bind a metal centre in a *trans*-fashion. Some DBFOX-based complexes proved to be particularly efficient in some catalytic transformations.[10] Herein, we wish to report on these syntheses as well as on the coordinating behaviour of this new type of ligands towards group 11 metals.

Results and discussion

Syntheses of ligands 2 and 3

Various methods are available for the synthesis of P=C double bonded systems. One of the most attractive approaches, which was initially developed in our laboratories for the synthesis of phosphaalkene complexes of metal carbonyls (M = Cr, Mo, W, Fe), is the well known phospha-Wittig reaction, a transformation that mimics the ubiquitous Wittig process.[11] This reaction which relies on the reactivity of phosphoranylidenephosphine complexes towards aldehydes was further extended to the synthesis of uncomplexed phosphaalkenes by Protasiewicz *et al.*[12] In practice, free phosphoranylidenephosphine reagents (phospha-Wittig) reagents are available through the reaction of PMe_3 with dichlorophosphines in the presence of zinc as reducing agent.[12] Among all methods available this approach offers several decisive advantages: its simplicity (a one-step process), the use of mild conditions and cheap reagents (Scheme 2).

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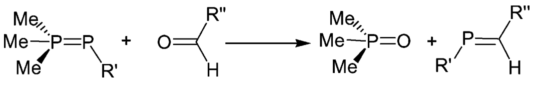
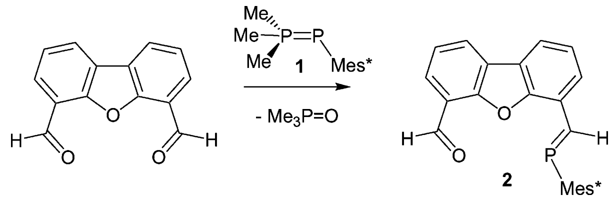
† Electronic supplementary information (ESI) available: View, cartesian coordinates and frequencies of the theoretical structures **I** and **II**. See http://dx.doi.org/10.1039/b508678g



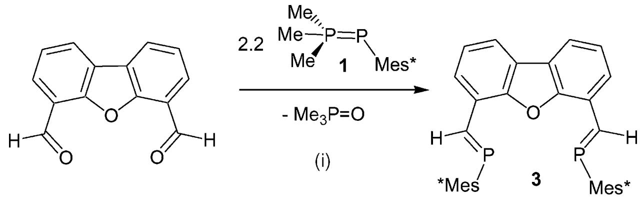
Scheme 2 The phospha-Wittig approach.

As a prerequisite to these syntheses, 4,6-bis(carbaldehyde)-dibenzofuran was synthesized according to a well-known reported procedure that involves the dimetallation of dibenzofuran with *n*-butyllithium followed by a trapping reaction with dimethylformamide.[13] The phospha-Wittig reagent **1** was conventionally prepared by reacting Mes*PCl$_2$ with PMe$_3$ (2.6 equiv.) in the presence of Zn as reductant in THF at 0 °C. Reaction of 1.1 equivalent of **1** with 4,6-bis(carbaldehyde)dibenzofuran readily occurred at room temperature to cleanly yield phosphaalkene **2**. After 3 h of reaction, analysis of the crude mixture by ^{31}P NMR spectroscopy revealed the presence of a very characteristic downfield shifted signal at 273.9 ppm. After extraction with dichloromethane, washings with water and crystallization from MeOH, compound **2** was isolated in a 60% yield as a very air stable pale yellow powder. The *E*-stereochemistry of **2** was confirmed by the analysis of the ^{1}H NMR spectrum which exhibits a doublet at 8.58 ppm (^2J(H–P) = 25.3 Hz). No trace of the *Z*-isomer was observed in the crude mixture (Scheme 3). The formulation proposed for **2** was confirmed by NMR and mass spectrometry as well as by elemental analyses.



Scheme 3 *Reagents and conditions*: (i) THF, RT, 3 h.

The bis-phosphaalkene derivative **3** was prepared following a similar strategy by using the phospha-Wittig reagent **1** in excess (2.2 equivalents). A prolonged reaction time (15 h) was needed to obtain a complete conversion. Importantly, ^{31}P NMR spectroscopy revealed that only one stereoisomer is formed. Compound **3** was isolated following a similar workup in a 50% yield as a very stable pale yellow solid. The structure of **3** was easily established on the basis of ^{1}H, ^{13}C NMR data, mass spectrometry and elemental analyses. As in **2**, the presence of a P=C double bond was evidenced by the presence of a downfield signal in ^{31}P NMR (δ(THF) = 273 ppm) (Scheme 4). The presence of two phosphaalkene moieties is proven first by ^{1}H NMR. The signal of the phosphaalkene appears as a deceptively simple doublet of doublet (AA′XX′ spin system) at 8.4 ppm ($\sum J$(H–P) = 42 Hz, $\sum$ means sum). In the ^{13}C NMR spectrum, the corresponding signal appears as the expected second-order signal at 167.1 ppm (AXX′ spin system, $\sum J$(C–P) = 51.7 Hz).



Scheme 4 *Reagents and conditions*: (i) THF, RT, 15 h.

Single crystals of compound **3** were obtained by crystallization in MeOH at room temperature. An X-ray crystal structure analysis was carried out and a view of one molecule of **3** is presented in Fig. 1 as well as the most relevant bond distances and bond angles. Crystal data and structural refinement details are presented in Table 1. The compound has crystallographically imposed twofold symmetry. As can be seen the *E*-stereochemistry of both phosphaalkene moieties is confirmed. Interestingly, one can note that two P=C bonds are coplanar with the dibenzofuran skeleton probably indicating that a weak delocalization occurs between the aromatic part of the molecules and the two P=C units. Besides, this is confirmed by the short C–C connection between the C9 carbon atoms and the C13 carbon atoms of the phosphaalkenes (d(C(9)–C(13)) = 1.454(2) Å). Apart from this, the structure of **3** deserves no special comments.

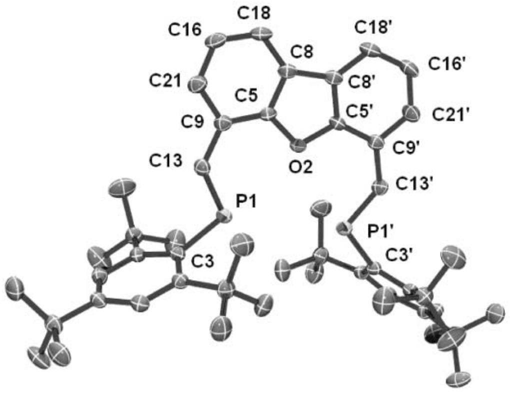


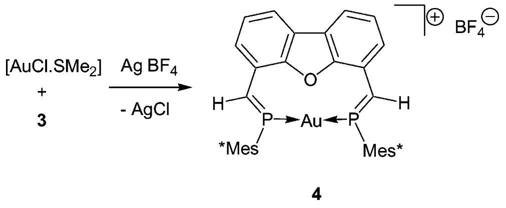
Fig. 1 ORTEP view of one molecule of **3** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. Atoms marked with a prime (′) are at equivalent position ($-1 - x, y, -1 - z$). Selected bond lengths (Å) and bond angles (°): C(13)–P(1) 1.674(3), C(3)–P(1) 1.852(1), C(13)–C(9) 1.454(2), C(9)–C(5) 1.405(2), C(5)–O(2) 1.379(1); C(3)–P(1)–C(13) 98.72(1), P(1)–C(13)–C(9) 128.5(1).

Table 1 Crystal and refinement parameters for **3** and **4**

	3	**4**
Formula	$C_{50}H_{66}OP_2$	$C_{50}H_{66}AuBF_4OP_2\cdot C_4H_{10}O$
M_r	744.97	1102.86
Crystal system	Monoclinic	Orthorhombic
Space group	$C2$	$P2_12_12_1$
a/Å	15.966(1)	11.647(1)
b/Å	10.407(1)	16.895(1)
c/Å	14.099(1)	27.329(1)
β/°	105.260(1)	90.00
Z	2	4
μ/cm^{-1}	0.130	2.846
Reflections measured	7551	27925
Reflections used	5376	13250
wR_2	0.0924	0.0701
R_1	0.0349	0.0340

Reactivity of 3 towards group 11 metals

In order to test the capacity of **3** to bind metals through a *trans* fashion, we focused our study on the coordination of group 11 cationic metal fragments which are known to form linear 14 VE ML_2 complexes. The gold complex **4** was readily prepared in one pot *via* a two-step sequence (Scheme 5).



Scheme 5 *Reagents and conditions*: THF, RT, 3 h.

The stoichiometric reaction of [AuCl·SMe_2] and ligand **3** in THF led to a pale yellow solution. A ^{31}P NMR of this mixture showed a very broad peak which revealed a weak interaction. Addition of solid $AgBF_4$ resulted in the very fast formation of characteristic silver salt indicating the end of chloride abstraction. ^{31}P NMR spectroscopy showed the formation of a single complex characterized by a singlet at 201 ppm (δ(**3**) = 273 ppm, $\Delta\delta$ = −72 ppm). The mixture was filtered through a pad of Celite and concentrated to give the desired complex **4** in near quantitative yield. The complex was fully characterized by usual NMR techniques as well as elemental analyses. Compared to the spectra of the starting ligand **3**, complex **4** varies only marginally. In particular, the phosphaalkene proton is upfield shifted to 8.2 ppm and appears as a virtual triplet (simplified AA′XX′ spin system), because the magnitude of the J(P–P) increases upon coordination. In the ^{13}C spectrum the two carbon atoms which are bound to the phosphorus atom are upfield shifted by *ca.* 10 ppm upon coordination. Single crystals of **4** were grown by a slow diffusion of diethyl ether in a THF solution of the complex. A view of one molecule of **4** is presented in Fig. 2 as well as the most relevant bond distances and bond angles. Crystal data and structural refinement details are presented in Table 1.

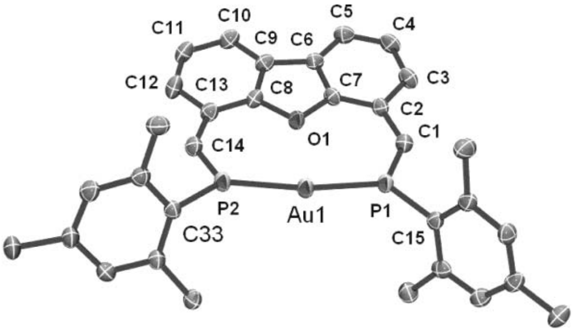
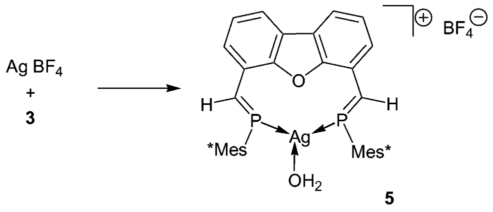


Fig. 2 ORTEP view of one molecule of **4** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. BF_4 counter ion and methyl groups of the *tert*-butyl substituents have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au(1)–P(1) 2.267(1), Au(1)–P(2) 2.267(1), Au(1)···O(1) 2.699, C(1)–P(1) 1.669(3), C(14)–P(2) 1.663(3), C(15)–P(1) 1.804(3), C(33)–P(2) 1.807(3), C(1)–C(2) 1.449(4), C(13)–C(14) 1.443(4), C(8)–O(1) 1.396(4), C(7)–O(1) 1.383(4); P(1)–Au(1)–P(2) 167.56(3), C(1)–P(1)–Au(1) 121.8(1), C(14)–P(2)–Au(1) 120.3(1), C(1)–P(1)–C(15) 112.3(2), C(15)–P(1)–Au(1) 125.9(1), C(13)–C(14)–P(2) 134.3(3), C(2)–C(1)–P(1) 133.0(3).

The only apparent feature of this complex is the significant deviation from linearity observed for the P–Au–P angle (167.56°). Moreover, this deviation brings the gold center away from the oxygen atom of the furan moiety. As will be seen further, this can be easily rationalized by considering a simple molecular orbital diagram.

We next investigated the coordination to silver, which was readily achieved by the stoichiometric reaction of ligand **3** with $AgBF_4$ (Scheme 6). After a few minutes, the ^{31}P NMR of the crude mixture proves the formation of a single complex at 204 ppm. Unlike many Ag^+ complexes, coupling of the two phosphorus atoms with both isotopes of Ag, namely Ag^{107} and Ag^{109} which both possess a spin of 1/2, was observed resulting in two sets of doublets (^1J(Ag^{109}–P) = 686 Hz and ^1J(Ag^{107}–P) = 596 Hz). After isolation, complex **5** was obtained as an air-stable solid. It was fully characterized by usual NMR techniques. In fact, a first surprising piece of information was given by a broad peak at 2.5 ppm in the ^{1}H NMR spectrum. This peak integrated for two protons which suggested the coordination of a water molecule. We verified that the same complex is formed when the reaction is carried out in air. Therefore, it seems likely that the water-free complex adopts a distorted linear geometry like the gold analogue described above. The silver centre then picks up water from the solvent to complete the coordination sphere yielding the observed complex which possesses a trigonal planar geometry. The presence of a water molecule was confirmed by elemental analyses. In the ^{1}H NMR spectrum also, the phosphaalkene proton appears as the expected signal for an AA′XX′ spin system (δ = 8.23 ppm, $\sum J$ = 40 Hz). In fact, the silver analogue gives very similar spectra than the gold complex.



Scheme 6 *Reagents and conditions*: CH_2Cl_2, air (traces of water), RT, 5 min.

Single crystals were obtained by a slow diffusion of hexanes into a CH_2Cl_2 solution of the complex, in air. We were both quite surprised and pleased to see in the structure (Fig. 3) that the coordination sphere of the metal had been completed by water during crystallisation. Indeed, this definitely proves that, unlike classical phosphaalkenes, the bulky derivatives are very robust toward hydrolysis, even once coordinated to a metal centre.

The P–Ag bond lengths Ag(1)–P(1) 2.388(1) Å, Ag(1)–P(2) 2.403(1) Å) are significantly longer than the P–Au bond lengths (Au(1)–P(1) 2.267(1) Å, Au(1)–P(2) 2.267(1) Å) as expected. The geometry at silver is trigonal planar ($\sum$angles = 358.24°) with a wide P(1)–Ag(1)–P(2) angle at 145.14(4)°. This increase in the angle (compared to the gold complex) is accompanied by an increase in the C=P–M angle from *ca.* 120 to *ca.* 130° (C(13)–P(1)–Ag(1) 131.1(2)). The fact that phosphaalkene ligands can

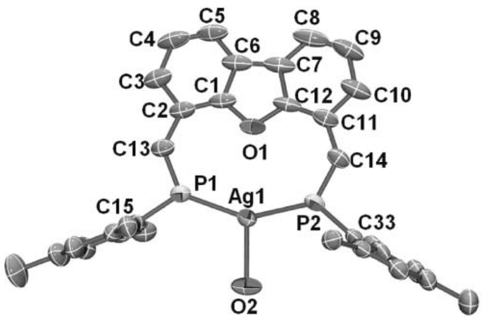
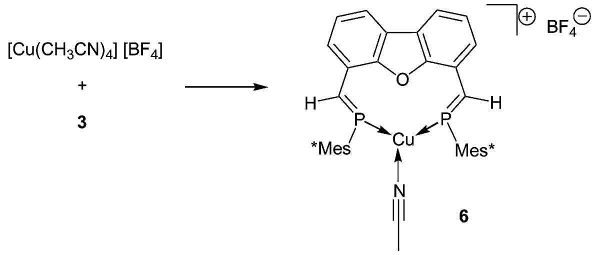


Fig. 3 ORTEP view of one molecule of **5** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. BF_4 counter ion and methyl groups of the *tert*-butyl substituents have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag(1)–P(1) 2.388(1), Ag(1)–P(2) 2.403(1), Ag(1)–O(2) 2.316(3), Ag(1)···O(1) 3.095, C(14)–P(2) 1.681(4), C(13)–P(1) 1.672(5), C(2)–C(13) 1.456(6), C(14)–C(11) 1.441(7), C(1)–O(1) 1.383(6), C(12)–O(1) 1.387(6), C(33)–P(2) 1.840(5), C(15)–P(1) 1.825(5); P(1)–Ag(1)–P(2) 145.14(4), P(1)–Ag(1)–O(2) 109.8(1), P(2)–Ag(1)–O(2) 103.3(1), C(14)–P(2)–Ag(1) 131.1(2), C(13)–P(1)–Ag(1) 130.6(2), C(11)–C(14)–P(2) 132.6(4), C(2)–C(13)–P(1) 132.1(4), C(13)–P(1)–C(15) 102.5(2).

accommodate readily such changes in coordination angles reflects the diffuse nature of the lone pair of sp^2 hybridized phosphorus.

To complete this investigation we examined the coordinating behaviour of **3** toward the catalytically relevant Cu(I) centre. Acetonitrile ligand was readily displaced from the $[Cu(CH_3CN)_4][BF_4]$ precursor to form a single complex **6** (Scheme 7). It appears as a singlet at 207 ppm in the ^{31}P NMR spectrum. This complex was fully characterized by usual NMR techniques as well as elemental analysis.



Scheme 7 *Reagents and conditions*: CH_2Cl_2, RT, 5 min.

Single crystals of complex **6** were obtained by slow diffusion of hexanes in a $CDCl_3$ solution of complex **6**. A view of one molecule of **6** is presented in Fig. 4 that also lists the most significant bond lengths and angles. Crystal data and structural refinement details are presented in Table 2.

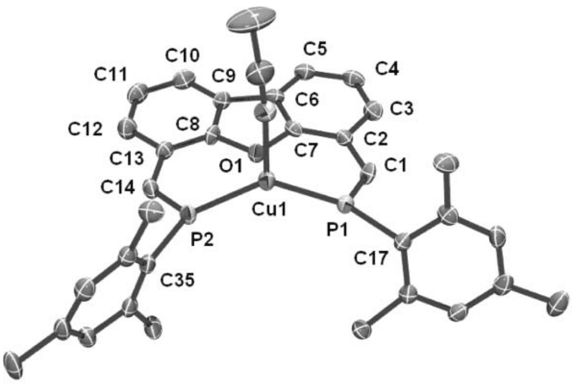


Fig. 4 ORTEP view of one molecule of **6** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. BF_4 counter ion and methyl groups of the *tert*-butyl substituents have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu(1)–P(1) 2.221(1), Cu(1)–P(2) 2.230(1), Cu(1)–N(1) 1.958(4), Cu(1)···O(1) 2.456, C(1)–P(1) 1.654(5), C(14)–P(2) 1.671(4), C(1)–C(2) 1.456(6), C(13)–C(14) 1.453(6), C(1)–O(1) 1.393(4), C(8)–O(1) 1.389(4), C(17)–P(1) 1.834(4), C(35)–P(2) 1.827(4); P(1)–Cu(1)–P(2) 132.60(4), P(1)–Cu(1)–N(1) 113.5(1), P(2)–Cu(1)–N(1) 113.7(1), C(1)–P(1)–Cu(1) 116.5(2), C(14)–P(2)–Cu(1) 120.6(2), C(2)–C(1)–P(1) 130.7(3), C(13)–C(14)–P(2) 127.3(3), Cu(1)–P(1)–C(17) 101.6(2).

As can be seen, the geometry at the copper center is trigonal planar ($\sum$angles = 359.8°) with a wide P(1)–Cu(1)–P(2) angle at 132.60(4)°. The P–Cu bond distances are normal at 2.221(1) and 2.230(1) Å. The other bond distances and angles are quite similar than the above mentioned ones, and therefore will not be further commented on. This complex possesses however a very significant feature, namely the metal centre is located well above the plane of the ligand, as clearly shown on the ORTEP plot (dihedral angle

Table 2 Crystal and refinement parameters for **5** and **6**

	5	**6**
Formula	$C_{50}H_{66}AgBF_4O_2P_2\cdot 1/2CH_2Cl_2$	$C_{52}H_{69}BCuF_4NOP_2\cdot 2CHCl_3$
M_r	1040.57	1175.11
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	35.058(3)	11.931(1)
b/Å	11.084(1)	14.527(1)
c/Å	30.013(3)	19.169(1)
a/°	90.00	107.920(1)
β/°	116.700(2)	92.030(1)
γ/°	90.00	109.710(1)
Z	8	2
μ/cm^{-1}	0.602	0.748
Reflections measured	17591	16842
Reflections used	7576	13870
wR_2	0.2282	0.1806
R_1	0.0724	0.0628

C2–C1–P1–Cu1 = 9°). This geometry results in a bond distance of 2.456 Å, more consistent with a weak interaction than a true bond. Indeed, typical Cu–O bond distances of 2.208 Å are found with neutral ligands such as carbaldehyde–pyridine coordination to the $[Cu(PPh_3)_2]^+$ fragment.[14] For several carboxylate complexes of the type $[Cu(PPh_3)_2(O_2CR)]$, Hart *et al.* have shown that the Cu–O=C linkage can vary from a true bond for R = CH_3 (2.257(7) Å) to a weak interaction for R = CHF_2 (2.465(6) Å) or R = CF_3 (2.545(5) Å).[15] In fact, for these two last cases, addition of ethanol resulted in the breaking of this carboxylate interaction and ethanol coordination. How can the geometry at the copper centre of our complex be rationalized? Being in sharp contrast to the other geometries of the Au and Ag complexes, this fact can not be fortuitous. Like in the case of **4** and **5**, this particular feature can be easily rationalized first through a qualitative molecular orbital diagram, and more quantitative DFT calculations.

Theoretical calculations

As previously noted, both Au and Ag complexes adopt a non linear coordination mode. Looking into the simple molecular orbital diagram of linear ML_2 complexes provided a lead toward the understanding of this peculiar geometry. Indeed, as in d^{10} ML_2 complexes all five d orbitals are filled, four-electron destabilizing interactions can occur between the $d_{x^2-y^2}$ and d_{xy} orbitals at the metal and the $2p_x$ (lone pair) and $2p_y$ (π-system) orbitals at the oxygen atom respectively for obvious symmetry reasons (Scheme 8). Note that the d_{z^2} also possesses the appropriate symmetry to interact with the $2p_y$ AO at oxygen. Thus in order to diminish these repulsive interactions, a bending of the P–Au–P is observed.

Theoretical calculations were carried out on a model complex **I** in which the Mes* groups were replaced by xylyl groups. A view of the optimized structure is presented in Fig. 5. Though the substitution scheme of the phosphorus atom is different, a reasonable agreement was found between theoretical and experimental data (Fig. 5). Thus, the P–Au bonds falls at 2.311 Å for 2.267(1) Å in **4** and the P–Au–P bending is relatively well reproduced (165.83° for 167.56(3)° in **4**). Examination of MOs allowed to check our hypothesis and as can be seen in the following figure several MOs account for this four-electron destabilizing interaction (see Fig. 6). The H-11 MO and H-13 correspond to the antibonding interaction between the $d_{x^2-y^2}$ and the d_{z^2} with the $2p_y$ AO at oxygen, respectively, whereas the H-12 is antibonding between the d_{xy} at Au and the $2p_x$ at O.

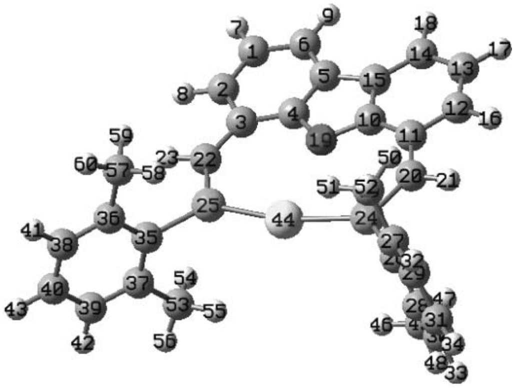


Fig. 5 Optimized geometry of the model complex **I**. Mes* groups at phosphorus have been replaced by xylyl groups. Selected bond lengths (Å) and bond angles (°): Au(44)–P(25) 2.311, P(25)–C(22) 1.682, C(22)–C(3) 1.445, C(3)–C(4) 1.409, C(4)–O(19) 1.371; P(24)–Au(44)–P(25) 165.826, Au(44)–P(25)–C(22) 121.050, P(25)–C(22)–C(3) 134.597, C(22)–C(3)–C(4) 128.947, C(3)–C(4)–O(19) 126.254.

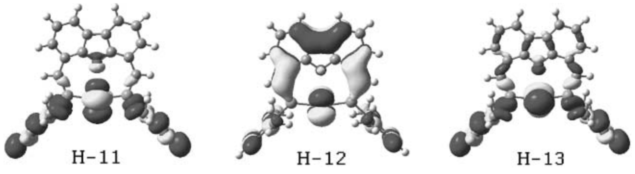
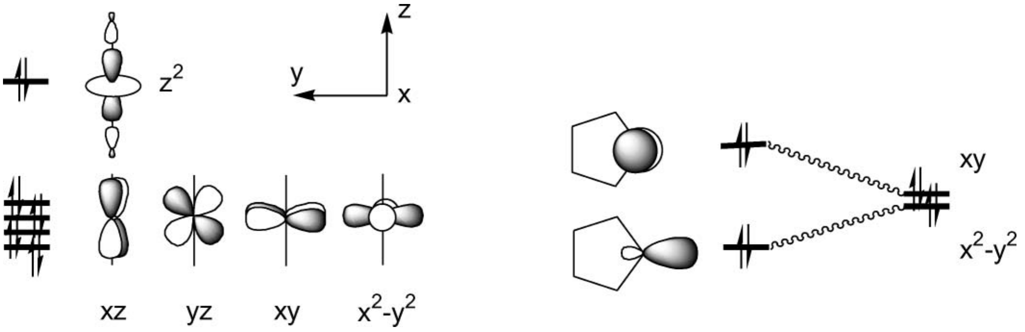


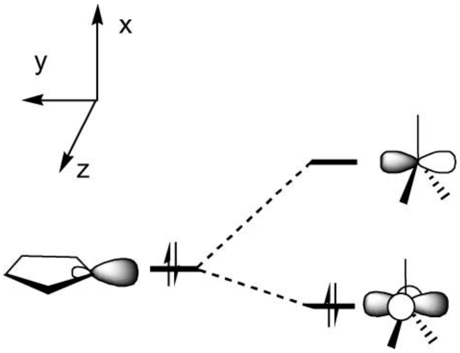
Fig. 6 H-11, H-12 and H-13 MO of complex **I**.

Having rationalized the geometry of the gold and silver complexes, we then turned our attention to the copper complex. The particular structural arrangement in complex **6** can be explained as follows. In d^{10} ML_3 16 VE complexes, the five d orbitals are also filled and but a vacant $3p_y$ orbital which is perpendicular to the plane defined by the three ligands is found as the LUMO. In complex **6**, this orbital points towards the lone pair at the oxygen atom. Note that the $d_{y^2-z^2}$ orbital which is involved in the bonding with the two phosphorus atoms has the right symmetry to interact with the oxygen lone pair (Scheme 9). Therefore the bonding between Cu and O can be described as a classical four-electron interaction involving three orbitals.

The theoretical structure of complex **6** was calculated. A first calculation carried out on the model complex featuring xylyl groups at phosphorus yielded a structure in which the O–Cu bond distance was found to be by far too long (2.638 Å in **II** *vs.* 2.456(3) Å in **6**). Therefore, supposing that in this case, the presence of



Scheme 8 Qualitative interaction diagram showing the four-electron destabilizing interactions occurring between the filled d-orbitals at the metal and $2p_x$ and $2p_y$ orbitals at the oxygen atom.



Scheme 9 Interaction diagram showing the two-electron stabilizing interaction occurring between the vacant $3p_y$-orbital at the metal and $2p_y$ orbital at the oxygen atom.

the two very bulky *tert*-butyl groups at the *ortho* positions would probably tend to pucker the copper metal towards the oxygen atom of the furan ligand, calculations were carried out on a complex featuring these two *t*-Bu groups. The optimization was carried out using the ONIOM method (B3PW91/UFF). A view of the optimized structure is presented in Fig. 7. As can be seen upon examining the theoretical data, there is a very good agreement with experimental metric parameters. Importantly, the Cu–O bond distance at 2.486 Å is rather well reproduced as well as the P–Cu–P angle (132.00 in **II** *vs.* 132.60° in **6**).

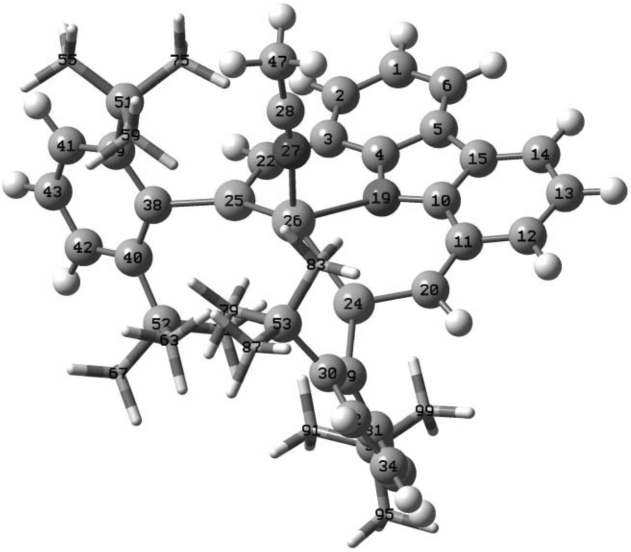


Fig. 7 Optimized geometry of the model complex **II**. Selected bond lengths (Å) and bond angles (°): Cu(26)–P(25) 2.288, P(25)–C(22) 1.683, C(22)–C(3) 1.448, C(3)–C(4) 1.406, C(4)–O(19) 1.380, Cu(26)–N(27) 2.054; P(24)–Cu(26)–P(25) 132.004, Cu(26)–P(25)–C(22) 118.546, P(25)–C(22)–C(3) 129.602, C(22)–C(3)–C(4) 127.453, C(3)–C(4)–O(19) 125.805, P(24)–Cu(26)–N(27) 115.341, P(25)–Cu(26)–N(27) 112.340, P(24)–Cu(26)–P(25) 132.003.

As expected, molecular orbital analysis revealed that a bonding interaction develops between the oxygen and the copper atom. As can bee seen in Fig. 8 the most important contribution to the bonding is provided by the interaction between the vacant $3p_y$ and $3d_{y^2-z^2}$ AOs at Cu and the $2p_y$ AO of the oxygen atom (HOMO-19).

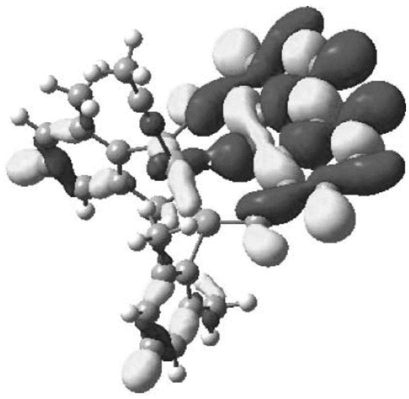


Fig. 8 A view of one of the MO describing the Cu–O bond in the model complex **II**. The methyl groups of the *t*-Bu substituents at supermesityl groups have been omitted for clarity.

Conclusion

In conclusion, we have synthesized a new *trans* spanning bidentate bis phosphaalkene ligand **3** in a one pot procedure from the readily available 4,6-bis(carbaldehyde)dibenzofuran. Using this same starting material, the mono-phosphaalkene mono-aldehyde **2** could also be synthesized, which opens the way to mixed ligands bearing one phosphaalkene moiety. This area is being pursued in our laboratories. Using the bidentate ligand **3**, the series of complexes of group 11 metals has been synthesized. In the gold and silver complexes **4** and **5**, respectively, a distortion form the linearity of the initial ML_2 fragment was observed, which in the case of complex **5** resulted in the coordination of a water molecule. This complex proves the robustness of the phosphaalkene ligands towards hydrolysis. The observed distortion, which has been rationalized by DFT calculations, results from a destabilizing interaction between the appropriate filled $d_{x^2-y^2}$ and d_{z^2} with the $2p_y$ AO at oxygen, and d_{xy} at Au with the $2p_x$ at oxygen. The catalytically relevant Cu(I) complex **6** was also synthesized. The geometry given by an X-ray structure analysis was rationalized by ONIOM calculations. In this case, a bonding interaction between, on one hand, empty $3p_y$-orbital and filled $3d_{y^2-z^2}$ at the copper and, on the other hand, filled $2p_y$ orbital at the oxygen atom, is responsible for the peculiar geometry. Catalytic tests with this complex are currently underway and will be reported in due course.

Experimental

General

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry ether from $CaCl_2$ and then NaH and dry CH_2Cl_2 from P_2O_5. $CDCl_3$ was dried from P_2O_5 and stored on 4 Å Linde molecular sieves. CD_2Cl_2 was used as purchased and stored in the glove-box. Nuclear magnetic resonance spectra were recorded on a Bruker 300 AVANCE spectrometer operating at 300.0 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C

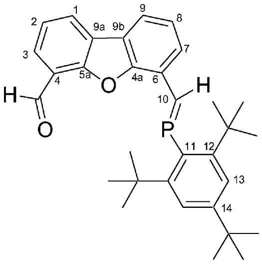
chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; v, virtual; b, broad. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer couple to a HP 5980 chromatograph by the direct inlet method. $[Cu(CH_3CN)_4BF_4]$[16] and $[AuCl(SMe_2)]$[17] were prepared according to reported procedures.

Phospha-Wittig reagent 1

To a mixture of Mes*PCl_2 (1.0 g, 2.9 mmol), Zn (1.0 g, 15.0 mmol) in THF (10 mL) at 0 °C, was syringed PMe_3 (1 M, 7.5 mmol, 7.5 mL). The crude mixture was allowed to warm to room temperature and was stirred for 3 h. The ^{31}P NMR spectrum showed the formation of the desired reagent which was used without further purification.

^{31}P NMR (121.5 MHz, THF, 298 K): δ 6.6 ppm (^{1}J(P–P) = 577.9, Mes*P), −132.5 ppm (^{1}J(P–P) = 577.9, PMe_3).

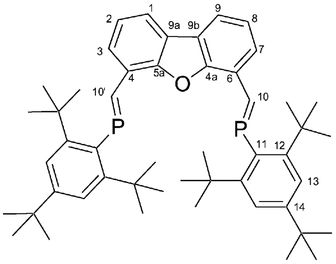
Synthesis of 4′-(supermesitylphosphanylidenemethyl)-6-(carbaldehyde)dibenzofuran 2. Reagent **1** was cooled to 0 °C and cannulated on a suspension of 4,6-bis(carbaldehyde)dibenzofuran (0.75 g, 3.3 mmol, 1.1 equivalent) at 0 °C in THF (10 mL). The crude mixture was stirred during 3 h and cooled to 0 °C. CH_2Cl_2, water and ice were then added. The organic phase was separated, dried over $MgSO_4$ and filtered. The solvent was then evaporated, MeOH was added which resulted in the formation of a precipitate which was filtered off and dried under vacuum. The title compound was obtained as a white solid. Yield: 50%, 0.80 g



^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.48 (s, 18H, *para* $C(CH_3)_3$), 1.67 (s, 36H, *ortho* $C(CH_3)_3$), 7.43 (t, 1H, ^{3}J(H–H) = 7.5, H_8), 7.51 (t, 1H, ^{3}J(H–H) = 7.3, H_2), 7.60 (s, 2H, H_{12}), 7.85 (dd, 1H, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 3.5, H_3), 7.92 (dd, 1H, ^{3}J(H–H) = 7.7, ^{4}J(H–H) = 1.4, H_7), 7.99 (dd, 1H, ^{3}J(H–H) = 7.7, ^{4}J(H–H) = 1.2, H_9), 8.22 (dd, 1H, ^{3}J(H–H) = 7.6, ^{4}J(H–H) = 1.2, H_1), 8.58 (d, 1H, ^{2}J(H–P) = 25.3, H_{10}) 10.75 (s, 1H, CHO). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 273.9 ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 30.34 (s, *para* $C(\mathit{C}H_3)_3$), 32.96 (d, ^{3}J(C–P) = 7.2, *ortho* $C(\mathit{C}H_3)_3$), 34.12 (s, *para* $\mathit{C}(CH_3)_3$), 37.42 (s, *ortho* $\mathit{C}(CH_3)_3$), 119.01 (d, ^{3}J(C–P) = 7.1, C_7), 120.31 (s, C_4 or C_{9b}), 121.20 (s, C_{13}, C_{15}), 122.23 (s, C_2), 122.38 (d, ^{4}J(C–P) = 2.8, C_{9a}), 122.98 (d, ^{4}J(C–P) = 3.9, C_8), 124.49 (d, ^{3}J(C–P) = 23.0, C_3), 124.66 (d, ^{2}J(C–P) = 14.5, C_6), 124.89 (s, C_9), 124.96 (s, C_{9b} or C_4), 125.80 (s, C_1), 138.96 (d, ^{1}J(C–P) = 54.4, C_{11}), 149.18 (s, C_{12}, C_{16}), 151.87 (d, ^{3}J(C–P) = 11.3, C_{5a}), 153.28 (s, C_{14}), 155.67 (s, C_{4a}), 166.60 (d, ^{1}J(C–P) = 39.0, C_{10}).

MS: 485 (M + H, 100%).

Synthesis of 4,6-bis(supermesitylphosphanylidenemethyl)dibenzofuran 3. Reagent **1** was cooled to 0 °C and cannulated on a suspension of 4,6-bis(carbaldehyde)dibenzofuran (0.27 g, 1.2 mmol, 0.4 equivalent) at 0 °C in THF (10 mL). The crude mixture was stirred during 18 h and cooled to 0 °C. CH_2Cl_2, water and ice were then added. The organic phase was separated, dried over $MgSO_4$ and filtered. The solvent was then evaporated, MeOH was added which resulted in the formation of a precipitate which was filtered off and dried under vacuum. The title compound was obtained as a white solid. Yield: 55%, 0.50 g.



^{1}NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.40 (s, 18H, *para* $C(CH_3)_3$), 1.56 (s, 36H, *ortho* $C(CH_3)_3$), 7.37 (t, 2H, ^{3}J(H–H) = 7.6, H_2, H_8), 7.50 (s, 4H, H_{13}), 7.77 (d, 2H, ^{3}J(H–H) = 5.3, H_3, H_7), 7.90 (d, 2H, ^{3}J(H–H) = 7.4, H_1, H_9), 8.48 (m, AA′XX′, m, $\sum J$ = 41.9, H_{10}, $H_{10'}$). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 271.5 ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K) δ 30.4 (s, *para* $C(\mathit{C}H_3)_3$), 33.0 (d, ^{4}J(C–P) = 3.0, *ortho* $C(\mathit{C}H_3)_3$), 34.1 (s, *para* $\mathit{C}(CH_3)_3$), 37.4 (s, *ortho* $\mathit{C}(CH_3)_3$), 118.94 (s, C_1, C_9), 121.01 (s, C_{13}), 122.36 (s, C_2, C_8), 123.70 (m, C_4, C_6, C_3, C_7), 124.57 (vt, AXX′, $\sum J$(C–P) = 14.4, C_{9a}, C_{9b}), 140.71 (m, AXX′, $\sum J$(C–P) = 62.7, C_{11}, $C_{11'}$), 148.90 (s, C_{12}), 151.55 (vt, AXX′, $\sum J$(C–P) = 12.0, C_{4a}, C_{5a}), 153.17 (s, C_{14}), 167.09 (m, AXX′, $\sum J$(C–P) = 51.7, C_{10}, $C_{10'}$). MS: 746 (M + H, 100%).

Synthesis of gold complex 4. $[AuCl(SMe_2)]$ (30 mg, 0.10 mmol) and ligand **3** (75 mg, 0.10 mmol) were dissolved in THF (3 mL). The solution was stirred for 20 min. $AgBF_4$ was added (19.8 mg, 0.10 mmol) and the solution was stirred for 12 h. The ^{31}P NMR spectrum of the crude mixture shows the formation of a unique product. The mixture was filtered on Celite and the solution was taken to dryness. The product was washed with hexanes and dried to yield a yellow powder. Yield: 92%, 87 mg. X-Ray quality crystals were obtained after diffusion of ether into a THF solution of the complex.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.40 (s, 18H, *para* $C(CH_3)_3$), 1.68 (s, 36H, *ortho* $C(CH_3)_3$), 7.58 (t, 2H, ^{3}J(H–H) = 7.6, H_2, H_8), 7.67 (s, 4H, H_{13}), 8.17 (t, ^{3}J(H–H) = 8.8, 2H, H_3, H_7), 8.37 (m, AA′XX′, m, $\sum J$ = 7.0, H_{10}, $H_{10'}$). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ 200.2. ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ 32.9 (s, *para* $C(\mathit{C}H_3)_3$), 36.5 (s, *ortho* $C(\mathit{C}H_3)_3$), 37.2 (s, *para* $\mathit{C}(CH_3)_3$), 40.6 (s, *ortho* $\mathit{C}(CH_3)_3$), 118.2 (s, $C_{9a,9b}$), 121.1 (m, $C_{1,2,8,9}$), 122.3 (s, C_{13}), 122.4 (s, $C_{4,6}$), 131.1 (m, $C_{3,7,11}$), 148.2 (AA′XX′, m, $\sum J$ = 8.0, $C_{4a,5a}$), 151.7 (s, C_{12}), 152.9 (s, C_{14}), 157.9 (AA′XX′, m, $\sum J$ = 69, $C_{10,10'}$).

Synthesis of silver complex 5. Ligand **3** (57 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (1 mL) and in the glove-box, solid $AgBF_4$ (15 mg, 0.07 mmol) was added. The initially colorless solution rapidly turned bright yellow. The ^{31}P NMR spectrum of the crude mixture shows the formation of a unique product. The solution was taken to dryness. The product was washed with hexanes and dried to yield a yellow powder. Yield: 95%, 57 mg. X-Ray quality crystals were obtained after diffusion of hexanes into a CH_2Cl_2 solution of the complex.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.39 (s, 18H, *para* $C(CH_3)_3$), 1.63 (s, 36H, *ortho* $C(CH_3)_3$), 2.52 (s, H_2O), 7.41 (d, 2H, $^3J(H–H) = 7.7$, $H_{1,9}$), 7.53 (t, $^3J(H–H) = 7.7$, 2H, $H_{2,8}$), 7.63 (s, 4H, H_{13}), 8.18 (dd, 2H, $^3J(H–H) = 7.7$, $^4J(H–P) = 1.3$, $H_{3,7}$), 8.23 (AA′XX′, m, 2H, $\sum J = 41.9$, $H_{10,10'}$). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 204.9 (d + d, $^1J(P–Ag) = 686$, $^1J(P–Ag) = 596$). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 31.7 (s, *para* $C(CH_3)_3$), 35.4 (d, $^4J(C–P) = 3.0$, *ortho* $C(CH_3)_3$), 36.1 (s, *para* $C(CH_3)_3$), 39.7 (s, *ortho* $C(CH_3)_3$), 122.2 (s, $C_{9a,9b}$), 123.8 (m, $C_{1,2,8,9}$), 125.1 (s, C_{13}), 125.7 (s, $C_{4,6}$), 129.2 (d, $^1J(P–C) = 15.5$, C_{11}), 133.8 (C), 153.4 (AXX′, m, $\sum J(C–P) = 7.5$, $C_{4a,5a}$), 154.2 (s, C_{12}), 156.3 (s, C_{14}), 169.6 (AXX′, m, $\sum J(C–P) = 40.3$, C_{10}).

Synthesis of copper complex 6. $[Cu(CH_3CN)_4][BF_4]$ (34.5 mg, 0.13 mmol) and ligand **3** (100 mg, 0.13 mmol) were dissolved in CH_2Cl_2 (7 mL). The ^{31}P NMR spectrum of the crude mixture shows the formation of a unique product. The volume of the solution was reduced, hexanes were added which resulted in the precipitation of a yellow solid. It was filtered, washed with hexanes then dried. Yield: 95%, 116 mg. X-Ray quality crystals were obtained after diffusion of hexanes into a $CDCl_3$ solution of the complex.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.38 (s, 18H, *para* $C(CH_3)_3$), 1.61 (s, 36H, *ortho* $C(CH_3)_3$), 7.34 (m, $H_{2,8}$), 7.50 (m, 2H, $H_{1,9}$), 7.61 (s, 4H, H_{13}), 8.10 (m, 4H, $H_{3,7,10,10'}$). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 207.6. ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 31.3 (s, *para* $C(CH_3)_3$), 34.9 (s, *ortho* $C(CH_3)_3$), 35.6 (s, *para* $C(CH_3)_3$), 39.0 (s, *ortho* $C(CH_3)_3$), 123.1 (s, $C_{9a,9b}$), 123.3 (s, $C_{1,2,8,9}$), 123.6 (s, C_{13}), 125.4 (s, $C_{4,6}$), 129.4 (d, $^1J(P–C) = 20$, C_{11}), 131.4 (m, $\sum J = 26$, $C_{3,7}$), 152.4 (AXX′, m, $\sum J(C–P) = 14$, $C_{4a,5a}$), 153.7 (s,C_{12}), 156.2 (s, C_{14}), 163.8 (AXX′, m, $\sum J(C–P) = 46$, C_{10}).

Computational details

All computations were performed using the Gaussian 03 suite of programs and gradient corrected density functional theory using the B3PW91 functional.[18,19] All optimizations were carried out using the 6-31 G(d) basis set for H, C, N, O, P. The basis set employed for the Cu and Au atoms incorporate the Hay and Wadt small-core relativistic effective core potential and double-ζ valence basis set.[20] For complex **II**, the ONIOM method was employed with the UFF force field (for methyl groups of the xylyl substituents).[21] Full optimizations were followed by analytical computation of the Hessian matrix to confirm the nature of the located minima on the potential energy surface. Minima were characterized by no imaginary frequency.

Crystallography

Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo-Kα ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. Experimental details are given in Tables 1 and 2. The crystal structure was solved using SIR 97[22] and SHELXL-97.[23] Molecular drawings were made using ORTEP III for Windows then POV-Ray.[24] contain the supplementary crystallographic data for this paper.

CCDC reference numbers 275394–275397.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b508678g

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