Coinage metal complexes with bridging hybrid phospine–NHC ligands: synthesis of di- and tetra-nuclear complexes†‡

Thomas Simler,a Pierre Braunstein*a and Andreas A. Danopoulos*a,b

A series of P–NHC-type hybrid ligands containing both PR₂ and N-heterocyclic carbene (NHC) donors on meta-bis-substituted phenylene backbones, L₁Cy, L₁Bu and L₁Ph (R = Cy, tBu, Ph, respectively), was accessed through a modular synthesis from a common precursor, and their coordination chemistry with coinage metals was explored and compared. Metallation of L₁Ph·n(HBr) (n = 1, 2) with Ag₂O gave the pseudo-cubane [Ag₄Br₄(L₁Ph)]₃, isostructural to [Ag₄Br₄(L₁Ph)] (R = Cy, tBu) (T. Simler, P. Braunstein and A. A. Danopoulos, Angew. Chem., Int. Ed., 2015, 54, 13691), whereas metallation of L₁Ph·n(BF₄) (R = Ph, tBu) led to the dinuclear complexes [Ag₄(L₁Ph)]₂(BF₄)₂ which, in the solid state, feature heteroleptic Ag centres and a ‘head-to-tail’ (HT) arrangement of the bridging ligands. In solution, interchange conversion with the homo-leptic ‘head-to-head’ (HH) isomers is facilitated by ligand fluxionality. ‘Head-to-tail’ [Cu₂Br₂(L₁Bu)] (R = Cy, tBu) dinuclear complexes were obtained from L₁Bu·nHBr and [Cu₂(Mes)₅], Mes = 2,4,6-trimethylphenyl, which also feature bridging ligands and heteroleptic Cu centres. Although the various ligands L₁ led to structurally analogous complexes for R = Cy, tBu and Ph, the rates of dynamic processes occurring in solution are dependent on R, with faster rates for R = Ph. Transmetallation of both NHC and P donor groups from [Ag₂Br₂(L₁Bu)]₃ to Au¹ by reaction with [AuCl(THT)] (THT = tetrahydrothiophene) led to L₁Bu transfer and to the dinuclear complex [Au₂Cl₂(L₁Bu)] with one L₁Bu ligand bridging the two Au centres. Except for the silver pseudo-cubanes, all other complexes do not exhibit metallophilic interactions.

Introduction

Phosphine and NHC donors are often compared because they readily coordinate to metal centres and display bonding analogies and tuneable stereo-electronic properties. However, despite the fact that both are considered as strong σ-donors, emerging evidence reveals subtly different σ-donating and π-accepting properties, diversifying across the periodic table. This can lead to transition metal complexes with beneficial catalytic properties, e.g. finely controlled lability and metal electronic tuning, stability of the catalytically active species etc.

The complementary roles of both types of donors participating in the same metal coordination sphere may enhance synergism, although counter examples have been described. The beneficial synergism may be enhanced if the hetero donors are part of a hybrid ligand. This background justifies synthetic efforts towards the design of new phosphine-functionalised NHC (P–NHC) complexes, with reported high activities in C–C coupling reactions (PdIV, RuII), amination of aryl chlorides (PdIII) and transfer hydrogenation of ketones (RuIII).

Among the P–NHC-type ligands, bidentate hybrid ligands with direct P–N bond, flexible alkyl, or more rigid and tuneable aryl spacer between the donors, have been described, respectively, have attracted most attention (Fig. 1). In particular, we and others have been interested in the meta-bis-substituted phenylene framework 1c–1d as potential precursor to non-symmetrical PC₆NHC ‘pincer’ complexes. Relevant PC₆NHC P pincer and P₂(C₉NHC)₂ macrocyclic ligands 2f–2g, respectively, have been described.

The coordination chemistry of P–NHC-type ligands has mainly been focussed on late transition metals; the few structurally characterized examples incorporating Ag⁺ or Cu⁺ are depicted in Fig. 2. This relative scarcity is surprising, considering the interest for air stable group 11 NHC.  

References

† Dedicated to the memory of Prof. Peter Hofmann, a dear colleague and friend who made major research advancements and contributed much to the promotion of chemistry.
‡ Electronic supplementary information (ESI) available: X-ray structure of [Ag₄(L₁Ph)]₃ and crystallographic summary table. CCDC 1445698-1445706. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00275g
complexes. Silver P–NHC complexes are usually obtained by the reaction of the corresponding imidazolium salts with Ag₂O, or by initial formation of the free carbene ligand followed by coordination to AgI. In addition to their structural diversity, they have proved to be efficient NHC transfer reagents to metals, such as RuII, RhI, PdII, and AuI, but in rare cases the transmetallation did not proceed neatly.

Interestingly, P–NHC-type copper(I) complexes are accessible by transmetallation from the corresponding AgI complexes and by other methodologies e.g. the coordination of the pre-formed free carbene to a labile CuI precursor, or the reaction of the imidazolium salt with precursors featuring a coordinated base (e.g. copper(i) acetate, mesitylcopper(i) [Cu₃(Mes)₃] and [CuN(SiMe₃)₂]).

Lastly, P–NHC gold(I) complexes are scarce (Fig. 3) but arise increasing interest due to their attractive photophysical properties and the occurrence of metallophilic interactions in their structures.

Extending our previous work on P-based NHC hybrid ligands, herein we report an efficient and modular access...
to the \(^8\)P–NHC-type (\(^8\)P = PCy\(_2\), PrBu\(_2\) or PPh\(_2\)) ligands (see 1d in Fig. 1) and their coinage metal complexes.

Results and discussion

Ligand synthesis

A synthetic strategy for the synthesis of phosphine imidazolium precursors employing silane (SiHMeCl\(_2\) or SiHCl\(_3\)) reduction\(^{20}\) of readily available phosphoryl-imidazolium salts has ample literature precedence,\(^{6,10,15,21}\) including attempted preparation of precursors of similar topology to those described below.\(^{12e}\) This methodology requires the use of excess silane reductants and forcing conditions, usually leading to moderate yields. Therefore, an alternative, wider scope synthetic strategy was developed, that is easily adaptable to different phosphine substituents (Scheme 1).

Starting from the imidazolium–bromobenzyl derivative A, the air-stable phosphonium–imidazolium salts LCy·2HBr and L\(^\text{PrBu}\)·2HBr were obtained by quaternisation of dicyclohexyl- and di-tert-butylphosphine in acetonitrile,\(^{12e}\) and converted to the corresponding phosphate-imidazolium salts L\(^\text{Cy}\)·HBr and L\(^\text{Bu}\)·HBr by treatment with NEt\(_3\). Successful single deprotonation was confirmed in the \(^1\)H-NMR spectra by the disappearance of the deshielded signal due to the acidic P–H proton (\(^1J_{P-H} \approx 480–490\) Hz). Singlets at \(\delta\) 5.8 and 32.0 ppm for LCy·HBr and L\(^\text{Bu}\)·HBr, respectively, were observed in the \(^{31}\)P{\(^1\)H}-NMR spectra. Due to the relative air-sensitivity of the trialkyl-phosphine products, borane-protection of the phosphine in LCy·HBr was carried out and yielded LCy·HBr·BH\(_3\) as an air-stable crystalline solid, the structure of which is shown in Fig. 4 (left).

When an analogous synthetic route was applied to L\(^\text{Ph}\)·HBr, it failed in the step of the direct quaternisation of diphenylphosphine by A owing to the lower nucleophilicity of the former. To circumvent the problem, lithium diphenylphosphide (LiPPh\(_2\)), generated in situ, was reacted with A at low temperature (Scheme 1). Formation of L\(^\text{Ph}\)·HBr was confirmed by a phosphorus resonance at \(\delta\) –8.5 ppm. In the different L\(^\text{R}\) precursors, the imidazolium backbone backbone protons usually gave
rise in the $^1$H-NMR spectra to apparent triplets (overlapping dd, $J_{HH} \approx 1.6–1.8$ Hz), and the NC$_2$H$_N$ signal was observed in the range $\delta 11.17–11.46$ ppm.

In the structure of the moderately air-stable LPh·HBr (Fig. 4, right) the imidazolium and central aryl ring planes form an angle of 13.4° (vs. 22.6° for LCy·HBr·BH$_3$). Other bond distances and angles are unremarkable. H-bonding interactions in the solid state were evidenced by a close contact between the NC$_2$H$_N$ proton and the bromide anion, in addition to the high directionality of the C–H⋯Br$^-$ interaction. Anion metathesis of LPh·HBr and L$_{tt}$Bu·HBr with excess NaBF$_4$ resulted in the corresponding LPh·HBF$_4$ and L$_{tt}$Bu·HBF$_4$ salts (see Experimental section). In their $^1$H-NMR spectra, the signal of the NC$_2$H$_N$ proton appeared shifted upfield ($\delta 9.05$ and $9.18$ ppm, respectively), consistent with weaker hydrogen bonding compared to the bromide salts.

**Formation of the free carbenes**

The free carbenes L$^\text{Cy}$, L$^\text{Bu}$ and L$^\text{Ph}$ were obtained by the double deprotonation of the corresponding phosphonium-imidazolium L$^R$·2HBr or the single deprotonation of phosphine-imidazolium L$^R$·HBr salts with stoichiometric amounts of KN(SiMe$_3$)$_2$ (Scheme 1). The free carbenes were obtained in high yields (79–90%) as very air sensitive, pentane soluble, dark green oils that turned red on standing for ca. 30 min at room temperature. The reason for such colour change is still unclear but probably linked to thermal and/or photochemical instability, however, the products of decomposition were not identified. Despite the difficulties associated with the long-term storage and handling of the isolated L$^\text{Cy}$, L$^\text{Bu}$ and L$^\text{Ph}$, unequivocal spectroscopic evidence for their identity and purity was obtained. Deprotonation and carbone formation was evidenced by the disappearance of the imidazolium signal in the $^1$H-NMR spectra of the oils and the observation of the NC$_2$N carbene resonance at $\delta 215.9–216.2$ ppm. Due to the difficult handling of LR, the synthesis of the coinage metal complexes described below is based on reactions with the imidazolium salt precursors L$^R$·n(HBr) ($n = 1, 2$).

**Synthesis and structure of silver complexes**

The availability of L$^R$·HBr opened the way for a comparative study of the coordination chemistry of L$^R$ as a function of R. Treatment of L$^\text{Ph}$·HBr with 1 mole equiv. of Ag$_2$O in acetonitrile, in the presence of 4 Å molecular sieves, afforded [Ag$_4$Br$_4$(L$^\text{Ph}$)$_2$] in low yields (<50%) after recrystallization from CH$_2$Cl$_2$/Et$_2$O (Scheme 2, route (a)). Upon formation of the
silver complex, the disappearance of the signal due to the acidic imidazolium proton and the downfield shift of the broad singlet at $\delta$ 3.2 ppm in the $^1$H-NMR and $^{31}$P-NMR spectrum, respectively, confirmed NHC formation and coordination of the P atom. The absence of P–Ag couplings ($^{107}$Ag 51.8% and $^{109}$Ag 48.2%, both $I = 1/2$) can be rationalised by a dynamic behaviour involving rapid P–Ag bond breaking/formation on the $^{31}$P-NMR timescale. $^{12e}$ In the $^{13}$C-NMR spectrum, the coordinated C$^{\text{NH}}$ was detected as a broad singlet, the coordinated CNHC was detected as a broad singlet at $\delta$ 51.8% and 109Ag 48.2%, both $I = 1/2$) can be rationalised by a dynamic behaviour involving rapid P–Ag bond breaking/formation on the $^{31}$P-NMR timescale. $^{12e}$ In the $^{13}$C-NMR spectrum, the coordinated C$^{\text{NH}}$ was detected as a broad singlet.

The absence of $^{13}$C–$^{107/109}$Ag coupling has been reported in related NHC–AgX clusters, $^{12d,e,23,26}$ and points towards dynamic behaviour in solution $^{27}$ and a high lability of the NHC–Ag bond. $^{16,28}$

The structure of [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$] (Fig. 5) corresponds to a distorted Ag$_4$Br$_4$ cubane cluster with alternating vertices of the cube being occupied by Ag and Br atoms. The two bridging L$^{\text{Ph}}$–L$^{\text{Ph}}$–NHC ligands each span the Ag···Ag diagonal of two parallel Ag$_2$Br$_2$ faces of the cube, forming 9-membered dimetallic cycles, as observed with a closely related phosphinite–NHC ligand $^{12a,e}$ and in the structures of [Ag$_4$Br$_4$(L$^R$)$_2$] (R = Cy, tBu) recently reported. $^{12e}$ All bromides are capping three Ag centres. The Ag···Ag separations (3.300(1) Å and 3.400(1) Å) are shorter than the sum of the van der Waals radii for Ag (3.44 Å), $^{29}$ implying weak d$^{10}$–d$^{10}$ interactions. $^{30}$ Related [Ag$_4$(halide)$_2$L$_2$] cubane structures have been described with L = phosphine ligands, $^{31}$ and recently obtained with bidentate ligands incorporating NHC donors (bis-NHC$^{23,26,32}$ or P–NHC-type$^{10g,12a,e}$ ligands). Containing non-symmetrical ligands, the observed molecular structure is chiral due to the lack of an improper axis of rotation (see Fig. 6); however, the two enantiomers are present in the asymmetric unit (related by the inversion centre of P$^1$).

Comparison of [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$] with the previously reported structures of [Ag$_4$Br$_4$(L$^R$)$_2$] (R = Cy, tBu) $^{12e}$ reveals that the substituents on the phosphorus have little influence on the adopted motif or the metrical data. For example, with L$^{\text{Ph}}$ and L$^6$, the Ag–C$^{\text{NH}}$ and Ag–P bond distances are comparable, while Ag–P is marginally longer in [Ag$_4$Br$_4$(L$^{\text{Bu}}$)$_2$] (difference <0.040 Å). A more notable difference is in the Ag···Ag separation in each bridged face of the pseudocubane (mean Ag···Ag ca. 3.350 Å for [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$], 3.188 Å for [Ag$_4$Br$_4$(L$^R$)$_2$] and 3.089 Å for [Ag$_4$Br$_4$(L$^{\text{Bu}}$)$_2$], leading to complexes with increased distortion from the idealised cubane geometry, which may be ascribed to intramolecular repulsions of the bulkier P-substituents. $^{33}$ Comparative metrical data for the different silver complexes are provided in Table 1.

In view of the similarity between [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$] and [Ag$_4$Br$_4$(L$^R$)$_2$] (R = Cy, tBu), the latter having been obtained from the corresponding phosphonium–imidazolium salts, we reasoned that better yields of [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$] should also be attainable by the reaction of L$^{\text{Ph}}$·2HBr with one mole equiv. Ag$_2$O. Indeed, the reaction of L$^{\text{Ph}}$·2HBr with Ag$_2$O afforded the expected cubane complex in very good yields (>80%). It is worth noticing that the method of choice for the preparation of L$^{\text{Ph}}$·2HBr consisted of protonation of L$^{\text{Ph}}$·HBr by dry HBr, generated in situ by methanolysis of an exactly stoichiometric amount of SiMe$_3$Br in dichloromethane under oxygen-free, controlled conditions (Scheme 2, route (b)). We also noted that the reaction of L$^{\text{Ph}}$·HBr with 0.5 mole equiv. Ag$_2$O in acetonitrile resulted in the formation of another silver complex featuring $^1$H NMR resonances distinct from [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$], the structure of which remains elusive to date.

Fig. 5 The molecular structure of [Ag$_4$Br$_4$(L$^{\text{Ph}}$)$_2$] with thermal ellipsoids at 40% probability. For clarity, H atoms are omitted and only the ipso carbons of the phenyl substituents in the lower ligand are shown. Selected metrical data are given in Table 1.
Table 1  Selected interatomic distances (Å) and angles [°] for the Ag(I) complexes \([\text{Ag}_2\text{Br}_4(L^\text{Ph})_2]\) and \([\text{Ag}_2(L^\text{t\text{-}Bu})_2]\)

|            | \([\text{Ag}_2\text{Br}_4(L^\text{Ph})_2]\) | \([\text{Ag}_2\text{Br}_4(L^\text{t\text{-}Bu})_2]\) | \([\text{Ag}_2\text{Br}_4(L^\text{Ph})_2]\) | \([\text{Ag}_2\text{Br}_4(L^\text{t\text{-}Bu})_2]\) |
|------------|--------------------------------------------|-------------------------------------------|---------------------------------------------|---------------------------------------------|
| \(\text{Ag}1\cdots\text{Ag}2\) | 3.101(1)                                   | 3.188(1)                                  | 3.400(1)                                   | 5.361(1)                                   |
| \(\text{Ag}1\cdots\text{Ag}3\) | 3.076(1)                                   | 3.188(1)                                  | 3.300(1)                                   | 5.508(1)/5.762(1)                          |
| \(\text{Ag}1\cdots\text{Ag}4\) | 3.821(1)                                   | 3.721(1)                                  | 3.761(1)                                   |                                             |
| \(\text{Ag}1\cdots\text{Ag}4\) | 3.712(1)                                   | 3.687(1)                                  | 3.562(1)                                   |                                             |
| \(\text{Ag}1\cdots\text{Br}1\) | 2.688(1)                                   | 2.880(1)                                  | 2.949(1)                                   |                                             |
| \(\text{Ag}1\cdots\text{Br}2\) | 3.006(1)                                   | 2.812(1)                                  | 2.748(1)                                   |                                             |
| \(\text{Ag}1\cdots\text{Br}4\) | 2.895(1)                                   | 2.708(1)                                  | 2.721(1)                                   |                                             |
| \(\text{Ag}2\cdots\text{P}1\)  | 2.422(1)                                   | 2.402(1)                                  | 2.407(1)                                   |                                             |
| \(\text{Ag}2\cdots\text{P}2\)  | 2.425(1)                                   | 2.391(1)                                  | 2.388(1)                                   |                                             |
| \(\text{Ag}1\cdots\text{C}1\)  | 2.148(4)                                   | 2.135(3)                                  | 2.147(5)                                   |                                             |
| \(\text{Ag}3\cdots\text{C}27\) | 2.123(4)                                   | 2.144(4)                                  | 2.127(5)                                   |                                             |
| N1-C1-N2   | 103.7(4)                                   | 109.3(3)                                  | 107.3(5)                                   | 104.6(1)                                   |
| N3-C3-N7   | 103.2(3)                                   | 103.3(3)                                  | 103.2(5)                                   | 105.1(5)                                   |

* Data taken from ref. 12. * There are two dinuclear complexes exhibiting similar metrical data in the asymmetric unit, the second set of values refers to the other molecule.

The crucial role of halides in the formation of the cubane structures described above raised the question of the possible reaction outcome under halide-free conditions. The reaction of \([\text{Ag}_2\text{L}^\text{Ph}]_2\) with 0.5 mole equiv. of \(\text{Ag}_2\text{O}\) in acetonitrile led to \([\text{Ag}_4\text{Br}_4(L^\text{Ph})_2](\text{BF}_4)_2\) (Scheme 3). Examination of its \(^{1}H\) and \(^{31}P\{^{1}H\}\ NMR spectra revealed an equilibrium involving two isomers in solution. Notably, dissolution in CD\(_2\)CN gave rise, in the \(^{31}P\{^{1}H\}\) NMR spectrum, to two sets of two doublets (total 8 lines) observed at \(\delta\) 21.3 (two doublets, \(J_{\text{P}-\text{Ag}} \approx 500\) Hz, \(J_{\text{P}-\text{Ag}} \approx 580\) Hz) and 11.2 ppm (two doublets, \(J_{\text{P}-\text{Ag}} \approx 475\) Hz, \(J_{\text{P}-\text{Ag}} \approx 550\) Hz) in a 1:1 ratio, respectively. Evaporation of the solution and re-dissolution in CD\(_2\)Cl\(_2\) led to a similar set of peaks but in a ca. 4:1 ratio, respectively. The reversibility of this procedure confirmed the solvent-dependency of the equilibrium. Due to limited solubility in CD\(_2\)CN, the \(^{13}C\{^{1}H\}\)-NMR spectrum was recorded in CD\(_2\)Cl\(_2\), where only the signals for the major isomer were clearly visible. In order to gain more insight into the structures of these two isomers, crystallisations from either CH\(_2\)Cl\(_2\) or CH\(_3\)CN solutions were attempted. Products corresponding to \([\text{Ag}_2(L^\text{Ph})_2](\text{BF}_4)_2\) (solvent) were obtained from both solvents, which crystallized in different space groups as ‘head-to-tail’ (HT) (heteroleptic) isomers with respect to the mutual arrangement of the ligands. However, the molecular structure of the products (Fig. 7, left and Fig. S1 in ESI†) revealed the same atom connectivity and very similar metrical data, indicating that only one and the same isomer crystallised (with a possible shift of the equilibrium between ‘head-to-head’ (HH) (homoleptic) and HT isomers upon crystallisation).

In the structure of \([\text{Ag}_2(L^\text{Ph})_2](\text{BF}_4)_2\cdot2\text{CH}_2\text{Cl}_2\) (Fig. 7, left), the two \(L^\text{Ph}\) ligands bridge two Ag metal centres (Ag1…Ag2 3.561(1) Å) in a ‘head-to-tail’ arrangement. The C–NHC-Ag–P angles slightly deviate from linearity (C1–Ag1–P1 121.3°) and the two NHC rings are not parallel, their mean planes forming an angle of 12.8°. Such an arrangement has already been observed in other P–NHC-silver complexes,\(^{10}\) the linear coordination geometry is also encountered in bis-NHC silver complexes with non-coordinating anions.\(^{13,14}\) The Ag–C\(_{\text{NHC}}\) bond distances follow trends observed for related complexes,\(^{23,24}\) being slightly longer in the NHC silver–halide clusters (mean ca. 2.137 Å)\(^{14}\) than in the complexes with non-coordinating anions (mean ca. 2.111 Å).\(^{13,14}\)

In order to gain insight into the solution behaviour of \([\text{Ag}_2(L^\text{Ph})_2](\text{BF}_4)_2\), the corresponding \([\text{Ag}_2(L^\text{t\text{-}Bu})_2](\text{BF}_4)_2\) was similarly prepared (Scheme 3). In this case too, \(^{1}H\) and \(^{31}P\{^{1}H\}\) NMR analysis in CD\(_2\)Cl\(_2\) revealed the presence of two isomers, in a 1:2 ratio, the nature of which could be determined by perusal of the \(^{13}C\{^{1}H\}\)-NMR spectrum. Spectra of sufficient quality were obtained by acquisition with a cryogenically cooled probe head. A complex pattern (10 lines in total) in the
region $\delta$ 180–177 ppm, corresponding to the $^{13}$C-NMR-$\text{Ag}$ signals was successfully simulated, revealing two different $^{13}$C-NMR-$\text{Ag}$ environments associated with the different isomers (Fig. 8): the two doublets centred at $\delta$ 178.8 ppm ($^{1}J_{C-107\text{Ag}} = 183$ Hz, $^{1}J_{C-109\text{Ag}} = 212$ Hz) were attributed to an isomer with homo-leptic Ag$^+$ centres and symmetrical NHC-$\text{Ag}$–NHC coordination (HH isomer), while two doublets of doublets at $\delta$ 178.5 ppm ($^{1}J_{C-107\text{Ag}} = 190$ Hz, $^{1}J_{C-109\text{Ag}} = 219$ Hz, $^{2}J_{P-C} = 62$ Hz) were assigned to the second and major isomer, with heteroleptic NHC-$\text{Ag}$–P connectivity (HT isomer). Further indication of the nature of the former isomer was obtained from the observation in $^{15}$C-NMR of ‘virtual’ triplets of the $X'_{1}A'X_{1}$ (X = X' = C, A = A' = P) spin system involving the carbon atoms directly bound to phosphorus, resulting from a strong $^{2}J_{P-A'P}$ coupling between trans-coordinated P donors.$^{35}$ Interestingly, for all $[\text{Ag}_{2}(\text{L})_{2}]^{2+}$(BF$_4$)$_2$ (R = Ph, tBu) complexes, the $^{1}$H-NMR signals for the NHC backbone protons were detected as apparent triplets, likely due to $^{3}J_{HH}$ coupling constants falling in the same range.$^{36}$

An X-ray diffraction study of $[\text{Ag}_{2}(\text{L}^{\text{Ph}})_{2}]$(BF$_4$)$_2$ also revealed a ‘head-to-tail’ coordination of the bidentate ligand (Fig. 7, right), with two crystallographically independent but very similar di-nuclear complexes in the unit cell (Table 1). The bond distances and angles in $[\text{Ag}_{2}(\text{L}^{\text{Ph}})_{2}]^{2+}$ for R = Ph and tBu are very close or within experimental error, showing that the nature of the P donor group has only little influence on the solid state structure.

Interestingly, Hofmann and co-workers recently reported the formation of P–NHC-type ‘head-to-head’ and ‘head-to-tail’
copper(II) complexes. Depending on the nature of NHC wingtip, either the homoleptic or the heteroleptic isomer was isolated. Mutual ‘trans-coordination’ of the NHC and P donors, electronically disfavoured, was rationalised by minimisation of the steric repulsion in the ‘head-to-head’ complex. Yet for these complexes, no ‘head-to-head’/‘head-to-tail’ isomerisation was detected in different NMR solvents.

Synthesis and structure of dinuclear copper(I) complexes

We have already reported the synthesis of tetranuclear, ladder-type P–NHC-type Cu(I) complexes by transmetallation from [Ag₄Br₄(L₆)₂] or by reaction of the phosphonium–imidazolium L·2HBr salts with mesitylcopper(I) [Cu₅(Mes)₅], which has been used before to form Cu(I) NHC complexes from imidazolium salts. The coordination chemistry of the L ligands with Cu(I) was further investigated by using the monoprotic proligands L·HBr.

Reaction of L·HBr (R = Ph, tBu, Cy) with [Cu₅(Mes)₅] resulted in the formation of the corresponding [Cu₂Br₂(L₂)] complexes in good yields (Scheme 4). Completion of the reaction was evidenced by ¹H NMR spectroscopy (i.e. disappearance of the imidazolium NC₄H₄N signal). For all three Cu(I) complexes, the ³¹P{¹H}-NMR spectra revealed a singlet assignable to the coordinated P donor, only slightly shifted from the position observed in the starting L·HBr. In the ¹³C{¹H}-NMR spectra, the Cu(I)–CNHC resonance was detected in the region δ 183–186 ppm, typical for Cu(I)–NHCs. The ¹H-NMR signal was observed as a doublet (JPC ≈ 46–47 Hz) for the dialkyl phosphine derivatives or as a broad signal for [Cu₂Br₂(L₆)]₂, possibly due to a different rate of fluxionality of the C–CNHC=Cu bonds in these two complexes. In the ¹H-NMR spectrum of [Cu₂Br₂(L₆)]₂, the line-shape of the signals for the methylene protons was field-dependent, pointing towards a dynamic process in solution.

The structures of [Cu₂Br₂(L₆)]₂ and [Cu₂Br₂(L₆)]·2CH₂Cl₂ were determined crystallographically and are depicted in Fig. 9. Both complexes crystallised as dimers with two L₆ ligands bridging the two copper centres, reminiscent of the coordination behaviour of the ligands in [Ag₂(L₆)](BF₄)₂. Both structures present a ‘head-to-tail’ arrangement for the NHC and P donors. The three-coordinate Cu centres adopt a distorted planar T-shaped coordination geometry, the third donor being a bromide. The Cu–CNHC distances, from 1.938(6) to 1.960(6) Å, and the Cu–P bond lengths lie within the range reported for related complexes. The large separation between the two Cu(I) centres (from 6.836(1) to 7.138(1) Å) can be traced to the large 1,3-phenylene spacer linking the NHC and phosphine donors.

In order to study further the dynamic behaviour of the Cu(I) complexes in solution, we undertook a variable temperature (VT) ¹H-NMR study of [Cu₂Br₂(L₆)] in CD₂Cl₂ prompted by its relatively simple line-shape compared to the L₆ and L₆.

Scheme 4 Synthesis of the dinuclear copper(I) complexes [Cu₂Br₂(L₆)]₂. Yields are based on L₆.

Fig. 9 The molecular structures of [Cu₂Br₂(L₆)] (left) and [Cu₂Br₂(L₆)]·2CH₂Cl₂ (right) with thermal ellipsoids at 40% probability. In [Cu₂Br₂(L₆)] only one Cy carbon and one disordered position for the nBu chain are shown for clarity. C atoms for the nBu, Cy and tBu groups are depicted as spheres of arbitrary radii. H atoms and crystallisation solvents have been removed for clarity. Selected metrical data are given in Table 2.
analогues (Fig. 10). At room temperature, very broad signals were observed at 600 MHz for the various protons, suggesting possible coalescence. Upon cooling to −41 °C, two sharp doublets at δ 1.43 and 0.86 ppm (9 H each) assignable to the tBu groups on P indicated a static structure (H_D). At this temperature, the signal of the methylene protons (H_C) was split into two complex multiplets, due to the geminal 2J_HH and 2J_PH coupling in an ABX (A = B = H, X = P) spin system. Interestingly, the NC2H protons (H_B) of the NHC wingtip also appeared as diastereotopic. The backbone H_A proton, closer to the aryl spacer, gives rise to a doublet at this temperature owing to 3J_HH coupling. For comparison, at 35 °C, one broad singlet (18 H) was assignable to the tBu groups on P and a doublet was observed for the methylene protons (H_C) in accordance with a relatively fast exchange of their positions on the NMR time scale. The spectral characteristics at lower temperature are in agreement with the solid-state structure being retained in solution. The dynamic behaviour at higher temperatures may have diverse origins, i.e. conformational changes in the dimeric structure involving flipping of the phenylene linker and/or the reversible formation of ‘head-to-head’ coordinated dimers by ligand (hemilability). The activation barrier corresponding to the fluxional behaviour of the tBu groups was found to be ΔG‡ = 56.5 ± 1.0 kJ mol⁻¹. Based on the current data there is no preference for any of the above explanations. The latter hypothesis is however less likely since only one singlet is observed in the 31P{1H}-NMR spectrum at room temperature. Recent work involving ligands with NHC and P donors held together by a CH2 linker ascribed stereo-isomerisations at the Cu centre to fluxionality.¹⁰

In contrast, the reaction of [Cu5(Mes)5] with the phosphonium–imidazolium L⁹⁻·2HBr, or the transmetallation of the corresponding [Ag4Br4(L⁸⁻)2] cubanes with 4 mole equiv. of [CuBr·SM^2] (R = Cy, tBu) gave rise to the tetranuclear clusters [Cu4Br4(L⁷⁻)2].¹²e Metrical data regarding the di- and tetranuclear Cu complexes are reported in Table 2.

The longer Cu−C(NHC) and Cu−P bond distances in the [Cu4Br4(L⁸⁻)2] complexes (mean distances ca. 1.948 and 2.228 Å, respectively) in comparison to the [Cu4Br4(LCy)2] cluster (1.903(5) Å and 2.211(2) Å) probably originate from the competition between mutually trans strong P and NHC σ-donors.

| Table 2 Selected interatomic distances (Å) and angles [°] for the copper complexes [Cu2Br2(L⁹⁻)2] (R = Cy, tBu) and comparison with [Cu4Br4(L⁷⁻)2]²a |
| --- |
| [Cu2Br2(L⁹⁻)2] | [Cu4Br4(L⁷⁻)2]²a |
| Cu1⋯Cu2 | 6.899(1) | 7.138(1)/6.836(1) |
| Cu1−Br1 | 2.497(1) | 2.453(1)/2.493(1) |
| Cu2−Br2 | 2.483(1) | 2.438(1)/2.493(1) |
| Cu1−P | 2.231(2) | 2.222(2)/2.230(2) |
| Cu2−P | 2.237(2) | 2.217(2)/2.230(2) |
| Cu1−C1 | 1.960(6) | 1.952(6)/1.947(6) |
| Cu2−C23/C27 | 1.938(6) | 1.943(6)/1.947(6) |
| P2−Cu1−Br1 | 114.8(1) | 109.7(1)/114.2(2) |
| P2−Cu1−C1 | 145.1(2) | 137.9(2)/107.5(1) |
| C1−Cu1−Br1 | 100.0(2) | 112.2(2)/110.1(2) |
| Σangles around Cu1 | 359.9 | 359.8/360.0 |
| Σangles around Cu2 | 360.0 | 360.0/360.0 |

²a Data taken from ref. 12e. There are two dinuclear complexes exhibiting similar metrical data in the asymmetric unit, the second set of values refers to the other molecule.
Synthesis and structure of a dinuclear gold(Ⅰ) complex

Since transmetallation of the silver cubane \([\text{Ag}_4\text{Br}_4(L^{\text{Bu}})_{2}]\) with Cu always led to tetranuclear complexes,12 we wondered what would happen with Au. Reaction of \([\text{Ag}_4\text{Br}_4(L^{\text{Bu}})_{2}]\) with 4 mole equiv. of \([\text{AuCl(THT)}]\) led to the homodinuclear gold complex \([\text{Au}_2\text{Cl}_2(L^{\text{Bu}})_{2}]\) (Scheme 5). 

\[ {^{13}}\text{C}\{^{1}H\}-\text{NMR spectral analysis supported the NHC transmetallation as a downfield singlet was detected at } 170.3 \text{ ppm, in a range typical for } \text{Au}^\text{I}-\text{CNHC} \] functionalities.40 A singlet at \( \delta 79.0 \text{ ppm in the } {^{31}}\text{P}\{^{1}H\}-\text{NMR spectrum also confirmed concomitant phosphate transfer to gold.} \]

However, a minor peak was observed at \( \delta 80.1 \text{ ppm and ascribed to analogous complexes originating from partial halide scrambling (Cl/Br); this was also supported by elemental analysis (cf. Experimental section).} \]

The structure of \([\text{Au}_2\text{Cl}_2(L^{\text{Bu}})_{2}]\) (Fig. 11) revealed an approximate linear coordination of the Au centres (P–Au–Cl: 177.7(1)° and \( \text{CNHC}–\text{Au–Cl}: 176.4(2)° \)), common for NHC gold(Ⅰ) complexes. The Au–C\( \text{CNHC} \) (1.985(5) \( \text{Å} \)) and Au–P (2.239(1) \( \text{Å} \)) bond distances are in the expected range.19,40 Contrary to a recent report by Koesly and co-workers on related P–NHC-type gold(Ⅰ) complexes (Fig. 3) obtained by transmetallation from the silver analogues,19 no intra- or inter-molecular Au–Au interactions were observed in the solid state for \([\text{Au}_2\text{Cl}_4(L^{\text{Bu}})]\).

Attempts to synthesise heterobimetallic silver–gold complexes proved unsuccessful, as the reaction of \([\text{Ag}_2\text{Br}_4(L^{\text{Bu}})_{2}]\) with 2 mole equiv. of \([\text{AuCl(THT)}]\) led to a mixture of products containing \([\text{Au}_2\text{Cl}_4(L^{\text{Bu}})]\).

Conclusion

The rational synthesis of a range of hybrid P–NHC-type (pro-) ligands with systematically varied substitution at P, provided insight into their coordination chemistry with coinage metals. The main features observed can be summarised as follows: (i) in all cases studied, the ligands bridge two metal centres, irrespective of the type of phosphine donor; (ii) in the presence of \( \text{Br}^- \), all silver complexes isolated adopt structures based on the \([\text{Ag}_2\text{Br}_4(L^{\text{R}})_{2}]\) motif comprising a distorted \( \text{Ag}_2\text{Br}_4 \) cubane core, bridging \( \text{L}^{\text{R}} \) ligands and weak metallophilic interactions; (iii) in the presence of the non-coordinating \( \text{BF}_4^- \), \([\text{Ag}_2\text{L}(\text{L}^{\text{R}})_{2}](\text{BF}_4)_2 \) complexes were obtained with bridging ‘head-to-tail’ ligand arrangement in the solid state and ‘head-to-tail’/‘head-to-head’ isomerisation in solution; (iv) the nature of the R substituent on the P end does not impact the structures of the Ag complexes characterised, but seems to influence the rates of dynamic processes in solution, presumably due to competition of electronic and steric factors of the P donor. The relative lability of the two types of donor ends in P–NHC-type hybrid ligands has been inferred from the nature of products obtained from the reaction of \([\text{Ag}_2\text{Br}_4(L^{\text{R}})_{2}] \) with \([\text{Ir(COD)}](\mu-\text{Cl})]_2^{12e} \) (v) dinuclear \([\text{Cu}_2\text{Br}_4(L^{\text{Bu}})_{2}]\) complexes with bridging ligands were easily accessible from \( \text{L}^{\text{R}}\text{HBr} \) and \([\text{Cu}_2(\text{Mes})_2]\) and are also non-rigid in solution; (vi) transmetallation of \([\text{Ag}_2\text{Br}_4(L^{\text{R}})_{2}] \) with \([\text{AuCl(THT)}]\) results in transfer of both donor groups of the hybrid P–NHC-type ligands, leading to the dinuclear \([\text{Au}_2\text{Cl}_4(L^{\text{Bu}})]\) complex.

Guided by the synthesis of non-symmetrical (pro)ligands and through the understanding of their emerging coordination chemistry, ligand alterations may be targeted to favour chelating and/or pincer rather than bridging coordination.
behaviour. In addition, the pre-organized tethering of the two types of strong σ-donors on the same skeleton (as on L²) will provide insight into the donor competition behaviour that may lead to (hemilabile or stable complexes with catalytic potential.¹²e

**Experimental section**

**General methods**

All air- and moisture-sensitive manipulations were performed under dry argon atmosphere using standard Schlenk techniques. THF and Et₂O were dried by refluxing over sodium/benzophenone ketyl and distilled under an argon atmosphere prior use. Methanol and ethanol were refluxed over CaH₂, distilled under an argon atmosphere and stored over 3 Å molecular sieves. Other solvents (pentane, CH₂Cl₂, toluene and acetonitrile) were dried by passing through columns of activated alumina and subsequently purged with argon. C₆D₆ and toluene-d₈ were distilled over KH; other deuterated solvents were dried over 4 Å (CD₂Cl₂ and CDCl₃) or 3 Å (CD₃OD) molecular sieves, degassed by freeze-pump-thaw cycles, and stored under argon. Mesityl copper(I)⁴¹ and [AuCl(THT)]⁴² were prepared according to literature methods and all other chemicals were obtained from commercial sources and used without further purification. The synthesis of 1-(3-(bromomethyl)phenyl)-3-butyl-1H-imidazol-3-ium bromide (L⁵⁻¹²²) has already been reported in a recent communication.¹²e

NMR spectra were recorded on Bruker spectrometers (AVANCE I – 300 MHz, AVANCE III – 400 MHz, AVANCE III – 600 MHz or AVANCE I – 500 MHz equipped with a cryogenic probe). Downfield shifts are reported in ppm as positive and referenced using signals of the residual proto solvents ¹H, the solvent ¹³C or externally ³¹P, ¹⁹F. All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet and br = broad. Unequivocal determination of ³¹P coupling constants in ambiguous cases was carried out by recording the ¹³C{¹H}-NMR spectra on two different field spectrometers. Assignments (Fig. 12) were determined either on the basis of unambiguous chemical shifts, coupling patterns and ¹³C-DEPT experiments or 2D correlations (¹H–¹H COSY, ¹H–¹³C HSQC, ¹H–¹³C HMBC). Spin-simulation was carried out using the DAISY module of the Topspin 2.1 software (BRUKER).

![Fig. 12 Atom numbering used for the assignment of the NMR resonances.](image)

Elemental analyses were performed by the “Service de micro-analyses”, Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas.

**Synthesis of 3-butyl-1-(3-(dicyclohexylphosphino)methylphenyl)-IH-imidazol-3-ium bromide (L⁵⁻¹²²-HBr).** To a solution of L⁵⁻¹²²·HBr (5.51 g, 9.63 mmol) in degassed methanol (15 mL) was added under argon a solution of NEt₃ (6.5 mL, 4.88 g, 48 mmol) in methanol (5 mL). After the resulting solution was stirred at r.t. for 1 h, all the volatiles were evaporated under reduced pressure. The oily residue was redissolved in CH₂Cl₂ and the solution was extracted three times with degassed water to remove the triethylammonium salt. The organic phase was dried over anhydrous MgSO₄ and concentrated under reduced pressure. Addition of a mixture of Et₂O and pentane precipitated L⁵⁻¹²²-HBr as a white powder that was isolated by filtration and dried under vacuum. Yield: 4.20 g (8.55 mmol), 89%. Anal. Calcd for C₂₆H₄₀BrN₂P (491.49): C, 63.54; H, 8.20; N, 5.70. Found: C, 63.04; H, 8.07; N, 5.64. ¹H NMR (500.13 MHz, CD₂Cl₂): δ 11.19 (t, ¹JHH = 1.6 Hz, 1H, CH₃mid. H2), 7.67 (d, ¹JHH = 7.8 Hz, 1H, CH₃arom. H7/H9), 6.74 (t, ¹JHH = ¹JHH = 1.7 Hz, 1H, CH₃mid. H8/H5), 7.60 (br s, 1H, CH₃arom. H11), 5.75 (t, ¹JHH = ¹JHH = 1.7 Hz, 1H, CH₃mid. H5/H4), 4.74 (t, ¹JHH = ¹JHH = 7.8 Hz, 1H, CH₃arom. H8), 7.42 (d, ¹JHH = 7.8 Hz, 1H, CH₃arom. H9/H7), 4.57 (t, ¹JHH = 7.4 Hz, 2H, NCH₂), 2.90 (br s, 2H, CH₂P), 1.98 (quint, ¹JHH = 7.5 Hz, 2H, NCH₂CH₂), 1.81–1.63 (m, 10H, Cy), 1.63–1.54 (m, 2H, Cy), 1.44 (sex, ¹JHH = 7.5 Hz, 2H, NCH₂CH₂CH₂), 1.31–1.06 (m, 10H, Cy), 0.99 (t, ¹JHH = 7.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂): δ 144.8 (d, ¹JPC = 10.0 Hz, CH₃mid. C10), 136.7 (CH₃mid. C2), 134.9 (C₆H₅mid. C6), 131.5 (d, ¹JPC = 7.1 Hz, CH₃mid. C8), 130.6 (CH₃mid. C7), 122.9 (CH₃mid. C12), 122.4 (d, ¹JPC = 8.2 Hz, CH₃mid. C11), 120.7 (CH₃mid. C15), 119.4 (CH₃mid. C14), 50.4 (NCH₂), 33.9 (d, ¹JPC = 14.9 Hz, CH₃), 32.6 (NCH₂CH₂), 30.2 (d, ¹JPC = 13.1 Hz, CH₂ Cy), 29.7 (d, ¹JPC = 9.1 Hz, CH₂ Cy), 29.3 (d, ¹JPC = 21.7 Hz, CH₂P), 27.64 (d, ¹JPC = 10.8 Hz, CH₂ Cy), 27.56 (d, ¹JPC = 8.3 Hz, CH₂ Cy), 26.8 (s, CH₂ Cy), 19.8 (NCH₂CH₂CH₂), 13.7 (CH₃). ³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂): δ 5.8.

**Synthesis of 3-butyl-1-(3-(dicyclohexylphosphino)methyl)-IH-imidazol-3-ium borane borane adduct (L⁵⁻¹²²-HBr-BH₃).** To a suspension of L⁵⁻¹²²·HBr (0.50 g, 1.0 mmol) in THF precooled at −10 °C was added dropwise BH₃·SMe₂ (0.55 mL of a 2.0 M THF solution, 1.1 mmol). The reaction mixture was allowed to reach r.t. and stirred for 2 h. All volatiles were evaporated under reduced pressure and the resulting white powder was washed with Et₂O and dried under vacuum. Yield: 0.50 g (0.99 mmol), 99%. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et₂O in a CH₂Cl₂ solution of L⁵⁻¹²²·HBr-BH₃. Anal. Calcd for C₂₆H₄₀BBR₃P (305.33): C, 61.80; H, 8.58; N, 5.54. Found: C, 61.50; H, 8.50; N, 5.52. ¹H NMR (300.13 MHz, CDCl₃): δ 11.42 (t, ¹JHH = 1.7 Hz, 1H, CH₃mid. H2), 7.91 (dm, ¹JHH = 8.0 Hz, 1H, CH₃arom. H7/H9), 7.80 (q, ¹JHH = ¹JHH = 1.8 Hz, 1H, CH₃mid. H11), 7.69 (t, ¹JHH = ¹JHH = 1.8 Hz, 1H, CH₃mid. H8/H5), 7.52 (t, ¹JHH = 7.9 Hz, 1H, CH₃arom. H8), 7.37 (t, ¹JHH = ¹JHH = 1.8 Hz, 1H, CH₃mid. H5/H4),
Synthesis of 3-butyl-1-(3-((diphenylphosphonio)methyl)phenyl)-1H-imidazol-3-ium bromide (LPh·HBr). To a solution of LPh·HBr in degassed methanol (15 mL) was added under argon a solution of NaBF₄ (2.75 g, 25 mmol) in methanol (5 mL). After the resulting solution was stirred at r.t. for 1 h, all the volatiles were evaporated under reduced pressure. The oily residue was redissolved in CH₂Cl₂ and the solution was extracted three times with degassed water to remove the triethylenammonium salt. The organic phase was dried over anhydrous MgSO₄ and concentrated under reduced pressure. Addition of a mixture of Et₂O and pentane precipitated LPh·HBr as a white powder that was isolated by filtration and dried under vacuum. Yield: 0.72 g (1.64 mmol), 65%. Anal. Calcd for C₃₅H₅₄BrN₂P (513.91): C, 65.33; H, 5.92; N, 6.00. Found: C, 65.14; H, 5.89; N, 5.84. 1H NMR (500.13 MHz, CD₂Cl₂): δ 11.17 (t, JHH = 1.6 Hz, 1H, CH₃imid. H2), 7.71 (s, 1H, CH₃imid. H11), 7.66 (t, JHH = 1.8 Hz, 1H, CH₃imid. H4/H5), 7.64 (d, JHH = 8.2 Hz, 1H, CH₃imid. H7/H9), 7.61 (t, JHH = JPh = 1.7 Hz, 1H, CH₃ Ph imid. C8), 7.52 (d, JHH = 7.8 Hz, 1H, CH₃ Ph imid. C7), 7.46 (t, JHH = 7.8 Hz, 1H, CH₃ Ph imid. H8), 4.57 (t, JHH = 7.2 Hz, 2H, NCH₃), 2.94 (d, JPH = 2.6 Hz, 2H, CH₂Ph), 1.97 (quint, JHH = JPh = 7.5 Hz, 2H, NCH₃ CH₂), 1.43 (sext, JHH = 7.5 Hz, 2H, NCH₃ CH₂), 1.13 (d, JPH = 11.0 Hz, 18H, C(CH₃)₃), 0.98 (t, JHH = 7.4 Hz, 3H, CH₃). 13C NMR (125.77 MHz, CD₂Cl₂): δ 146.0 (d, JPC = 13.7 Hz, Caryl, C10), 136.6 (CH₃imid. C2), 134.8 (Caryl, C6), 131.8 (d, JPC = 8.7 Hz, Caryl, C4), 130.5 (CH₃imid., C13), 123.0 (CH₃imid. H8), 122.7 (d, JPC = 9.7 Hz, CH₃imid. H7), 120.8 (CH₃imid. C14), 119.2 (CH₃imid. C22), 50.4 (NCH₃), 32.6 (NCH₃ CH₂), 32.2 (d, JPC = 22.2 Hz, C(H₂)), 29.9 (d, JPC = 13.3 Hz, C(H₂)), 28.7 (d, JPC = 25.2 Hz, CH₂Ph), 19.8 (NCH₃ CH₉CH₃), 13.7 (C). 31P[H] NMR (161.98 MHz, CD₂Cl₂): δ 32.0.

Synthesis of 3-butyl-1-(3-((di-tert-butylphosphonio)methyl)-phenyl)-1H-imidazol-3-ium tetrafluoroborate (LPh₂HBF₄). A solution of LPh·HBr (0.55 g, 1.25 mmol) and NaBF₄ (2.75 g, 25 mmol) in degassed ethanol was stirred overnight and evaporated to dryness. The oily residue was redissolved in CH₂Cl₂ and the solution was extracted three times with degassed water. The organic phase was dried over anhydrous MgSO₄ and concentrated under reduced pressure to afford a low melting point solid that was directly used in the next step. Yield: 0.40 g (0.90 mmol), 73%. 1H NMR (400.13 MHz, CD₂Cl₂): δ 9.18 (s, 1H, CH₃imid. H2), 7.63–7.55 (m, 3H, CH₃imid. H4/H5 + CH₃imid. H7/H9 + CH₃imid. H11), 7.49 (t, JHH = 7.8 Hz, 1H, CH₃imid. H8), 7.47 (t, JHH = JPh = 1.8 Hz, 1H, CH₃ Ph imid. H5/H4), 7.40 (d, JHH = JPh = 7.8 Hz, 1H, CH₃ Ph imid. H7/H9), 4.37 (t, JHH = 7.5 Hz, 2H, NCH₃), 2.95 (d, JPh = 2.7 Hz, 2H, CH₂Ph), 1.95 (quint, JHH = JPh = 7.5 Hz, 2H, NCH₃ CH₂), 1.45 (sext, JHH = JPh = 7.5 Hz, 2H, NCH₃ CH₂), 1.15 (d, JHH = 11.0 Hz, 6H, Caryl), 0.41 (br d, JHH = 7.3 Hz, 3H, CH₃). 31P[H] NMR (161.98 MHz, CD₂Cl₂): δ 37.4. 13C NMR (125.77 MHz, CD₂Cl₂): δ −1.0 (quint, JHH = 1.3 Hz).
equiv. (resp. 2.1 equiv.) of KN(SiMe3)2 in diethyl ether (10 mL). The organic phase was dried over degassed water. The solution remained unchanged. 1H NMR (400.13 MHz, toluene-d8): δ 8.20 (s, 1H, CHarom, H11), 7.67 (d, JHH = 7.8 Hz, 1H, CHarom, H7/H9), 7.22 (d, JHH = 7.6 Hz, 1H, CHarom, H9/H7), 7.15 (t, JHH = 7.8 Hz, 1H, CHarom, H8), 7.06 (d, JHC = 1.6 Hz, 1H, CHarom, H4/H5), 6.44 (br s, 1H, CHarom, H5/H4). 3.87 (t, JHP = 7.2 Hz, 2H, NCH3), 2.74 (s, 2H, CH2P), 1.84–1.75 (m, 2H, CH2P), 1.74–1.47 (m, 10H, CH2C2), 1.60 (quint, JHH = 7.4 Hz, 2H, NCH2CH2), 1.28–1.04 (m, 10H, CH2C2), 1.18 (sext, JHH = 7.4 Hz, 2H, NCH2CH2CH3), 0.78 (t, JHH = 7.3 Hz, 3H, CH3). 31P{1H} NMR (161.98 MHz, C6D6): δ 0.0.

Synthesis of 3-butyl-1-(3-((diphenylphosphino)methyl)-phenyl)-imidazol-2-ylidene (L0). Following the general procedure, L0 was synthesised from L0H2HBr (0.53 g, 1.02 mmol) and KN(SiMe3)2 (0.42 g, 2.12 mmol). Yield: 0.29 g (0.81 mmol), 79% (dark brown oil). 1H NMR (400.13 MHz, toluene-d8): δ 8.09 (q, JHH = JHP = 1.7 Hz, 1H, CHarom, H11), 7.58 (d, JHH = 7.9 Hz, 1H, CHarom, H7/H9), 7.23 (d, JHH = 7.8 Hz, 1H, CHarom, H4/H5), 6.52 (d, JHC = 1.6 Hz, 1H, CHarom, H11), 7.09 (d, JHH = 1.7 Hz, 1H, CHarom, H9/H7), 7.11 (t, JHH = 7.8 Hz, 1H, CHarom, H8), 5.81 (d, JHC = 1.6 Hz, 1H, CHarom, H4/H5), 3.85 (t, JHH = 7.3 Hz, 2H, NCH3), 2.71 (d, JHH = 2.3 Hz, 2H, CH2P), 1.60 (quint, JHH = 7.4 Hz, 2H, NCH2CH2), 1.19 (sext, JHH = 7.5 Hz, 2H, NCH2CH2CH3), 1.02 (d, JPH = 10.7 Hz, 18H, C(CH3)3), 0.79 (t, JHH = 7.4 Hz, 3H, CH3). 13C{1H} NMR (100.62 MHz, toluene-d8): δ 215.9 (CPh), 143.3 (d, JPC = 13.0 Hz, 142.9, 129.0, 127.3 (d, JDC = 9.7 Hz, 122.3 (d, JDC = 8.6 Hz), 119.7, 117.9, 116.9, 51.2 (NCH3), 34.0 (NCH2CH3), 31.9 (d, JDC = 24.3 Hz, C(CH3)3), 30.0 (d, JDC = 13.6 Hz, C(CH3)3), 29.1 (d, JDC = 25.8 Hz, CH2P), 20.2 (NCH2CH2CH3), 13.9 (CH3). 31P{1H} NMR (161.98 MHz, C6D6): δ 33.1.

Synthesis of 3-butyl-1-(3-((dicyclohexylphosphino)methyl)-phenyl)-imidazol-2-ylidene (L1). Following the general procedure, L1 was synthesised from L1H2HBr (0.057 g, 0.12 mmol) and KN(SiMe3)2 (0.026 g, 0.13 mmol). Yield: 0.040 g (0.10 mmol), 84% (dark-green oil). 1H NMR (300.17 MHz, C6D6): δ 7.78 (dm, JHH = 7.9 Hz, 1H, CHarom, H7/H9), 7.72 (q, JHH = JHP = 1.7 Hz, 1H, CHarom, H11), 7.39–7.30 (m, 4H, CHPh, 7.07–7.01 (m, 6H, CHarom), 7.01 (t, JHH = 7.8 Hz, 1H, CHarom, H8), 6.89 (d, JHH = 1.7 Hz, 1H, CHarom, H4/H5), 6.85 (dm, JHH = 7.8 Hz, 1H, CHarom, H9/H7), 6.44 (d, JHC = 1.7 Hz, 1H, CHarom, H5/H4), 3.86 (t, JHH = 7.2 Hz, 2H, NCH3), 3.24 (s, 2H, CH2P), 1.60 (quint, JHH = 7.3 Hz, 2H, NCH2CH2), 1.18 (sext, JHH = 7.4 Hz, 2H, NCH2CH2CH3), 0.79 (t, JHH = 7.4 Hz, 3H, CH3). 13C{1H} NMR (75.49 MHz, C6D6): δ 216.1 (CPh), 142.9, 139.09 (d, JPC = 16.5 Hz, CPh), 139.05 (d, JPC = 8.2 Hz), 133.4 (d, JDC = 18.6 Hz, CPh), 129.2 (d, JDC = 1.6 Hz), 128.8 (CPh), 128.6 (d, JDC = 6.4 Hz, CPh), 127.0 (d, JDC = 6.8 Hz), 122.0 (d, JDC = 6.7 Hz), 119.7, 118.8 (d, JDC = 2.7 Hz), 116.9, 51.2 (NCH2CH3), 36.3 (d, JDC = 16.8 Hz, CH3P), 33.8 (NCH2CH3), 20.0 (NCH2CH2CH3), 13.9 (CH3). 31P{1H} NMR (161.98 MHz, C6D6): δ –9.9.
Synthesis of the tetranuclear silver cluster \([\text{Ag}_2(\mu_1-\text{Br})_2(\mu_2-\text{PPh}_2\text{NC},\kappa\text{P}\text{NC}^{\text{NITRO}})](\text{BF}_4)_2\) (route b). L\(^{\text{Ph}}\)-2HB (0.40 g, 0.72 mmol) and Ag\(_2\)O (0.185 g, 0.80 mmol) were charged into a Schlenk flask along with molecular sieves 4 Å. Degassed acetonitrile (20 mL) was added and the mixture was stirred for 2 days at 40 °C under exclusion of light. After evaporation of the solvent under reduced pressure, the remaining slurry was extracted twice with CH\(_2\)Cl\(_2\), and the resulting solution was filtered over Celite® and concentrated to ca. 1 mL. Complex \([\text{Ag}_2(\mu_1-\text{Br})_2(\mu_2-\text{PPh}_2\text{NC},\kappa\text{P}\text{NC}^{\text{NITRO}})](\text{BF}_4)_2\) was precipitated by addition of Et\(_2\)O. The white powder was collected by filtration and dried under vacuum. Yield: 0.46 g (0.30 mmol), 83% based on the ligand. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et\(_2\)O in a CH\(_2\)Cl\(_2\) solution of the complex. Anal. Calcd for \(\text{C}_{52}\text{H}_{52}\text{Ag},\text{Br}_4\text{N}_4\text{P}_2\): C, 50.42; H, 4.50; N, 4.53. Found: C, 50.98; H, 4.42; N, 4.72. Examination of the \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra revealed the presence of the “head-to-tail” and “head-to-head” isomers in a ca. 4:1 \(\text{H}/\text{HH}\) ratio in CD\(_2\)Cl\(_2\) (see text) and 1:1 in CD\(_3\)CN.

\(^1\text{H}\) NMR (400.13 MHz, CD\(_2\)CN): \(\delta\) 0.80 (br q, \(\text{j}_{\text{HH}} = \text{j}_{\text{HAg}} = 1.7 \text{ Hz}, 0.8\text{H}, \text{CH}_{\text{mid}}\)), 6.73–7.22 (m, 11.6\text{H}, CH\(_{\text{arom}}\)), 7.17 (t, \(\text{j}_{\text{HH}} = \text{j}_{\text{HAg}} = 1.7 \text{ Hz}, 0.8\text{H}, \text{CH}_{\text{mid}}\)), 7.09 (t, \(\text{j}_{\text{HH}} = 7.9 \text{ Hz}, 0.2\text{H}, \text{CH}_{\text{arom}}\)), 7.04 (t, \(\text{j}_{\text{HH}} = 7.8 \text{ Hz}, 0.8\text{H}, \text{CH}_{\text{mid}}\)), 6.92 (s, 0.2H, CH\(_{\text{arom}}\)), 6.60 (d, \(\text{j}_{\text{HH}} = 7.7 \text{ Hz}, \text{CH}_{\text{arom}}\)), 4.30 (t, \(\text{j}_{\text{HH}} = 7.3 \text{ Hz}, 0.4\text{H}, \text{NCH}_{2}\)), 3.93 (Ab part of an ABX spin system with \(A = B = H\) and \(X = P\)) = 10.5, 4.6 Hz, CH\(_{2}\)), 3.89–3.82 (br s, 0.4H, CH\(_{2}\)), 1.91 (quint, \(\text{j}_{\text{HH}} = 7.4 \text{ Hz}, 0.4\text{H}, \text{NCH}_{2}\)), 1.82 (quint, \(\text{j}_{\text{HH}} = 7.4 \text{ Hz}, 1.6\text{H}, \text{NCH}_{2}\)), 1.40 (sex, \(\text{j}_{\text{HH}} = 7.4 \text{ Hz}, 2\text{H}, \text{NCH}_{2}\)), 1.03 (t, \(\text{j}_{\text{HH}} = 7.3 \text{ Hz}, 0.6\text{H}, \text{CH}_{2}\)), 0.96 (t, \(\text{j}_{\text{HH}} = 7.4 \text{ Hz}, 2.4\text{H}, \text{CH}_{2}\)). \(^{31}\text{P}\) NMR (125.77 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) peak not observed, 140.7 (CH\(_{arom}\)), 137.6 (CH\(_{arom}\)), 133.6 (d, \(\text{J}_{\text{H_P}} = 14.6 \text{ Hz}, \text{J}_{\text{H_P}} = 2.3 \text{ Hz}, \text{CH}_{\text{Ph}}\)), 132.1 (d, \(\text{J}_{\text{PC}} = 1.8 \text{ Hz}, \text{H}_{\text{Ph}}\)), 130.4 (d, \(\text{J}_{\text{PC}} = 5.4 \text{ Hz}, \text{CH}_{\text{arom}}\)), 129.9 (d, \(\text{J}_{\text{PC}} = 2.9 \text{ Hz}, \text{CH}_{\text{arom}}\)), 129.8 (d, \(\text{J}_{\text{PC}} = 10.4 \text{ Hz}, \text{CH}_{\text{Ph}}\)), 129.1 (d, \(\text{J}_{\text{PC}} = 36.7 \text{ Hz}, \text{J}_{\text{PC}} = 4.4 \text{ Hz}, \text{CH}_{\text{Ph}}\)), 126.3 (d, \(\text{J}_{\text{PC}} = 8.4 \text{ Hz}, \text{CH}_{\text{arom}}\)), 122.8 (d, \(\text{J}_{\text{PC}} = 5.5 \text{ Hz}, \text{CH}_{\text{arom}}\)), 122.7 (d, \(\text{J}_{\text{PC}} = 4.0 \text{ Hz}, \text{CH}_{\text{arom}}\)), 122.2 (d, \(\text{J}_{\text{PC}} = 6.3 \text{ Hz}, \text{CH}_{\text{arom}}\)), 52.3 (NCH\(_3\)), 34.4 (d, \(\text{J}_{\text{PC}} = 17.1 \text{ Hz}, \text{CH}_{3}\)), 33.9 (NCH\(_3\)), 19.9 (NCH\(_3\)).

**General procedure for the synthesis of silver(i) complexes \([\text{Ag}(\text{L}^{\text{Ph}})](\text{BF}_4)_2\)**

\(\text{L}^{\text{Ph}}\)-HBF\(_4\) and Ag\(_2\)O (0.55 equiv.) were charged in a Schlenk flask along with molecular sieves 4 Å. Degassed acetonitrile (15 mL) was added and the mixture was stirred for 2 days at 40 °C under exclusion of light. After evaporation of the solvent under reduced pressure, the remaining slurry was extracted twice with CH\(_2\)Cl\(_2\) and the resulting solution was filtered over Celite® and concentrated to ca. 1 mL. The complex \([\text{Ag}(\text{L}^{\text{Ph}})](\text{BF}_4)_2\) was precipitated with diethyl ether. The white powder was collected by filtration and dried under vacuum.

**Synthesis of \([\text{Ag}(\mu_1-\text{PPh}_2\text{NC},\kappa_\text{P}\text{NC}^{\text{NITRO}})](\text{BF}_4)_2\) (route b).** Following the general procedure, \([\text{Ag}(\text{L}^{\text{Ph}})](\text{BF}_4)_2\) was synthesised from \(\text{L}^{\text{Ph}}\)-HBF\(_4\) (0.12 g, 0.25 mmol) and Ag\(_2\)O (0.032 g, 0.14 mmol). Yield: 0.13 g (0.11 mmol), 85% based on the ligand. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et\(_2\)O in a CH\(_2\)Cl\(_2\) solution of the complex. Anal. Calcd for \(\text{C}_{52}\text{H}_{52}\text{Ag},\text{Br}_4\text{N}_4\text{P}_2\cdot0.6\text{CH}_2\text{Cl}_2\): C, 51.06%; H, 4.50%; N, 4.53%.
Under reduced pressure, the solid residue was washed with room temperature. The resulting clear solution was stirred at 183 Hz, \( \text{J}_\text{CNMR} \) (125.77 MHz, CD2Cl2): \( \delta \) 178.8 (two doublets, \( \text{J}_\text{pH} = 17.4 \text{ Hz}, \text{CH(C)} \)), \( \delta \) 1.29 (d, \( \text{J}_\text{pH} = 14.7 \text{ Hz}, \text{CH(C)} \)), \( \delta \) 1.04 (t, \( \text{J}_\text{HH} = 7.3 \text{ Hz}, \text{H}1, \text{H}3 \)), \( \delta \) 1.01 (t, \( \text{J}_\text{HH} = 7.4 \text{ Hz}, \text{H}2, \text{H}3 \)). \( 1^1\text{H} \) NMR (121.49 MHz, CD2Cl2): \( \delta \) 34.7 \( \text{br d}, \text{J}_\text{Cp} = 12.9 \text{ Hz}, \text{major} \text{C}_{\text{C}3} \), \( \delta \) 1.78 (two doublets, \( \text{J}_\text{pH} = 17.4 \text{ Hz}, \text{CH(C)} \)).

Following the general procedure, \([\text{CuBr}_2\text{L}^{(5\text{L})}]_2\) was synthesised from L5-BBr (0.18 g, 0.41 mmol) and mesityl copper (0.078 g, 0.43 mmol). Yield: 0.18 g (0.17 mmol), 85% based on the ligand. Single crystals suitable for X-ray diffraction were obtained by slow slow diffusion of toluene in a CH2Cl2 solution of the complex. Anal. Calcd for \( \text{Cu}_{16}\text{H}_{24}\text{Br}_2\text{N}_6\text{P}_4\text{C}_{100} \text{H}_{4} \): C, 55.66; H, 4.86; N, 4.92. Better elemental analyses and single crystals suitable for X-ray diffraction studies could not be obtained despite several attempts. \( 1^1\text{H} \) NMR (400.13 MHz, CD2Cl2): \( \delta \) 8.12 (d, \( \text{J}_\text{HH} = 7.3 \text{ Hz}, \text{H}1, \text{CH}(_{\text{C}2}) \)), \( \delta \) 7.44 (s, 1H, CH(_{\text{C}6}) H11), \( \delta \) 7.01 (t, \( \text{J}_\text{HH} = 7.6 \text{ Hz}, \text{H}1, \text{CH}(_{\text{C}6}) \)), \( \delta \) 2.98 (br s, 2H, NCH2CH2), \( \delta \) 1.78 (two doublets, \( \text{J}_\text{pH} = 7.4 \text{ Hz}, 2 \text{H}, \text{H}2, \text{H}3 \)).

Synthesis of \([\text{CuBr}[(\mu-\text{PPPh}_2\text{-NHC}k\text{xp}k\text{NHC})_2]]_2\) \([\text{CuBr}L^{(5\text{P})}]_2\) was synthesised from L5-BBr (0.13 g, 0.27 mmol) and mesityl copper (0.057 g, 0.31 mmol). Yield: 0.13 g (0.12 mmol), 90% based on the ligand. Anal. Calcd for \( \text{Cu}_{16}\text{H}_{24}\text{Br}_2\text{N}_6\text{P}_4\text{C}_{100} \text{H}_{4} \): C, 57.62; H, 5.02; N, 5.17. Found: C, 55.66; H, 4.86; N, 4.92. Better elemental analyses and single crystals suitable for X-ray diffraction studies could not be obtained despite several attempts. \( 1^1\text{C} \) NMR (250 MHz, CD2Cl2): \( \delta \) 183.7 (br s, \( \text{J}_\text{pH} = 13.8 \text{ Hz}, \text{CH}(_{\text{C}6})_3 \)), \( \delta \) 133.7 (d, \( \text{J}_\text{pH} = 25.4 \text{ Hz}, \text{CH}(_{\text{C}6})_3 \)), \( \delta \) 129.4 (CH(_{\text{C}6})_3), \( \delta \) 128.9 (d, \( \text{J}_\text{pH} = 8.5 \text{ Hz}, \text{CH}(_{\text{C}6})_3 \)), \( \delta \) 124.1 (br s, CH(_{\text{C}6})_3), \( \delta \) 99.2 (br s, CH(_{\text{C}6})_3), \( \delta \) 85.8 (t, \( \text{J}_\text{HH} = 7.3 \text{ Hz}, \text{H}1, \text{CH}(_{\text{C}6}) \)). \( 1^1\text{H} \) NMR (121.49 MHz, CD2Cl2): \( \delta \) 9.8.
Synthesis of [Au₄Cl₄(μ-P(tBu)₂)-NHCH₂P(3CNH)] ([Au₄Cl₄L₄₉])

To a solution of [Ag₄Br₄(L₄₉)] (0.076 g, 0.052 mmol) in CH₂Cl₂ (5 mL) was added a solution of [AuCl(THT)] (4 equiv., 0.066 g, 0.21 mmol) in CH₂Cl₂ (2 mL) under protection against light. A white precipitate appeared instantaneously and the resulting suspension was stirred overnight. Filtration through Celite® and evaporation of the solvent afforded [Au₄Cl₄L₄₉] as a white powder. Yield: 0.083 g (0.10 mmol), 97%. Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of Et₂O in a CH₂Cl₂ solution of the complex. Anal. Calc. for C₂₂H₃₅Au₂BrCl₂N₉P (823.34): C, 32.09; H, 4.28; N, 3.40. Found: C, 31.25; H, 4.13; N, 3.24. These experimental values fit better with the formula C₄₉H₆₅Au₂BrCl₂N₉P (845.57): C, 31.25; H, 4.17; N, 3.31, corresponding to partial halide exchange between AgBr and AuCl.¹

¹H NMR (400.13 MHz, CD₂Cl₂): δ 7.89 (s, 1H, CH₃om. H11), 7.74 (d, J₃HH = 1.6 Hz, 1H, CH₃mid.), 7.73 (d, J₃HH = 7.9 Hz, 1H, CH₃om.), H7/H9), 7.55 (d, J₃HH = 7.9 Hz, 1H, CH₃om. H9/H7), 7.47 (t, 1H, J₃HH = 7.9 Hz, 1H, CH₃om. H8), 7.18 (d, J₃HH = 1.9 Hz, 1H, CH₃mid.), 4.27 (t, J₃HH = 7.3 Hz, 2H, NCH₂H₂), 3.37 (d, J₃HH = 11.0 Hz, 2H, CH₂P). 19.6 (j, J₃HH = 7.4 Hz, 2H, NHC₆H₅CH₃) 1.42 (s, J₃HH = 7.4 Hz, 2H, NHC₆H₅CH₃) 1.39 (d, J₃HH = 15.1 Hz, 18H, C₆H₃(C₆H₃)₉), 0.99 (t, J₃HH = 7.4 Hz, 3H, CH₃).¹

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References
1 (a) E. Peris and R. H. Crabtree, Coord. Chem. Rev., 2004, 248, 2239–2246; (b) L. Cavallo, A. Correa, C. Costabile and H. Jacobsen, J. Organomet. Chem., 2005, 690, 5407–5413;
P. Nägeli, U. Herrlich, F. Rominger and P. Hofmann, Organometallics, 2013, 32, 181–191; (c) P. G. Ai, A. A. Danopoulos, P. Braunstein and K. Yu Monakhov, Chem. Commun., 2014, 50, 103–105; (d) C. C. Brown, F. Rominger, M. Limbach and P. Hofmann, Inorg. Chem., 2015, 54, 10126–10140; (e) P. G. Ai, A. A. Danopoulos and P. Braunstein, Inorg. Chem., 2015, 54, 3722–3724.

10 (a) W. A. Herrmann, C. Köcher, L. J. Grooßen and G. R. J. Artus, Chem. – Eur. J., 1996, 2, 1627–1636; (b) A. A. Danopoulos, S. Winston, T. Gelbrich, M. B. Hursthouse and R. P. Tooze, Chem. Commun., 2002, 482–483; (c) J. Wolf, A. Labande, J.-C. Daran and R. Poli, J. Organomet. Chem., 2006, 691, 433–443; (d) J. Wolf, A. Labande, J.-C. Daran and R. Poli, Eur. J. Inorg. Chem., 2008, 3024–3030; (e) G. Song, X. Li, Z. Song, J. Zhao and H. Zhang, Chem. – Eur. J., 2009, 15, 5535–5544; (f) E. Kühnel, I. V. Shishkov, F. Rominger, T. Oeser and P. Hofmann, Organometallics, 2012, 31, 8000–8011; (g) M. Brill, E. Kühnel, C. Scribani, F. Rominger and P. Hofmann, Dalton Trans., 2013, 42, 12861–12864; (h) M. Brill, D. Marrwitz, F. Rominger and P. Hofmann, J. Organomet. Chem., 2015, 775, 137–151.

11 (a) E. Bappert and G. Helmchen, Synlett, 2004, 1789–1793; (b) C.-C. Ho, S. Chatterjee, T.-L. Wu, K.-T. Chan, Y.-W. Chang, T.-H. Hsiao and H. M. Lee, Organometallics, 2009, 28, 2837–2847; (c) I. Abdellah, Y. Canac, C. D. Mboyi, C. Duhayon and R. Chauvin, J. Organomet. Chem., 2015, 776, 149–152.

12 (a) M. Raynal, X. Liu, R. Pattacini, C. Vallée, H. Olivier-Bourgigou and P. Braunstein, Dalton Trans., 2009, 7288–7293; (b) B. Vabre, Y. Canac, C. Duhayon, R. Chauvin and D. Zargarian, Chem. Commun., 2012, 48, 10446–10448; (c) X. Liu and P. Braunstein, Inorg. Chem., 2013, 52, 7367–7379; (d) B. Vabre, Y. Canac, C. Lepetit, C. Duhayon, R. Chauvin and D. Zargarian, Chem. – Eur. J., 2015, 21, 17403–17414; (e) T. Simler, P. Braunstein and A. A. Danopoulos, Angew. Chem., Int. Ed., 2015, 54, 13691–13695.

13 (a) H. M. Lee, J. Y. Zeng, C.-H. Hu and M.-T. Lee, Inorg. Chem., 2004, 43, 6822–6829; (b) S. Gischig and A. Togni, Organometallics, 2005, 24, 203–205; (c) T. Steinke, B. K. Shaw, H. Jong, B. O. Patrick and M. D. Fryzuk, Organometallics, 2009, 28, 2830–2836; (d) D. A. Vaalyaev, O. A. Filippov, N. Lugar, G. Lavigne and N. A. Ustynyuk, Angew. Chem., Int. Ed., 2015, 54, 6315–6319.

14 The Cambridge Structural Database, accessed Jan. 2016: F. Allen, Acta Crystallogr., Sect. B: Struct. Sci., 2002, 58, 380–388.

15 (a) P. L. Chiu and H. M. Lee, Organometallics, 2005, 24, 1692–1702; (b) H. Salem, M. Schmitt, U. Herrlich, E. Kühnel, M. Brill, P. Nägeli, A. L. Bogado, F. Rominger and P. Hofmann, Organometallics, 2013, 32, 29–46; (c) A. Marchenko, H. Koidan, A. Hurieva, O. Kuprijeva, Y. Vlasenko, A. Kostyuk, C. Tubaro, A. Lenarda, A. Biffs and C. Graiff, J. Organomet. Chem., 2014, 771, 14–23.

16 H. M. J. Wang and I. J. B. Lin, Organometallics, 1998, 17, 972–975.
