Coinage metal complexes with bridging hybrid phosphine–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, LCy, LRBu and LPh (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 LPh-ni(HBr) (n = 1, 2) with Ag2O gave the pseudo-cubane [Ag8Br8(LPh)8], isostructural to [Ag4Br4(LPh)4] (R = Cy, tBu) (T. Simler, P. Braunstein and A. A. Danopoulos, Angew. Chem., Int. Ed., 2015, 54, 13691), whereas metallation of LPh-HBF4 (R = Ph, tBu) led to the dinuclear complexes [Ag2(LPh)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, interconversion with the homo- leptic ‘head-to-head’ (HH) isomers is facilitated by ligand fluxionality. ‘Head-to-tail’ [Cu2Br2(LPh)2] (R = Cy, tBu) dinuclear complexes were obtained from LPh-HBr and [Cu5(Mes)5], Mes = 2,4,6-trimethylphenyl, which also feature bridging ligands and heteroleptic Cu centres. Although the various ligands LPh 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 [Ag8Br8(LPh)8] to AuI by reaction with [AuCl(THT)] (THT = tetrahydrothiophene) led to LRBu transfer and to the dinuclear complex [Au2Cl2(LPh)2] with one LPh ligand bridging the two Au centres. Except for the silver pseudo-cubanes, all other complexes do not exhibit metallophilic interactions.

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 (PdII, RuII), amination of aryl chlorides (PdII) 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, 1a and 1b, 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 PCC(NHC, ‘pincer’) complexes. Relevant PCC(NHC-P pincer and P2(CNHC)2 macrocyclic ligands 2f and 3, 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+, CuI or CuII are depicted in Fig. 2. This relative scarcity is surprising, considering the interest for air stable group 11 NHC.
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, a, RhI, a, PdII, f, g, 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 Cu³ precursor, or the reaction of the imidazolium salt with precursors featuring a coordinated base (e.g. copper(ii) acetate, mesitylcopper(i) [Cu₅(Mes)₅] and [CuN(SiMe₃)₂]).

Lastly, P–NHC gold(I) complexes are scarce (Fig. 3) but arouse 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 P–NHC-type (PCy₂, PrBu₂, or PPh₂) 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 (SiHMeCl₂ or SiHCl₃) reduction²⁰ of readily available phosphoryl-imidazolium salts has ample literature precedence,⁶b,¹⁰a,¹⁵b,²¹ including attempted preparation of precursors of similar topology to those described below.¹²c 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 LtBu·2HBr were obtained by quaternisation of dicyclohexyl- and di-tert-butylphosphine in acetonitrile,¹²c and converted to the corresponding phosphate-imidazolium salts LCy·HBr and LtBu·HBr by treatment with NEt₃. Successful single deprotonation was confirmed in the ¹H-NMR spectra by the disappearance of the deshielded signal due to the acidic P–H proton (¹J_P–H ≈ 480–490 Hz). Singlets at δ 5.8 and 32.0 ppm for LCy·HBr and LtBu·HBr, respectively, were observed in the ³¹P {¹H}-NMR spectra. Due to the relative air-sensitivity of the triaryl-phosphine products, borane-protection of the phosphine in LCy·HBr was carried out and yielded LCy·HBr·BH₃ as an air-stable crystalline solid, the structure of which is shown in Fig. 4 (left).

When an analogous synthetic route was applied to LPh·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 (LiPPh₂), generated in situ, was reacted with A at low temperature (Scheme 1). Formation of LPh·HBr was confirmed by a phosphorus resonance at δ −8.5 ppm. In the different LR precursors, the imidazolium backbone protons usually gave

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**Scheme 1**

Introduction of phosphine moieties to obtain hybrid P-NHC-type ligands. The synthesis of LCy·2HBr and LtBu·2HBr has been reported in a previous communication.¹²c
rise in the $^1$H-NMR spectra to apparent triplets (overlapping dd, $J_{HH} \approx 1.6–1.8$ Hz), and the NC$_3$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$_3$H$_N$ proton and the bromide anion, in addition to the high directionality of the C–H···Br$^-$ interaction.$^{22}$ Anion metathesis of LPh·HBr and LtBu·HBr with excess NaBF$_4$ resulted in the corresponding LPh·HBF$_4$ and LtBu·HBF$_4$ salts (see Experimental section). In their $^1$H-NMR spectra, the signal of the NC$_3$H$_N$ proton appeared shifted upfield ($\delta$ 9.05 and 9.18 ppm, respectively)$^{23}$, consistent with weaker hydrogen bonding compared to the bromide salts.

**Formation of the free carbenes**

The free carbenes L$^{Cy}$, L$nBu$ and L$^{Ph}$ were obtained by the double deprotonation of the corresponding phosphonium-imidazolium L$^R$-2HBr or the single deprotonation of phosphine-imidazolium L$^Ph$-HBr salts with stoichiometric amounts of KN(SiMe$_3$)$_4$ (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$^R$, 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$^{Ph}$-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$^{Ph}$)$_2$] 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 δ 3.2 ppm in the 1H-NMR and 31P-NMR spectrum, respectively, confirmed NHC formation and coordination of the P atom. The absence of P–Ag couplings (107Ag 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 31P-NMR timescale.\(^{12e}\) In the 13C-NMR spectrum, the coordinated C\(^{\text{NHC}}\) was detected as a broad singlet at δ 186.5 ppm, in the typical range for NHC–Ag complexes.\(^{25}\) The absence of 13C–107/109Ag coupling has been reported in related NHC–AgX clusters,\(^{12a,e,23,26}\) and points towards dynamic behaviour in solution\(^{27}\) and a high lability of the NHC–Ag bond.\(^{16,28}\)

The structure of [Ag\(_4\)(halide)\(_4\)L\(_2\)] (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\(_{\text{Ph}}\)–P–CNHC ligands each span the Ag⋯Ag diagonal of two parallel Ag\(_2\)Br\(_2\) faces of the cube, forming 9-membered dometalocycles, as observed with a closely related phosphinite–NHC ligand\(^{12a,c}\) and in the structures of [Ag\(_4\)(halide)\(_4\)L\(_2\)] (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)\(_4\)L\(_2\)] cubane structures have been described with L = phosphine ligands,\(^{14}\) and recently obtained with bidentate ligands incorporating NHC donors (bis-NHC\(^{13a,c,32}\) or P–NHC–type\(^{10g,12a,c,e}\) 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 P1).

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\(_S\), the Ag–C\(^{\text{NHC}}\) and Ag–P bond distances are comparable, while Ag–P is marginally longer in [Ag\(_4\)Br\(_4\)(L\(_{\text{Ph}}\))\(_2\)] (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\(_{\text{Ph}}\))\(_2\)] and 3.089 Å for [Ag\(_4\)Br\(_4\)(L\(_S\))\(_2\)], 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\(_S\))\(_2\)] (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.

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**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.
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 LPh-HBF₄ with 0.5 mole equiv. of Ag₂O in acetonitrile led to the complex [Ag₂(L₄Ph)₂(BF₄)₂] (Scheme 3). Examination of its ¹H and ³¹P{¹H} NMR spectra revealed an equilibrium involving two isomers in solution. Notably, dissolution in CD₃CN gave rise, in the ³¹P{¹H} NMR spectrum, to two sets of two doublets (total 8 lines) observed at δ 21.3 (two doublets, ⁴J_P-Ag ≈ 500 Hz, ⁴J_P-Ag ≈ 580 Hz) and 11.2 ppm (two doublets, ⁵J_P-Ag ≈ 475 Hz, ⁵J_P-Ag ≈ 550 Hz) in a 1 : 1.1 ratio, respectively. Evaporation of the solution and re-dissolution in CD₂Cl₂ 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 CD₃CN, the ¹³C{¹H}-NMR spectrum was recorded in CD₂Cl₂ 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 CH₂Cl₂ or CH₃CN solutions were attempted. Products corresponding to [Ag₂(L₄Ph)₂(BF₄)₂(solvent)] were obtained from both solvents, which crystallized in different space groups as ‘head-to-tail’ (HT) (hetero-leptic) 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 crystallized (with a possible shift of the equilibrium between ‘head-to-head’ (HH) (homoleptic) and HT isomers upon crystallisation).

In the structure of [Ag₂(L₄Ph)₂(BF₄)₂]·2CH₂Cl₂ (Fig. 7, left), the two L₄Ph ligands bridge two Ag metal centres (Ag₁…Ag₂ 3.561(1) Å) in a ‘head-to-tail’ arrangement. The C₄NHC—Ag—P angles slightly deviate from linearity (C₁—Ag₁—P1 172.7(2)°) 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-type silver complexes,¹⁰g,¹₂c,¹₅b the linear coordination geometry is also encountered in bis-NHC silver complexes with non-coordinating anions.²₃,³⁴ The Ag—C₄NHC bond distances follow trends observed for related complexes,²₅d 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).¹⁴

In order to gain insight into the solution behaviour of [Ag₂(L₄Ph)₂(BF₄)₂], the corresponding [Ag₂(L₄Ph)₂(BF₄)₂] was similarly prepared (Scheme 3). In this case too, ¹H- and ³¹P{¹H}-NMR analysis in CD₂Cl₂ revealed the presence of two isomers, in a 1 : 2 ratio, the nature of which could be determined by perusal of the ¹³C{¹H}-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

### Scheme 3

**Synthesis of the silver complexes** [Ag₂(L₄Ph)₂(BF₄)₂] (R = Ph, tBu) and ‘head-to-tail’ (HT)/‘head-to-head’ (HH) isomerisation in solution (see text). Yields are based on L₄Ph.

### Table 1

Selected interatomic distances (Å) and angles [°] for the Ag(I) complexes [Ag₄Br₄(L₄Ph)₂] and [Ag₂(L₄Ph)₂(BF₄)₂]·2CH₂Cl₂

<table>
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<th>Complex</th>
<th>Interatomic Distances (Å)</th>
<th>Αngle (°)</th>
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<tr>
<td>[Ag₄Br₄(L₄Ph)₂]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag1…Ag2</td>
<td>3.101(1)</td>
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</tr>
<tr>
<td>Ag1…Ag3</td>
<td>3.076(1)</td>
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</tr>
<tr>
<td>Ag1…Ag4</td>
<td>3.821(1)</td>
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</tr>
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<td>Ag1…Ag5</td>
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<td></td>
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<tr>
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<tr>
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<td>Ag1—Br4</td>
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<td>2.381(1)</td>
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<tr>
<td>[Ag₂(L₄Ph)₂(BF₄)₂]</td>
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<tr>
<td>[Ag₂(L₄Ph)₂(BF₄)₂]·2CH₂Cl₂</td>
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<td>Ag1—P1</td>
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<tr>
<td>Ag2—P2</td>
<td>2.113(6)</td>
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* 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.
region $\delta$ 180–177 ppm, corresponding to the $C^{NHC}$–Ag signals was successfully simulated, revealing two different $C^{NHC}$–Ag environments associated with the different isomers (Fig. 8): the two doublets centred at $\delta$ 178.8 ppm ($^{1}J_{C-107Ag} = 183$ Hz, $^{1}J_{C-109Ag} = 212$ Hz) were attributed to an isomer with homoleptic Ag$^{+}$ centres and symmetrical NHC–Ag–NHC coordination (HH isomer), while two doublets of doublets at $\delta$ 178.5 ppm ($^{1}J_{C-107Ag} = 190$ Hz, $^{1}J_{C-109Ag} = 219$ Hz, $^{2}J_{P-Ag-C} = 62$ Hz) were assigned to the second and major isomer, with heteroleptic NHC–Ag–P connectivity (HT isomer). Further indication of the nature of the former isomer was obtained from the observation in $^{13}C$-NMR of ‘virtual’ triplets of the $X_{m}AA'X'_{n}$ ($X = X' = C$, $A = A' = P$) spin system involving the carbon atoms directly bound to phosphorus, resulting from a strong $^{2}J_{P-Ag-P}$ coupling between trans-coordinated P donors.\(^{35}\)

Interestingly, for all $[Ag_{2}(L^{Ph})_{2}](BF_{4})_{2}$ (R = Ph, tBu) complexes, the $^1$H-NMR signals for the NHC backbone protons were detected as apparent triplets, likely due to $^{3}J_{HAg}$ and $^{2}J_{HH}$ coupling constants falling in the same range.\(^{36}\)

An X-ray diffraction study of $[Ag_{2}(L^{Ph})_{2}](BF_{4})_{2}$ also revealed a ‘head-to-tail’ coordination of the bidentate ligand (Fig. 7, right), with two crystallographically independent but very similar dinuclear complexes in the unit cell (Table 1). The bond distances and angles in $[Ag_{2}(L_{R})_{2}]^{2+}$ 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(i) 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\(^{1}\) complexes by transmetallation from \([\text{Ag}_4\text{Br}_4(\text{LR})_2]\) or by reaction of the phosphonium–imidazolium \(\text{LR}\cdot2\text{HBr}\) salts with mesitylcopper(I) \([\text{Cu}_5(\text{Mes})_5]\), which has been used before to form Cu\(^{1}\) NHC complexes from imidazolium salts. The coordination chemistry of the \(\text{LR}\) ligands with Cu\(^{1}\) was further investigated by using the monoprotic proligands \(\text{LR}\cdot\text{HBr}\).

Reaction of \(\text{LR}\cdot\text{HBr} (\text{R} = \text{Ph}, \text{tBu}, \text{Cy})\) with \([\text{Cu}_5(\text{Mes})_5]\) resulted in the formation of the corresponding \([\text{Cu}_2\text{Br}_2(\text{LR})_2]\) complexes in good yields (Scheme 4). Completion of the reaction was evidenced by \(^1\text{H}\) NMR spectroscopy (i.e. disappearance of the imidazolium \(\text{NCN}\) signal). For all three Cu\(^{1}\) complexes, the \(31\text{P}\{^1\text{H}\}\)-NMR spectra revealed a singlet assignable to the coordinated P donor, only slightly shifted from the position observed in the starting \(\text{LR}\cdot\text{HBr}\). In the \(13\text{C}\{^1\text{H}\}\)-NMR spectra, the Cu\(^{1}\)–C\(\text{NHC}\) resonance was detected in the region \(\delta 183–186\) ppm, typical for Cu\(^{1}\)–NHCs. The \(\text{CNHC}\) signal was observed as a doublet \((J_{\text{PC}} \approx 46–47\) Hz) for the dialkyl phosphine derivatives or as a broad signal for \([\text{Cu}_2\text{Br}_2(\text{LPh})_2]\), possibly due to a different rate of fluxionality of the \(\text{C}_{\text{NHC}}\)–Cu bonds in these two complexes. In the \(^3\text{H}\)-NMR spectrum of \([\text{Cu}_2\text{Br}_2(\text{L}^{\text{nu}})\text{Ph}_2]\), the line-shape of the signals for the methylene protons was field-dependent, pointing towards a dynamic process in solution.

The structures of \([\text{Cu}_2\text{Br}_2(\text{L}^{\text{Cy}})_2]\) and \([\text{Cu}_2\text{Br}_2(\text{L}^{\text{nu}})\text{Ph}_2]\) were determined crystallographically and are depicted in Fig. 9. Both complexes crystallised as dimers with two \(\text{LR}\) ligands bridging the two copper centres, reminiscent of the coordination behaviour of the ligands in \([\text{Ag}_2(\text{LR})_2][\text{BF}_4]\). 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–C\(\text{NHC}\) 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\(^{1}\) 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\(^{1}\) complexes in solution, we undertook a variable temperature (VT) \(^1\text{H}\) NMR study of \([\text{Cu}_2\text{Br}_2(\text{L}^{\text{nu}})\text{Ph}_2]\) in CD\(_2\)Cl\(_2\) prompted by its relatively simple line-shape compared to the \(\text{L}^{\text{Ph}}\) and \(\text{L}^{\text{Cy}}\) complexes.
analogues (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 (H₉). At this temperature, the signal of the methylene protons (H₈) was split into two complex multiplets, due to the geminal 2JHH and 2JHP coupling in an ABX (A = B = H, X = P) spin system. Interestingly, the NC₃H₂ protons (H₇) of the NHC wingtip also appeared as diastereotopic. The backbone H₆ proton, closer to the aryl spacer, gives rise to a doublet at this temperature owing to 3JHH 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 (H₇) 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’ co-ordinated dimers by ligand (hemi)lability. 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 [Cu₂(Mes)₂] with the phosphonium–imidazolium L⁻²HBr, or the transmetallation of the corresponding [Ag₄Br₄(L⁻³)] cubanes with 4 mole equiv. of [CuBr·SMe₂] (R = Cy, tBu) gave rise to the tetranuclear clusters [Cu₄Br₄(L⁻³)]₂.¹²e Metrical data regarding the di- and tetranuclear Cu² complexes are reported in Table 2.

The longer Cu–C₃NHC and Cu–P bond distances in the [Cu₄Br₄(L⁻³)] complexes (mean distances ca. 1.948 and 2.228 Å, respectively) in comparison to the [Cu₂Br₂(L⁻⁵)] 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(L⁻³)]₂ (R = Cy, tBu) and comparison with [Cu₄Br₄(L⁻³)]₂

<table>
<thead>
<tr>
<th></th>
<th>[Cu₂Br₂(L⁻³)]₂</th>
<th>[Cu₂Br₂(L⁻⁵)]_2⁡ab</th>
<th>[Cu₄Br₄(L⁻³)]₂</th>
</tr>
</thead>
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<tr>
<td>Cu₁⋯Cu₂</td>
<td>6.899(1)</td>
<td>7.138(1)/6.836(1)</td>
<td>2.790(1)</td>
</tr>
<tr>
<td>Cu₁⋯Br₁</td>
<td>2.497(1)</td>
<td>2.453(1)/2.493(1)</td>
<td>2.442(1)</td>
</tr>
<tr>
<td>Cu₂⋯Br₂</td>
<td>2.483(1)</td>
<td>2.438(1)/2.493(1)</td>
<td>2.503(1)</td>
</tr>
<tr>
<td>Cu₁⋯P₂</td>
<td>2.231(2)</td>
<td>2.222(2)/2.230(2)</td>
<td></td>
</tr>
<tr>
<td>Cu₂⋯P₁</td>
<td>2.237(2)</td>
<td>2.217(2)/2.230(2)</td>
<td>2.211(2)</td>
</tr>
<tr>
<td>C₁⋯Cu₁</td>
<td>1.960(6)</td>
<td>1.952(6)/1.947(6)</td>
<td>1.903(5)</td>
</tr>
<tr>
<td>Cu₂⋯C₂/C₂7</td>
<td>1.938(6)</td>
<td>1.943(6)/1.947(6)</td>
<td></td>
</tr>
<tr>
<td>P₂⋯Cu₁−Br₁</td>
<td>114.8(1)</td>
<td>109.7(1)/142.4(2)</td>
<td></td>
</tr>
<tr>
<td>P₂⋯Cu₁–C₁</td>
<td>145.1(2)</td>
<td>137.9(2)/107.5(1)</td>
<td></td>
</tr>
<tr>
<td>C₁⋯Cu₁–Br₁</td>
<td>100.0(2)</td>
<td>112.2(2)/110.1(2)</td>
<td></td>
</tr>
<tr>
<td>∑ angles around Cu₁</td>
<td>359.9</td>
<td>359.8/360.0</td>
<td></td>
</tr>
<tr>
<td>∑ angles around Cu₂</td>
<td>360.0</td>
<td>360.0/360.0</td>
<td></td>
</tr>
</tbody>
</table>

a Data taken from ref. 12. b 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 \(\text{Cu}^+)\) always led to tetranuclear complexes,\(^{12}\) we wondered what would happen with \(\text{Au}^+)\). Reaction of \([\text{Ag}_4\text{Br}_4(L^{\text{Bu}})_2]\) with 4 mole equiv. of \([\text{AuCl}(\text{THT})]\) led to the homodinuclear gold complex \([\text{Au}_2\text{Cl}_2(L^{\text{Bu}})]\) (Scheme 5). \(^{31}\text{C}^1\text{H})\)-NMR spectral analysis supported the NHC transmetallation as a downfield singlet was detected at \(\delta\) 170.3 ppm, in a range typical for \(\text{Au}^+)\-C^\text{NHC}\) functionalities.\(^{40}\) A singlet at \(\delta\) 79.0 ppm in the \(^{31}\text{P}^1\text{H})\)-NMR spectrum also confirmed concomitant phosphine transfer to gold. However, a minor peak was observed at \(\delta\) 80.1 ppm and ascribed to analogous complexes originating from partial halide scrambling (\(\text{Cl}/\text{Br}\)); this was also supported by elemental analysis (cf. Experimental section).

The structure of \([\text{Au}_2\text{Cl}_2(L^{\text{Bu}})]\) (Fig. 11) revealed an approximate linear coordination of the \(\text{Au}^+)\) centres (P–Au–Cl: 177.7(1)° and C^\text{NHC}–Au–Cl: 176.4(2)°), common for \(\text{NHC}\) gold(i) complexes. The Au–C^\text{NHC} (1.985(5) Å) and Au–P (2.239(1) Å) bond distances are in the expected range.\(^{19,40}\) Contrary to a recent report by Roesky 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 \(\text{Au}–\text{Au}\) 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 \([\text{Ag}_4\text{Br}_4(L^{\text{Bu}})_2]\) with 2 mole equiv. of \([\text{AuCl}(\text{THT})]\) 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 \([\text{Ag}_4\text{Br}_4(L^{\text{Bu}})_2]\) motif comprising a distorted \(\text{Ag}_4\text{Br}_4\) cubane core, bridging \(L^R\) ligands and weak metallophilic interactions; (iii) in the presence of the non-coordinating \(\text{BF}_4^-)\), \([\text{Ag}_4(L^R)_2][(\text{BF}_4)_2]\) 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 \([\text{Ag}_4\text{Br}_4(L^R)_2]\) with \([\text{Ir(COD)}(\mu-\text{Cl})]_2\)\(^{12}\) (v) dinuclear \([\text{Cu}_2\text{Br}_2(L^R)_2]\) complexes with bridging ligands were easily accessible from \(L^R\)-HBr and \([\text{Cu}_2(\text{Mes})_2]\) and are also non-rigid in solution; (vi) transmetallation of \([\text{Ag}_4\text{Br}_4(L^R)_2]\) with \([\text{AuCl}(\text{THT})]\) 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.\textsuperscript{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 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. CD₆D₆ and toluene-δ₈ were distilled over KH; other deuterated solvents were dried over 4 Å (CD₂Cl₂ and CDCl₃) or 3 Å (CD₃OD) molecular sieves, deceased by freeze–pump–thaw cycles, and stored under argon. Mesityl copper(II)\textsuperscript{13} and [AuCl(THT)]\textsuperscript{12} 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-bromomethylphenyl)-3-butyl-1H-imidazol-3-ium bromide (A), L⁵⁵₂Br⁻, 1⁴⁵⁸₂₄Br⁻, [AgBr₂(L⁵⁸₂)], [AgBr₂(L⁶⁹₂)] and [CuBr₂(L⁷⁰₂)] has already been reported in a recent communication.\textsuperscript{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 protio solvent (¹H), the solvent (¹³C) or externally (³¹P, ¹¹B). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicities 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 JPC 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).

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)methyl-phenyl)-1H-imidazol-3-ium bromide (L⁵⁵₂-HBr).** To a solution of L⁵⁵₂·2HBr (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 L⁵⁵₂-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 C₂₆H₄₉BrN₅P (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, JHH = 1.6 Hz, 1H, CH₉imid. H₂), 7.67 (d, JHH = 7.8 Hz, 1H, CH₉arom. H7/H9), 7.64 (t, JHH = 1.7 Hz, 1H, CH₉imid. H4/H5), 7.60 (br s, 1H, CH₉arom. H11), 7.57 (t, JHH = 1.7 Hz, 1H, CH₉imid. H5/H4), 7.47 (t, JHH = 1.7 Hz, 1H, CH₉arom. H8), 7.42 (d, JHH = 7.8 Hz, 1H, CH₉imid. H9/H7), 4.57 (t, JHH = 7.4 Hz, 2H, NCH₂), 2.90 (br s, 2H, CH₂P), 1.98 (quint, JHH = 7.5 Hz, 2H, NCH₂CH₂), 1.81–1.63 (m, 10H, Cy), 1.63–1.54 (m, 2H, Cy), 1.44 (sext, JHH = 7.5 Hz, 2H, NCH₂CH₂CH₂), 1.31–1.06 (m, 10H, Cy), 0.99 (t, JHH = 7.4 Hz, 3H, CH₃). ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂): δ 144.8 (d, JPC = 10.0 Hz, CH₉arom. C10), 136.7 (CH₉imid. C2), 134.9 (CH₉arom. C6), 131.5 (d, JPC = 7.1 Hz, CH₉arom.), 130.6 (CH₉arom.), 122.9 (CH₉arom.), 122.4 (d, JPC = 8.2 Hz, CH₉arom.), 120.7 (CH₉arom.), 119.4 (CH₉arom.), 50.4 (NCH₂), 33.9 (d, JPC = 14.9 Hz, CH₂Cy), 32.6 (NCH₂CH₂), 30.2 (d, JPC = 13.1 Hz, CH₂Cy), 29.7 (d, JPC = 9.1 Hz, CH₂Cy), 29.3 (d, JPC = 21.7 Hz, CH₃P), 27.64 (d, JPC = 10.8 Hz, CH₂Cy), 27.56 (d, JPC = 8.3 Hz, CH₂Cy), 26.8 (s, CH₂Cy), 19.8 (NCH₂CH₂CH₂), 13.7 (CH₃). ³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂): δ 5.8.

**Synthesis of 3-butyl-1-(3-(dicyclohexylphosphino)methyl-phenyl)-1H-imidazol-3-ium bromide borane adduct (L⁵⁵₂-HBr·BH₃).** To a suspension of L⁵⁵₂-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 L⁵⁵₂-HBr·BH₃. Anal. Calcd. for C₂₆H₄₉BrN₅P (503.33): 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, JHH = 1.7 Hz, 1H, CH₉imid. H2), 7.91 (dm, JHH = 8.0 Hz, 1H, CH₉arom. H7/H9), 7.80 (q, JHH = JPH = 1.8 Hz, 1H, CH₉arom. H11), 7.69 (t, JHH = JHH = 1.8 Hz, 1H, CH₉imid. H5/H4), 7.52 (t, JHH = 7.9 Hz, 1H, CH₉arom. H8), 7.37 (t, JHH = JHH = 1.8 Hz, 1H, CH₉imid. H5/H4).

![Fig. 12 Atom numbering used for the assignment of the NMR resonances.](Image 1)

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overnight and evaporated to dryness. 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 evaporated to dryness under reduced pressure. Addition of a mixture of Et2O and pentane precipitated Lm-HBr as a white powder that was isolated by filtration and dried under vacuum. Yield: 0.72 g (1.64 mmol), 65%. Anal. Caled for C23H28BrN4P (439.41): C, 60.13; H, 8.26; N, 6.38. Found: C, 59.90; H, 8.23; N, 6.87. 1H NMR (500.13 MHz, CD2Cl2): δ 11.17 (t, JHH = 1.6 Hz, 1H, CHimid. H2), 7.71 (s, 1H, CHarom. H11), 7.66 (t, JHH = 1.8 Hz, 1H, CHimid. H4/H5), 7.64 (d, JHH = 8.2 Hz, 1H, CHarom. H7/H9), 7.61 (t, JHH = JHF = 1.7 Hz, 1H, CHimid. H5/H4), 7.52 (d, JHF = 7.8 Hz, 1H, CHarom. H9/H7), 7.46 (t, JHH = 7.8 Hz, 1H, CHarom. H8), 4.57 (t, JHF = 7.2 Hz, 2H, CH2), 2.94 (d, JHF = 2.6 Hz, 2H, CH2P), 1.97 (quint, JHF = JHF = 7.5 Hz, 2H, NCH2CH2), 1.43 (sext, JHF = 7.5 Hz, 2H, NCH2CH2), 1.13 (d, JPH = 11.0 Hz, 18H, C(CH3)3), 0.98 (t, JHH = 7.4 Hz, 3H, CH3). 13C {1H} NMR (125.77 MHz, CD2Cl2): δ 146.0 (d, JPC = 13.7 Hz, 1H, CHarom. C10), 136.6 (CHimid. C2), 134.8 (CHarom. C6), 131.8 (d, JPC = 8.7 Hz, CHarom.), 130.5 (CHarom.), 123.0 (CHarom.), 122.7 (d, JPC = 9.7 Hz, CHarom.), 120.8 (CHarom.), 119.2 (CHarom.), 50.4 (NCH2), 32.6 (NCH2CH2), 32.2 (d, JPC = 22.2 Hz, C(CH3)2), 29.9 (d, JPC = 13.3 Hz, C(CH3)3), 28.7 (d, JPC = 25.2 Hz, CH2P), 19.8 (NCH2CH2CH3), 13.7 (CH3). 31P {1H} NMR (161.98 MHz, CD2Cl2): δ 32.0.

Synthesis of 3-butyl-1-[(d-tert-butylphosphino)methyl]-phenyl]-1H-imidazol-3-ium bromide (LPh-HBr). To a solution of LPh-HBr (0.35 g, 0.73 mmol) in CH2Cl2 (10 mL) was added methanol (0.1 mL, 79 mg, 2.5 mmol) and, dropwise, bromotrimethylsilane (0.11 mL, 128 mg, 0.84 mmol). After 2 h of stirring at room temperature, the solution was concentrated to ca. 2 mL under reduced pressure. Addition of Et2O precipitated LPh-HBr as an off-white powder that was collected by filtration and dried under vacuum. Yield: 0.40 g (0.72 mmol), 98%. 1H NMR (500.13 MHz, CD2Cl2): δ 11.19 (t, JHH = 1.7 Hz, 1H,
CH\textsubscript{mid} (H2), 10.89 (br d, \(\delta\) 7.8 Hz, NC\textsubscript{3}), 9.64 (s, CH\textsubscript{mid}, H3), 8.38 (br s, 1H, CH\textsubscript{amorn}, H11), 8.27 (dd, \(\delta\) 14.0 Hz, \(\delta\) 7.5 Hz, 4H, CH\textsubscript{PPm}), 7.76 (dt, \(\delta\) 8.3 Hz, \(\delta\) 7.5 Hz, 1H, CH\textsubscript{amorn}, H7), 7.67–7.61 (m, 3H, CH\textsubscript{amorn} H9 + 2 CH\textsubscript{PPm}), 7.54 (dt, \(\delta\) 7.9 Hz, \(\delta\) 7.7 Hz, JH = 3.2 Hz, 4H, CH\textsubscript{PPm}), 7.52 (overlapping t, \(\delta\) 8.3 Hz, 1H, CH\textsubscript{mid} H4), 6.90 (t, \(\delta\) 7.7 Hz = 8.8 Hz, 1H, CH\textsubscript{amorn}, H8), 5.01 (d, \(\delta\) 9.1 Hz = 16.1 Hz, 2H, CH\textsubscript{PPm}), 4.41 (t, \(\delta\) 7.4 Hz = 2H, NCH\textsubscript{2}), 1.97 (quint, \(\delta\) 8.0 Hz = 14.0 Hz, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 1.40 ( sext, \(\delta\) 7.9 Hz = 7.5 Hz, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 0.96 (t, \(\delta\) 7.4 Hz = 7.4 Hz, 3H, CH\textsubscript{3}).

**Synthesis of 3-butyl-1-(3-((diphenylphosphino)methyl)phenyl)-imidazol-2-ylidine (L\textsubscript{1Hm}**). Following the general procedure, L\textsubscript{1Hm} was synthesised from L\textsubscript{1Hm}·2HBr (0.53 g, 1.02 mmol) and KN(SiMe\textsubscript{3})\textsubscript{2} (0.42 g, 2.12 mmol). Yield: 0.29 g (81 mmol), 79% (dark brown oil).

**Synthesis of 3-butyl-1-(3-((dicyclohexylphosphino)methyl)phenyl)-imidazol-2-ylidine (L\textsubscript{1cH})**. Following the general procedure, L\textsubscript{1cH} was synthesised from L\textsubscript{1cH}·2HBr (0.057 g, 0.12 mmol) and KN(SiMe\textsubscript{3})\textsubscript{2} (0.026 g, 0.13 mmol). Yield: 0.040 g (10 mmol), 84% (dark-green oil).

**Synthesis of 3-butyl-1-(3-((dicyclohexylphosphino)methyl)phenyl)-imidazol-2-ylidine (L\textsubscript{1cH})**. Following the general procedure, L\textsubscript{1cH} was synthesised from L\textsubscript{1cH}·2HBr (0.20 g, 0.41 mmol) and KN(SiMe\textsubscript{3})\textsubscript{2} (0.088 g, 0.44 mmol). Yield: 0.15 g (37 mmol), 90%. The oil turned green over a period of 1 h even when stored under inert atmosphere, however spectroscopic data remained unchanged. \(^1\)H NMR (400.13 MHz, CD\textsubscript{4}D\textsubscript{2}): \(\delta\) 8.20 (s, 1H, CH\textsubscript{amorn}, H11), 7.67 (d, \(\delta\) 7.4 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H7/H9), 7.22 (d, \(\delta\) 7.9 Hz = 7.6 Hz, 1H, CH\textsubscript{amorn} H5/H6), 7.37–7.35 (m, 4H, CH\textsubscript{PPm}), 7.07–7.01 (m, 6H, CH\textsubscript{PPm}), 7.01 (t, \(\delta\) 7.8 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H7/H9), 7.04 (m, \(\delta\) 7.8 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H5/H6), 7.00 (q, \(\delta\) 7.5 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H4/H5), 6.94 (br s, 1H, CH\textsubscript{amorn}, H11), 3.38 (d, \(\delta\) 8.0 Hz = 7.8 Hz, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 2.54 (t, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}), 1.93 (s, 2H, CH\textsubscript{PPm}), 1.76 (d, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}), 1.38 (m, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}).

**Synthesis of 3-butyl-1-(3-((dicyclohexylphosphino)methyl)phenyl)-imidazol-2-ylidine (L\textsubscript{1cH})**. Following the general procedure, L\textsubscript{1cH} was synthesised from L\textsubscript{1cH}·2HBr (0.20 g, 0.41 mmol) and KN(SiMe\textsubscript{3})\textsubscript{2} (0.088 g, 0.44 mmol). Yield: 0.15 g (37 mmol), 90%. The oil turned green over a period of 1 h even when stored under inert atmosphere, however spectroscopic data remained unchanged. \(^1\)H NMR (400.13 MHz, CD\textsubscript{4}D\textsubscript{2}): \(\delta\) 8.20 (s, 1H, CH\textsubscript{amorn}, H11), 7.67 (d, \(\delta\) 7.4 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H7/H9), 7.22 (d, \(\delta\) 7.9 Hz = 7.6 Hz, 1H, CH\textsubscript{amorn} H5/H6), 7.37–7.35 (m, 4H, CH\textsubscript{PPm}), 7.07–7.01 (m, 6H, CH\textsubscript{PPm}), 7.01 (t, \(\delta\) 7.8 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H7/H9), 7.04 (m, \(\delta\) 7.8 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H5/H6), 7.00 (q, \(\delta\) 7.5 Hz = 7.8 Hz, 1H, CH\textsubscript{amorn} H4/H5), 6.94 (br s, 1H, CH\textsubscript{amorn}, H11), 3.38 (d, \(\delta\) 8.0 Hz = 7.8 Hz, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 2.54 (t, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}), 1.93 (s, 2H, CH\textsubscript{PPm}), 1.76 (d, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}), 1.38 (m, \(\delta\) 7.7 Hz = 7.3 Hz, 2H, CH\textsubscript{PPm}).
Synthesis of the tetranuclear silver cluster \([\text{Ag}_2(\mu-\text{Br})_2(\mu-\text{PPPh}_2\text{NC} H_2\text{KpXen}}\text{N}_2)]\) \((\text{route (b)})\). \(\text{L}^{\text{PP}}\)-2HBF\(_4\) (0.40 g, 0.72 mmol) and Ag\(_2\O\) (0.185 g, 0.80 mmol) were charged in 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\(^\text{\textregistered}\) and concentrated to \(ca.\) 1 mL. Complex \([\text{Ag}_2(\mu-\text{PPPh}_2\text{N})_2])\) 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 C\(_{52.53}\)H\(_{70}\)Ag\(_2\B_2\F_8\)N\(_4\)P\(_2\): C, 51.06; H, 4.50; N, 4.53. Found: C, 50.98; H, 4.42; N, 4.72. Examination of the \(^1\H\) and \(^{31}\P\{^1\H\}\) NMR spectra revealed the presence of the "head-to-tail" and "head-to-head" isomers in a ca. 4:1 H/H ratio in CD\(_2\)Cl\(_2\) (see text) and \(1:1\) in CD\(_3\)CN. \(^1\H\) NMR (400.13 MHz, CD\(_3\)CN): \(\delta\) 8.00 (br q, \(J_{\text{HH}} = 4.0 \text{ Hz}, 0.8H, \text{CH}_{\text{imid.}}, H11)), 7.64 (t, \(J_{\text{HH}} = J_{\text{HAg}} = 1.7 \text{ Hz}, 0.8H, \text{CH}_{\text{imid.}}, H11)), 7.63–7.72 (m, 11.6H, CH\(_{\text{imid.}}\)), 7.17 (t, \(J_{\text{HH}} = J_{\text{HAg}} = 1.7 \text{ Hz}, 0.8H, \text{CH}_{\text{imid.}}\)), 7.09 (t, \(J_{\text{HH}} = 0.7 \text{ Hz}, 0.2H, \text{CH}_{\text{imid.}}, H8)), 7.04 (t, \(J_{\text{HH}} = 0.8 \text{ Hz}, 0.8H, \text{CH}_{\text{imid.}}, H8)), 6.92 (s, 0.2H, CH\(_{\text{imid.}}\)), 6.60 (dd, \(J_{\text{HH}} = 7.7 \text{ Hz, CH}_{\text{imid.}}, H7\)), 4.30 (t, \(J_{\text{HH}} = 1.7 \text{ Hz, 1.6H, CH}_{2}\)), 3.89–3.82 (br s, 0.4H, CH\(_{2}\)), 1.91 (quint, \(J_{\text{HH}} = 7.4 \text{ Hz}, 0.4H, \text{NCH}_{2}\)). 1\(\text{P}\{^1\H\}\) NMR (161.98 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 324.1 (dd, \(J_{\text{PH}} = 4.4 \text{ Hz, CPH})\)).

General procedure for the synthesis of silver(l) complexes \([\text{Ag}_2(\text{PP})_2])\) \((\text{BF}_4)_2\). \(\text{L}^{\text{PP}}\)-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\(^\text{\textregistered}\) and concentrated to \(ca.\) 1 mL. The complex \([\text{Ag}_2(\text{PP})_2])\) \((\text{BF}_4)_2\) was precipitated with diethyl ether. The white powder was collected by filtration and dried under vacuum.

Synthesis of \([\text{Ag}[\mu-\text{PPPh}_2\text{NC} \text{H}_2\text{KpXen}}\text{N}_2])\) \((\text{BF}_4)_2\) \((\text{route (b)})\). Following the general procedure, \([\text{Ag}_2(\mu-\text{PP})_2])\) \((\text{BF}_4)_2\) was synthesised from \(\text{L}^{\text{PP}}\)-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 C\(_{52.53}\)Ag\(_2\B_2\F_4\text{P}_2\text{N}_2\): C, 51.06; H, 4.50; N, 4.53. Found: C, 50.98; H, 4.42; N, 4.72. Examination of the \(^1\H\) and \(^{31}\P\{^1\H\}\) NMR spectra revealed the presence of the "head-to-tail" and "head-to-head" isomers in a ca. 4:1 H/H ratio in CD\(_2\)Cl\(_2\) (see text) and 1:1 in CD\(_3\)CN. \(^1\H\) NMR (400.13 MHz, CD\(_3\)CN): \(\delta\) 7.67–7.25 (m, 11.6H, CH\(_{\text{imid.}}\)), 7.17 (t, \(J_{\text{HH}} = J_{\text{HAg}} = 1.7 \text{ Hz}, 0.8H, \text{CH}_{\text{imid.}}\)), 7.09 (t, \(J_{\text{HH}} = 0.7 \text{ Hz, 0.2H, CH}_{\text{imid.}}, H8)), 7.04 (t, \(J_{\text{HH}} = 0.8 \text{ Hz, 0.8H, CH}_{\text{imid.}}, H8)), 6.92 (s, 0.2H, CH\(_{\text{imid.}}\)), 6.60 (dd, \(J_{\text{HH}} = 7.7 \text{ Hz, CH}_{\text{imid.}}, H7\)), 4.30 (t, \(J_{\text{HH}} = 1.7 \text{ Hz, 1.6H, CH}_{2}\)), 3.89–3.82 (br s, 0.4H, CH\(_{2}\)), 1.91 (quint, \(J_{\text{HH}} = 7.4 \text{ Hz}, 0.4H, \text{NCH}_{2}\)), 1.82 (quint, \(J_{\text{HH}} = 7.4 \text{ Hz, 1.6H, NCH}_{2}\)). 1\(\text{P}\{^1\H\}\) NMR (161.98 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 252.5 (two doublets, \(J_{\text{P-WA}} = 503 \text{ Hz, } \text{J}_{\text{P-WAg}} = 581 \text{ Hz, integrating for 0.8P})\), 17.6 (two doublets, \(J_{\text{P-WA}} ≈ 515 \text{ Hz, } \text{J}_{\text{P-WAg}} ≈ 595 \text{ Hz, integrating for 0.2P})\). \(^{13}\text{B}\) NMR (128.38 MHz, CD\(_2\)Cl\(_2\)) \(\delta = 0.9 \text{ (quint, } \text{J}_{\text{BF}} = 1.5 \text{ Hz})\).

H NMR (400.13 MHz, CD\(_2\)CN): \(\delta\) 7.67–7.25 (m, 13.6H, CH\(_{\text{aron.}}\)), 7.14–6.68 (br s, 2H, CH\(_{\text{aron.}}\)), 6.82–6.60 (br s, 0.4H, CH\(_{\text{aron.}}\)), 5.45 (s, 0.4H, residual CH\(_2\)Cl\(_2\)), 4.20 (t, \(J_{\text{HH}} = 7.3 \text{ Hz, 2H, CH}_{2}\)), 3.70 (br s, 2H, CH\(_{2}\)), 1.91–1.69 (br s, 2H, CH\(_2\)), 1.37 (six, \(J_{\text{HH}} = 7.4 \text{ Hz, 2H, NCH}_{2}\)). 1\(\text{H}\) NMR (161.98 MHz, CD\(_3\)CN): \(\delta\) 21.3 (two doublets, \(J_{\text{P-WA}} ≈ 500 \text{ Hz, } \text{J}_{\text{P-WAg}} ≈ 580 \text{ Hz, integrating for 1.0P})\), 11.2 (two doublets, \(J_{\text{P-WA}} ≈ 475 \text{ Hz, } \text{J}_{\text{P-WAg}} ≈ 550 \text{ Hz, integrating for 1.1P})\).
Following the general procedure, [CuBr₂(L₄)]₂ was synthesised from L⁵⁻HBr (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 diffusion of toluene in a CH₂Cl₂ solution of the complex. Anal. Calcd for C₃₄H₇₀Br₂Cu₂N₄P₂ (1003.90): C, 52.64; H, 7.03; N, 5.58. Found: C, 52.61; H, 7.22; N, 5.67. ¹H NMR (400.13 MHz, CDCl₃): δ 8.12 (d, JHH = 7.3 Hz, 1H, CH₃Ar, H7), 7.44 (s, 1H, CH₃Ar, H11), 7.17 (t, JHH = 7.6 Hz, 1H, CH₃Ar, H8), 7.08 (d, JHH = 7.7 Hz, 1H, CH₃Ar, H9), 6.93 (d, JHH = 1.4 Hz, 1H, CH₃Ar, H4), 6.67 (s, 1H, CH₃Ar, H5), 2.98 (br d, JHH = 7.4 Hz, 2H, CH₂P), 2.01 (q, JHH = 7.6 Hz, 2H, NCH₂CH₂C₅H₃), 1.50 (s, JHH = 7.4 Hz, 2H, NCH₂CH₂C₅H₃), 1.56-0.98 (br s, 18H, C(CH₃)₂). ³¹P¹H NMR (119.98 MHz, CDCl₃): δ 73.65. Anal. Calcd for C₃₄H₇₀Br₂Cu₂N₄P₂ (1003.90): C, 52.64; H, 7.03; N, 5.58. Found: C, 52.61; H, 7.22; N, 5.67. ¹H NMR (400.13 MHz, CDCl₃): δ 8.12 (d, JHH = 7.3 Hz, 1H, CH₃Ar, H7), 7.44 (s, 1H, CH₃Ar, H11), 7.17 (t, JHH = 7.6 Hz, 1H, CH₃Ar, H8), 7.08 (d, JHH = 7.7 Hz, 1H, CH₃Ar, H9), 6.93 (d, JHH = 1.4 Hz, 1H, CH₃Ar, H4), 6.67 (s, 1H, CH₃Ar, H5), 2.98 (br d, JHH = 7.4 Hz, 2H, CH₂P), 2.01 (q, JHH = 7.6 Hz, 2H, NCH₂CH₂C₅H₃), 1.50 (s, JHH = 7.4 Hz, 2H, NCH₂CH₂C₅H₃), 1.56-0.98 (br s, 18H, C(CH₃)₂). ³¹P¹H NMR (119.98 MHz, CDCl₃): δ 73.65. Anal. Calcd for C₃₄H₇₀Br₂Cu₂N₄P₂ (1003.90): C, 52.64; H, 7.03; N, 5.58. Found: C, 52.61; H, 7.22; N, 5.67. ¹H NMR (400.13 MHz, CDCl₃): δ 8.12 (d, JHH = 7.3 Hz, 1H, CH₃Ar, H7), 7.44 (s, 1H, CH₃Ar, H11), 7.17 (t, JHH = 7.6 Hz, 1H, CH₃Ar, H8), 7.08 (d, JHH = 7.7 Hz, 1H, CH₃Ar, H9), 6.93 (d, JHH = 1.4 Hz, 1H, CH₃Ar, H4), 6.67 (s, 1H, CH₃Ar, H5), 2.98 (br d, JHH = 7.4 Hz, 2H, CH₂P), 2.01 (q, JHH = 7.6 Hz, 2H, NCH₂CH₂C₅H₃), 1.50 (s, JHH = 7.4 Hz, 2H, NCH₂CH₂C₅H₃), 1.56-0.98 (br s, 18H, C(CH₃)₂). ³¹P¹H NMR (119.98 MHz, CDCl₃): δ 73.65. Anal. Calcd for C₃₄H₇₀Br₂Cu₂N₄P₂ (1003.90): C, 52.64; H, 7.03; N, 5.58. Found: C, 52.61; H, 7.22; N, 5.67. ¹H NMR (400.13 MHz, CDCl₃): δ 8.12 (d, JHH = 7.3 Hz, 1H, CH₃Ar, H7), 7.44 (s, 1H, CH₃Ar, H11), 7.17 (t, JHH = 7.6 Hz, 1H, CH₃Ar, H8), 7.08 (d, JHH = 7.7 Hz, 1H, CH₃Ar, H9), 6.93 (d, JHH = 1.4 Hz, 1H, CH₃Ar, H4), 6.67 (s, 1H, CH₃Ar, H5), 2.98 (br d, JHH = 7.4 Hz, 2H, CH₂P), 2.01 (q, JHH = 7.6 Hz, 2H, NCH₂CH₂C₅H₃), 1.50 (s, JHH = 7.4 Hz, 2H, NCH₂CH₂C₅H₃), 1.56-0.98 (br s, 18H, C(CH₃)₂). ³¹P¹H NMR (119.98 MHz, CDCl₃): δ 73.65.
Synthesis of [Au2Cl2(µ-P(bu)]2(NHC,κPC,κ′-NHC)] ([Au2Cl2Lnu]).

To a solution of [Ag2Br2(Lnu)] (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 [Au2Cl2Lnu] 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. Calcd for C22H35Au2ClN2P 787.1552, found 787.1547.

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X-ray crystallography

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Summary of the crystal data, data collection and refinement are given in Table S1 (see ESI†).

Data sets for Lph-HBr, Lcy-HBr-H2b, [Ag2(Lph)2][BF4]−, [Ag2(Lph)2][BF4]−·2CH2Cl2, [Cu2Br2(Lcy)]2 and [Au2Cl2Lnu] were collected at 173(2) K on a Bruker APEX-II CCD Duo diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). Data sets for [Ag2(Lph)2]2[BF4]−, [Ag2(Lph)2]2[BF4]−·2CH2Cl2, [Cu2Br2(Lcy)]2 and [Au2Cl2Lnu] were collected at 173(2) K on a Kappa CCD diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). Specific comments for each data set are given below. The cell parameters were determined using DENZO‡ (Kappa) or APEX2‡‡ (APEX-II) softwares.

The structures were solved by direct methods using the program SHELXS-97 (compounds Lph-HBr-H2b, Lph-HBr, Cu2Br2(Lcy)2, Cu2Br2(Lcy)2·2CH2Cl2 and [Cu2Br2(Lcy)2·2CH2Cl2]·2CH2Cl2) or SHELXS-2013 (complexes [Ag2Br2(Lph)2]2[BF4]−·2CH2Cl2, [Ag2(Lph)2][BF4]−, [Ag2(Lph)2][BF4]−·2CH2Cl2, [Ag2(Lph)2][BF4]−] and [Au2Cl2Lnu]).‡ The refinement and all further calculations were carried out using SHELX-97 (compounds Lph-HBr, [Cu2Br2(Lcy)]2, [Cu2Br2(Lcy)2·2CH2Cl2] and [Cu2Br2(Lcy)2·2CH2Cl2]·2CH2Cl2) or SHELXL-2013 (all other compounds).‡‡ The H-atoms were introduced into the geometrically calculated positions (SHELXL-97 or SHELXL-2013 procedures) unless stated otherwise. Non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2.

The following special comments apply to the models of the structures:

Lph-HBr: A SQUEEZE procedure‡ was applied and the residual electron density was assigned to one half disordered molecule of CH2Cl2.

[Ag2Br2(Lph)2]: A SQUEEZE procedure‡ was applied and the residual electron density was assigned to two disordered molecules of acetonitrile. The structure of this complex can be found in the ESI†.

[Ag2(Lph)2][BF4]−·2CH2Cl2: thermal motions affect the alkyl chains on the ligands. The carbons atoms C49, C50 and C73 are disordered on two positions. The carbon atom C48 is also disordered on two positions but C48 and C48B have been imaged at the same position to avoid short contacts between the H-atoms and subsequent alerts in the Checkcif. A SQUEEZE procedure‡ was applied and the residual electron density was assigned to one and a half disordered molecules of CH2Cl2.

[Cu2Br2(LCy)2]: The asymmetric unit contains one and a half molecules of the complex. The alkyl atoms C6 and C7 are disordered on two positions.

[Cu2Br2(Lnu)2]·2CH2Cl2: The space group is chiral (P21) and the value of Flack parameter is −0.008.‡‡ A SQUEEZE procedure‡ was applied and the residual electron density was assigned to one disordered molecule of toluene.

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References


