Phosphine-substituted 1,2,3-triazoles as P,C- and P,N-ligands for photoluminescent coinage metal complexes†‡

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A series of homo- and hetero-polynuclear coinage metal complexes based on a phosphine-substituted 1,2,3-triazole system is presented. Besides the P,N-ligand 1-benzyl-4-(diphenylphosphanyl)-1H-1,2,3-triazole (LPN), the P,C-donor ligand 1-benzyl-4-(diphenylphosphanyl)-3-methyl-1H-1,2,3-triazole (LPC), featuring a potential mesoionic carbene moiety, was obtained by methylation of LPN. Starting from the monogold chloride complexes AuCl(LP/N/LPC), the syntheses of a heterotrinuclear Au2Cu complex as well as a digold carbene complex are described. The multinuclear complexes show metallophilic interactions. Their photophysical properties were investigated by temperature-dependent photoluminescence (PL) measurements. In particular, the digold complex shows interesting PL properties including narrow exciton peaks arising in the excitation and emission spectra below 50 K. These might be related to the molecular ‘chains’ in the crystal structure of the digold complex, formed by phenyl ligand stacking.

Introduction

Carbenes and particularly imidazole-based N-heterocyclic carbenes (NHCs) are presently well established ligands which have been widely used in organometallic chemistry for the last three decades.1,2 Their strong σ-donor properties allow the formation and stabilization of organometallic complexes comprising almost every metal or metalloid.3–7 Typically, NHCs serve as spectator ligands, however, reactions transforming the NHC itself (such as a ring expansion) are known as well.8–12 Their great application potential has led to further development of ligands with tailor-made steric and electronic properties derived from classical NHCs. These include remote, abnormal, cyclic alkylamino and mesoionic carbenes (Scheme 1).13–20 The latter are either based on substituted imidazole, pyrazole or 1,2,3-triazole backbones, respectively.21,22

The 1,2,3-triazol-5-ylidenes (Scheme 1, type E) are typically stronger donors than their 1,2,4-triazolylidene isomers and other five-membered NHCs.23–25 They can be readily prepared on a multi-gram scale by using the well-established CuAAC “click” reaction. The variety of substituents on the carbon and nitrogen atoms, which aﬀect the steric and electronic properties, is very large and practically only limited by the stability of the parent azide and alkyne precursors (Scheme 2).22,26,27

The free carbenes are generated by deprotonation of (typically N3-alkylated) triazolium salts.22 A donor-substituted triazolium salt thus exhibits orthogonal donor sites for subsequent and controllable coordination of metals. Following this concept, we herein present a methylated phosphine-substituted 1,2,3-triazol-5-ylidene LPC, as well as a phosphine-sub-

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Scheme 1 Schematic drawing of NHC types: classical N-heterocyclic (NHCs; A), remote (rNHC; B), abnormal (aNHC; C), cyclic alkylamino (caAC; D) and mesoionic carbenes (MIC; E).
Results and discussion

The synthesis of the two ligands \( \text{LP}^\text{PC} \) and \( \text{LP}^\text{PN} \) was achieved by a stepwise synthetic procedure, starting from ethynyldiphenylphosphine and benzylazide in a CuAAC click reaction.\(^{59}\) As trivalent phosphines are known to react with azides to yield phosphazenes (Staudinger reduction),\(^{60,61}\) the phosphine was first converted to the corresponding ethynylidiphenylphosphine oxide 1, using aqueous \( \text{H}_2\text{O}_2 \).\(^{52}\) The subsequent click reaction between 1 and benzylazide gave the phosphinoxide-substituted triazole 2 in 78% yield (for crystal structure, see Fig. S2†). In the next step, 2 was alkylated with methyl trifluoromethanesulfonate (MeOTf) in \( \text{CH}_2\text{Cl}_2 \) to give the \( \text{N} \)-methylated triazolium salt 3. Upon methylation, a broad resonance at \( \delta = 15.2 \) ppm is observed in the \(^{31}\text{P}\{\text{H}\} \) NMR spectrum of compound 3, which is significantly broadened compared to the sharp resonance at \( \delta = 16.6 \) ppm for 2. The broadening may be attributed to the delocalization of the positive charge. Although minor impurities were detected in the NMR spectra, compound 3 was used without further purification. In the last step, the reduction of 2 and 3 to \( \text{LP}^\text{PN} \) (4) and \( \text{LP}^\text{PC}\text{H}^+\cdot\text{OTf}^- \) (5) respectively, was conducted with PhSiH\(_3\) as reducing agent (Scheme 4).\(^{63}\) In the \(^{31}\text{P}\{\text{H}\} \) NMR spectrum, the two ligands \( \text{LP}^\text{PN} \) and \( \text{LP}^\text{PC}\text{H}^+\cdot\text{OTf}^- \) exhibit almost identical chemical shifts at \( \delta = -31.9 \) ppm (\( \text{LP}^\text{PN} \)) and \( -31.5 \) ppm (\( \text{LP}^\text{PC}\text{H}^+\cdot\text{OTf}^- \)).

The respective monogold chloride complexes of \( \text{LP}^\text{PN} \) and \( \text{LP}^\text{PC}\text{H}^+\cdot\text{OTf}^- \) were obtained by reaction with [AuCl(tht)] (tht = tetrahydrothiophene) (Scheme 5). After workup, [AuCl(\( \text{LP}^\text{PN} \))] (6) and [AuCl(\( \text{LP}^\text{PC}\text{H}^+\cdot\text{OTf}^- \))] (7) were obtained as colorless solids in yields of 73% (6) and 68% (7).
The reaction can be easily monitored by $^{31}$P{¹H} NMR spectroscopy. Chemical shifts of $\delta = 6.96$ (6) and 12.5 ppm (7) indicate the coordination of the corresponding phosphines to the metal atoms. Note that a downfield shift in the range of 30–40 ppm is characteristic upon coordination of arylphosphines to AuCl.64,65

Complex 6 crystallizes in the trigonal space group $P3_121$ with additional solvent molecules (CH$_2$Cl$_2$ and tetrahydrothiophene, for details refer to ESI, Fig. S1†) in the asymmetric unit (Fig. 1). The Au1–Cl1 (2.270(3) Å) and P1–Au1 (2.213(3) Å) bond lengths are in the typical range for chloro phosphine nates, for which strong aurophilic interactions have been reported.66

The $P^N$ angle P1–N3–N4 is nearly identical to the N–C–N angle in, e.g., dinuclear gold amides, for which strong aurophilic interactions have been reported.55,67,68

Complex 7 crystallizes in the monoclinic space group $P2_1/n$ as an Au–Au connected dimer with two additional CH$_2$Cl$_2$ molecules in the asymmetric unit (Fig. 2). The Au1–Au2 contact of 3.1074(2) Å indicates aurophilic interactions of medium strength.69 As already seen for 6, the Au–Cl and P–Au bond lengths (Au1–Cl1 2.2791(11) Å, Au1–P1 2.2262(10) Å, Au2–Cl2 2.2983(10) Å, Au2–P2 2.2254(10) Å) are in the expected range. However, while the P1–Au1–Cl1 bond angle (177.74(4)°) is close to the typical linear coordination, the P2–Au2–Cl2 angle (169.60(4)°) deviates by approximately 10°. This is rather unusual but may be explained by crystal packing effects. Compared to 6, the introduction of positive charge by methylating results in two effects: (i) aurophilic interactions are observed in 7 while 6 remains monomeric in the solid state. This supports the general assumption that the neighbouring atoms, as well as the symmetry and nature of the ligand strongly influence the aurophilicity phenomenon;44,70,71 (ii) the methyl group has a considerable impact on the chemical shift in the $^{31}$P{¹H} NMR spectrum. A downfield shift of 5.50 ppm relative to the unmethylated derivative 6 is observed for 7.

For the synthesis of a defined multimetallic complex, [AuCl (L$^{PN}$)] (6) was further reacted with [Cu(MeCN)$_4$]PF$_6$ to give the heterotrinuclear complex [Cu(AuCl(L$^{PN}$))$_2$(thf)$_2$]PF$_6$ (8) (Scheme 6).

The heterotrinuclear complex 8 crystallizes in the monoclinic space group $P2_1/n$ with two additional THF molecules in the asymmetric unit (Fig. 3). The central Cu(i) atom is co-
ordinated in a distorted octahedral fashion by the trans-located N3 and N6 atoms of the triazoles (Cu1–N3 1.944(13) Å, Cu1–N6 1.923(13) Å, the two Au(i) centers (Au1–Cu1 3.069(2) Å, Au2–Cu1 3.200(2) Å), as well as two thf molecules in a cis-coordination mode. The Cu1–N3 and Cu1–N6 distances are in the range of comparable Cu(i) triazole complexes.72,73 The copper atom and the two gold atoms form a triangle with interior angles of 54.52(4)° (Cu1–Au1–Au2), 58.10(4)° (Cu1–Au2–Au1) and 67.37(4)° (Au1–Cu1–Au2). The intermetallic distances are close to comparable complexes showing heterometallophilic interactions between Au and Cu.74,75 Due to the change in the chemical environment, primarily in the methylated triazolium salt [AuCl(LPCH)]OTf (Scheme 7), the formation of a carbene is conducted by deprotonation of the second donor site of [AuCl(LPN)] (Scheme 6). For this purpose, 7 was reacted with AgOAc, whereby AgCl precipitates and the (LPCH)− moiety is deprotonated by the acetate to form the mesoionic carbene. Intramolecular stabilization of the Au+ is not favoured and thus, dimerization to the digold complex [Au2(LPCH)2](OTf)2 occurs (Scheme 7).

Complex 9 crystallizes in the triclinic space group P1 with half of a molecule in the asymmetric unit (Fig. 4). As expected, the formation of the dinuclear arrangement with a linear coordination of phosphines and carbenes to the gold atoms (C2–Au1–P1 176.8(10)°) is observed. The carbene–gold bond length (Au1–C2 2.037(3) Å) is in the common range. The intermetallic contact Au1–Au1′ 2.9513(3) Å is short, indicating strong aurophilic interactions.76-78 In the 31P{1H} NMR spectrum of 9, a chemical shift of δ = 21.1 ppm is detected, which is shifted downfield by 8.6 ppm compared to the precursor 7, due to the change in the chemical environment, primarily in the trans-located ligand (Cl− vs. carbene). In gold carbene complexes, the carbene carbon atoms typically exhibit a chemical shift of around 180–210 ppm in the 13C{1H} NMR spectrum. For 9, unfortunately no resonance could be detected above 135 ppm.56,79

In a parallel experiment, the starting compound ethynylidiphenylphosphine (Ph2P–C==C–H) was reacted to the known gold chloride complex [AuCl(Ph2P–C==C–H)]80 instead of oxidizing the phosphine for the subsequent CuAAC reaction. Besides the ‘click product’ [AuCl(LPN)] (6), a dinuclear species, consisting of a dimeric gold triazolide complex (10), was identified as well (Scheme 8).

During the reaction, the precipitation of a large amount of a colorless solid is observed, which is not soluble in common organic solvents and could not be identified unambiguously. Slow evaporation of the supernatant results in the crystallization of products 6 and 10. A rational synthesis of complex 10, however, including several attempts from different starting materials (including 6 and 4 (LPN)) and varying conditions, failed so far. Thus 10 was characterized by single crystal X-ray diffraction only.

Complex 10 crystallizes in the monoclinic space group P21/c with half of a molecule in the asymmetric unit (Fig. 5). The bi-
metallic complex displays the neutral and non-methylated analogue to 9. Since the triazole scaffold is not alkylated, 10 is not a gold carbene complex, but a gold triazolide. The gold carbon bond lengths of 9 (Au1–C2 2.037(3) Å) and 10 (Au1–C2 2.036(4) Å), however, do not differ significantly. The intermetallic distance Au1–Au1’ 2.9615(7) Å is close to that in 9, indicating strong aurophilic interactions as well.

Photoluminescence properties
The heterotrimetallic complex 8 and the digold complex 9 show, respectively, relatively bright yellow and blue-white photoluminescence (PL) in the solid state at ambient temperature, while the other presented compounds were found to be less efficient or virtually non-luminescent under similar UV excitation.

The PL properties of 8 and 9 were therefore studied in more detail. PL spectra of 8 show a broad, featureless emission centred at 580 nm, which is typical of charge-transfer transitions. It moderately enhances in intensity and practically does not change spectrally by decreasing the temperature from 295 to 20 K (Fig. 6). Under nanosecond-pulsed laser excitation at 337 nm, the emission decays monoexponentially with τ = 14 and 8 μs at T = 20 and 295 K, respectively (Fig. S9‡), indicating phosphorescence. A PL quantum yield, ϕ(295 K), of 9% was determined at ambient temperature using an integrating sphere and excitation at 350 nm. It increases to about 35% at low temperatures, according to the temperature-dependent PL spectra (Fig. 6). Compound 9 emits a broad phosphorescence centred at around 440 (480) nm at 18 K (295 K), with a weak vibronic structure at low temperatures, as presented in Fig. 7. The PL decay approximately follows monoexponential curves with τ ≈ 15 and 0.7 μs at 18 and 295 K, respectively (Fig. S10‡). The PL intensity monotonically decreases by a factor of ~25 by increasing the temperature from 18 to 295 K, thus correlation with the faster decay. Correspondingly, a smaller quantum yield ϕ(295 K) = 4% was determined for 9 in comparison to 8.

However, it approaches ~100% below 50 K as estimated from the temperature-dependent spectra (Fig. 7). For both 8 and 9, the PL may be assigned to triplet metal-to-ligand charge transfer (MLCT) states. In a first approximation, these excited states are localized within the corresponding molecular entities.

Perhaps the most interesting PL feature of 9 are narrow bands arising at the onsets of excitation and emission spectra at temperatures below 50 K (Fig. 7). These bands peak at 358.4 and 363.5 nm, respectively (T = 18 K), corresponding to a small Stokes shift of ca. 50 meV. The width (FWHM) of these PLE
and PL bands is about 2–3 and 5–6 nm (20–30 and 50–60 meV), respectively. The decay of the 363 nm emission under pulsed laser excitation at 337 nm also proceeds on a microsecond time scale, but, in difference to the major PL band at ~440 nm, is clearly nonexponential. It can be well fit by the stretched exponential function of the form \( y = y_0 \times e^{-\left(\frac{t}{\tau}\right)^n} \) with \( \tau = 70 \mu s \) and \( n = 0.51 \) at 18 K. The decay at 363 nm is notably slowed down by further cooling of 9 down to 3.7 K (Fig. S10†), whereas the PL spectra and decay of the broad band remain nearly unchanged (Fig. S11†). The low-temperature PLE and PL spectra demonstrate sidebands to the phonon replica. Their frequencies are indicated in Fig. S11†.

The sharp PLE and PL bands of 9 resemble those observed for free excitons in some low-dimensional materials, for instance, in 1D and 2D lead halide perovskites.\(^{82,83}\) Accordingly, we tentatively assign these features to free (or relatively delocalized) excitons in 9. A delocalization might be related to the \( \pi \)-stacking between the phenyl groups of the neighbouring molecules in solid 9 (Fig. S7†). Especially at low temperatures, this may provide for a rigid, chain-like intermolecular structure. The microsecond-long emission decay indicates triplet excitons. The excitation–emission Stokes shift (see above) thus corresponds to the singlet–triplet exciton energy separation of ca. 50 meV.

**Conclusions**

By a facile synthetic procedure, two imidazole-based ligands \( \text{L}^{\text{PN}} \) and \( \text{L}^{\text{PC}^-}\text{H}^-\text{OTf}^- \) were obtained. They display different donor site combinations for selective metal coordination while having a similar structural geometry. Both ligands were converted to their respective mono gold chloride complexes [AuCl \( (\text{L}^{\text{PN}}) \)] (6) and [AuCl(\text{L}^{\text{PC}^-}\text{H})\text{OTf}^-] (7). Compound 6 was used for further coordination to Cu(i) to yield a heterotrimetallic Au₂Cu complex 8, exhibiting moderate metallophilic interactions. However, strong aurophilic interactions were observed in the dinuclear gold carbene complex 9, obtained by deprotonation and chloride abstraction of the triazolium salt 7. Furthermore, the photoluminescence (PL) properties of the multimetallic complexes 8 and 9 were investigated in the solid state. These compounds show relatively bright, spectrally broad, yellow and blue-white phosphorescence, respectively. In addition, the low-temperature PL spectra of 9 demonstrate narrow excitation and emission bands with a linewidth of about 20–30 and 50–60 meV, respectively, and a Stokes shift of about 50 meV. These were tentatively assigned to free (or relatively delocalized) excitons in 9. To the best of our knowledge, this is the first observation of such features for gold and other coinage metal complexes.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


