www.eurjic.org

An Easily Accessible Chiral Carbodiphosphorane and its Coinage Metal Complexes

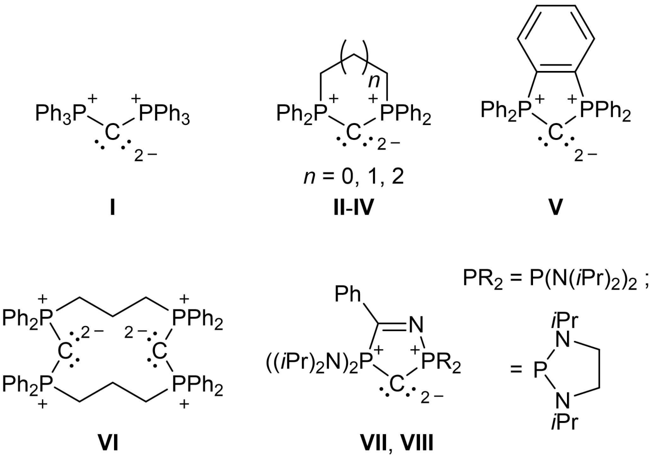
Tobias Dunaj,[a] M.Sc.Chloé Krampe,[a, b] B.Sc.Jasmin Heinrichs,[a] Fabian Müller,[a] Bernhard Neumüller,[a] Xiulan Xie,[a] and Istemi Kuzu*[a]

Dedicated to Prof. Wolfgang Petz on the occasion of his 84th birthday.

Herin, the high yielding synthesis of the chiral carbodiphosphorane (**3**) prepared in a two-step procedure from commercially available (*R*)-BINAP (([1,1′-binaphthalene]-2,2′-diyl)bis(diphenylphosphane), BINAP) and dibromomethane is presented. In the first reaction step, the bis phosphonium salt **1**[Br]$_2$ is obtained, which is subsequently deprotonated either with potassium hydroxide to yield the mono phosphonium salt **2**[Br], or with potassium hexamethyldisilazide to produce **3**. Moreover, coinage metal complexes of **3** were prepared *via* reaction with CuCl (**4**^{Cu}, **5**^{Cu}, **6**^{Cu}), Cu(OTf)·toluene$_{0.5}$ (**7**^{Cu}) or AuCl·(tht) (**5**^{Au}, **6**^{Au}). The prepared compounds were characterised by NMR- and IR-spectroscopy, mass spectrometry, elemental analysis, single crystal X-ray diffraction and UV/Vis spectroscopy. Photoluminescence emission spectra were obtained for most of the complexes (**3**, **4**^{Cu}, **5**^{Cu}, **6**^{Cu} and **6**^{Au}).

Introduction

The first carbodiphosphorane (CDP), $(Ph_3P)_2C$ (**I**, Scheme 1), was prepared in 1961 and immediately raised questions about the bonding situation present in the compound.[1] A combined theoretical and experimental study performed in 2006 concluded, that CDPs are best described as compounds were formal Carbon(0) atoms with two electron lone pairs are stabilized by two σ-donating phosphane ligands.[2] Such stabilised C(0) species are called *carbones* to distinguish them from carbenes.[3] Since the preparation of **I**, several functionalities have been introduced to CDPs. Examples include compounds where one or several phenyl substituents were exchanged for amide,[4,5–7] pyridyl[8–10] or halide[6,7,11] substituents. By the reaction of $(Ph_2P)_2CH_2$ and $BrCH_2(CH_2)_nCH_2Br$ ($n=0$–2) and subsequent deprotonation, the first cyclic CDPs (**II**–**IV**, Scheme 1) have been prepared.[12] In recent studies, the cyclic CDP **III** (Scheme 1) was used for catalytic hydroboration reactions.[13,14] In a synthetic approach similar to the preparation of **II**–**IV**, a compound with an 1,3-diphosphaindane framework has been identified, which can be considered a cyclic CDP with an aromatic backbone (**V**, Scheme 1). However, compound **V** is stable only below −30 °C.[15] Recently, a twelve membered compound with two CDP moieties (**VI**, Scheme 1) has been synthesized and its reactivity with ECl_3 (E = B, Al, Ga) studied.[16] Cyclic CDPs can also have multiple additional functional groups, for example in the five membered compounds **VII** and **VIII** shown in scheme 1.[17]



Scheme 1. Examples for literature known (cyclic) Carbodiphosphoranes.

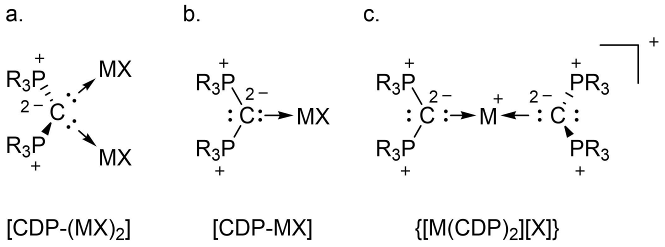
Several coinage metal halide complexes of CDPs have been reported in the literature. Within these compounds different coordination modes depending on the CDP and coinage metal halide stoichiometry have been realized. Upon using a 1:2 stoichiometry, two electron pairs on the central carbon atom form dative bonds to a coinage metal halide unit respectively (Scheme 2a). This motif has been identified with the coinage

---

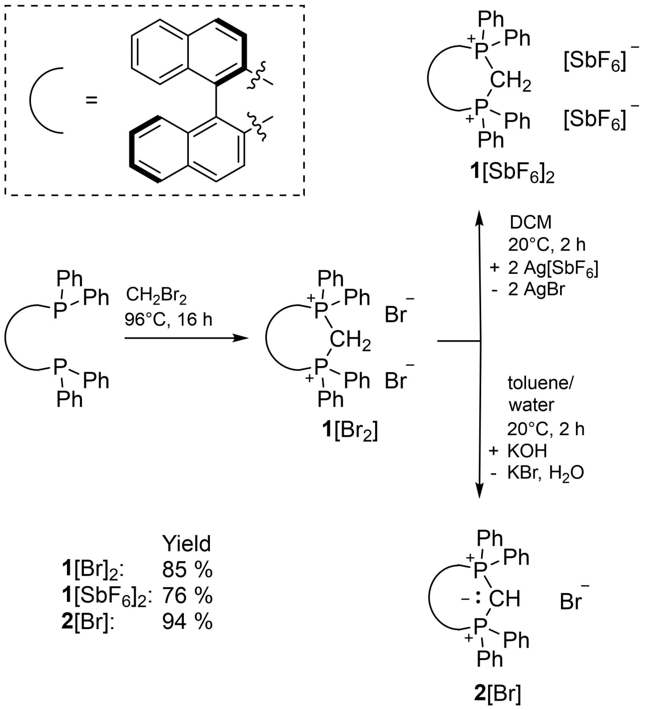
[a] *Dr. T. Dunaj, M.S.C. Krampe, B.S.J. Heinrichs, Dr. F. Müller, Prof. Dr. B. Neumüller, Dr. X. Xie, Dr. I. Kuzu*
Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35043 Marburg, Germany
E-mail: istemi.kuzu@chemie.uni-marburg.de

[b] *M.S.C. Krampe*
Current address: Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202400170



Scheme 2. Coordination modes that have previously been observed in adducts of carbodiphosphoranes and coinage metal halides. M = Cu, Ag, Au; X = Cl, Br, I.



Scheme 3. Synthesis of the bis phosphonium bromide salt **1**[Br]$_2$, the bis phosphonium hexafluoroantimonate **1**[SbF$_6$]$_2$ and the mono phosphonium bromide salt **2**[Br].

metal halides CuX (X = Cl, Br, I) and AuCl, where compounds have been structurally characterized in past reports.[9,18–21] It is noteworthy, that photoluminescence was observed in some of the copper complexes which has been investigated in an extensive study.[21] Using a 1:1 stoichiometry of the CDP and MX (M = Cu, Ag, Au, X = Cl), the coordination mode depicted in scheme 2b is observed.[18,22–24] The group of *Baceiredo* et al. could show, that these compounds can successfully be used in catalytic hydroamination and hydroalkoxylation reactions, upon exchange of a halide for an alkoxy ligand.[24] The third known bonding motif has been achieved when a 2:1 stochiometric of CDP and CuI or AgCl is used in reactions. In both reported compounds, the coinage metal cation is linearly coordinated by two CDP ligands (scheme 2c).[25,26]

It is noted here, that BINAP based phosphane-phosphonium and phosphane-phosphonium ylides have been used for the preparation of transition metal complexes in the past.[27]

In this work, the synthesis of an unprecedented helically chiral CDP with a (*R*)-BINAP backbone (**3**) with a cyclic 2H-1,3-diphosphepinediium diylide structural motif is reported. Compound **3** is accessible from commercially available starting materials in a twostep procedure in high yields. The intermediate products **1**[Br]$_2$ and **2**[Br] have also been isolated and characterized. Moreover, the reactivity with respect to the coordination to CuX (X = Cl, OTf) and AuCl is explored, and the obtained compounds, featuring all bonding motifs in scheme 2, have been isolated and characterized. Also, the photophysical properties of selected compounds have been examined *via* UV/Vis spectroscopy and photoluminescence emission measurements.

Results and Discussion

Preparation of (R)-BINAP-CDP (3)

In literature procedures, the preparation of reference compound **I** or the cyclic compounds **II–IV** *via* reaction of a bisphosphane precursor and CH$_2$Br$_2$ is described.[15,28] Based on this approach, (*R*)-BINAP is dissolved in CH$_2$Br$_2$ and, after reflux, standard work up and subsequent recrystallization, the bis phosphonium salt **1**[Br]$_2$ is obtained in high yield (scheme 3). Compound **1**[Br]$_2$ shows a broad singlet in the ^{31}P NMR spectrum at 19.6 ppm, in a similar range as the reference compounds **I**$^{2+}$ and **II**$^{2+}$ (18.4 and 30.7 ppm).[15,29] In the ^{1}H and ^{13}C NMR spectra, triplets corresponding to the CH$_2$ unit are found at 7.38 ppm ($^{2}J_{PH}$ = 13.5 Hz) and 24.5 ppm ($^{1}J_{PC}$ = 50.1 Hz), respectively (DCM-d$_2$). The ^{1}H NMR resonance signal is also similar to reference compound **I**$^{2+}$ (6.79 ppm, t, $^{2}J_{PH}$ = 16.4 Hz, in CD$_3$OD).[29] In the ESI(+) mass spectrum, only one fragment can be observed and identified which corresponds to [**1**-H]$^{+}$, hence **2**$^{+}$. Unless otherwise mentioned, this is the only signal observed for all other prepared compounds in this manuscript. Crystals of **1**[Br]$_2$ suitable for single crystal X-ray diffraction were obtained from an NMR tube monitoring the reaction progress. Compound **1**[Br]$_2$ crystallizes in the asymmetric space group $P2_1$ with Z = 2 and co-crystalline CH$_2$Br$_2$ and H$_2$O (Figure 2a). The bromide anions, the CH$_2$ group and the water molecule form a planar square in the crystal structure through hydrogen bromide contacts (Br–H: 254(2)–261.34(1) pm, Figure 1). The P1-C1 and P2-C1 bond lengths in **1**[Br]$_2$ are 181.2(5) and 181.9(5) pm, which are very similar to other structurally characterized compounds containing a dicationic [(R$_3$P)$_2$CH$_2$]$^{2+}$ (R = Aryl, Alkyl) moiety.[18,30,31] The P1-C1-P2 angle is 112.5(2)°, which is similar to the double-protonated compound **III**$^{2+}$ (113.1(2)°), bearing a six membered cycle.[32] Chemical shifts, coupling constants and structural parameters of **1**[Br]$_2$ and all subsequently prepared compounds in this manuscript are summarized in table 1.

To further investigate the ion interaction in solution and in the solid state, the bromide anions in **1**[Br]$_2$ were replaced with weakly coordinating anions by reaction with Ag[SbF$_6$], leading to the formation of **1**[SbF$_6$]$_2$ (scheme 3). Anion exchange leads to no significant changes in of the chemical shift of the CH$_2$

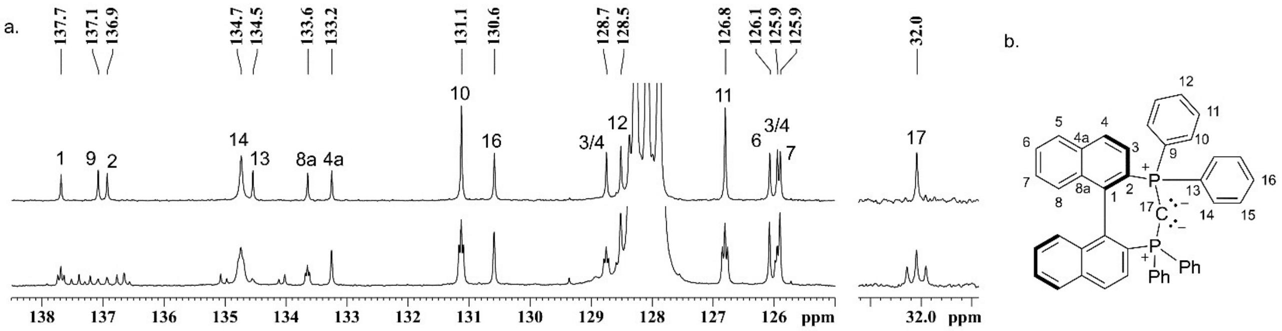


Figure 1. a. Top: Excerpts of the $^{13}C\{^1H,^{31}P\}$ NMR spectrum of **3**. Bottom: Excerpts of the $^{13}C\{^1H\}$ NMR spectrum of **3**. b. Labelling scheme for the assignment of signals.

Table 1. Left: $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR chemical shifts of the central P_2CX_n (X = H, CuCl, AuCl, *n* = 1, 2) unit of all prepared compounds. Unless otherwise specified, NMR spectra were measured in CD_2Cl_2. Right: Selected bond lengths and bond angles of all structurally characterised compounds in this manuscript.

Compound	$^{31}P\{^1H\}$ /ppm	^1H ($^2J_{PH}$) /ppm (Hz)	$^{13}C\{^1H\}$ ($^1J_{PC}$) /ppm (Hz)	d(P-C1) /pm	∡ (P1-C1-P2) /°	d(C1-M) /pm	d(M1⋯M1′) /pm
1[Br]$_2$	19.6	7.38 (13.5)	24.6 (50.1)	181.2(5) 181.9(5)	112.5(2)	–	–
1[SbF$_6$]$_2$	16.7	5.13 (13.1)	23.8 (53.4)	180.8(7)–182.8(7)	113.9(4)–115.7(4)	–	–
2[Br]	20.8	2.21 (2.8)	6.0 (113.9)	174.1(11) 170.9(12)	117.2(7)	–	–
3	1.3[a]	–	32.0 (11.7)[a]	166.1(2) 166.7(2)	112.61(12)	–	–
4^{Cu}	23.0	–	9.7 (40.5)	173.2(2) 175.0(5)	113.0(2)	193.9(5) 194.0(4)	255.16(8)
5^{Cu}	17.2[a]	–	–[b]	169.8(2) 170.4(2)	112.35(11)	189.2(2)	–
6^{Cu}	16.5	–	15.3 (52.9)	167.0(3) 167.0(3)	113.4(2)	191.0(2)	–
4^{Au}	21.1	–	7.0 (44.7)	174.9(13)–176.6(13)	115.2(7)	206.2(12)–210.3(12)	292.09(7)
5^{Au}	17.5	–	25.2 (71.0)	172(2) 172(2)	112.2(12)	199(2)	–

[a] Measured in C_6D_6. [b] not observed.

group in the ^{13}C NMR spectrum (t, 23.8 ppm, $^1J_{PC}$ = 53.4 Hz). However, a significant change is observed in the ^1H NMR spectrum. where a triplet signal is now observed at 5.13 ppm ($^2J_{PH}$ = 13.1 Hz) in DCM-d$_2$. This indicates the presence of contact ion pairs for **1**[Br]$_2$ and a separated ion pair for **1**[SbF$_6$]$_2$ in DCM solution. As expected, these results indicate a weaker cation-anion interaction in **1**[SbF$_6$]$_2$. Crystals of **1**[SbF$_6$]$_2$ were obtained from a $CDCl_3$ solution inside a NMR tube. The compound crystalizes in the space group $P2_12_12_1$ with three **1**[SbF$_6$]$_2$ units and two $CDCl_3$ molecules in the asymmetric unit. The P–C1 bond lengths and the P1-C1-P2 angles are very similar to those in compound **1**[Br]$_2$.

Deprotonation of **1**[Br]$_2$ with an aqueous solution of potassium hydroxide (KOH, 1 mol/L) selectively leads to the mono phosphonium salt **2**[Br]. After workup, **2**[Br] is obtained in 94% yield in the form of a colorless solid. in the ^1H and ^{13}C NMR spectra, resonance signals for the CH group in **2**[Br] are observed as triplets at 2.21 ppm ($^2J_{PH}$ = 2.7 Hz) and 6.0 ppm ($^1J_{PC}$ = 113.5 Hz), respectively. A resonance signal corresponding to the phosphorus atom is observed at 20.7 ppm in the ^{31}P NMR spectrum, fitting well to literature known compounds like [(Ph$_3$P)$_2$CH][Br] (25.7 ppm).[33] Crystals of **2**[Br] suitable for single crystal X-ray diffraction were obtained from layering of a DCM solution with *n*-pentane at 4 °C ($P2_12_12_1$, Z = 4, Figure 2b). As expected, the P–C1 bond lengths in **2**[Br] (174.1(11) and 170.9(12) pm) are shorter than in **1**[Br]$_2$ and fit well to structurally characterized compounds containing a [(Ph$_3$P)$_2$CH]$^+$ cation.[25,31,34] However, the P1-C1-P2 bond angle of 117.2(7) ° in **2**[Br] is more acute than in the comparable compounds (128.4(2)–132.0(1) °).[25,34,35] This is probably due to the seven-membered ring system and the torsion of the BINAP unit.

For the twofold deprotonation of **1**[Br]$_2$ two equivalents of potassium hexamethyldisilazide (KHMDS) are added to a suspension of **1**[Br]$_2$ in toluene at −30 °C (scheme 4). After workup, the desired (*R*)-BINAP-CDP **3** is isolated in the form of an orange solid in 82% yield.

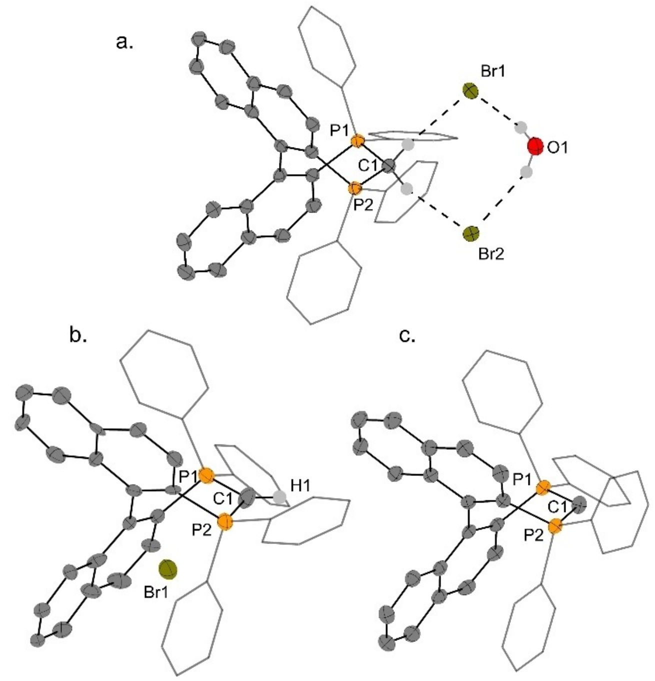
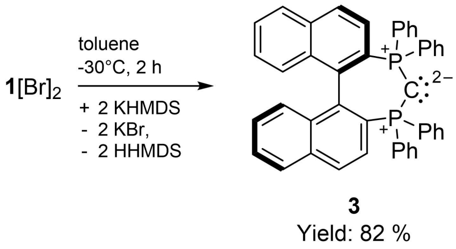


Figure 2. Molecular structure of a. **1**[Br]$_2$, b. **2**[Br] and c. **3** in the crystal. Co-crystalline solvent molecules in **2**[Br] and hydrogen atoms besides those at C1 and of a water molecule in a. are omitted for clarity. Ellipsoids are shown at the 50 % probability level. Selected bond lengths [pm] and angles [°] for **1**[Br]$_2$: P1-C1 181.2(5), P2-C1 181.9(2), P1-C1-P2 112.5(2). Selected bond lengths [pm] and angles [°] for **2**[Br]$_2$: P1-C1 174(1), P2-C1 170.9(12), P1-C1-P2 117.2(6). Selected bond lengths [pm] and angles [°] for **3**: P1-C1 166.1(2), P2-C1 166.7(2), P1-C1-P2 112.61(12).



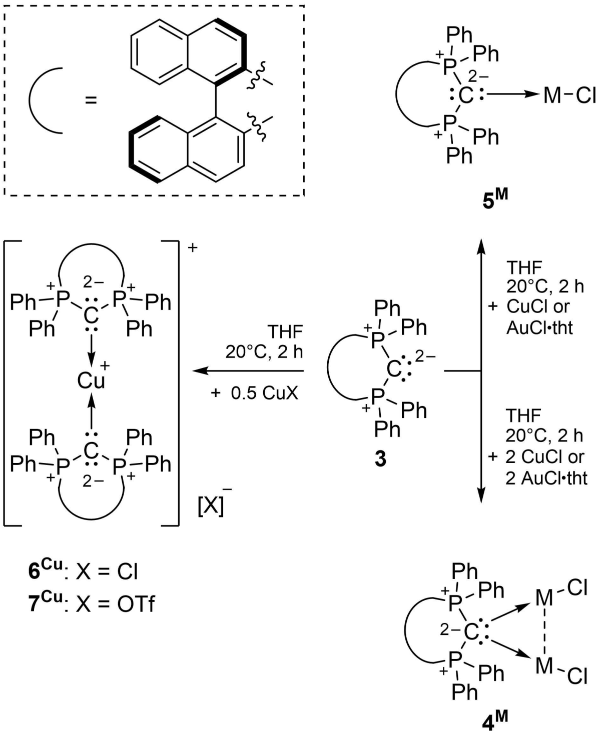
Scheme 4. Synthesis of the Carbodiphosphorane **3**.

Single crystals of **3** in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit were obtained from a mixture of toluene and *n*-pentane at −30 °C (Figure 2c). The P–C1 bond lengths in **3** (166.1(2) and 166.7(2) pm) fit very well other structurally characterized carbodiphosphoranes like reference or six-membered **III**.[36,37] But they are significantly shorter than in the previously discussed cationic compounds $\mathbf{1}^{2+}$ and $\mathbf{2}^{+}$. In the series of $\mathbf{1}^{2+}$–$\mathbf{2}^{+}$–**3** the P–C1 bond lengths decrease from 181.9 via 174.1 to 166.7 pm which nicely corresponds to the increasing bond order in the compounds: with the incremental cumulation of electron pairs at the central carbon atom C1, more and more electron density is available for donation into the vacant anti-bonding P-C^{Ph} orbitals, which leads to shorter P–C1 bond lengths in this series.[2,36,38,39] Moreover, a non-negligible amount of electrostatic compression from P$^+$ and C$^-$ must be considered.[39] NMR spectra of **3** were measured in C_6D_6. The ^{31}P NMR spectrum shows a resonance signal with a chemical shift of 1.3 ppm, which is in good agreement with reference compound **I** (−2.8 ppm) or the seven membered CDP **IV** (−1.7 ppm).[29,36] In the ^{13}C NMR spectrum, the expected resonance signals for the phenyl and napthyl substituents are observed. Moreover, a triplet at 31.5 ppm with a coupling constant of 11.4 Hz is observed, which is tentatively assigned to the "carbone-C"-atom. However, in reference compounds, this signal is shifted towards slightly higher fields (22 to −7 ppm). The $^1J_{PC}$ coupling constant is on the lower end of the observed range in carbodiphosphoranes ($^1J_{PC}$ = 11–305 Hz).[5,7,17,21,29,40] The assignment was verified by acquisition of a ^{13}C{^{1}H,^{31}P} NMR spectrum with broadband decoupling on ^{1}H and ^{31}P simultaneously. The experiment was realized with a Bruker triple resonance broad band probe (TBI). There, instead of the triplet, a singlet was observed. The chemical shift and low $^1J_{PC}$ coupling constant might be rationalized by the hindered rotation and fixed P-C-P angle in the molecule leading to a less favorable orbital overlap for the coupling. This method was also applied to reference compound (**I**), were a similar change of the triplet to a singlet in the ^{13}C NMR spectrum was observed. The later experiment is a reproduction of a known reference work.[29]

The orange compound **3** was also analyzed *via* UV/Vis spectroscopy in a toluene solution. A first absorption maximum is observed at a wavelength of 450 nm which fits the visually observed orange color. As it is known that the BINAP ligand shows room temperature photoluminescence (RTP),[41] the RTP-properties of the crystalline **3** were probed. After excitation with a 405 nm laser, emission at ~690 nm is observed in the emission spectrum (Figure 4). This is redshifted compared to the free (*R*)-BINAP which shows a dual emission at ~520 nm (95 %) and ~680 nm (5 %) after excitation with 360 nm UV light.[41] Quantum yield or determination of lifetimes of the excited states for further characterization are not obtainable with the used setup. Nonetheless, this makes the chiral **3** interesting for potential applications as emitter of circularly polarized light.

Reactions of 3 with CuCl and AuCl.

For the preparation of coinage metal complexes, **3** is reacted with CuCl or [AuCl(tht)] (tht = tetrahydrothiophene) in THF at room temperature. Depending on stoichiometry between **3** and CuCl, different phosphorus containing species were observed in the ^{31}P NMR spectra of the corresponding reaction solutions. One minor product, which was always observed in small quantities in the ^{31}P NMR spectrum, was identified as the protonated species $\mathbf{2}^{+}$, even though the reactions were performed using rigorously dried solvents and a glovebox or standard Schlenk techniques. Single crystals of **2**[Cl] and **2**[CuCl$_2$] suitable for single crystal X-ray diffraction were obtained during attempted product crystallizations from the reaction mixtures (see supporting information). During our experiments, it was possible to isolate three different compounds from the reaction of **3** and CuCl. Upon performing the reaction using a 1:2 ratio of **3** and CuCl, formation of a light-yellow precipitate is observed. The precipitate was unambiguously identified as **4**^{Cu} *via* single crystal X-ray diffraction (see Scheme 5). Here, two CuCl moieties are coordinated by the CDP ligand. Compound **4**^{Cu} crystalizes in the orthorhombic space group $P2_12_12_1$ with one molecule of benzene in the asymmetric unit (Figure 3a). The elongated P–C1 bond lengths in **4**^{Cu} (173.2(2) and 175.0(5) pm) compared to **3** (166.7 pm) point to a four-electron-coordination-mode of the ligand **3** in complex **4**^{Cu}.[42,43] The C–Cu bond lengths of 194.1(5) and 194.2(5) pm are in agreement to other compounds of the form $[(R_3P)_2C(CuX)_2]$ (X = Cl-I; 195.6(3)–207.5(1) pm).[9,21] The Cu···Cu distance of 255.05(9) and the Cu–C–Cu angle of 82.1(2) ° also fits the reference compounds and hints at cuprophilic interactions between the copper centers (sum of van der Waals radii: 280 pm; distance in the Cu_2 dimer in the gas phase: 222 pm).[9,21,44,45] All expected resonance signals are observed in the ^1H and ^{13}C NMR spectra with the triplet signal for the carbone-C atom at 9.7 ppm ($^1J_{PC}$ = 40.5 Hz) in the ^{13}C NMR spectrum. The ^{31}P NMR spectrum shows a singlet at 23.0 ppm. The UV/Vis spectrum in DCM shows an absorption maximum at ~380 nm which fits to the pale-yellow color of the compound. In a previous report, the photoluminescence of two rigid CDP-$(CuX)_2$ complexes has been investigated by Sundermeyer *et al.*, where emission maxima at 510 and 540 nm were observed. These were ascribed to thermally activated delayed fluorescence (TADF) emissions.[9] Therefore, the photoluminescence properties of the prepared complexes were investigated. The emission spectra of **4**^{Cu} were recorded, whereby an emission with a maximum at 650 nm was observed after excitation with a 405 nm laser (Figure 4). The observed emission is significantly more red-shifted compared to the reference compounds prepared by Sundermeyer *et al.* and slightly red shifted compared to **3**.[9] Currently the underlying mechanism of



Scheme 5. Synthesis the copper complexes **4**^{Cu}-**7**^{Cu} and the gold complexes **5**^{Au} and **6**^{Au}.

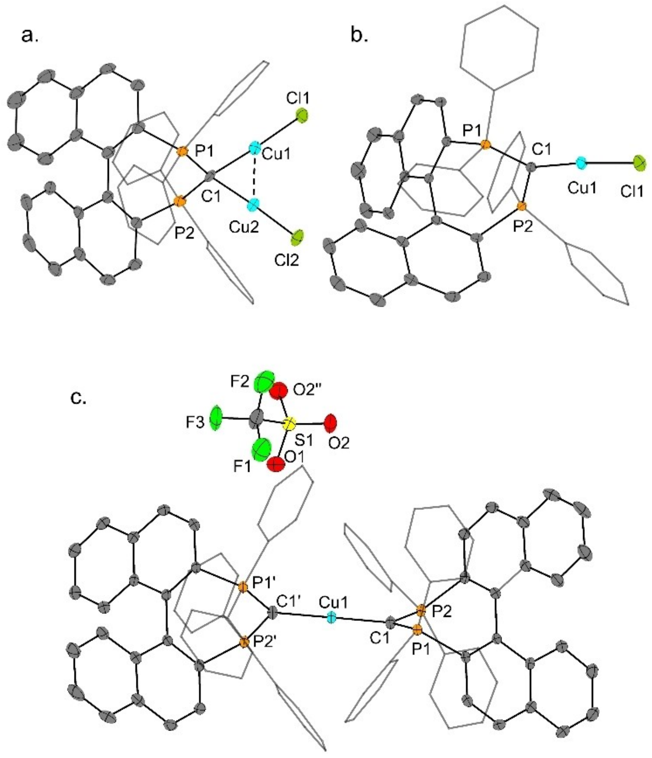


Figure 3. Molecular structure of a. **4**^{Cu}, b. **5**^{Cu} and c. **7**^{Cu} in the crystal structure. Co-crystalline solvent molecules and hydrogen atoms are omitted. Moreover, disorder is not shown for clarity. The atoms in c. labelled with an apostrophe are symmetry generated by using 1-x, y, 1-z and those labelled with a double apostrophe by using -x, y, 1-z. Selected bond lengths [pm] and angles [°] for **4**^{Cu}: C1-Cu1 193.9(5), C1-Cu2 194.0(4), Cu1-Cl1 212.27(5), Cu2-Cl2 211.88(12), Cu1-Cu2 255.16(8), P1-C1 173.2(2), P2-C1 175.0(5), C1-Cu1-Cl1 177.0(1), C1-Cu2-Cl2 175.7(1), Cu1-C1-Cu2 82.3(2), P1-C1-P2 113.0(2). Selected bond lengths [pm] and angles [°] for **5**^{Cu}: C1-Cu1 189.1(2), Cu1-Cl1 212.27(5), P1-C1 169.8(2), P2-C1 170.4(2), C1-Cu1-Cl1 175.16(6), P1-C1-P2 112.35(11). Selected bond lengths [pm] and angles [°] for **7**^{Cu}: C1-Cu1 191.0(2), P1-C1 167.0(3), P2-C1 167.0(3), C1-Cu-C1' 179.1(8), P1-C1-P2 113.4(2).

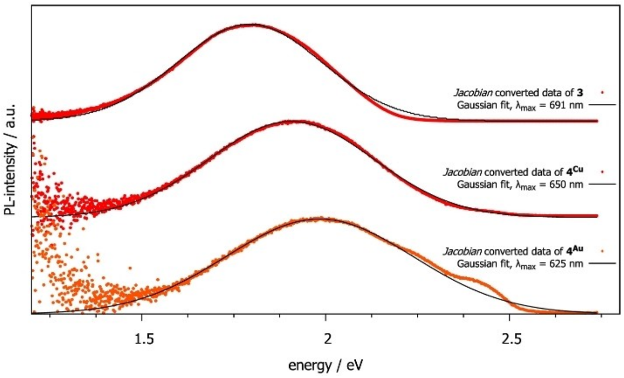


Figure 4. Normalized emission spectra of solid **3** (top), solid **4**^{Cu} (center) and solid **4**^{Au} (bottom) after irradiation with a 405 nm laser room temperature.

the emission is under investigating. It might be related to TADF emissions, to the BINAP moiety itself, or both.[9,41]

Upon reaction of **3** and CuCl in 1:1 stoichiometry, **5^{Cu}** is obtained (see Scheme 5). The crude product obtained in the reaction contains impurities which were identified as **4^{Cu}** and **6^{Cu}**. Analytically pure and crystalline **5^{Cu}** was obtained by recrystallization from toluene. The orange compound shows a singlet resonance signal in the ^{31}P NMR spectrum at 17.2 ppm in C_6D_6 (18.0 ppm in CD_2Cl_2), which is in agreement with the chemical shift of the structurally similar, literature known reference compound $[(Ph_3P)_2C\text{-}CuCl]$ (16.5 ppm in CD_2Cl_2).[22] However, the triplet resonance signal for the central carbon-C atom in the ^{13}C NMR spectrum is not observed for **5^{Cu}**. UV/Vis investigations reveal an absorption band at ~450 nm fitting to the orange color. The RTP emission spectra show a maximum at ~660 nm (Figure S4.3), which is in between that of **3** and **4^{Cu}**. Compound **5^{Cu}** crystallizes in the space group $P2_1$ with $Z=4$ (Figure 3b). The P–C1 bond lengths (169.8(2) and 170.4(2) pm) are considerably smaller than in **4^{Cu}** (173.2(2) and 175.0(5) pm)). This is due to the fact that in **5^{Cu}** (and **5^{Au}**, vide infra) only one lone pair (σ-symmetry) on C1 coordinates to the metal center. Therefore, **3** acts as a two-electron donor ligand. The remaining lone pair (π-symmetry) on the central carbon atom C1 is still available for π back-donation to the BINAP moiety, i.e. into vacant anti-bonding P-C^{Ph} orbitals. Hence, the P–C1 bond order is only slightly reduced, yielding in only slightly elongated P–C1 bond lengths in **5^{Cu}** compared to **3**. The C-Cu bond length is 189.1(2) pm and the C–Cu–Cl bond angle is 175.12(7) °, corroborating a linear complexation at the copper center. This is similar to $[(Ph_3P)_2C\text{-}CuCl]$ (C–Cu: 190.6(1) pm; C–Cu–Cl: 178.2(1) °).[23]

When CuCl is treated with two equivalents of **3** in THF, precipitation of the homoleptic complex [CDP-Cu-CDP]Cl (**6^{Cu}**) is observed (see Scheme 5). The compound shows a chemical shift at 16.5 ppm (CD_2Cl_2) in the ^{31}P NMR spectrum which corresponds well to the literature known complex $[Cu(C(PPh_3)_2)_2]I$ (15.8 ppm).[26] The resonance signal of the carbone-C atom is observed at 15.3 ppm (triplet, $^1J_{PC}=52.9$ Hz). In the UV/Vis spectrum an absorption maximum is observed at ~460 nm, which is very similar to **5^{Cu}** and also fits the observed orange color. DCM solutions of **6^{Cu}** show visible orange photoluminescence. The RTP emission spectrum of solid **6^{Cu}** reveals a photoluminescence maximum at ~660 nm after excitation with a 405 nm laser (Figure S4.4), which is also similar to **5^{Cu}**. Crystals of **6^{Cu}** were obtained from a THF solution at −20 °C. However, the quality of the x-ray diffraction data obtained was not sufficient for a robust structural analysis.

To be able to evaluate the molecular structure of cation **6**$^+$, the chloride anion was exchanged for a triflate anion ($CF_3SO_3^-$, OTf^-). By reaction of **3** with $Cu(OTf)_2\cdot toluene_{0.5}$ in THF, the corresponding complex [CDP–Cu-CDP][OTf] (**7^{Cu}**, see Scheme 5) could be obtained in 85 % yield. The anion exchange does not influence the chemical shifts in the ^{1}H, ^{13}C or ^{31}P NMR spectra of the cation in CD_2Cl_2 solution at all. From this it is concluded, that **6^{Cu}** and **7^{Cu}** are at hand as solvent separated ion pairs in CD_2Cl_2 solutions. By comparison of the IR spectra of **6^{Cu}** and **7^{Cu}**, stretching modes of the triflate anion can be identified at 1267 cm^{-1}, 1221 cm^{-1}, 1140 cm^{-1} and 1029 cm^{-1}. The absorption band at 1267 cm^{-1} is tentatively assigned to the $\nu[SO_3(E)]$ vibration which is similar to the vibration in Ag[OTf] (1270 cm^{-1}) or Na[OTf] (1280 cm^{-1}), where ionic, non-covalently bound triflate anions can be assumed.[46] The presence of an ionic moiety in the solid state was confirmed by single crystal X-ray diffraction measurements. Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of toluene into a solution of **7^{Cu}** in THF. Compound **7^{Cu}** crystalizes in the monoclinic space group *I*2 with half a formula unit and one molecule of toluene in the asymmetric unit (Figure 3c). The copper atom is positioned on the C_2 axis, so that a second ligand is symmetry generated by 1-x, y, 1-z. The Cu1-C1 bond length is 191.0(2) pm, which is very similar to the previously described compounds **4^{Cu}** and **5^{Cu}** and indicative of minimal steric hindrance between the two ligands. The same holds true for the P–C1 bond lengths. Both are 167.0(3) pm long, which is significantly smaller than in **4^{Cu}** and only marginally smaller than in **5^{Cu}**. This can also be rationalized by the remaining lone pair in π-symmetry, which is available for π back donation to the BINAP moiety (vide supra). The C1-Cu1-Cl1 bond angle is 179.1(8) °, hence the copper atom is linearly coordinated. The planes spanned by P1-Cu1-P2 and P1′-Cu1-P2′ show an angle of 55 °. This is much smaller than in the reference compound $[Cu(C(PPh_3)_2)_2]I$ (66 °) and might be attributed to packing effects of the ligands as they are sterically very similar.[26]

Similar reactivity was observed in reactions of **3** with [AuCl(tht)]. After addition of two equivalents of [AuCl(tht)] to **3**, [(*R*)-BINAP-CDP-(AuCl)$_2$] (**4^{Au}**, see Scheme 5) is obtained in the form of a colorless precipitate. The ^{31}P NMR spectrum of compound **4^{Au}** shows a chemical shift of 21.1 ppm, while a triplet resonance signal for the carbone-C atom is observed at 7.0 ppm ($^1J_{PC}=44.7$ Hz). Similar to all previously discussed compounds, the main signal in the ESI(+) mass spectrum relates to **2**$^+$. However, another fragment identified as [**4^{Au}**−AuCl+H]$^+$ is observed. NMR spectra show all expected signals with a triplet resonance signal for the P–C–P unit at 7.0 ppm ($^1J_{PC}=44.7$ Hz) in the ^{13}C NMR spectrum. Single crystals suitable for X-ray diffraction were obtained either by slow diffusion of *n*-hexane into a solution of **4^{Au}** in pyridine or **4^{Au}** in DCM at room temparature, or by layering of a DCM solution of **4^{Au}** with *n*-pentane at −20 °C (see supporting information). Only the best quality structure is discussed within this manuscript, which was obtained from DCM and *n*-hexane at room temperature. There, **4^{Au}** crystalizes in the orthorhombic space group $P2_12_12_1$ with one molecule of **4^{Au}** and one molecule of DCM in the asymmetric unit (Figure 5a). The gold atoms show linear coordination with C1-Au–Cl bond angles of 177.5(3) and 178.7(4) °. The C–Au bond lengths are 206.2(12) to 210.3(12) pm, which is similar to the literature known reference compound $[(Ph_3P)_2C\text{-}(AuCl)_2]$ (207.8(3) and 207.3(3) pm).[19] As seen in complex **4^{Cu}**, the elongated P–C1 bond lengths in **4^{Au}** (174.9(13) and 176.6(13) pm) are about nine pm longer than those in non-coordinating **3** (166.1(2) and 166.7(2) pm), which clearly substantiates the four electron donor mode of the ligand. The Au···Au distance is 292.09(7) pm and lies in the range for aurophilic interactions (sum of Van der Waals radii:

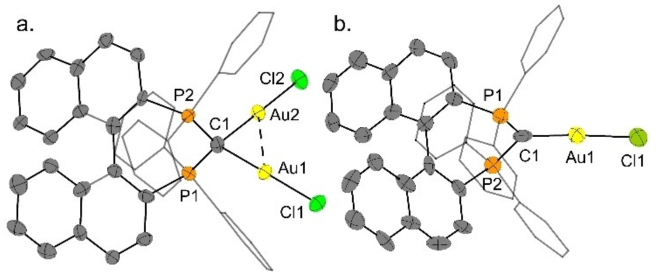


Figure 5. Molecular structure of a. 4^{Au} and b. 5^{Au} in the crystal structure. Co-crystalline solvents and hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°] for 4^{Au}: C1-Au1 206.2(12), C1-Au2 210.3(12), Au1-Cl1 227.9(3), Au2-Cl2 229.9(3), Au1-Au2 292.09(7), P1-C1 174.9(13), P2-C1 176.6(13), C1-Au1-Cl1 177.5(3), C1-Au2-Cl2 178.7(4), Au1-C1-Au2 89.1(5), P1-C1-P2 115.2(7). Selected bond lengths [pm] and angles [°] for 5^{Au}: C1-Au1 199(2), Au1-Cl1 230.2(5), P1-C1 172(2), P2-C1 172(2), C1-Au1-Cl1 175.5(6), P1-C1-P2 112.2(12).

380 pm; sum of covalent radii in two coordinate Au(I): 250 pm).[45,47] Moreover, it is significantly smaller than in the reference compound $[(Ph_3P)_2C\text{-}(AuCl)_2]$ (314.32(2) pm).[19] The colorless complex **4**$^{\mathbf{Au}}$ was also investigated using UV/Vis spectroscopy where an absorption maximum was found at 341 nm. This is slightly blue shifted compared to the structurally similar complex **4**$^{\mathbf{Cu}}$ and relates nicely to the colorlessness of the compound. Photoluminescence emission spectra with a maximum at 625 nm was recorded, which is blue shifted compared to **3** and **4**$^{\mathbf{Cu}}$ (Figure 4).

The (*R*)-BINAP-CDP-AuCl complex (**5**$^{\mathbf{Au}}$) is obtained as a red precipitate in low yield (10%). In the ^{31}P NMR spectrum, a resonance signal with a chemical shift of 17.5 ppm is observed, which is very similar to the CuCl complex **5**$^{\mathbf{Cu}}$. A resonance signal corresponding to the carbone-C atom is at hand at 25.2 ppm (triplet, $^1J_{PC}=71.0$ Hz) in the ^{13}C NMR spectrum. Crystals suitable for single crystal X-ray diffraction were obtained from layering of a DCM solution with *n*-pentane at −20 °C ($P2_12_12_1$, Z = 4, figure 5b). The gold atom in **5**$^{\mathbf{Au}}$ shows linear coordination with a C–Au–Cl bond angle of 175.5(6) °. The C1-Au1 bond length is 199(2) pm, which is in the range of literature known carbone-C–Au bond lengths of linear coordinated gold complexes (201.8(6)–208.2(2) pm).[8,18,19,24] As seen in the series of Cu complexes above (**4**$^{\mathbf{Cu}}$, **5**$^{\mathbf{Cu}}$, **7**$^{\mathbf{Cu}}$), the P–C1 bond length in **5**$^{\mathbf{Au}}$ (172 pm) lies in between the values found for **4**$^{\mathbf{Au}}$ and **3**. In the UV/Vis spectrum a maximum is observed at ~445 nm which is again similar to the related copper compound **5**$^{\mathbf{Cu}}$ and fitting to the red color.

The linear coinage metal halide complexes **5**$^{\mathbf{Cu}}$ and **5**$^{\mathbf{Au}}$ were used for the determination of the percent buried volume (% V_{bur}) of **3**, a property related to the steric demand of a donor ligand.[48] When normalizing the C1-M1 bond length to 200 pm, the %V_{bur} values for ***5***$^{\boldsymbol{Cu}}$ and ***5***$^{\boldsymbol{Au}}$ add up to 41.6% and 38.9%, respectively. This is very similar to the value obtained for the reference compound **I** (%$V_{bur}=41.9$) and larger than in $((Ph_2Me)_2P)_2C$ (%$V_{bur}=35.0$).[42,49]

Conclusions

Herein, an easily feasible high yielding synthesis of an unprecedented chiral carbodiphosphorane (CDP) with a (*R*)-BINAP backbone (**3**) is presented. Starting from commercially available (*R*)-BINAP and dibromomethane, the bis phosphonium salts **1**[Br]$_2$ and **1**[SbF$_6$]$_2$, the mono phosphonium salt **2**[Br] and finally the CDP **3** were obtained in high yields.

The coordination chemistry of **3** was explored in reactions with CuX (X = Cl, OTf) and AuCl·(tht). Depending on stoichiometry, complexes with different coordination motifs were obtained: (*R*)-BINAP-CDP-(MCl)$_2$ (M = Cu (**4**$^{\mathbf{Cu}}$), Au (**4**$^{\mathbf{Au}}$)), (*R*)-BINAP-CDP-MCl (M = Cu (**5**$^{\mathbf{Cu}}$), Au (**5**$^{\mathbf{Au}}$)) and [Cu{(*R*)-BINAP-CDP}$_2$]Cl (**6**$^{\mathbf{Cu}}$). The obtained compounds were investigated in solution (NMR spectroscopy, mass spectrometry and UV/Vis absorption spectroscopy) and in the solid state (IR spectroscopy, elemental analysis and single crystal X-ray diffraction). Moreover, photophysical properties of **3** and selected coinage metal complexes were examined by room temperature photoluminescence emission spectroscopy.

In the past, CDPs and transition metal CDP complexes have been used in catalytic transformations, such as hydroamination, hydroalkoxylation or hydoborations.[14,24] The results presented are intended to spark interest for the use of chiral CDPs or their transition metal complexes in asymmetric catalysis. Moreover, the coordination chemistry towards silver salts, which was beyond the scope of this article, should be examined.

Experimental Section

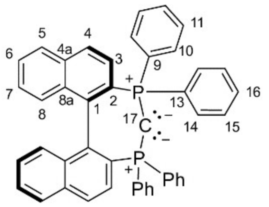
General Considerations: Unless otherwise specified, all manipulations were carried out under argon atmosphere using standard Schlenk and glovebox technique. All solvents used in the reactions and for crystallisations were dried *via* standard techniques, distilled and stored under argon.[50] Solvents were never stored longer than three weeks before use. Dibromomethane was distilled once before use. (*R*)-BINAP, Ag[SbF$_6$], KHMDS and Cu(OTf)·toluene$_{0.5}$ were used as received from a commercial source. CuCl, AuCl·tht and $(Ph_3P)_2C$ (**I**) were prepared according to literature procedures.[51]

NMR spectra were recorded using a Bruker Avance III HD 250MHz, a Bruker Avance II 300 MHz, a Bruker Avance III 500 MHz or a Avance III HD 500 MHz spectrometer at 300K. ^{1}H and ^{13}C chemical shifts were referenced to SiMe$_4$ using the signals of the residual protons of the deuterated solvent ($\delta^1H=5.32$ (CD$_2$Cl$_2$), 7.16 (C$_6$D$_6$); $\delta^{13}C=53.84$ (CD$_2$Cl$_2$), 128.06 (C$_6$D$_6$)) as secondary reference. Spectra of heteronuclei were referenced using the Ξ scale[52] employing 85% H$_3$PO$_4$ (^{31}P) and CFCl$_3$ (^{19}F) as secondary references. The labelling scheme for the resonance signals of ligand **3** in the NMR spectra is given in the scheme 6. Observed signals corresponding to virtual triplets are labelled with the abbreviation *vt*.[53] The *J* values given in this case represent the apparent coupling between adjacent peaks.

IR-spectra were run on a ALPHA FT-IR spectrometer by Bruker using the attenuated total reflectance (ATR) mode.

Mass spectrometry was conducted on a Thermo Fischer Scientific LTQ-FT Ultra (ESI) and a Jeol AccuTOF GCv (LIFDI) .

Elemental analysis was performed on an Elementar Vario MicroCube.



Scheme 6. Labelling scheme for the assignment of resonance signals of the (*R*)-BINAP-CDP moiety in the NMR spectra.

UV/Vis spectra were measured in DCM or toluene using an Analytik-Jena Specord S 600 spectrometer in the range from 1000 nm up to 250 nm.

Photoluminescence spectra were obtained on an Avantes AvaSpec-ULS2048CL-EVO-RS-UA spectrometer featuring a 2048-pixel CMOS detector with a bandwidth of 200 to 1100 nm. The excitation source is a diode laser of tuneable power emitting at 405 nm.

Single-crystal X-ray diffraction analysis was conducted using a Stoe IPDS2 ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å), a Stoe IPDS2T ($Mo_{K\alpha}$), a Stoe StadiVari ($Cu_{K\alpha}$, $\lambda = 1.54178$ Å), a Bruker D8 Quest ($Mo_{K\alpha}$) or a Bruker D8 Venture ($Mo_{K\alpha}$, $Cu_{K\alpha}$) diffractometer. Structures were solved by intrinsic phasing using SHELXT-2015. Structures were refined through full-matrix-least-squares against F^2 using SHELXL-2015. All structures were solved and refined by using the OLEX2 platform.[54] Structural data was deposited in the CCDC database.[55]

Synthesis of 1[Br]$_2$. (*R*)-BINAP (8.0 g, 12.9 mmol, 1.0 eq) is suspended in 40 ml of dibromomethane and the reaction mixture is stirred under reflux for 20 hours. Subsequently the resulting light-yellow solution is concentrated to 10 ml and 250 ml of toluene are added. The resulting pale-yellow precipitate is separated *via* filtration and washed with toluene (4×10 ml). After removal of volatiles under reduced pressure**1**[Br]$_2$ is obtained as a pale-yellow solid containing minor impurities in >99% yield. Analytically pure, colourless **1**[Br]$_2$, is obtained by layering of a concentrated solution in hot methanol with ethyl acetate. Crystaline yield: 85% Crystals suitable for single crystal X-ray diffraction were obtained from an NMR tube of the reaction mixture in CH_2Br_2 . **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 8.45$ (dd, $^3J_{HH} = 8.0$ Hz, $^3J_{PH} = 13.2$ Hz, 4H, H^{14}), 8.01 (br s, 4H, H^{10}), 7.91 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{PH} = 2.0$, Hz, 2H, H^4), 7.81 (d, $^3J_{HH} = 8.3$ Hz, 2H, H^5), 7.68 (t, $^3J_{HH} = 7.1$ Hz, 2H, H^6), 7.66 (t, $^3J_{HH} = 6.2$ Hz, 2H, H^{16}), 7.57 (dt, $^3J_{HH} = 7.9$ Hz, $^4J_{PH} = 3.4$ Hz, 4H, H^{15}), 7.43 (t, $^3J_{HH} = 7.7$ Hz, 2H, H^7), 7.38 (t, $^2J_{PH} = 13.5$ Hz, 2H, H^{17}), 7.32 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{PH} = 12.8$ Hz, 2H, H^3), 7.05–7.12 (m, 4H, H^8, H^{12}), 6.93 (br s, 4H, H^{11}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 141.8$ (br s, C^1), 136.2 (s, C^{16}), 136.1 (m, C^{4a}), 135.5 (s, C^{14}), 133.7 (s, C^{12}), 132.7 (m, C^4), 132.5 (m, C^{8a}), 132.1 (m, C^{10}), 131.1 (s, C^6), 130.9 (m, C^{15}), 129.6 (s, C^7), 129.3 (s, C^5, C^{11}), 127.8 (s, C^8), 127.5 (br s, C^3), 117.2 (d, $^1J_{PC} = 87.4$ Hz, C^2), 114.6 (d, $^1J_{PC} = 115.2$ Hz, C^9), 114.9 (d, $^1J_{PC} = 91.2$ Hz, C^{13}), 24.6 (t, $^1J_{PC} = 50.1$ Hz, C^{17}) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2):$\delta = 19.6$ ppm. **Elemental analysis** calcd (%) for [$C_{45}H_{34}Br_2P_2$] (796.52 g/mol): C 67.86; H 4.30; found: C 67.52; H 4.50. **IR** (cm^{-1}): 3038 (m), 3002 (m), 2631 (m), 1582 (w), 1554 (w), 1500 (w), 1485 (m), 1435 (w), 1370 (s), 1321 (w), 1218 (w), 1178 (w), 1163 (w), 1142 (s), 1100 (s), 1027 (s), 995 (m), 948 (s), 878 (s), 847 (s), 826 (s), 810 (s), 794 (s), 747 (s), 737 (s), 721 (m), 704 (m), 685 (s), 645 (s), 608 (m), 549 (w), 535 (m), 497 (s), 454 (s), 417 (m). **HR-MS** ESI(+): m/z 635.2042 [$C_{45}H_{33}P_2$]$^+$, calcd 635.2057.

Synthesis of 1[SbF$_6$]$_2$. Compound **1**[Br]$_2$ (200 mg, 0.25 mmol, 1.0 eq) is dissolved in 4 ml of DCM and Ag[SbF$_6$] (173 mg, 0.50 mmol, 2.0 eq) dissolved in 4 ml of DCM is added whereupon formation of a pale-yellow solid precipitate is observed, which is removed *via* filtration. Afterwards, *n*-pentane is added to the filtrate and a colourless solid is precipitated. After decanting of the liquids, the remaining solid is washed with *n*-pentane and dried under reduced pressure. Compound **1**[SbF$_6$]$_2$ is obtained in 76% yield. Crystals suitable for single crystal X-ray diffraction were obtained from a solution in $CDCl_3$ inside an NMR tube. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 8.02$ (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{PH} = 2.5$ Hz, 2H, H^4), 7.91–7.96 (m, 2H, H^{16}), 7.85 (d, $^3J_{HH} = 7.8$ Hz, 2H, H^8), 7.79–7.86 (m, 8H, H^{14}, H^{15}), 7.24 (t, $^3J_{HH} = 7.6$ Hz, 2H, H^7), 7.51 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{PH} = 13.2$ Hz, 2H, H^3), 7.47 (dt, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, 2H, H^6), 7.40 (dd, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 13.9$ Hz, 4H, H^{10}), 7.21 (t, $^3J_{HH} = 7.6$ Hz, 2H, H^{12}), 7.03–7.07 (m, 4H, H^{11}), 7.04 (d, $^3J_{HH} = 8.6$ Hz, 2H, H^5), 5.13 (t, $^3J_{PH} = 13.1$ Hz, 2H, H^{17}). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 141.8$ (vt, $J = 6.7$ Hz, C^1), 137.1 (s, C^{16}), 136.5 (s, C^{4a}), 134.9 (s, C^{12}), 134.3 (m, C^{14}), 133.4 (m, C^4), 132.8 (m, C^{8a}), 131.9 (m, C^{15}), 131.8 (s, C^7), 130.8 (m, C^{10}), 130.2 (m, C^{11}, C^6), 129.6 (s, C^5), 127.7 (s, C^{16}), 127.2 (m, C^3), 114.7 (m, C^{13}), 114.5 (m, C^2) 113.0 (m, C^9), 23.8 (t, $^1J_{PC} = 53.4$ Hz, C^{17}) ppm. **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): $\delta = 16.7$ ppm. **Elemental analysis** calcd (%) for [$C_{45}H_{34}F_{12}P_2Sb_2$] (1108.22 g/mol): C 48.77; H 3.09; found: C 48.31; H 3.26. **IR** (cm^{-1}): 3067 (w), 2913 (w), 2165 (w), 2113 (w), 1981 (w), 1584 (w), 1555 (w), 1504 (w), 1485 (w), 1439 (m), 1373 (w), 1320 (w), 1263 (w), 1220 (w), 1166 (w), 1102 (m), 1027 (w), 998 (w), 947 (w), 878 (w), 849 (w), 818 (w), 781 (w), 767 (w), 735 (m), 705 (w), 689 (w), 651 (s), 535 (m), 494 (s), 445 (w). **HR-MS** ESI(+): m/z 635.2047 [$C_{45}H_{33}P_2$]$^+$, calc. 635.2057.

Synthesis of 2[Br]. Compound **1**[Br]$_2$ (200 mg, 0.25 mmol) is suspended in 6 ml toluene and 10 ml of a 1 M solution of KOH in water are added. The reaction mixture is stirred for 15 minutes at room temperature. Solids are separated by filtration and washed with water (3×6 ml) and diethylether (3×6 ml). After drying under reduced pressure, Compound **2**[Br] is obtained as colourless solid in 94% yield. Crystals suitable for single crystal X-ray diffraction were obtained from layering of a DCM solution with *n*-hexane at 4 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 7.90$ (dd, $^3J_{HH} = 7.4$ Hz, $^3J_{PH} = 12.2$ Hz, 4H, H^{14}), 7.84 (t, $^3J_{HH} = 7.5$ Hz, 2H, H^{16}), 7.91 (d, $^3J_{HH} = 8.5$ Hz, 2H, H^4), 7.72 (dt, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 2.2$ Hz, 4H, H^{15}), 7.69 (d, $^3J_{HH} = 8.6$ Hz, 2H, H^5), 7.45 (t, $^3J_{HH} = 7.2$ Hz, 2H, H^6), 8.01 (dt, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 6.4$ Hz, 4H, H^{10}), 7.20 (dt, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.1$ Hz, 2H, H^7), 7.12 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{PH} = 12.2$ Hz, 2H, H^3), 6.95 (t, $^3J_{HH} = 7.4$ Hz, 2H, H^{12}), 6.85 (br t, $^3J_{HH} = 7.8$ Hz, 4H, H^{11}), 6.82 (d, $^3J_{HH} = 8.6$ Hz, 2H, H^8), 2.21 (t, $^2J_{PH} = 2.8$ Hz, 1H, H^{17}), ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 141.8$ (vt, $J = 6.7$ Hz, C^1), 134.7 (s, C^{16}), 134.6 (vt, $J = 5.7$ Hz, C^{14}), 134.0 (s, C^{4a}), 132.3 (vt, $J = 4.8$ Hz, C^{8a}), 131.9 (s, C^{12}), 131.3 (vt, $J = 6.1$ Hz, C^4), 132.1 (vt, $J = 5.6$ Hz, C^{10}), 130.3 (vt, $J = 6.7$ Hz, C^{15}), 128.8 (s, C^6), 128.7 (s, C^5), 128.5 (m, $^3J_{PC} + {}^5J_{PC =}$6.6 Hz, C^{11}), 128.1 (s, C^7), 127.9 (s, C^8), 127.1 (m, C^2), 125.5 (m, C^9), 124.8 (vt, $J = 5.2$ Hz, C^3), 122.8 (m, C^{13}), 6.0 (t, $^1J_{PC} = 113.9$ Hz, C^{17}) ppm. **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2): $\delta = 20.8$ ppm. **Elemental analysis** calcd (%) for [$C_{45}H_{33}Br_1P_2 \cdot CH_2Cl_2$] (800,54 g/mol): C 69.02; H 4.41; found: C 69.39; H 4.33. **IR** (cm^{-1}): 3052 (w), 3016 (w), 2917 (w), 1584 (w), 1556 (w), 1501 (w), 1480 (w), 1432 (m), 1371 (w), 1316 (w), 1280 (w), 1185 (s), 1163 (w), 1124 (s), 1100 (w), 1025 (w), 998 (m), 961 (m), 942 (m), 877 (w), 851 (w), 831 (m), 812 (m), 794 (m), 754 (s), 719 (s), 696 (s), 667 (m), 646 (m), 622 (m), 609 (w) 581 (w), 550 (m), 525 (m), 503 (s), 457 (m), 447 (m), 415 (m). **HR-MS** ESI(+): m/z 635.2036 [$C_{45}H_{33}P_2$]$^+$, calc. 635.2052.

Synthesis of 3. Compound **1**[Br]$_2$ (1.54 g, 1.93 mmol, 1 eq) is suspended in 20 ml of toluene at −30 °C. During dropwise addition of KHMDS (0.81 g, 4.06 mmol, 2.1 eq) in 30 ml toluene, the reaction mixture turns orange. The reaction mixture is allowed to reach room temperature over 2 hours and solids are removed *via* filtration. Upon concentration of the filtrate and addition of *n*-pentane an orange solid precipitates from solution. The solid is separated, washed with *n*-pentane and dried under reduced pressure at 80 °C. Compound **3** is obtained as an orange solid in 82% yield. Crystals suitable for single crystal X-ray diffraction are obtained by layering of a concentrated solution in toluene with *n*-pentane at −30 °C. **^{1}H NMR** (500 MHz, C$_6$D$_6$): $\delta = 8.66$ (br m, 4H, H^{14}), 7.71 (br dd, $^{3}J_{HH} = 7.2$ Hz, $^{3}J_{PH} = 10.9$ Hz, 4H, H^{10}), 7.30–7.17 (m, 12H, H^{15}, H^{8}, H^{3}, H^{4}, H^{16}), 7.07 (d, $^{3}J_{HH} = 8.6$ Hz, 2H, H^{5}), 7.01 (dt, $^{3}J_{HH} = 7.4$ Hz, $^{4}J_{HH} = 1.1$ Hz, 2H, H^{7}), 6.83 (dt, $^{3}J_{HH} = 7.7$ Hz, $^{4}J_{HH} = 1.2$ Hz, 2H, H^{6}), 6.41–6.52 (m, 6H, H^{11}, H^{12}). **^{13}C{^{1}H,^{31}P} NMR** (126 MHz, C$_6$D$_6$): 137.3 (s, C^{1}), 137.1 (s, C^{9}), 136.9 (s, C^{2}), 134.7 (s, C^{14}), 134.5 (s, C^{13}), 133.6 (s, C^{8a}), 133.2 (s, C^{4a}), 131.1 (s, C^{10}), 130.6 (s, C^{16}), 128.7 (s, C^{3} or C^{4}), 128.5 (s, C^{12}), 126.8 (s, C^{11}), 126.8 (s, C^{6}), 125.9 (s, C^{3} or C^{4}), 125.9 (s, C^{7}), 32.0 (s, C^{17}), C^{5}, C^{8} and C^{15} are below the C$_6$D$_6$ signal. **^{13}C{^{1}H} NMR** (126 MHz, C$_6$D$_6$): 137.3 (vt, $J = 6.5$ Hz, C^{1}), 137.1 (m, C^{9}), 136.9 (m, C^{2}), 134.7 (br m, C^{14}), 134.5 (m, C^{13}), 133.6 (vt, $J = 4.2$ Hz, C^{8a}), 133.2 (s, C^{4a}), 131.1 (vt, $J = 4.4$ Hz, C^{10}), 130.6 (s, C^{16}), 128.7 (m, C^{3} or C^{4}), 128.5 (s, C^{12}), 126.8 (vt, $J = 6.6$ Hz, C^{11}), 126.8 (s, C^{6}), 125.9 (m, C^{3} or C^{4}), 125.9 (s, C^{7}), 32.0 (t, $^{1}J_{PC} = 11.7$ Hz, C^{17}). C^{5}, C^{8} and C^{15} are below the C$_6$D$_6$ signal. **^{31}P{^{1}H} NMR** (202 MHz, C$_6$D$_6$): $\delta = 1.3$ ppm. **Elemental analysis** calcd (%) for [C$_{45}$H$_{32}$P$_2$] (800,54 g/mol): C 85.16; H 5.08; found: C 85.10; H 5.40. **IR** (cm^{-1}): 3046 (w), 1584 (w), 1552 (w), 1498 (w), 1476 (w), 1434 (m), 1333 (w), 1303 (w), 1256 (w), 1215 (w), 1160 (w), 1144 (m), 1135 (s), 1118 (w), 1090 (m), 1064 (m), 1025 (w), 997 (w), 961 (w), 921 (w), 890 (w), 845 (w), 818 (w), 803 (w), 790 (w), 743 (s), 709 (w), 690 (s), 667 (m), 642 (w), 621 (w), 605 (w), 551 (w), 526 (m), 503 (s), 471 (w), 446 (m), 408 (w). **HR-MS** ESI(+): m/z 635.2036 [C$_{45}$H$_{33}$P$_2$]$^{+}$, calcd 635.2052.

Synthesis of 4^{Cu}. Compound **3** (150 mg, 0.23 mmol, 1 eq) and CuCl (47 mg, 0.47 mmol, 2 eq) are suspended in 6 ml THF. Upon stirring for 2 hours at room temperature, a pale-yellow precipitate has formed, which is separated by decanting of the solution. The remaining solid is washed several times with Et$_2$O and dried under reduced pressure. The raw product is taken up in 2 ml DCM, filtered, and the filtrate is layered with *n*-pentane at room temperature. After 2 days pale-yellow crystals of **4^{Cu}**, which were dried under reduced pressure at 60 °C, are obtained in 45 % yield. **^{1}H NMR** (500 MHz, CD$_2$Cl$_2$): $\delta = 8.30$ (ddd, $^{3}J_{HH} = 8.1$ Hz, $^{3}J_{PH} = 11.5$ Hz, $^{4}J_{HH} = 1.2$ Hz, 4H, H^{14}), 7.87 (dd, $^{3}J_{HH} = 8.6$ Hz, $^{4}J_{HH} = 1.2$ Hz, 2H, H^{4}), 7.69–7.79 (m, H^{3}, H^{5}, H^{10}, H^{16}), 7.68 (dt, $^{3}J_{HH} = 7.8$ Hz, $^{4}J_{PH} = 2.2$ Hz, H^{15}), 7.43 (dt, $^{3}J_{HH} = 7.6$ Hz, $^{4}J_{HH} = 1.0$ Hz, 2H, H^{7}), 7.08 (dt, $^{3}J_{HH} = 7.7$ Hz, $^{4}J_{HH} = 1.3$ Hz, 2H, H^{6}), 6.79–6.90 (m, 6H, H^{11}, H^{12}), 6.62 (d, 2H, $^{3}J_{HH} = 8.6$ Hz, H^{8}). **^{13}C{^{1}H} NMR** (126 MHz, CD$_2$Cl$_2$): $\delta = 138.1$ (vt, $J = 6.7$ Hz, C^{1}), 135.0 (vt, $J = 5.4$ Hz, C^{14}), 134.3 (s, C^{4a}), 134.1 (s, C^{16}), 132.3 (vt, $J = 4.8$ Hz, C^{8a}), 131.5 (br s, C^{10}), 131.0 (s, C^{12}), 130.8 (vt, $J = 6.1$ Hz, C^{4}), 129.7 (vt, $J = 6.7$ Hz, C^{15}), 128.9 (m, C^{2}), 128.5-128.6 (m, C^{5}, C^{7}), 128.2 (vt, $J = 6.2$ Hz, C^{11}), 128.0 (s, C^{8}), 127.5 (s, C^{6}), 127.2 (m, C^{9}), 125.5 (m, C^{13}), 125.4 (vt, $J = 4.3$ Hz, C^{3}), 9.7 (t, $^{1}J_{PC} = 40.5$ Hz, C^{17}) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD$_2$Cl$_2$): $\delta = 23.0$ ppm. **Elemental analysis** calcd (%) for [C$_{45}$H$_{32}$Cl$_2$Cu$_2$P$_2$] (832,69 g/mol): C 64.91; H 3.87; found: C 64.79; H 3.89. **IR** (cm^{-1}): 3052 (w), 1585 (w), 1555 (w), 1502 (w), 1478 (w), 1434 (m), 1372 (w), 1316 (w), 1260 (w), 1217 (w), 1161 (w), 1094 (m), 1027 (w), 998 (w), 959 (m), 945 (w), 928 (w), 874 (w), 849 (w), 814 (m), 775 (w), 741 (s), 715 (m), 691 (s), 667 (m), 646 (w), 622 (w), 608 (w), 580 (w), 556 (w), 545 (w), 499 (s), 473 (w), 444 (w), 421 (w), 408 (w). **HR-MS** LIFDI(+): m/z 635.20701 [C$_{45}$H$_{33}$P$_2$]$^{+}$, calcd 635.20575.

Synthesis of 5^{Cu}. Compound **3** (300 mg, 0.47 mmol, 1 eq) is suspended in 10 ml THF and added to CuCl (47 mg, 0.47 mmol, 1 eq) at room temperature. While the reaction mixture is stirred for 2 hours, the solution clears. Little leftover suspended solids are separated *via* filtration and the filtrate is concentrated. After layering with diethylether, compound **5^{Cu}** is obtained in the form of an orange solid in 84 % yield. Crystals suitable for single crystal X-ray diffraction are obtained from an oversaturated solution in toluene. **^{1}H NMR** (500 MHz, C$_6$D$_6$): $\delta = 8.66$ (br m, 4H, H^{14}), 7.71 (br m, 4H, H^{10}), 7.22–6.99 (m, 12H, H^{15}, H^{8}, H^{3}, H^{4}, H^{16}), 6.98 (dt, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.0$ Hz, 2H, H^{7}), 6.81 (d, $^{3}J_{HH} = 8.5$ Hz, 2H, H^{5}), 6.73 (dt, $^{3}J_{HH} = 7.6$ Hz, $^{4}J_{HH} = 1.2$ Hz, 2H, H^{6}), 6.47 (t, $^{3}J_{HH} = 7.1$ Hz, 2H, H^{12}), 6.37 (t, $^{3}J_{HH} = 7.1$ Hz, 4H, H^{11}). **^{13}C{^{1}H} NMR** (126 MHz, C$_6$D$_6$): 138.1 (vt, $J = 6.6$ Hz, C^{1}), 134.7 (vt, $J = 5.2$ Hz, C^{14}), 133.3 (s, C^{4a}), 132.8 (vt, $J = 4.3$ Hz, C^{8a}), 132.5 (s, C^{16}), 132.3 (m, C^{13}), 131.6 (m, C^{9}), 131.4 (vt, $J = 4.9$ Hz, C^{10}), 129.7 (s, C^{12}), 129.6 (m, C^{3} or C^{4}), 127.5 (s, C^{8}), 127.2 (vt, $J = 5.2$ Hz, C^{11}), 126.9 (s, C^{7}), 126.9 (s, C^{6}), 126.1 (m, C^{3} or C^{4}), C^{5} and C^{15} are below the C$_6$D$_6$ signal, C^{2} and C^{17} are not observed. **^{31}P{^{1}H} NMR** (202 MHz, C$_6$D$_6$): $\delta = 17.2$ ppm. **Elemental analysis** calcd (%) for [C$_{45}$H$_{32}$Cl$_1$Cu$_1$P$_2$] (733,69 g/mol): C 73.67; H 4.40; found: C 73.81; H 4.55. **IR** (cm^{-1}): 3046 (w), 1585 (w), 1556 (w), 1495 (w), 1480 (w), 1436 (m), 1316 (w), 1256 (w), 1216 (w), 1178 (w), 1166 (w), 1095 (m), 1056 (m), 1023 (w), 996 (w), 945 (w), 881 (m), 858 (w),814 (m) 775 (w), 737 (s), 716 (m), 691 (s), 667 (m), 643 (w), 622 (w), 607 (w), 561 (w), 552 (w), 523 (w), 509 (s), 502 (s), 471 (m), 456 (w), 445 (w), 414 (w). **HR-MS** LIFDI(+): m/z 635.20759 [C$_{45}$H$_{33}$P$_2$]$^{+}$, calcd 635.20575.

Synthesis of 6^{Cu}. Compound **3** (175 mg, 0.28 mmol, 1 eq) is suspended in 3 ml THF and CuCl (14 mg, 0.14 mmol, 0.5 eq) suspended in 2 ml THF is added at room temperature. The reaction mixture is stirred for 2 hours at room temperature whereupon a bright orange precipitate is obtained. The solid is separated *via* decanting of the mother liquor and dried under reduced pressure, giving **6^{Cu}** in the form of an orange solid. Additional product is obtained through storage of the mother liquor at −20 °C giving a total yield of 79 %. Analytically pure material is obtained through crystallisation from a THF solution at −20 °C. **^{1}H NMR** (500 MHz, CD$_2$Cl$_2$): $\delta = 7.83$ (m, 4H, H^{14}), 7.54 (d, $^{3}J_{HH} = 8.5$ Hz, 2H, H^{5}), 7.47 (d, $^{3}J_{HH} = 8.6$ Hz, 2H, H^{4}), 7.33 (br s, 4H, C^{10}), 7.30 (dt, $^{3}J_{HH} = 7.5$ Hz, $^{4}J_{HH} = 0.9$ Hz, 2H, H^{7}), 7.05–7.10 (m, 6H, H^{15}, H^{16}), 7.03 (dt, $^{3}J_{HH} = 7.7$ Hz, $^{4}J_{HH} = 1.2$ Hz, 2H, H^{6}), 6.82 (t, $^{3}J_{HH} = 7.1$ Hz, 2H, H^{12}), 6.74 (br s, 4H, C^{11}), 6.70 (m, 2H, H^{3}), 6.73 (d, 2H, $^{3}J_{HH} = 8.5$ Hz, H^{8}). **^{13}C{^{1}H} NMR** (126 MHz, CD$_2$Cl$_2$): $\delta = 138.0$ (vt, $J = 6.5$ Hz, C^{1}), 134.0 (vt, $J = 4.8$ Hz, C^{14}), 133.3 (s, C^{4a}), 132.5 (vt, $J = 4.3$ Hz, C^{8a}), 132.0 (m, C^{9}), 131.7 (s, C^{16}), 131.6 (br s, C^{10}), 130.4 (m, C^{2}), 130.1 (s, C^{12}), 129.6 (vt, $J = 5.0$ Hz, C^{4}), 129.6 (m, C^{13}), 128.7 (vt, $J = 6.2$ Hz, C^{15}), 128.2 (s, C^{5}), 128.2 (s, C^{8}), 127.4 (s, C^{7}), 127.3 (br m, C^{11}), 126.9 (s, C^{6}), 125.4 (vt, $J = 4.3$ Hz, C^{3}), 15.3 (t, $^{1}J_{PC} = 52.9$ Hz, C^{17}). **^{31}P{^{1}H} NMR** (202 MHz, CD$_2$Cl$_2$): $\delta = 16.5$ ppm. **Elemental analysis** calcd (%) for [C$_{90}$H$_{64}$Cl$_1$Cu$_1$P$_4$·3C$_4$H$_8$O$_1$] (733,69 g/mol): C 77.31; H 5.60; found: C 77.27; H 6.01. **IR** (cm^{-1}): 3045 (w), 2971 (w), 2855 (w), 1584 (w), 1554 (w), 1500 (w), 1478 (w), 1434 (w), 1370 (w), 1308 (w), 1257 (w), 1217 (w), 1159 (w), 1096 (s), 1055 (m), 1022 (m), 996 (w), 946 (w), 877 (m) 855 (w), 813 (w), 741 (s), 713 (m), 691 (s), 667 (m), 643 (w), 621 (w), 607 (w), 562 (w), 552 (w), 524 (m), 503 (s), 472 (w), 453 (w), 407 (w). **HR-MS** ESI(+): m/z 635.2039 [C$_{45}$H$_{33}$P$_2$]$^{+}$, calcd 635.2052.

Synthesis of 7^{Cu}. Compound **3** (150 mg, 0.24 mmol, 1 eq) is suspended in 3 ml THF and Cu(OTf)·toluene$_{0.5}$ (31 mg, 0.12 mmol, 0.5 eq) suspended in 2 ml THF is added at room temperature. The reaction mixture is stirred for 2 hours at room temperature. Thenn-pentane is added whereupon an orange precipitate is obtained. The solid is separated *via* decanting of the mother liquor and dried under reduced pressure, giving **7^{Cu}** in the form of an orange solid. Additional product is obtained through storage of the mother liquor at −20 °C giving a total yield of 85 %. Analytically pure material is obtained through crystallisation from a saturated THF solution at −20 °C. **^{1}H NMR** (500 MHz, CD$_2$Cl$_2$): $\delta = 7.83$ (m, 4H, H^{14}), 7.54 (d, $^{3}J_{HH} = 8.5$ Hz, 2H, H^{5}), 7.47 (d, $^{3}J_{HH} = 8.6$ Hz, 2H, H^{4}), 7.33 (br s, 4H, C^{10}), 7.30 (dt, $^{3}J_{HH} = 7.5$ Hz, $^{4}J_{HH} = 0.9$ Hz, 2H, H^{7}), 7.05–7.10 (m, 6H, H^{15}, H^{16}), 7.03 (dt, $^{3}J_{HH} = 7.7$ Hz, $^{4}J_{HH} = 1.2$ Hz, 2H, H^{6}), 6.82 (t, $^{3}J_{HH} = 7.1$ Hz, 2H, H^{12}), 6.74 (br s, 4H, C^{11}), 6.70 (m, 2H, H^{3}), 6.73 (d, 2H, $^{3}J_{HH} = 8.5$ Hz, H^{8}). **^{13}C{^{1}H} NMR** (126 MHz, CD$_2$Cl$_2$): $\delta = 138.0$ (vt, $J = 6.5$ Hz, C^{1}), 134.0 (vt, $J = 4.8$ Hz, C^{14}), 133.3 (s, C^{4a}), 132.5 (vt, $J = 4.3$ Hz, C^{8a}), 132.0 (m, C^{9}), 131.7 (s, C^{16}), 131.6 (br s, C^{10}), 130.4 (m, C^{2}), 130.1 (s, C^{12}), 129.6 (vt, $J = 5.0$ Hz, C^{4}), 129.6 (m, C^{13}), 128.7 (vt, $J = 6.2$ Hz, C^{15}), 128.2 (s, C^{5}), 128.2 (s, C^{8}), 127.4 (s, C^{7}), 127.3 (br m, C^{11}), 126.9 (s, C^{6}), 125.4 (vt, $J = 4.3$ Hz, C^{3}), 15.3 (t, $^{1}J_{PC} = 52.9$ Hz, C^{17}). **^{31}P{^{1}H} NMR** (202 MHz, CD$_2$Cl$_2$): $\delta = 16.5$ ppm. **^{19}F NMR** (282 MHz,

CD_2Cl_2): $\delta = 79.9$ ppm. **Elemental analysis** calcd (%) for $[C_{90}H_{64}Cl_1Cu_1P_4 \cdot C_4H_8O_1]$ (733,69 g/mol): C 73.42; H 4.67; found: C 73.17; H 5.09. **IR** (cm^{-1}): 3051 (w), 2967 (w), 2860 (w), 1586 (w), 1555 (w), 1501 (w), 1479 (w), 1436 (w), 1371 (w), 1315 (w), 1267 (m), 1221 (w), 1140 (w), 1097 (w), 1057 (w), 1029 (m) 996 (w), 946 (w), 878 (w), 855 (w), 814 (w), 775 (w), 741 (m) 714 (w), 691 (s) 667 (w), 634 (s) 607 (w), 571 (w), 562 (w), 552 (w), 503 (s) 475 (w), 453 (w). **HR-MS** ESI(+): m/z 635.2028 $[C_{45}H_{33}P_2]^+$, calcd 635.2052.

Synthesis of $\mathbf{4^{Au}}$. [AuCl(tht)] (202 mg, 0.63 mmol, 2 eq) is suspended in 1 ml THF and compound **3** (200 mg, 0.32 mmol, 1 eq) suspended in 7 ml THF is added at room temperature. After the addition, a colourless solid starts precipitating. The reaction mixture is stirred further for 2 hours and the solid is separated by decanting of the solution. The remaining colourless solid is washed several times with Et_2O and dried under reduced pressure. Compound $\mathbf{4^{Au}}$ is obtained in 92% yield. Crystals suitable for single crystal X-ray diffraction are obtained from a solution in DCM which was layered with *n*-pentane at −20 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 8.42$ (ddd, $^3J_{HH} = 7.9$ Hz, $^3J_{PH} = 11.8$ Hz, $^4J_{HH} = 1.3$ Hz, 4H, H^{14}), 8.11 (dd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 10.1$ Hz, 2H, H^3), 7.96 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{PH} = 1.2$ Hz, 2H, H^4), 7.74 (dt, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ 2H, H^{16}), 7.70 (d, $^3J_{HH} = 8.4$ Hz, 2H, H^5), 7.60 (m, $^3J_{HH} = 7.9$ Hz, 4H, H^{15}), 7.39 (dt, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.0$ Hz, 2H, H^7), 6.97 (dt, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, H^6), 6.77 (br m, 6H, H^{11} H^{12}), 6.42 (d, 2H, $^3J_{HH} = 8.6$ Hz, H^8), H^{10} is not observed. **^{13}C {^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 140.1$ (vt, $J = 6.9$ Hz, C^1), 136.0 (vt, $J = 5.1$ Hz, C^{14}), 134.6 (s, C^{4a}), 134.2 (s, C^{16}), 132.2 (m, C^{8a}), 132.2 (br m, C^{10}), 133.4 (vt, $J = 5.2$ Hz, C^4), 130.9 (br m, C^{12}), 131.9 (vt, $J = 6.4$ Hz, C^{15}), 128.9 (s, C^7), 128.6 (s, C^5), 128.2 (vt, $J = 6.4$ Hz, C^{11}), 128.1 (s, C^8), 127.9 (m, C^2), 127.4 (s, C^6), 126.9 (m, C^{13}), 125.7 (vt, $J = 3.9$ Hz, C^3), 124.9 (m, C^9), 7.0 (t, $^1J_{PC} = 44.7$ Hz, C^{17}) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): $\delta = 21.1$ ppm. **IR** (cm^{-1}): 3051 (w), 1584 (w), 1554 (w), 1502 (w), 1478 (w), 1433 (m), 1371 (w), 1316 (w), 1259 (w), 1218 (w), 1188 (w), 1161 (w), 1137 (w), 1090 (m), 1028 (w), 997 (w), 948 (w), 920 (w), 873 (w), 847 (w), 813 (w), 797 (m), 741 (s), 714 (m), 692 (s), 667 (m), 644 (w), 624 (w), 605 (w), 548 (w), 498 (s), 477 (w), 444 (w), 416 (w). **Elemental analysis** calcd (%) for $[C_{45}H_{32}Au_2Cl_2P_2]$ (1099,53 g/mol): C 49.16; H 2.93; found: C 49.18; H 2.96. **HR-MS** ESI(+): m/z 635.2045 $[C_{45}H_{33}P_2]^+$, calcd 635.2052; m/z 867.1387 $[C_{45}H_{33}P_2Au_1Cl_1]^+$; calcd 867.1406.

Synthesis of $\mathbf{5^{Au}}$. Compound **3** (225 mg, 0.35 mmol, 1 eq) is dissolved in 10 ml THF and [AuCl(tht)] (108 mg, 0.34 mmol, 0.95 eq) suspended in 3 ml THF is added at room temperature. After stirring for some seconds, the reaction mixture becomes clear. Upon further stirring for 2 hours, a red solid precipitate is formed. Removal of liquids *via* decanting and washing of the remaining solid with diethyl ether yields $\mathbf{5^{Au}}$ in 10% yield. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 7.90$ (ddd, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 11.8$ Hz, $^4J_{HH} = 1.1$ Hz, 4H, H^{14}), 7.57 (d, $^3J_{HH} = 8.1$ Hz, 2H, H^5), 7.52 (d, $^3J_{HH} = 8.6$ Hz, 2H, H^4), 7.27–7.36 (m, 8H, H^6, H^{15}, H^{16}), 7.24 (br s, 4H, C^{10}), 7.39 (dt, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, H^7), 6.87 (m, 2H, H^3), 6.82 (t, $^3J_{HH} = 7.3$ Hz, 2H,H^{12}), 6.73 (d, 2H, $^3J_{HH} = 8.6$ Hz, H^8), 6.68 (br s, 4H, C^{11}). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 138.1$ (vt, $J = 6.5$ Hz, C^1), 134.6 (vt, $J = 4.8$ Hz, C^{14}), 133.3 (s, C^{4a}), 132.7 (m, C^{8a}), 131.9 (vt, $J = 6.4$ Hz, C^{15}), 131.3 (br s, C^{10}), 129.8–131.2 (m, C^2, C^9, C^{13}), 130.2 (s, C^{12}), 129.8 (vt, $J = 4.3$ Hz, C^4), 128.1–128.3 (m, C^5, C^8, C^{16}), 127.5 (s, C^6), 127.4 (br s, C^{11}), 127.1 (s, C^7), 125.6 (vt, $J = 4.3$ Hz, C^3), 25.2 (t, $^1J_{PC} = 71.0$ Hz, C^{17}). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): $\delta = 17.5$ ppm. **IR** (cm^{-1}): 3045 (w), 2973 (w), 1584 (w), 1554 (w), 1500 (w), 1478 (w), 1434 (w), 1370 (w), 1311 (w), 1257 (w), 1218 (w), 1159 (w), 1096 (s), 1054 (m), 1022 (m), 995 (m), 877 (m), 854 (m), 841 (w), 813 (m), 775 (w), 741 (s), 713 (m), 691 (s), 667 (m), 643 (w), 621 (w), 607 (w), 552 (w), 523 (w), 502 (s), 471 (m), 452 (m), 406 (w). **Elemental analysis**: on several attempts, no sufficient elemental analysis was obtained, likely due to solvent impurities. **HR-MS** ESI(+): m/z 635.2046 $[C_{45}H_{33}P_2]^+$, calcd 635.2052; m/z 867.1393 $[C_{45}H_{33}P_2Au_1Cl_1]^+$; calcd 867.1406.

Supporting Information

The data that support the findings of this work are available in the supporting information of this article: general considerations, experimental protocols, NMR spectra, IR spectra, UV/Vis spectra, photoluminescence spectra, calculations for percent buried volume and crystallographic data. Some references have also been cited within the supporting information (Ref. [48,55]).

Acknowledgements

The German Research Foundation (DFG) is gratefully acknowledged for financial support (KU3348/3-1). I.K. and T.D. thank Jörn Münzer, Eva-Katharina Homberger and Dr. Sergei Ivlev for the collection of single crystal X-ray data of **2**[Cl]$\cdot C_7H_8$, **2**[$CuCl_2$], **3**, $\mathbf{4^{Cu}}\cdot C_6D_6$, $\mathbf{5^{Cu}}\cdot C_7H_8$, and $\mathbf{7^{Cu}}\cdot 2\,C_7H_8$. Moreover, we thank Cornelia Mischke for the collection of NMR data and Meng Yang of the Heine group for the collection of photoluminescence emission spectra. I. K. would like to thank Prof. S. Dehnen and Prof. C. Lichtenberg for generous support. Fruitful discussions with Prof. W. Petz are acknowledged. This work was supported by the Philipps-Universität Marburg. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Carbodiphosohoranes · Chiral Ligands · Coinage metal complexes · Room Temperature Photoluminescence

[1] F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539.
[2] R. Tonner, F. Oxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem. Int. Ed.* **2006**, *45*, 8038.
[3] a) G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597; b) R. Tonner, G. Heydenrych, G. Frenking, *ChemPhysChem* **2008**, *9*, 1474.
[4] a) A. Kroll, H. Steinert, L. T. Scharf, T. Scherpf, B. Mallick, V. H. Gessner, *Chem. Commun.* **2020**, *56*, 8051; b) R. Appel, K. Waid, *Z. Naturforsch. B* **1981**, *36*, 131; c) W. Plass, M. Spahn, G. Heckmann, E. Fluck, *Z. Naturforsch.* **1992**, *47*, 947; d) S. Ullrich, B. Kovačević, B. Koch, K. Harms, J. Sundermeyer, *Chem. Sci.* **2019**, *10*, 9483.
[5] R. Appel, U. Baumeister, F. Knoch, *Chem. Ber.* **1983**, *116*, 2275.
[6] R. Appel, U. Baumeister, *Z. Naturforsch. B* **1980**, *35*, 513.
[7] E. Fluck, B. Neumüller, R. Braun, G. Heckmann, A. Simon, H. Borrmann, *Z. Anorg. Allg. Chem.* **1988**, *567*, 23.
[8] M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* **2013**, *49*, 3140.
[9] M. Klein, N. Demirel, A. Schinabeck, H. Yersin, J. Sundermeyer, *Molecules* **2020**, *25*, 3990.
[10] W. Su, S. Pan, X. Sun, L. Zhao, G. Frenking, C. Zhu, *Dalton Trans.* **2019**, *48*, 16108.
[11] R. Appel, H.-D. Wihler, *Chem. Ber.* **1978**, *111*, 2054.

[12] H. Schmidbaur, T. Costa, B. Milewski-Mahrla, U. Schubert, *Angew. Chem. Int. Ed.* **1980**, *19*, 555.

[13] B. A. Janda, J. A. Tran, D. K. Chang, G. C. Nerhood, O. Maduka Ogba, A. L. Liberman-Martin, *Chem. Eur. J.* **2024**, *30*, e202303095.

[14] C. R. Aversa-Fleener, D. K. Chang, A. L. Liberman-Martin, *Organometallics* **2021**, *40*, 4050.

[15] G. A. Bowmaker, R. Herr, H. Schmidbaur, *Chem. Ber.* **1983**, *116*, 3567.

[16] K. Saito, S. Kusumoto, K. Nozaki, *Chem. Eur. J.* **2023**, *29*, e202302060.

[17] S. Marrot, T. Kato, H. Gornitzka, A. Baceiredo, *Angew. Chem.* **2006**, *118*, 2660.

[18] S. Yogendra, S. Schulz, F. Hennersdorf, S. Kumar, R. Fischer, J. J. Weigand, *Organometallics* **2018**, *37*, 748.

[19] J. Vicente, A. R. Singhal, P. G. Jones, *Organometallics* **2002**, *21*, 5887.

[20] G. Ma, M. J. Ferguson, R. McDonald, R. G. Cavell, *Organometallics* **2010**, *29*, 4251.

[21] M. Klein, J. Sundermeyer, *Organometallics* **2021**, *40*, 2090.

[22] H. Schmidbaur, C. E. Zybill, G. Müller, C. Krüger, *Angew. Chem. Int. Ed.* **1983**, *22*, 729.

[23] G. Müller, C. Krüger, C. Zybill, H. Schmidbaur, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1141.

[24] R. Corberán, S. Marrot, N. Dellus, N. Merceron-Saffon, T. Kato, E. Peris, A. Baceiredo, *Organometallics* **2009**, *28*, 326.

[25] W. Petz, F. Öxler, B. Neumüller, *J. Organomet. Chem.* **2009**, *694*, 4094.

[26] W. Petz, B. Neumüller, S. Klein, G. Frenking, *Organometallics* **2011**, *30*, 3330.

[27] a) P. Leglaye, B. Donnadieu, J.-J. Brunet, R. Chauvin, *Tetrahedron Lett.* **1998**, *39*, 9179; b) Z. Yao, X. Lin, R. Chauvin, L. Wang, E. Gras, X. Cui, *Chin. Chem. Lett.* **2020**, *31*, 3250; c) C. Canal, C. Lepetit, M. Soleilhavoup, R. Chauvin, *Afinidad* **2004**, *61*, 298.

[28] a) C. Zybill, G. Mueller, *Organometallics* **1987**, *6*, 2489; b) J. S. Driscoll, D. W. Grisley, J. V. Pustinger, J. E. Harris, C. N. Matthews, *J. Org. Chem.* **1964**, *29*, 2427.

[29] M. Gruber, W. Bauer, H. Maid, K. Schöll, R. R. Tykwinski, *Inorg. Chim. Acta* **2017**, *468*, 152.

[30] a) W. P. Jensen, H. Gehrke, D. R. Jones, I.-H. Suh, R. A. Jacobsen, *Z. Kristallogr. – Cryst. Mater.* **1996**, *211*, 829; b) R. Dobrovetsky, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 2516; c) M. Abdalilah, R. Zurawinski, Y. Canac, B. Laleu, J. Lacour, C. Lepetit, G. Magro, G. Bernardinelli, B. Donnadieu, C. Duhayon, M. Mikolajczyk, R. Chauvin *Dalton Trans.* **2009**, *40*, 8493; d) R. Ganguly, V. Jevtovic, *Acta Crystallogr. Sect. E* **2017**, *73*, 1259; e) C. Gurnani, A. L. Hector, E. Jager, W. Levason, D. Pugh, G. Reid, *Dalton Trans.* **2013**, *42*, 8364; f) L. Miao, A. Yeganeh-Salman, J. Yeung, D. W. Stephan, *Dalton Trans.* **2022**, *51*, 14049; g) W. Petz, K. Dehnicke, N. Holzmann, G. Frenking, B. Neumüller, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1702; h) W. Petz, K. Dehnicke, B. Neumüller, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1761; i) W. Petz, M. Fahlbusch, E. Gromm, B. Neumüller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 682; j) W. Petz, B. Neumüller, *X-Ray Struct. Anal. Online* **2021**, *37*, 33; k) J. K. Schuster, D. K. Roy, C. Lenczyk, J. Mies, H. Braunschweig, *Inorg. Chem.* **2019**, *58*, 2652; l) S. Stallinger, C. Reitsamer, W. Schuh, H. Kopacka, K. Wurst, P. Peringer, *Chem. Commun.* **2007**, *5*, 510; m) J. Walker, R. Poli, *Polyhedron* **1989**, *8*, 1293.

[31] W. Petz, B. Neumüller, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2331.

[32] P. G. Jones, S. Jager, *CCDC 699280: Experimental Crystal Structure Determination*, Cambridge Crystallographic Data Centre, **2010**, doi: 10.5517/ccrgnf8.

[33] K. Lauritsen, H. Vogt, L. Riesel, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1103.

[34] W. Petz, C. Kutschera, S. Tschan, F. Weller, B. Neumüller, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1235.

[35] W. Petz, B. Neumüller, *Z. Anorg. Allg. Chem.* **2012**, *638*, 987.

[36] H. Schmidbaur, T. Costa, B. Milewski-Mahrla, U. Schubert, *Angew. Chem.* **1980**, *92*, 557.

[37] a) S. Böttger, M. Gruber, J. E. Münzer, G. M. Bernard, N.-J. H. Kneusels, C. Poggel, M. Klein, F. Hampel, B. Neumüller, J. Sundermeyer, V. K. Michaelis, R. Tonner, R. R. Tykwinski, I. Kuzu, *Inorg. Chem.* **2020**, *59*, 12054; b) P. J. Quinlivan, G. Parkin, *Inorg. Chem.* **2017**, *56*, 5493; c) A. T. Vincent, P. J. Wheatley, *J. Chem. Soc., Dalton Trans.* **1972**, *5*, 617.

[38] S. Marrot, T. Kato, H. Gornitzka, A. Baceiredo, *Angew. Chem. Int. Ed.* **2006**, *45*, 2598.

[39] R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260.

[40] a) M. S. Hussain, H. Schmidbaur, *Z. Naturforsch. B* **1976**, *31*, 721; b) H. Schmidbaur, O. Gasser, M. S. Hussain, *Chem. Ber.* **1977**, *110*, 3501; c) A. Wohlleben, H. Schmidbaur, *Angew. Chem.* **1977**, *89*, 428.

[41] X. Wu, C.-Y. Huang, D.-G. Chen, D. Liu, C. Wu, K.-J. Chou, B. Zhang, Y. Wang, Y. Liu, E. Y. Li, P.-T. Chou, *Nat. Commun.* **2020**, *11*, 2145.

[42] K. Flosdorf, D. Jiang, L. Zhao, B. Neumüller, G. Frenking, I. Kuzu, *Eur. J. Inorg. Chem.* **2019**, *2019*, 4546.

[43] J. E. Münzer, P. Oña-Burgos, F. M. Arrabal-Campos, B. Neumüller, R. Tonner, I. Fernández, I. Kuzu, *Eur. J. Inorg. Chem.* **2016**, *2016*, 3852.

[44] a) N. V. S. Harisomayajula, S. Makovetskyi, Y.-C. Tsai, *Chem. Eur. J.* **2019**, *25*, 8936; b) J. Ho, K. M. Ervin, W. C. Lineberger, *J. Chem. Phys.* **1990**, *93*, 6987; c) P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.

[45] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[46] a) G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17; b) H. Brger, K. Burczyk, A. Blaschette, *Monatsh. Chem.* **1970**, *101*, 102; c) M. G. Miles, G. Doyle, R. P. Cooney, R. S. Tobias, *Spectrochim. Acta Part A* **1969**, *25*, 1515.

[47] a) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370; b) A. Bayler, A. Schier, G. A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 7006; c) G. A. Bowmaker, H. Schmidbaur, S. Krüger, N. Rösch, *Inorg. Chem.* **1997**, *36*, 1754.

[48] a) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759; b) L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286.

[49] W. Petz, F. Weller, J. Uddin, G. Frenking, *Organometallics* **1999**, *18*, 619.

[50] C. Chai, *Purification of Laboratory Chemicals*, Elsevier Science & Technology, **2003**, pp. 95–635.

[51] a) G. Brauer, *Handbook of Preparative Inorganic Chemistry V1*, Elsevier Science, **1963**, pp. 1005–1006; b) C. K. Mirabelli, R. K. Johnson, D. T. Hill, L. F. Faucette, G. R. Girard, G. Y. Kuo, C. M. Sung, S. T. Crooke, *J. Med. Chem.* **1986**, *29*, 218; c) R. Appel, F. Knoll, W. Miche, W. Morbach, H.-D. Wihler, H. Veltmann, *Chem. Ber.* **1976**, *109*, 58.

[52] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Magn. Reson. Chem.* **2002**, *40*, 489.

[53] W. H. Hersh, *J. Chem. Educ.* **1997**, *74*, 1485.

[54] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112; c) G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3; d) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3.

[55] Deposition Numbers 2339428 (**1**$[Br]_2\cdot CH_2Br_2\cdot H_2O$), 2339477 (**1**$[SbF_6]_2\cdot 0.67\ CDCl_3$), 2339429 (**2**[Br]), 2339431 (**2**$[Cl]\cdot CH_2Cl_2$), 2339479 (**2**$[Cl]\ \cdot C_7H_8$), 2339478 (**2**$[CuCl_2]$), 2339482 (**3**), 2339480 (**4**$Cu\cdot C_6D_6$), 2339483 (**5**$Cu\cdot C_7H_8$), 2339481 (**7**$^{Cu}\cdot C_7H_8$), 2339484 (**4**$^{Au}\cdot 2\ C_5H_5N_1$), 2339674 (**4**$^{Au}\cdot 1.5\ CH_2Cl_2$), 2342569 (**4**$^{Au}\cdot CH_2Cl_2$), 2339427 (**5**$^{Au}\cdot 2\ CH_2Cl_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Manuscript received: March 27, 2024
Revised manuscript received: May 23, 2024
Accepted manuscript online: May 27, 2024
Version of record online: July 12, 2024