ORGANOMETALLICS

Low-Nuclearity Alkynyl d¹⁰ Clusters Supported by Chelating **Multidentate Phosphines**

Andrey Belyaev,[†] Thuy Minh Dau,[†] Janne Jänis,[†] Elena V. Grachova,[‡] Sergey P. Tunik,^{*,‡} and Igor O. Koshevoy*^{,†}

[†]Department of Chemistry, University of Eastern Finland, Joensuu, 80101, Finland [‡]St. Petersburg State University, 7/9 Universitetskaya nab., 199034 St. Petersburg, Russia

Supporting Information

ABSTRACT: The coordination chemistry of the tri- and tetradentate chelating phosphines (2-PPh₂C₆H₄)₂P(O)Ph (P^3O) and $(2-PPh_2C_6H_4)_3P$ (P^4) with respect to d^{10} copper subgroup metal ions has been investigated. Depolymerization of $(MC_2R)_n$ (M = Cu, Ag) with P^4 affords the series of monoand trinuclear complexes $(P^4)CuC_2Ph$ (1), $(P^4)Cu_3(C_2Ph)_3$ (2), $(P^4)Ag_3(C_2Ph)$ (Hal)₂ (Hal = Cl (3), Br (4), I (5)). Reactions of the M⁺ (M = Cu, Ag) ions with $(M'C_2R)_n$ (M' = Cu, Ag, Au) acetylides in the presence of P^4 yield the family of dinuclear species $[(P^4)MM'(C_2R)]^+$ (6–12), which comprise the Cu_2/Ag_2 (6, 7; R = Ph), AuCu (8-10; R = Ph, $C(OH)Me_2$, $C(OH)Ph_2$), and AuAg (11, 12; R = Ph, $C(OH)Ph_2$) metal cores. A related triphosphine, (2-



 $PPh_2C_6H_4)_2PPh$ (P³), applied in a similar protocol undergoes partial oxidation and leads to the heterotrimetallic clusters $[\{(P^3O)M\}_2Au(C_2R)_2]^+$ (M = Cu, R = C(OH)Ph₂, 13; M = Ag, R = C(OH)Ph₂, 14; M = Ag, R = Ph, 15), which can be prepared more efficiently starting from the oxidized ligand P^3O . The structures of the complexes 1-4 and 6-15 were established by single-crystal X-ray crystallography. According to the variable-temperature ¹H and ³¹P $\{^{1}H\}$ NMR experiments, compounds 1-12 demonstrate fluxional behavior in solution. The title complexes do not show appreciable luminescence in solution at 298 K, and the photophysical properties of 1–15 were studied in the solid state. The observed phosphorescence (Φ_{em} up to 0.46, λ_{em} from 440 to 635 nm) is assigned to cluster-centered transitions mixed with some MLCT d $\rightarrow \pi^*(alkynyl)$ character.

INTRODUCTION

Metal-metal bonds represent unique types of interactions that have been extensively used for the construction of numerous multimetallic compounds. The availability of single-crystal diffraction analysis as a routine method of structural characterization made possible careful analysis of the M-M noncovalent bonding and, consequently, rational and predictable supramolecular design of sophisticated metal-containing architectures.¹ The presence of several metal ions or atoms in one molecular entity often brings a distinct cooperative effect and leads to the emergence of physical and chemical properties which cannot be accessed by a simple combination of the monometallic components.² Such synergistic functionality has significantly driven the experimental and theoretical efforts that have impressively advanced the fundamental chemistry of metal-rich aggregates (clusters and nanoparticles), which have also been applied in catalysis,³ fabrication of photonic devices,⁴ visualization,⁵ and detection techniques.⁶ In this respect, particular interest has been paid to closed-shell attractive forces, for which the general term "metallophilicity" was proposed by Pyykkö.⁷ These metal-metal interactions suggested remarkably rich opportunities for the design of

photofunctional compounds and materials comprising combinations of d⁸ (Pt^{II}) and d¹⁰ metal (Cu^I, Ag^I, Au^I) ions.⁸

Due to the relative weakness of $d^{10}-d^{10}$ metallophilic bonds, which are comparable in strength to hydrogen bonds (ca. 15-40 kJ/mol),^{7,9} an additional stabilization of the polymetallic assemblies is often required. This goal can be achieved (a) in a spontaneous manner by forming an extended network of M-M interactions leading to high-nuclearity clusters and polymers^{1f,10} and (b) by using appropriate (element)-organic bridging ligands, which support effective contact between the metal atoms and simultaneously provide a way to control the geometry of the resulting frameworks on the molecular level.^{1f,g}

The choice of ligand environment is largely dictated by the affinity of the binding groups to the particular metal ions in given oxidation states. The anionic alkynyl ligands serve as popular building blocks for the preparation of d¹⁰ coinage-metal clusters primarily due to a pronounced tendency of the $-C \equiv$ CR moiety to coordinate in a few σ, π -bridging modes and therefore to support the metallophilic interactions.^{3c,10a,c,11} Tertiary phosphines as ancillary soft donors are also frequently

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utilized as bridging ligands and have no less important influence on the arrangement of the metal core and, consequently, on the physical properties of the cluster complexes. Analysis of the structurally characterized d¹⁰ polymetallic M_x (M = Cu, Ag, Au; $x \ge 2$) alkynyl phosphine compounds permits distinguishing three main synthetic strategies depending on the denticity and stereochemistry of the templating phosphine ligands (Chart 1).

Chart 1. Three Types of d¹⁰ Coinage-Metal Alkynyl-Phosphine Clusters



In the type A clusters a homoleptic alkynyl core is supported by the external shell of di-/triphosphines with substantial spatial separation of the PR_2R' coordinating functions.^{4c,12} For the **B** species ligands with short spacers (bis(diphenylphosphino)methane and related bi- and tridentate phosphines with similar geometry) providing intermetallic distances in the range 2.8– 3.4 Å are used on a periphery of metal–alkynyl frameworks.^{4d,13}

The **A** and **B** approaches often produce medium- to highnuclearity compounds, which exhibit intense luminescence. In the case of monophosphine-stabilized clusters (**C**) a minimal assembly of two metal centers occurs under favorable conditions rendered by the ligand sphere,¹⁴ though formation of larger species cannot be excluded.¹⁵ The former compounds were shown to be useful in homogeneous catalysis because of their lability and thus easy generation of active species.¹⁶

To increase the kinetic and photodynamic stability of lownuclearity complexes, it seemed feasible to employ chelating oligophosphines, which are capable of saturating the coordination vacancies of the constituting metal ions and concurrently prevent their dissociation in solution. However, chelating phosphines have been predominantly used for the synthesis of monometallic coordination d¹⁰ compounds but not for that of alkynyl complexes with metallophilic bonding, as there are only a few examples¹⁷ with very scarce photophysical data.¹⁸

In the present contribution, we demonstrate the so far poorly explored possibility of utilizing oligodentate chelating phosphine ligands for the preparation of low-nuclearity luminescent complexes of Cu^{I} , Ag^{I} , and Au^{I} . We have systematically synthesized a series of di- and trinuclear homo- and heterometallic alkynyl compounds and carried out structural and photophysical studies to correlate the luminescence behavior with the molecular structures of the novel species.

RESULTS AND DISCUSSION

Homometallic Neutral Complexes. The tetradentate phosphine $(2\text{-PPh}_2\text{C}_6\text{H}_4)_3\text{P}$ (P^4) readily reacts with polymeric copper phenylacetylide, $(\text{CuC}_2\text{Ph})_m$, in s 1:1 molar ratio to give the yellow mononuclear complex (P^4)CuC₂Ph (1) in high yield (Scheme 1). Using the same reagents in a 1:3 stoichiometry affords the trinuclear cluster (P^4)Cu₃(C₂Ph)₃ (2) in a moderate yield due to the formation of appreciable amounts of 1 as a side product. Attempts to prepare analogous silver compounds were unsuccessful, and only the trinuclear chloride-alkynyl cluster (P^4)Ag₃(C₂Ph)Cl₂ (3) could be isolated from a reaction carried out in dichloromethane. Complex 3 is obviously generated as a result of halide subtraction from the solvent. Using a nonchlorinated medium did not allow us to obtain the alkynyl-only silver complexes with a P^4 ligand, presumably because of their intrinsic instability.

Optimization of the reaction conditions of the synthesis of 3 (Scheme 2) that involve utilization of a 1:2 molar mixture of $(AgC_2Ph)_n/AgCl$ as starting reagent improved the yield and permitted the synthesis of bromide (4) and iodide (5) homologues of 3. It has to be noted that the P^4 ligand has virtually not been used for the synthesis of copper subgroup metal compounds, with only one example of $[(P^4)Cu]BF_4$ described to date.¹⁹

Complexes 1-4 have been characterized crystallographically (Figure 1 and Figure S1 in the Supporting Information; selected bond lengths are given in Table S2 in the Supporting Information). In the monometallic 1 the P^4 phosphine is

Scheme 1. Synthesis of Complexes 1-5



Scheme 2. Synthesis of Complexes $6-12^a$



coordinated to the metal center in a tridentate mode, thus having one pendant $-PPh_2$ group with a P(3)-Cu(1) separation of 3.958 Å. Together with the σ -bound $-C\equiv CPh$ moiety the ligand sphere saturates four coordination vacancies of the copper ion, which adopts a distorted-tetrahedral geometry in a fashion similar to that of $(P^3)CuC_2R$ compounds $(P^3 = (PPh_2C_6H_4)_2PPh)$ reported recently.²⁰

Nearly equilateral triangular cores are found in the M₃ clusters 2-4; the metal-metal distances are comparable to the corresponding values determined for other copper^{12a,15c,21} and silver^{21c,22} alkynyl compounds that are indicative of effective metallophilic interactions. The metal-metal bonds are additionally supported by the $\mu_{2\nu}\sigma$ -bridging alkynyl (2–4) and halide (3, 4) ligands, which are located on the edges of the trimetallic triangles. The tetraphosphine ligand in 2-4 occupies a capping position over the cluster framework. Each of the terminal PPh₂ groups is coordinated to the metal vertex, thus bridging all metal-metal contacts; the M-PPh₂ bond lengths (2.132-2.225 Å for Cu-P and 2.378-2.418 Å for Ag-P) are slightly shorter than those in 1 but are within the normal range reported for the congener species.^{12a,15c,21,22,22d} However, the central phosphorus atom P(2) of the P^4 ligand is only poorly involved in binding to the metal ions, as the shortest separations P(2)-M are 2.723 and 2.883 Å for 2 and 3, respectively. Moreover, in cluster 4 the P(2) donor is placed roughly over the center of the Ag_3 skeleton with P(2)-Ag distances of 3.127–3.291 Å that significantly exceed the conventional interval of P–Ag bonds.

The NMR spectroscopic data for compounds 1-5 are generally consistent with the solid-state structures, which are retained in solution, though they appear to be stereochemically nonrigid in fluid medium (see the Experimental Section and Table S5 in the Supporting Information for the ${}^{31}P{}^{1}H$ NMR spectroscopic parameters). The ³¹P NMR spectrum of complex 1 at 298 K displays two resonances with a 3:1 ratio of relative intensities (Figure S2 in the Supporting Information) that points to the equivalence of the terminal PPh₂ groups due to their fast exchange. Cooling the sample to 193 K slows down the dynamic process and causes the appearance of three signals of 2:1:1 integral intensities, one of which is considerably shifted to a high-field region (-24.5 ppm) and obviously corresponds to the noncoordinated PPh_2 arm. Copper cluster 2 demonstrates the expected ³¹P NMR pattern with two multiplets at -10.8 (d, $3PPh_2$) and -14.6 ppm (q, $P(C_6H_4PPh_2)_3)$, broadened at 298 K. Lowering the temperature to 193 K does not change the number of signals and their multiplicity, which suggest a symmetrical coordination of the P^4 phosphine on the Cu_3 core.

The phosphorus NMR spectra of **3–5** are very much alike (Figure S3 in the Supporting Information), each of which displays a low-field doublet (-5.4 to -6.8 ppm) accompanied by a high-field unresolved multiplet (-33.0 to -33.9 ppm), assigned to PPh₂ and $P(C_6H_4PPh_2)_3$ fragments, respectively, on the basis of the relative intensities. The presence of only one signal arising from terminal diphenylphosphine groups and the absence of detectable ${}^{31}P{-}^{107,109}Ag$ couplings can be explained in terms of fast intramolecular dynamics, tentatively ascribed to a merry-go-round rotation of the tetraphosphine over the Ag₃ coordinating framework. Attempts to freeze this motion were not completely successful, as even at 183 K the ${}^{31}P$ NMR pattern remains complicated and hardly interpretable presumably due to the presence of several forms.

The ¹H NMR data are also compatible with the composition and structure of the complexes 1-5 found in the solid state. However, because of the fluxionality of these species and the presence of similar aromatic protons, the signals of which appear in a quite narrow region, these spectra are insufficiently resolved and therefore are much less informative than the data of ³¹P NMR measurements.

Homo- and Heterometallic Cationic Complexes. The availability of a noncoordinated $-PPh_2$ function in complex 1



Figure 1. Molecular views of complexes 1, 2, and 4. Thermal ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity.



Figure 2. Molecular views of complexes 6, 7, and 12. Thermal ellipsoids are shown at the 50% probability level. Counterions and H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms in 7: (') 2 - x, 2 - y, 1 - z.

prompted us to investigate the possibility of its binding to another metal center using different combinations of d¹⁰ ions. For this purpose, the phosphine P^4 was coupled with a stoichiometric amount of the suitable polymeric phenylacetylide (MC₂R)_n (M = Cu, Ag, Au), followed by the addition of AgPF₆ or Cu(NCMe)₄PF₆ salt to produce a series of dinuclear cationic compounds **6–12** of the general formula [(P^4)MM'(C₂R)]PF₆ (Scheme 2).

The solid-state structures of all complexes 6-12 have been determined by XRD analysis; see Figure 2 and Figure S4 in the Supporting Information. These species adopt a similar structural motif (except 7), in which a bimetallic unit MM' is supported by the P^4 phosphine and the σ,π -bridging coordination of the C≡CR fragment. One metal center having a σ -bonded alkynyl ligand is connected to the P(1) donor of a PPh₂ arm and therefore is found in a formally two-coordinate environment. The second d¹⁰ ion is chelated by the remaining three phosphorus atoms of the P^4 ligand and is additionally linked to the π system of the C=C triple bond to attain a pseudotetrahedral geometry. The metal-metal distances found in 6–12 (Table S3 in the Supporting Information) are normal for the Cu–Cu, 12a,15c,21 Ag–Ag, 21c,22 Au–Cu, 12b,13e,23 and Au– Ag^{4c,12c,g} interactions observed for the corresponding alkynyl compounds, indicating the presence of effective metallophilic bonding in the title species. The coordination of alkynes in 6-12 is also not exceptional, and the related structural parameters correlate well with previous reports.^{4c,12b,c,g,13e,23}

The binding fashion of the P^4 tetraphosphine in 6–12 somewhat resembles that in trinuclear clusters 2–4. While the –PPh₂ moieties are located at normal distances from the metal ions, the central P(2) atoms show clearly larger P–M separations, which exceed 2.7 Å for P(2)–Ag contacts in 11 and 12 and thus become weakly bonding.

The silver cluster 7 differs from other congeners of this series. In the solid state it possesses a tetranuclear Z-shaped flat Ag_4 skeleton as a result of dimerization of two $[(P^4)-Ag_2(C_2Ph)]^+$ cations via the formation of supplementary Ag-Ag and Ag-C=C bonds. Because of this fusion the alkynyl

ligands in 7 have $\mu_3 \cdot \eta^1 \cdot \eta^1 \cdot \eta^2$ -bridging positions, which have been observed in high-nuclearity silver clusters and polymers.²⁴

Electrospray ionization mass spectrometry (ESI-MS) measurements, however, did not detect the presence of the dicationic $[{(P^4)Ag_2(C_2Ph)}_2]^{2+}$ molecular form of 7 (Figure S5 in the Supporting Information) and show only the signal at m/z 1129.08 of the monocation, pointing to a possible dissociation of 7 into the bimetallic $[(P^4)Ag_2(C_2Ph)]^+$ units, which are analogous to other dinuclear complexes of types **6**– **12**. For the rest of these clusters the results of ESI-MS studies are completely compatible with compositions found in the solid state and display the dominant signals at m/z 1041.14 (**6**), 1175.18 (**8**), 1157.19 (**9**), 1281.22 (**10**), 1219.15 (**11**), and 1325.20 (**12**); the isotopic distributions match well the calculated patterns (Figure S5).

The room-temperature ³¹P NMR spectra of 6 and 7 indicate that these homometallic complexes demonstrate intramolecular fluxionality in solution. At 298 K the copper compound 6 shows a low-field multiplet centered at -9.5 ppm and a very broad unresolved bump in the range from 5 to -4 ppm (Figure S6 in the Supporting Information). The spectroscopic pattern becomes clearly interpretable at 193 K, with all PPh₂ groups of the P^4 being inequivalent (Figure 3). This observation is in accordance with the solid-state structure of 6, where all coordinated phosphorus atoms occupy stereochemically different positions (see Figure 2 and the inset in Figure 3). The silver congener 7 displays a similar behavior, with the scrambling rate being considerably higher in comparison with the dynamics observed in 6. The ³¹P room-temperature spectrum (Figure S7 in the Supporting Information) displays a pattern which corresponds to the high-temperature limit of the PPh₂ group movement about the skeleton to give two signals of 1:3 relative intensity that fit an idealized symmetry of the tetraphosphine coordinated to the $\{Ag_2(C_2Ph)\}$ moiety. The high-field quartet $(\delta - 29.1 \text{ ppm}, {}^{3}J_{\text{PP}} = 144 \text{ Hz})$ is due to the central phosphorus atom coupled to three equivalent lateral PPh₂ groups, whereas the low-field multiplet (δ –1.3 ppm, broadened dt) with poorly resolved couplings to P(2) and two silver nuclei corresponds to the scrambled diphenylphosphino groups $({}^{3}J_{PP} = 144 \text{ Hz and}$

D



Figure 3. ${}^{31}P{}^{-31}P$ COSY NMR spectrum of complex 6 (199 K, 162 MHz, CD₂Cl₂). The inset shows the assignment scheme and spin-spin coupling network. The top 1D projection (brown) shows a simulated spectrum (${}^{2}J(P(3){}-P(4)) = 57$ Hz, ${}^{3}J(P(3/4){}-P(2)) = 82$ Hz, ${}^{3}J(P(1){}-P(2)) = 113$ Hz).

dynamically averaged ${}^{1}J_{AgP} =$ ca. 200 Hz). In contrast to the case for **6**, fast motion of the ligands could not be completely frozen even at 193 K and produced three broadened doublets (δ 0.6, -2.4, and -7.7 ppm, ${}^{1}J_{PAg}$ in the range 300–500 Hz) assigned to diphenylphosphino fragments, along with a high-field distorted quartet (δ -31.4 ppm, ${}^{3}J_{PP} =$ ca. 150 Hz) arising from the central P(2) nucleus (Figure S7). Independently of the temperature, the resonance of the P(2) atom in 7 exhibits nearly no characteristic P–Ag magnetic coupling, evidencing an extremely weak interaction between this phosphorus atom and the silver ion or even indicating breakage of the corresponding bond in solution. Crystallographic data obtained (vide supra) also point to a poor P(2)–Ag bonding, in accord with which the P(2)–M bond lengths in complexes **6**–12 are systematically longer than the related distances PPh₂–M.

The gold–copper compounds 8–10 adopt essentially the same structural arrangement (Figure S4 in the Supporting Information) and exhibit nearly identical ³¹P{¹H} NMR spectra (see the Experimental Section). In contrast to the case for 6 and 7, these heterometallic species retain their rigid structures in solution at room temperature, which is indicated by the presence of four well-resolved multiplets (Figure S8 in the Supporting Information). Analysis of the $J_{\rm PP}$ = values and comparison of the chemical shifts with those of other Au–Cu phosphine complexes described earlier^{14b,25} allows for an easy assignment of the low-field doublets (35.2–35.7 ppm) to Aucoordinated PPh₂ groups, while three higher field resonances (δ 8.7 to -6.8 ppm) in each of the spectra correspond to Cubound phosphorus atoms.

The solution behavior of Ag–Au complexes 11 and 12 resembles that of 6 and 7, revealing fast intramolecular dynamics at room temperature on the NMR time scale (Figure 4 and Figure S9 in the Supporting Information). At the low-temperature limit (193 K) the ³¹P NMR spectra of 11 and 12



Figure 4. (A) ³¹P–³¹P COSY NMR spectrum of complex **12** (193 K, 162 MHz, CD₂Cl₂). The inset shows the assignment scheme and spin–spin coupling network. The top 1D projection (green) shows a simulated spectrum $({}^{2}J(P(3)-P(4)) = 75 \text{ Hz}, {}^{3}J(P(3/4)-P(2)) = 148$ and 166 Hz, ${}^{3}J(P(1)-P(2)) = 68 \text{ Hz}$). (B) VT ${}^{31}P{}^{1}H{}$ NMR spectra of complex **12** (162 MHz, CD₂Cl₂).

suggest that both compounds exist in one low-symmetry form, which corresponds to the motif found in the solid state (Figure 2 and Figure S4 in the Supporting Information). The spectroscopic patterns for **11** and **12** feature AQQ'X spin systems, additionally complicated by ^{107/109}Ag-³¹P couplings of two lateral phosphorus atoms (Figure 4 and Figure S9).

Analogously to the assignment in 8–10, a low-field doublet for 11 and 12 (δ 31.6 and 31.8 ppm) is ascribed to the P(1) atom bound to the gold ion and coupled to the P(2) nucleus. Two remaining PPh₂ groups (δ 1.1–1.3 and 5.5 ppm) are evidently bound to the Ag(I) center, as the corresponding multiplets from P(3) and P(4) atoms demonstrate typical coupling constants J_{AgP} for the $^{107/109}$ Ag-containing isotopomers. The high-field resonance (P(2), δ –7.7 and –9.8 ppm for 11 and 12, respectively) displays only the phosphorus–phosphorus splitting, pointing to a negligible P(2)–Ag interaction that is in line with long P(2)–Ag(1) separations determined in the solid state (see Table S3 in the Supporting Information). Heterotrimetallic Cationic Complexes. In order to extend the synthetic strategy, we employed a related triphosphine, bis (2 - diphenylphosphinophenyl)-phenylphosphine (P^3) ,²⁰ in an attempt to prepare trinuclear complexes—congeners of the bimetallic compounds 6-12 (Scheme 3). The hypothesized approach involved reacting the

Scheme 3. Synthesis of Complexes 13–15^a



^{*a*}Conditions: CH₂Cl₂/acetone, 3 h, 298 K.

 P^3 ligand with $[Cu(NCMe)_4]^+$ or Ag⁺ triflates to produce the coordinatively unsaturated species $[M(P^3)]^+$, followed by a reaction with the anionic dialkynyl complexes $[Au-(C_2R)_2]^-PPN^+$. The latter were generated in situ according to the "acac method" developed by Vicente.²⁶ However, no target complexes, depicted in Scheme 3 (top), could be isolated. Instead, for the gold–silver mixture a very small amount of the trinuclear complex $[\{(P^3O)Ag\}_2Au(C_2C(OH)-Ph_2)_2]CF_3SO_3$ containing partially oxidized phosphine ($P^3O = bis(2-(diphenylphosphino)phenyl)phenylphosphine oxide) was obtained upon recrystallization. Following the same protocol with the <math>P^3O$ ligand²⁷ allowed for the preparation of the $[\{(P^3O)M\}_2Au(C_2R)_2]CF_3SO_3$ compounds 13–15 in considerably improved yields (Scheme 3, bottom).

Crystallographic studies revealed that these compounds possess a gold(I) dialkynyl anion decorated with two cationic $[M(P^3O)]^+$ (M = Cu, Ag) units, which are held together by means of gold-metal and π -C=C-metal bonding (Figure 5 and Figure S10 in the Supporting Information). The metal ions in 13–15 form an ideal linear arrangement, as well as the central $[Au(C_2R)_2]^-$ rod (the M-Au-M and C(1)-Au-C(1') angles are 180.0°). The intermetallic and metal-ligand distances are in the normal range determined for the congener coinage-metal complexes^{4c,12b,cg,13e,23} and are comparable to the corresponding parameters found for compounds 6–12 (Table S4 in the Supporting Information). The relatively long P=O···M contacts in 13–15 are close to those observed in the mononuclear halide species $M(P^3O)$ Hal (M = Cu, Ag),²⁷ pointing to rather loose O–M interactions. It should be noted that clusters 13 and 14 with hydroxyl-alkynyl ligands are



Figure 5. Molecular views of complexes 13 and 15. Thermal ellipsoids are shown at the 50% probability level. Counterions and H atoms (except the O-H atoms) are omitted for clarity. Symmetry transformations used to generate equivalent atoms ('): in 13, -x, -y, -z; in 15, 1 - x, -y, 1 - z.

furthermore stabilized by effective $-O-H\cdots O=P$ hydrogen bonding between the alkynyl and phosphine oxide moieties, which is indicated by short $O(1)\cdots O(2)$ separations (2.806 and 2.787 Å for 13 and 14, respectively).

An ESI-MS investigation of 13-15 shows the presence of molecular ions with m/z 2029.36 (13), 2117.36 (14), and 1905.26 (15) (Figure S11 in the Supporting Information). However, in the case of 15 a significant fragmentation can be observed which presumably results from a lower stability of this complex in comparison with that of 13 and 14 due to the absence of efficient intramolecular hydrogen bonding.

The NMR data obtained at room temperature confirm that the structures of 13–15 found in the solid state are retained. Their ³¹P spectra exhibit a pattern which consists of two signals with a 1:2 ratio of relative intensities. The low-field resonance (δ 42.3, 38.5, and 37.6 ppm for 13–15, respectively) corresponds to the phosphine oxide function, while a highfield multiplet of double intensity (δ –12.5, –2.4 and –2.2

Table 1. Solid-State Photophysical Properties of 1-15

	298 K						77 K	
	$\lambda_{\rm ex}$ nm	$\lambda_{\rm em}$, nm	Φ^a	$\tau_{av}, \mu s^b$	$k_{\rm r}, {\rm \ s}^{-1} {\rm \ c}$	$k_{nr} s^{-1} d$	λ_{ex} nm	$\lambda_{\rm em}$, nm
1	415	635	0.03	1.1	2.5×10^{4}	9.0×10^{5}	331	633
2	329	583	0.05	1.3	3.5×10^{4}	7.1×10^{5}	325	490, 535, 588
3	298, 374	533	0.08	3.7	2.2×10^4	2.5×10^{5}	325	431, 453, 463, 474, 500
4	325, 365	510	0.1	1.2	8.4×10^4	7.3×10^{5}	340	515
5	325, 376	555	0.17	1.7	9.8×10^4	4.7×10^{5}	310, 370	542
6	305, 373	480	0.36	8.3	4.4×10^{4}	7.7×10^{4}	294, 370	475
7	327, 382	480	0.13	1.5	8.1×10^4	5.7×10^{5}	330, 385	511
8	340, 370	520	0.16	5.5	2.9×10^{4}	1.5×10^{5}	366	547
9	340, 366	495	0.21	3.3	6.2×10^{4}	2.4×10^{5}	344	490
10	337, 371	485	0.26	2.8	9.2×10^{4}	2.6×10^{5}	321, 385	485
11	335, 385	465	0.04	0.6	7.9×10^4	1.7×10^{5}	335	477
12	330, 375	450	0.31	11.4	2.7×10^{4}	6.1×10^{4}	330	451
13	372	532	0.30	2.5	1.2×10^{5}	2.8×10^{5}	365	523
14	330 sh, 365	485	~0.01	1.7	$\sim 5.0 \times 10^{3}$	$\sim 5.8 \times 10^{5}$	325	488
15	354, 400, 428	440, 481	0.46	5.2	8.8×10^{4}	1.0×10^{5}	332, 400, 415, 432	437, 458, 469, 482

^{*a*}The uncertainty of the quantum yield measurement is in the range of ±5% (an average of three replica). ^{*b*}Average emission lifetime for all of the complexes except 13 for the two-exponential decay determined by the equation $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$; A_i = weight of the *i* exponent. ^{*c*} k_r values were estimated by Φ/τ_{obs} . ^{*d*} k_{nr} values were estimated by $k_r(1 - \Phi)/\tau_{obs}$.

ppm) is generated by the equivalent metal-bound PPh₂ groups with typical $^{107/109} Ag - ^{31} P$ splitting observed for silver-containing compounds 14 and 15.

The OH resonances in the ¹H NMR spectra of **13** and **14** are found at δ 6.22 and 6.40 ppm and therefore show a large lowfield shift with respect to those of complexes **10** and **12** having the same $-C \equiv CC(OH)Ph_2$ alkyne, for which the OH signals were found at δ 2.40 and 2.84 ppm. This dramatic difference supports the presence of a strong O-H…O attraction in **13** and **14** in solution. The aromatic region of the proton spectra is compatible as well with the solid-state structures of **13–15**, though the signals are visibly broadened for **15** evidently because of a lower rigidity of its framework.

Solid-State Photophysical Properties. The title complexes exhibit room-temperature luminescence in the solid state but virtually are not emissive in solution under ambient conditions. The fluxional behavior of complexes 1-12 may introduce effective nonradiative deactivation of the excited states, resulting in severe quenching of luminescence in the fluid medium. The trinuclear clusters 13-15 possess intrinsically flexible frameworks based on the P^3O ligand, which was recently shown to induce emission-free relaxation.²⁷ The photophysical data are summarized in Table 1; the corresponding spectra are presented in Figures 6-8 (298 K) and Figures S12-S14 in the Supporting Information (77 K). The excitedstate lifetimes for all of the compounds lie in the range from 0.6 to 11.4 μ s, which implies a triplet parentage of photoemission; this assignment is also supported by significant Stokes shifts exceeding 100 nm.

The mononuclear complex 1 displays a broad emission band of low intensity ($\Phi = 0.03$) in the orange-red region (λ 635 nm), which is comparable to the characteristics of the triphosphine-based alkynyl Cu(P^3)C₂Ph congener ($\Phi = 0.06$, λ 602 nm).²⁰

The tricopper compound **2** produces a somewhat stronger luminescence ($\Phi = 0.05$), which is blue-shifted in relation to **1** (λ 583 nm). A comparison to other copper alkynyl clusters^{12a} allows for a tentative assignment of the emission to Cu₃centered electronic transitions mixed with MLCT d(Cu) $\rightarrow \pi^*$ (C=CPh) character. Cooling these samples to 77 K leads to



Figure 6. Normalized solid-state excitation (dotted lines) and emission (solid lines) spectra of 1–6 at 298 K.



Figure 7. Normalized solid-state excitation (dotted lines) and emission (solid lines) spectra of 7-12 at 298 K.



Figure 8. Normalized solid-state excitation (dotted lines) and emission (solid lines) spectra of 13-15 at 298 K.

a visible increase in emission energy for **2** and the appearance of a vibronic structure, the progression of which (ν ca. 1730 cm⁻¹) indicates substantial contribution of the C=CPh fragments into the frontier orbitals.

The trisilver complexes 3-5 expectedly display a substantial blue shift of emission bands in comparison to the isostructural copper analogue 2 in both room- and low-temperature experiments. The emission profiles of silver alkynyl halide clusters 3-5 (Figure 6) under ambient conditions constitute featureless bands, the intensity of which follows the order I (0.17, 5) > Br (0.1, 4) > Cl (0.08, 3). At 77 K fine vibrational structure can be seen for the chloride derivative 3, the maximum of the emission band being blue-shifted from 533 to 431 nm. In contrast, the temperature influence on the spectroscopic patterns of 4 and 5 is quite minor. Alterations of emission energies within the series 3-5 may be associated with a contribution of halide ligands to the excited states, which originate from a mixture of XLCT/XMCT and MLCT transitions.²⁸ This assumption is supported by the clearly visible effect of halides on emission energies at 77 K: λ_{max} (Cl) $< \lambda_{max}$ (Br) $< \lambda_{max}$ (I). However, at room temperature there is no obvious dependence of λ_{\max} as a function of Hal, which is generally in line with other reports on silver phosphine-halide luminophores.^{27,28}

The homometallic alkynyl-phosphine copper and silver complexes **6** and 7, which are shown separately in Figures 6 and 7 to avoid congestion, display closely analogous excitation and identical emission spectra at 298 K (λ 480 nm) with moderately good quantum yields (Φ = 0.36 and 0.13) and relatively long lifetimes (τ = 8.3 and 1.5 μ s).

At 77 K the dicopper complex **6** shows a typical small blue shift of excitation and emission bands, whereas the silver complex 7, which exists in a tetranuclear form in the solid state, exhibits a considerable red shift of the emission maximum (λ 511 nm) conceivably due to a contraction of the metal–metal distances in the cluster core.²⁹ The luminescence of structurally similar Au–M bimetallic species **8–12** is clearly dependent on the nature of the heterometal M (Figure 7).

The gold-copper compounds 8-10 display systematically lower emission energies with respect to their silver counterparts 11 and 12 that can be explained by stabilization of the groundstate HOMO levels in the case of Ag-containing complexes. This effect of copper vs silver leads to a reduced HOMO- LUMO gap in the Au-Cu species and thus red-shifted emission, which has been noticed earlier for other Au-Cu/ Ag heterometallic assemblies.³⁰ The electronic characteristics of the $-C \equiv CR$ groups affect the optical properties of the title materials as well. The alkynyl ligands functionalized with hydroxyl groups tend to cause a hypsochromic shift of emission, which ultimately gives a deep blue color for 12 (λ 450 nm) at a decent quantum efficiency ($\Phi = 0.31$). This effect can be presumably attributed to the difference in electronic properties of aromatic and hydroxyaliphatic alkynyls, as well as weak noncovalent interactions in the solid state, facilitated by the presence of polar OH groups. The trinuclear species 13 and 15 are intensely luminescent with quantum yields of 0.30 and 0.46, respectively. Similarly to the dinuclear compounds, the Au-Cu cluster 13 shows a lower emission energy (λ 532 nm, Figure 8). The Au–Ag complex 15 displays the highest energy emission within the entire series 1-15 (λ 440 nm), indicative of a low-lying ground-state level. The poorly resolved vibronic structure of the emission band of 15 at 298 K, which is significantly enhanced at 77 K (Figure S14 in the Supporting Information), proves a substantial contribution of the intraligand transitions to the emissive excited states.

CONCLUSIONS

We investigated the preparation of a series of low-nuclearity alkynyl clusters of d^{10} coinage metals, stabilized by the tetradentate chelating phosphine P^4 ligand. Application of the polymeric phenylacetylides of copper and silver as starting materials affords neutral mononuclear (P^4)MC₂Ph (1, M = Cu) or trinuclear $(P^4)M_3(C_2Ph)_{3-x}Hal_x$ (2-5) complexes. The combination of $(M'C_2R)_n$ (M' = Cu, Ag, Au) acetylides with M^+ (M = Cu, Ag) ions results in the assembly of a range of dinuclear cationic compounds $[(P^4)MM'(C_2R)]^+$ (6–12). Crystallographic analysis of these species indicates that in the di- and trinuclear clusters the tetraphosphine coordinates predominantly in a tridentate mode, where the central phosphorus donor is poorly involved in binding to the metal centers. Complexes 1-12 were found to be stereochemically nonrigid in solution and were characterized by variabletemperature NMR spectroscopic measurements to confirm that their structures were retained in the fluid medium. Attempts to synthesize heterotrimetallic compounds employing a congener phosphine of a lower denticity, P^3 , and dialkynyl anionic precursors $[Au(C_2R)_2]^-$ led to the formation of target metal frameworks only via partial oxidation of the triphosphine, giving the clusters $[{(P^{3}O)M}_{2}Au(C_{2}R)_{2}]^{+}$ (13–15). Complexes 1-15 are virtually nonluminescent in solution, and their photoemissive properties were studied in the solid state at 298 and 77 K to reveal weak to moderately intense phosphorescence (Φ_{em} up to 0.46), which covers the range from 440 to 635 nm under ambient conditions. The optical behavior of the title compounds expectedly depends on both the composition and structure of the metal core and the characteristics of the ligand environment. In particular, the copper-containing complexes display a systematic red shift of the emission maxima in comparison to the silver congeners, while the electronic properties of the alkynyl −C≡CR groups, utilized in this study, have a less pronounced effect, which is reflected by a hypsochromic shift upon changing the R substituent from aromatic to hydroxyaliphatic. For most of the compounds the radiative excited states are tentatively assigned to clustercentered transitions mixed with some MLCT d $\rightarrow \pi^*(alkyne)$ character, while the spectroscopic profile of complex 15

indicates that the ³IL transitions are substantially engaged in the observed luminescence.

EXPERIMENTAL SECTION

General Information. (2-Bromophenyl)diphenylphosphine,³¹ bis-(2-(diphenylphosphino)phenyl)phenylphosphine oxide (P^3O) ,²⁷ and the complexes $(CuC_2Ph)_m^{32} (AgC_2Ph)_m^{33} AuC_2R$ (R = Ph, -C(OH) $(CH_3)_2$, $-C(OH)Ph_2$),³⁴ and $[Au(acac)_2]PPN$ (acac = acetylacetonate)³⁵ were synthesized according to the published procedures. Tetrahydrofuran (THF) was distilled over Na-benzophenone ketyl under a nitrogen atmosphere prior to use. Other reagents and solvents were used as received. The solution ¹H, ³¹P{¹H}, and ¹H-¹H COSY NMR spectra were recorded on a Bruker Avance 400 spectrometer. Mass spectra were determined on a Bruker micrOTOF 10223 instrument in the ESI⁺ mode. Microanalyses were carried out in the analytical laboratory of the University of Eastern Finland.

Tris(2-diphenylphosphino)phenylphosphine (P⁴). The ligand was obtained via a modified protocol.³⁶ The synthesis was carried out under a nitrogen atmosphere. A solution of 2-(bromophenyl)diphenylphosphine (1.5 g, 4.4 mmol) in THF (20 mL) was cooled to -78 °C, and a 1.6 M solution of n-BuLi (3.0 mL, 4.8 mmol) was added within 10 min to give a light yellow solution. It was stirred for 1 h at -78 °C and then treated dropwise with neat PCl₃ (0.20 g, 1.45 mmol). The pale reaction mixture was stirred below -70 °C for 2 h and overnight at room temperature, quenched with methanol (2 mL), and evaporated. The yellow residue was washed with methanol (3 \times 15 mL), dried, dissolved in dichloromethane, and passed through a pad of silica gel (150 mesh, 2×5 cm). The resulting solution was diluted with ethanol and slowly evaporated at +5 °C to afford a colorless crystalline material (0.73 g, 61%). The spectroscopic data are identical with those reported earlier.³⁷ ³¹P{¹H} NMR (CDCl₃, 298 K, δ): AB₃ spin system -22.5 (³J_{PP} = 145 Hz, 1P), -14.1 (³J_{PP} = 145 Hz, 3P). ¹H NMR (CDCl₃, 298 K, δ): 7.72 (m, 1H), 7.19 (m, 13H), 7.07 (m, 10H), 6.8 (m, 2H).

(P^4)CuC₂Ph (1). A mixture of (CuC₂Ph)_n (12.2 mg, 0.074 mmol) and P^4 (60 mg, 0.074 mmol) in dichloromethane (10 cm³) was stirred for 2 h in the absence of light. The resulting bright yellow solution was filtered through Celite and evaporated. The solid residue was recrystallized by gas-phase diffusion of diethyl ether into a dichloromethane solution of I at 278 K to afford yellow crystalline material (66 mg, 92%). ³¹P{¹H} NMR (CD₂Cl₂,193 K, δ): -24.5 (m, 1P, noncoordinated PPh₂), 0.4 (m, 1P, $P(C_6H_4PPh_2)_3$, 6.2 (m, 2P, PPh₂). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.59 (br m, 5H), 7.42 (dm, ³J_{HH} = 7.1 Hz, 2H), 7.08-7.39 (m, 37H), 7.04 (t, ³J_{HH} = 7.5 Hz, 3H). Anal. Calcd for $C_{62}H_4$, P_4 Cu: C, 76.03; H, 4.84. Found: C, 75.85; H, 4.89.

(*P*⁴)Cu₃(C₂Ph)₃ (2). This complex was prepared similarly to 1 from $(CuC_2Ph)_n$ (37.0 mg, 0.224 mmol) and *P*⁴ (60 mg, 0.074 mmol). Yellow crystalline material (51 mg, 53%). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): -10.8 (d br, ³*J*_{PP} = ca. 73 Hz, 3P, PPh₂), -14.6 (q br, ³*J*_{PP} = ca. 73 Hz, 1P *P*(C₆H₄PPh₂)₃). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.83 (br, 6H), 7.60 (t, ³*J*_{HH} = 7.9 Hz, 6H), 7.37–7.24 (m, 12H), 7.21 (t, ³*J*_{HH} = 7.4 Hz, 3H), 7.19–7–12 (m, 15H), 7.08 (t, ³*J*_{HH} = 7.4 Hz, 6H), 7.03 (t, ³*J*_{HH} = 7.9 Hz, 3H), 6.35 (br, 3H). Anal. Calcd for C₇₆H₅₇P₄Cu₃: C, 71.58; H, 4.39. Found: C, 71.39; H, 4.48.

 (P^4) Ag₃(C₂Ph)X₂ (X = Cl, Br, I). A mixture of P^4 (60.0 mg, 0.074 mmol), AgC₂Ph (30.8 mg; 0.074 mmol), and AgX (0.147 mmol) in dichloromethane (15 cm³) was stirred for 5 h in the absence of light. The solution was filtered through Celite and evaporated, and the solid residue was purified by recrystallization.

 $(P^4)Ag_3(C_2Ph)Cl_2$ (**3**). Recrystallized by gas-phase diffusion of diethyl ether into a dichloromethane solution of **3** at 278 K to give a colorless crystalline material (73 mg, 75%). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): -5.4 (d, ³J_{PP} = 155 Hz, 3P, PPh₂), -33.0 (br, 1P, P(C₆H₄PPh₂)₃). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.50 (m br, 14H), 7.35 (m br, 9H), 7.22–7.06 (m, 15H), 7.03 (m br, 3H), 6.86 (t, ³J_{HH} = 7.5 Hz, 3H), 6.60 (m br, 3H). Anal. Calcd for C₆₂H₄₇Cl₂P₄Ag₃: C, 56.83; H, 3.62. Found: C, 56.59; H, 3.77.

 $(P^4)Ag_3(C_2Ph)Br_2$ (4). Recrystallized by gas-phase diffusion of diethyl ether into an acetone/dichloromethane (1/1 v/v mixture) solution of

4 at 278 K to give a colorless crystalline material (87 mg, 84%). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): -6.6 (d, ³J_{PP} = 161 Hz, 3P, PPh₂), -33.9 (br, 1P, P(C₆H₄PPh₂)₃). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.48 (m br, 14H), 7.39 (m br, 9H), 7.25–7.16 (m, 6H), 7.15–7.03 (m, 12H), 6.80 (t br, ³J_{HH} = ca. 7.0 Hz, 3H), 6.49 (br, 3H). Anal. Calcd for C₆₂H₄₇Br₂P₄Ag₃: C, 53.22; H, 3.39. Found: C, 53.10; H, 3.21.

 $(P^4)Ag_3(C_2Ph)I_2$ (5). Recrystallized by gas-phase diffusion of diethyl ether into an acetone/dichloromethane (2/1 v/v mixture) solution at 278 K to give a colorless crystalline material (74 mg, 67%). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): -6.8 (d, ³J_{PP} = 153 Hz, 3P, PPh₂), -32.4 (br, 1P, P(C₆H₄PPh₂)₃). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.35–7.55 (m, 23H), 7.25–7.05 (m, 18H), 6.77 (m br, 3H), 6.41 (m br, 3H). Anal. Calcd for C₆₂H₄₇I₂P₄Ag₃: C, 49.87; H, 3.17. Found: C, 50.03; H, 3.14.

 $[(P^4)Cu_2(C_2Ph)]PF_6$ (6). Freshly prepared $(CuC_2Ph)_n$ (12.3 mg, 0.074 mmol) was suspended in acetone (5 cm³), and a solution of P^4 (60.0 mg, 0.074 mmol) in dichloromethane (5 cm³) was added. The reaction mixture was stirred for 30 min in the absence of light, and a solution of Cu(NCMe)₄PF₆ (27.6 mg, 0.074 mmol) in acetone (5 cm³) was added. The resulting light greenish reaction mixture was stirred for 30 min and evaporated, and the residue was recrystallized by gas-phase diffusion of pentane into a dichloromethane solution of 6 at 278 K to give yellow greenish crystalline material (49 mg, 56%). ESI-MS (m/z): $[M]^+$ 1041.14 (calcd 1041.12). ³¹P{¹H} NMR (CD₂Cl₂, 199 K, δ): 5.4 (dd, ${}^{2}J_{PP} = 57$ and ${}^{3}J_{PP} = 82$ Hz, 1P, PPh₂), 3.6 (d, ${}^{3}J_{PP} =$ 113 Hz, 1P, PPh₂), -2.4 (dd, ${}^{2}J_{PP} = 57$ and ${}^{3}J_{PP} = 82$ Hz, 1P, PPh₂), $-6.9 (dt, {}^{3}J_{PP} = 82 and 113 Hz, 1P, P(C_{6}H_{4}PPh_{2})_{3}), -144.6 (sept, 1P,$ PF₆). ¹H NMR (CD₂Cl₂, 199 K, δ): 7.70 (dd, ³J_{HP} 10.9 Hz, ³J_{HH} = 7.7 Hz, 2H), 7.58-7.39 (m, 14H), 7.39-7.25 (m, 4H), 7.24-7.01 (m, 20 H), 6.98 (t, ${}^{3}J_{HH}$ = 7.1 Hz, 2H), 6.78 (m, 1H), 6.62 (dd, ${}^{3}J_{HP}$ 10.6 Hz, ${}^{3}J_{\rm HH}$ = 7.8 Hz, 2H), 6.45 (m, 1H), 6.19 (m, 1H). Anal. Calcd for C₆₂H₄₇F₆P₅Cu₂: C, 62.68; H, 3.99. Found: C, 62.41; H, 4.11.

 $[(P^4)_2Ag_4(C_2Ph)_2](PF_6)_2$ (7). A solution of AgPF₆ (18.7 mg; 0.074 mmol) in acetone (5 cm³) was added to a mixture of AgC₂Ph (15.4 mg; 0.074 mmol) and P^4 (60.0 mg, 0.074 mmol) in dichloromethane (5 cm³). The resulting solution was stirred for 2 h in the absence of light and then evaporated, and the residue was recrystallized by gasphase diffusion of pentane into an acetone solution of 7 at 278 K to give a colorless crystalline material (66 mg, 70%). ESI-MS (m/z): $[0.5M]^+$ 1129.08 (calcd 1129.07). ³¹P{¹H} NMR (acetone- d_{6} , 298 K, $δ): -1.3 (br, dt, {}^{3}J_{PP} = 144 Hz, av. {}^{1}J_{PAg} ca. 200 Hz, 3P, PPh_{2}), -29.1 (q, {}^{3}J_{PP} = 144 Hz, 1P, P(C_{6}H_{4}PPh_{2})_{3}), -144.8 (sept, 1P, PF_{6}).$ ${}^{31}P{}^{1}H$ NMR (acetone- d_6 , 193 K, δ): 0.6 (dd br, ${}^{3}J_{PP}$ = ca. 148 Hz, ¹J_{PAg} ca. 510 Hz, 1P, PPh₂), -2.4 (d br, ¹J_{PAg} ca. 300 Hz, 1P, PPh₂), -7.7 (d br, ${}^{1}J_{PAg}$ ca. 390 Hz, 1P, PPh₂), -31.4 (q, ${}^{3}J_{PP}$ = 148 Hz, 1P, $P(C_6H_4PPh_2)_3)$, -144.8 (sept, 1P, PF₆). ¹H NMR (acetone- d_6 , 298 K, δ): 7.60 (m, 9H), 7.47 (m, 6H), 7.43-7.28 (m, 14H), 7.27-7.20 (m, 9H), 7.15-7.08 (m, 6H), 6.81 (m, 3H). Anal. Calcd for C62H47F6P5Ag2: C, 58.33; H, 3.71. Found: C, 57.96; H, 3.83.

 $[(P^4)AuM(C_2R)]PF_6$ Complexes (M = Cu, Ag; R = Ph, -C(OH)(CH₃)₂, -C(OH)Ph₂). Au(C₂R) (0.074 mmol) was suspended (dissolved for R = -C(OH)Ph₂) in dichloromethane (5 cm³), and P⁴ (60.0 mg, 0.074 mmol) was added, followed by a solution of AgPF₆ or Cu(NCMe)₄PF₆ (0.074 mmol) in acetone (5 cm³). The reaction mixture was stirred for 2 h in the absence of light. The resulting transparent solution was evaporated, and the crude solid was recrystallized by a gas-phase diffusion of diethyl ether into a dichloromethane (5, 7–9) or acetone (6) solution of the corresponding complex at 278 K.

 $[(P^4)AuCu(C_2Ph)]PF_6$ (8). Yellow crystalline material (66 mg, 68%). ESI-MS (m/z): $[M]^+$ 1175.18 (calcd 1175.16). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): 35.5 (d, ³J_{PP} = 48 Hz, 1P, Au-PPh₂), 7.6 (ddd, ³J_{PP} = 138, 125, 48 Hz, 1P, P(C₆H₄PPh₂)₃), 1.6 (dd br, ³J_{PP} = 138 and ²J_{PP} = 54 Hz, 1P, PPh₂), -5.8 (dd br, ³J_{PP} = 125 and ²J_{PP} = 54 Hz, 1P, PPh₂), -144.6 (sept, 1P, PF₆). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.67 (m, 2H), 7.61–7.18 (m, 28H), 7.15–7.09 (m, 5H), 7.09–6.97 (m, 7H), 6.93 (dd, ³J_{HP} 11.7 Hz, ³J_{HH} = 6.5 Hz, 1H), 6.62 (m, 3H), 6.37 (dd, ³J_{HP} 11.0 Hz, ³J_{HH} = 6.7 Hz, 1H). Anal. Calcd for C₆₂H₄₇F₆P₅AuCu: C, 56.35; H, 3.59. Found: C, 56.44; H, 3.70. $[(P^4)AuCu(C_2C(OH) (CH_3)_2)]PF_6 (9). Yellow crystalline material (80 mg, 83%). ESI-MS (m/z): [M]⁺ 1157.19 (calcd 1157.17). ³¹P{¹H} NMR (CD_2Cl_2, 298 K, <math>\delta$): 35.7 (d, ³J_{PP} = 47 Hz, 1P, Au-PPh₂), 8.7 (ddd, ³J_{PP} = 135, 127, 47 Hz, 1P, PPh₂), 1.4 (dd br, ³J_{PP} = 135 and ²J_{PP} = 65 Hz, 1P, PPh₂), -6.7 (dd, ³J_{PP} = 127 and ²J_{PP} = 65 Hz, 1P, PPh₂), -6.7 (dd, ³J_{PP} = 127 and ²J_{PP} = 65 Hz, 1P, PPh₂), -144.6 (sept, 1P, PF₆). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.65 (m, 2H), 7.60–7.42 (m, 13H), 7.37 (m, 4H), 7.32–7.16 (m, 12H), 7.15–7.02 (m, 6H), 6.93 (dd, ³J_{HP} 11.6 Hz, ³J_{HH} = 6.7 Hz, 1H), 6.82 (dd, ³J_{HH} = 8.2, 8.6 Hz, 2H), 6.59 (t, ³J_{HH} = 6.6 Hz, 1H), 6.37 (dd, ³J_{HP} 10.1 Hz, ³J_{HH} = 6.6 Hz, 1H), 1.47 (s br, OH, 1H), 1.33 (s, CH₃, 3H), 1.30 (s, CH₃, 3H). Anal. Calcd for C₅₉H₄₉OF₆P₅AuCu: C, 54.37; H, 3.79. Found: C, 54.46; H, 4.42.

 $[(P^4)AuCu(C_2C(OH)Ph_2)]PF_6$ (10). Yellow crystalline material (75 mg, 71%). ESI-MS (m/z): [M]⁺ 1281.22 (calcd 1281.20). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): 35.2 (d, ³J_{PP} = 49 Hz, 1P, PPh₂), 7.0 (ddd, ³J_{PP} = 137, 132, 49 Hz, 1P, P(C₆H₄PPh₂)₃), 2.1 (dd, ³J_{PP} = 137 and ²J_{PP} = 61 Hz 1P, PPh₂), -6.8 (dd, ³J_{PP} = 132 and ²J_{PP} = 61 Hz, 1P, PPh₂), -144.6 (sept, 1P, PF₆). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.67 (dd, ³J_{HH} = 7.8, 8.5 Hz, 2H), 7.62–7.48 (m, 10H), 7.47–7.32 (m, 8H), 7.29 (t, ³J_{HH} = 7.6 Hz, 1H), 7.25–7.14 (m, 14H), 7.11–6.91 (m, 10H), 6.80 (dd, ³J_{HP} 11.7 Hz, ³J_{HH} = 6.6 Hz, 1H), 6.58 (dd, ³J_{HH} = 7.6, 7.0 Hz, 1H), 6.42–6.32 (m, 3H), 2.40 (s, OH, 1H). Anal. Calcd for C₆₉H₅₃OF₆P₅AuCu: C, 58.05; H, 3.74. Found: C, 57.59; H, 3.71.

 $\begin{bmatrix} (P^{2}) & AuAg(C_{2}Ph) \end{bmatrix} PF_{6} (11).$ Yellow crystalline material (73 mg, 73%). ESI-MS (m/z): [M]⁺ 1219.15 (calcd 1219.13). ³¹P{¹H} NMR (CD₂Cl₂, 192 K, δ): AQQ'X spin system ³J_{AX} = 67 Hz, ³J_{QX} = 158 Hz, ³J_{QX} = 139 Hz, ²J_{Q'Q} = 78 Hz; 31.8 (d, 1P, Au-PPh₂), 1.1 (m, ¹J¹⁰⁹_{AgP} = 422 Hz, ¹J¹⁰⁷_{AgP} = 370 Hz, 1P, PPh₂), -5.5 (m, ¹J¹⁰⁹_{AgP} = 417 Hz, ¹J¹⁰⁷_{AgP} = 360 Hz, 1P, PPh₂), -7.7 (m, 1P, P(C₆H₄PPh₂)₃), -144.6 (sept, 1P, PF₆). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.61–7.50 (m, 9H), 7.40 (m, 9H), 7.45–7.13 (m, 29H), 7.11 (br, 3H), 7.01 (br, 3H), 6.76 (br, 3H). Anal. Calcd for C₆₂H₄₇F₆P₅AuAg: C, 54.53; H, 3.47. Found: C, 54.84; H, 3.80.

[AuAg(P⁴)(C₂C(OH)Ph₂)]PF₆ (12). Colorless crystalline material (85 mg, 78%). ESI-MS (*m*/*z*): [M]⁺ 1325.20 (calcd 1325.18). ³¹P{¹H} NMR (CD₂Cl₂, 192 K, δ): AQQ'X spin system ³J_{AX} = 68 Hz, ³J_{QX} = 166 Hz, ³J_{QX} = 148 Hz, ²J_{Q'Q} = 75 Hz; 31.6 (d, 1P, Au–PPh₂), 1.3 (m, ¹J¹⁰⁹_{AgP} = 430 Hz, ¹J¹⁰⁷_{AgP} = 374 Hz, 1P, PPh₂), -5.5 (m, ¹J¹⁰⁹_{AgP} = 417 Hz, ¹J¹⁰⁷_{AgP} = 360 Hz, 1P, PPh₂), -9.8 (m, 1P, P(C₆H₄PPh₂)₃), -144.6 (sept, 1P, PF₆). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.60 (m, 6H), 7.54 (t, ³J_{HH} = 7.3 Hz, 6H), 7.48 (dd, ³J_{HH} = 8.3, 1.1 Hz, 2H), 7.3–6.9 (m br, 35H), 6.70 (br, 3H), 2.84 (s, OH, 1H). Anal. Calcd for C₆₉H₅₃OF₆P₅AuAg: C, 56.31; H, 3.63. Found: C, 56.26; H, 3.94.

 $[(P^3O)_2AuM_2(C_2R)_2]CF_3SO_3$ Complexes (M = Cu, Ag; R = $-C(OH)Ph_2$, Ph). A degassed solution of $[Au(acac)_2]PPN$ (47 mg, 0.05 mmol) and HC₂R (0.11 mmol) in dichloromethane (5 cm³) was stirred under a nitrogen atmosphere for 3 h in the absence of light. Then a separately prepared mixture of Cu(NCMe)₄CF₃SO₃ (38 mg; 0.1 mmol) or AgCF₃SO₃ (26 mg; 0.1 mmol) and P³O (65 mg, 0.1 mmol) in acetone (5 cm³) was added, and the reaction solution was stirred for an additional 3 h. The solvents were evaporated, and the residue was washed with methanol (2 × 2 cm³) and recrystallized.

[(**P**³**O**)₂AuCu₂(C₂C(OH)Ph₂)₂]CF₃SO₃ (**13**). Recrystallization by gasphase diffusion of diethyl ether into an acetone solution of **13** at 278 K gave yellow crystalline material (73 mg, 67%). ESI-MS (*m*/*z*): [M]⁺ 2029.36 (calcd 2029.34). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, δ): 42.3 (s, 2P, P(O)Ph), -12.5 (s, 4P, PPh₂). ¹H NMR (CD₂Cl₂, 298 K, δ): 7.66 (t, ³J_{HH} = 7.3 Hz, 2H), 7.60 (dm, ³J_{HH} = 8.2 Hz, 8H), 7.50 (ddd, ³J_{HH} = 7.8, 7.3, ⁴J_{HP} 3.3 Hz, 4H), 7.37 (dd, ³J_{HP} 11.8 Hz, ³J_{HH} = 7.8 Hz, 4H), 7.34–7.15 (m, 24H), 7.13 (t, ³J_{HH} = 7.5 Hz, 4H), 7.04 (t, ³J_{HH} = 7.5 Hz, 4H), 6.95 (dt, ³J_{HH} = 7.5, 7.6 Hz, 8H), 6.74 (dd, ³J_{HH} = 7.5, 7.2 Hz, 8H), 6.72 (m, 4H), 6.22 (s, OH, 1H). Anal. Calcd for C₁₁₅H₈₈F₃O₇P₆SAuCu₂: C, 63.33; H, 4.07. Found: C, 63.25; H, 4.15.

[(**P**³**O**)₂AuAg₂(C₂C(OH)Ph₂)₂]CF₃SO₃ (14). Recrystallization by gasphase diffusion of diethyl ether into a dichloromethane/methanol (1/1 v/v mixture) solution of 14 at 278 K gave colorless crystalline material (63 mg, 56%). ESI-MS (*m*/*z*): [M]⁺ 2117.36 (calcd 2117.29). ³¹P{¹H} NMR (CDCl₃, 298 K, δ): 38.5 (t, ³J_{PP} = 6.6 Hz, 2P, P(O)Ph), -2.4 (dd, ¹J¹⁰⁰_{AgP} = 410 Hz, ¹J¹⁰⁷_{AgP} = 356 Hz, ³J_{PP} = 6.6 Hz, 4P, PPh₂). ¹H

NMR (CDCl₃, 298 K, δ): 7.64 (d, ³J_{HH} = 6.9 Hz, 8H), 7.53 (t, ³J_{HH} = 7.3, 2H), 7.35 (m, 12H), 7.28–7.04 (m, 48H), 7.00 (dt, ³J_{HH} = 7.5 Hz, 4H), 6.88 (m, 4H), 6.79 (dd, ³J_{HH} = 7.5, 7.1 Hz, 8H), 6.40 (s, OH, 1H). Anal. Calcd for C₁₁₅H₈₈F₃O₇P₆SAuAg₂: C, 60.86; H, 3.91. Found: C, 60.84; H, 3.96.

 $[(P^3O)_2AuAg_2(C_2Ph)_2]CF_3SO_3$ (15). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane/methanol (1/1 v/v mixture) solution of 15 at 278 K gave colorless crystalline material (63 mg, 61%). ESI-MS (*m*/*z*): [M]⁺ 1905.26 (calcd 1905.20). ³¹P{¹H} NMR (CD_2Cl_2 298 K, δ): 37.6 (s, 2P, P(O)Ph), -2.2 (d, ¹J₁₆₇_{AgP} = 400 Hz, ¹J₁₆₇_{AgP} = 349 Hz, 4P, PPh₂). ¹H NMR (CD_2Cl_2 298 K, δ): 7.63–7.36 (*m*, 20H), 7.34–7.12 (*m*, 40H), 7.01 (*m*, 12H), 6.93 (br, 4H). Anal. Calcd for C₁₀₁H₇₆F₃O₅P₆SAuAg₂: C, 58.97; H, 3.72. Found: C, 58.96; H, 3.76.

X-ray Structure Determination. The crystals of 1–4 and 6–15 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 120 or 150 K. The X-ray diffraction data were collected on Bruker SMART APEX II, Bruker Kappa Apex II, and Bruker Kappa Apex II Duo diffractometers using Mo K α radiation ($\lambda = 0.71073$ Å). The APEX2 (2009 #15764) program package was used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-2013³⁸ programs with the WinGX³⁹ graphical user interface. A semiempirical absorption correction (SADABS)⁴⁰ was applied to all data. Structural refinements were carried out using SHELXL-2014.³⁸

Some phenyl rings in 1, 11, and 12 and PF_6^- and $CF_3SO_3^-$ counterions in 11 and 13–15 were modeled to be disordered between two sites each. A series of displacement and geometry constraints and restraints were applied to these moieties. The C=C carbon atoms in 1, 3, and 4 were constrained so that their U_{ij} components were approximately equal, while in 1 and 3 these atoms were also restrained so that their U_{ij} values approximated isotropic behavior.

The crystallization solvent was lost from the crystals of 2, 4, 7, 8, 12, 14, and 15 and could not be reliably determined. The contribution of missing solvent to the calculated structure factors was taken into account by using a SQUEEZE routine of PLATON⁴¹ and was not included in the unit cell content. In addition, some of the partially lost solvent molecules (CH_2Cl_2 in 3, 8, and 12, acetone in 4, diethyl ether in 11) were refined with 0.5 occupancy.

All H atoms in 1–4 and 6–15 were positioned geometrically and constrained to ride on their parent atoms, with O–H = 0.84 Å, C–H = 0.95–0.99 Å, and $U_{\rm iso} = 1.2-1.5U_{\rm eq}$ (parent atom). The crystallographic details are summarized in Table S1 in the Supporting Information.

Photophysical Measurements. The steady-state emission and excitation spectra of complexes **1–15** in the solid state at 298 and 77 K was carried out on FluoroMax 4 and FluoroLog 3 Horiba spectrofluorometers. The emission was excited using xenon lamps (300 and 450 W). Two LEDs (maximum of emission at 340 and 390 nm) were used in pulse mode to pump luminescence for the lifetime measurements at room temperature (pulse width 1.2 nm, repetition rate 100 Hz to 10 kHz). The absolute emission quantum yields of powder samples were determined using a FluoroLog 3 Horiba spectrofluorometer and a Quanta-phi integration sphere.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00701.

Crystal data for 1-4 and 6-15, molecular views of selected complexes, additional NMR and ESI-MS spectra, and excitation and emission spectra (PDF) Crystal data for 1-4 and 6-15 (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail for S.P.T.: stunik@inbox.ru. *E-mail for I.O.K.: igor.koshevoy@uef.fi.

Notes

The authors declare no competing financial interest.

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