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Water-Soluble Phosphine Capable of Dissolving Elemental Gold: The Missing Link between 1,3,5-Triaza-7-phosphaadamantane (PTA) and Verkade's Ephemeral Ligand

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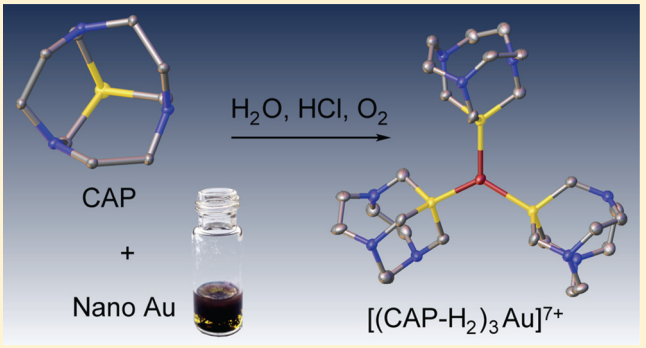
Supporting Information

ABSTRACT: We herein describe a tricyclic phosphine with previously unreported tris(homoadamantane) cage architecture. That water-soluble, air- and thermally stable ligand, 1,4,7-triaza-9-phosphatricyclo[5.3.2.1^{4,9}]tridecane (hereinafter referred to as CAP) exhibits unusual chemical behavior toward gold and gold compounds: it readily reduces Au(III) to Au(0), promotes oxidative dissolution of nanocrystalline gold(0) with the formation of water-soluble trigonal CAP−Au(I) complexes, and displaces cyanide from $[Au(CN)_2]^-$ affording triangular $[Au(CAP)_3]^+$ cation. From the stereochemical point of view, CAP can be regarded as an intermediate between 1,3,5-triaza-7-phosphaadamantane (PTA) and very unstable aminophosphine synthesized by Verkade's group: hexahydro-2*a*,4*a*,6*a*-triaza-6*b*-phosphacyclopenta[*cd*]pentalene. The chemical properties of CAP are likely related to its anomalous stereoelectronic profile: combination of strong electron-donating power (Tolman's electronic parameter 2056.8 cm^{-1}) with the low steric demand (cone angle of 109°). CAP can be considered as macrocyclic counterpart of PTA with the electron-donating power approaching that of strongest known phosphine electron donors such as P(*t*-Bu)$_3$ and PCy$_3$. Therefore, CAP as sterically undemanding and electron-rich ligand populates the empty field on the stereoelectronic map of phosphine ligands: the niche between the classic tertiary phosphines and the sterically undemanding aminophosphines.



1. INTRODUCTION

Gold is playing an important role in the coordination chemistry of phosphines: compounds containing Au−P bonds share for more than 7% of metal−phosphine complexes comprised in CCDC database.[1] The great interest for that class of organometallics is accounted not only for "pure chemistry" aspects[2] but also for their applications in homogeneous catalysis,[3] development of anticancer and antimicrobial metallodrugs[4] and luminophores.[5] A majority of the gold−phosphine complexes are those containing tertiary phosphines[1−5] that can be explained by the relative stability of the latter ligands.[6] Tertiary phosphines are widely used for stabilizing mixed-valence Au(0)−Au(I) clusters and gold nanoparticles obtained via reduction of Au(III) and Au(I) with borohydrides and hydrazine.[2,7] However, tertiary phosphines themselves are not capable of reducing Au compounds to elemental gold: the reactions are stopped at the stage of Au(I) phosphine complexes.[2,7,8] Phosphine ligands are known for the high affinity for gold[2,7] but the Au−P bonding in gold−phosphine complexes is weaker than Au−CN in gold−cyanide[8] and Au−S in gold−sulfur ligand complexes.[9−11] Therefore, to the best of our knowledge, tertiary phosphines are not capable of dissolving elemental gold via complexation-promoted Au(0)/Au(I) oxidation pathways like cyanide ions[8] and sulfur-based ligands.[9,10]

In the course of an ongoing research of polyamine ligands, we succeeded in synthesizing a new symmetric cage-like triazaphosphine: an example of previously unreported tris(homoadamantane) cage architecture. The title compound **1**, 1,4,7-triaza-9-phosphatricyclo[5.3.2.1^{4,9}]tridecane is hereinafter referred to as CAP due to characteristic cap-like shape of its cage (Figure 1a). CAP is a solid, freely handled, water-soluble, air- and thermally stable phosphine: the set of properties known for the favorite hydrosoluble phosphine ligands such as sulfonate-modified triphenylphosphines[12] and PTA (1,3,5-triaza-7-phosphaadamantane).[13] CAP exhibits unusual chemical behavior toward gold and its compounds: it is capable of reducing Au(III) to Au(0), readily dissolving nanocrystalline gold(0) with the formation of water-soluble Au(I) complexes and displacing cyanide from $[Au(CN)_2]^-$ yielding triangular $[Au(CAP)_3]^+$ cation. From the stereochemical point of view,

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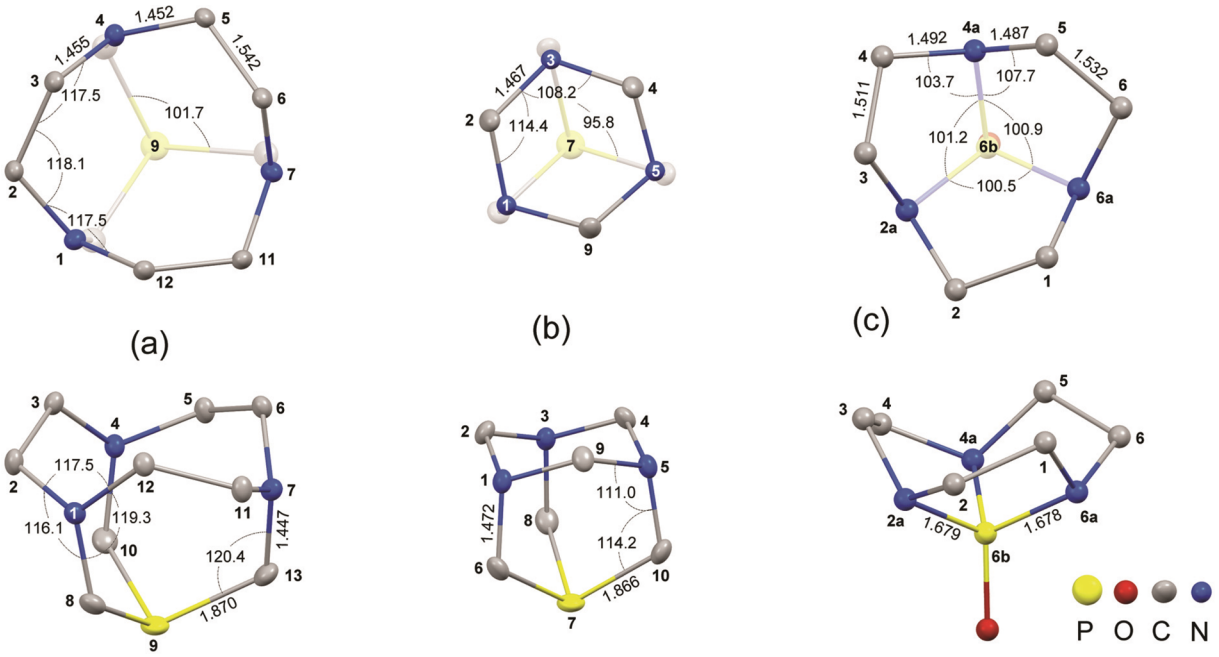
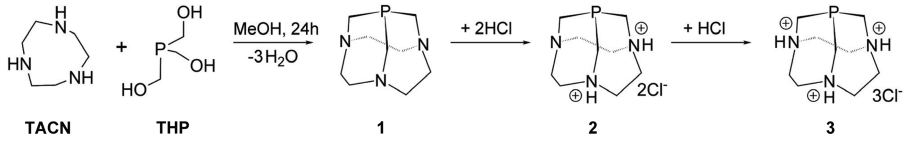


Figure 1. Ring conformations, atomic numbering schemes, selected bond distances (Å) and angles (deg) in the solid-state structures of (a) CAP **1**, (b) PTA, and (c) *P*-oxide of Verkade's aminophosphine. Note nine-membered (1,4,7-triazacyclononane) macrocycle in the cages of CAP and Verkade's ligand. Displacement ellipsoids in CAP and PTA are shown at the 50% probability level. Projections approximately parallel (top row) and perpendicular (bottom row) to the 3-fold axes. The back atoms at the top row are depth cued. Hydrogen atoms have been omitted for clarity. X-ray structural data: this study (a and b); ref 14b (c). Drawing: CCDC Mercury 3.3 (ref 15).

Scheme 1. Synthetic Route to CAP (1) and Its N-Protonated Hydrochlorides 2 and 3



CAP represents the cage architecture intermediate between PTA (Figure 1b) and the ephemeral aminophosphine described by Verkade's group in 1979: hexahydro-2*a*,4*a*,6*a*-triaza-6*b*-phosphacyclopenta[*cd*]pentalene (the structure of its *P*-oxide is presented in Figure 1c).[14] Computational DFT studies reveal that CAP possesses unusual combination of stereoelectronic properties: very low value of calculated Tolman's electronic parameter (TEP) of 2056.8 cm^{-1} and low steric bulk with the cone angle of 109°. Therefore, CAP can be ranked as one of the strongest known phosphine electron donors with rather low contribution for the steric effect.[16] The unusual chemical profile of CAP is further extended by its polyamine function related to the three readily protonable tertiary nitrogens (Scheme 1). Herein we present the basic primary results of CAP studies, with the emphasis on its gold complexes chemistry.

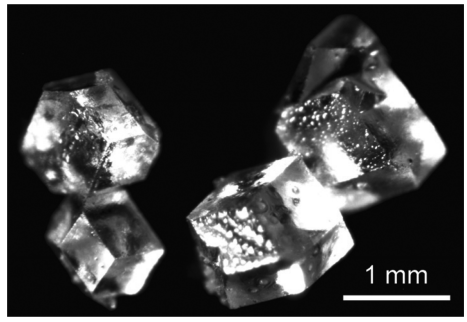


Figure 2. Dodecahedral crystals of CAP (the free ligand **1**) obtained via condensation of 1,4,7-triazacyclononane (TACN) and tris-(hydroxymethyl)phosphine (THP).

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. The free ligand **1** (Figures 1 and 2) is readily prepared via one-step Mannich-type condensation of 1,4,7-triazacyclononane (TACN) and tris-(hydroxymethyl)phosphine (THP) (Scheme 1). The general approach for that kind of condensations between amines and THP has been developed in the course of flameproofing textiles research[17] and later adopted for the synthesis of PTA[13] and THP-derived aminomethylphosphines.[18] The synthesis of **1** does not require inert atmosphere or water-free reagents and can be carried out under ambient conditions. Among several solvents tested as reaction media, water, MeOH, EtOH, *i*-PrOH and MeCN gave substantial yields of CAP, but crude reaction mixtures were always contaminated with white amorphous intractable byproducts. The use of acetone or THF did not afford CAP at all but only resulted in formation of insoluble powdery amorphous substances. Finally, methanol has been selected as the best choice for preparative purposes due to better yields, lesser amounts of amorphous (polymeric?) byproducts and easily proceeded crystallization of **1**. Formation of intractable impurities can be minimized by using the diluted (~1 wt %) starting solutions of TACN and THP. After air evaporation of reaction mixtures, **1** crystallizes as brilliant

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dodecahedral crystals (Figure 2) with faint phosphine odor. It is air-stable and can be stored unchanged in glass vial at room temperature for at least one year. The solubility of **1** in water is ~2 g/100 mL (0.1 M), that is by the order lower than the solubility of PTA.[13c] However, the aqueous solutions of CAP obtained by evaporation of crude THP-TACN reaction mixtures can be concentrated to slurries containing up to ~20 wt % of **1** prior to the onset of precipitation of its crystals. The obvious discrepancy in solubilities can be accounted for by the basicity of the free ligand (as it is discussed below) resulting in the uptake of atmospheric CO_2 due to partial formation of unstable highly soluble carbonate salts; the latter are decomposed upon further evaporation of solutions. The existence of CAP carbonates in its concentrated crude slurries is evidenced by weak effervescence of such solutions observed upon addition of diluted HCl. **1** is soluble in MeOH (~1.5 g/100 mL), EtOH, *i*-PrOH, MeCN and has no observable solubility in acetone, THF, benzene, toluene and hexane. It is very well (more than 10 g/100 mL) soluble in CH_2Cl_2 and $CHCl_3$. The solutions of **1** are air-stable and do not require special precautions for their handling.

CAP is thermally stable phosphine: **1** is melted at ~50 °C and evaporates smoothly in Ar atmosphere between 200 and 300 °C without decomposition (Figure 3). Therefore, the thermal stability of CAP is comparable with that of PTA which is known to decompose at 260 °C.[13c]

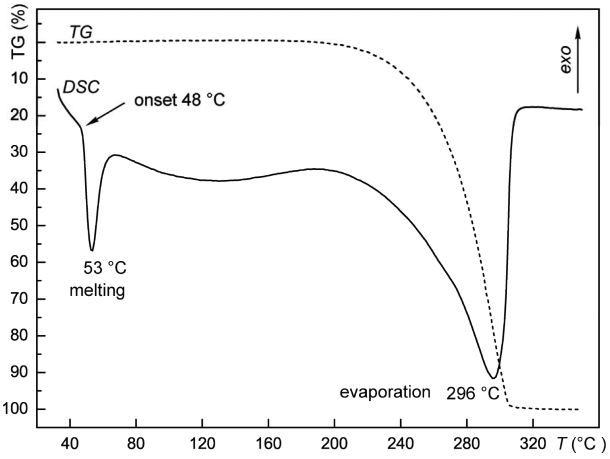

Figure 3. TG and DSC curves for **1** recorded under Ar flow.

2.2. CAP, PTA, and Verkade's Aminophosphine. The molecule of CAP (Figure 1a) is an example of simple but hitherto unreported cage-like architecture: tricyclo[5.3.2.1^{4,9}]-tridecane or tris(homoadamantane). From the stereochemical point of view, the cage of CAP can be considered as an intermediate between PTA (Figure 1b and ref 19) and the ephemeral aminophosphine synthesized by Verkade's group in 1979.[14a] The latter ligand, hexahydro-2*a*,4*a*,6*a*-triaza-6*b*-phosphacyclopenta[*cd*]pentalene (or, according to the former IUPAC nomenclature, 1,4,7-triaza-10-phosphatricyclo-[5.2.1.0^{4,10}]decane) is reported to be extremely unstable: the efforts to isolate it were unsuccessful,[14a] and even isolation of its *P*-oxide requires the special precautions.[14b] However, solid-state structures of both *P*-sulfide[14a] and *P*-oxide[14b] of Verkade's aminophosphine could be determined thereby allowing the comparison of cage architectures. The CAP and Verkade's ligand (Figure 1) are obviously similar due to presence of 1,4,7-triazacyclononane ([9]aneN$_3$) macrocycle[20] embedded in their cages. On the other hand, the comparison of CAP (with its large [9]aneN$_3$ ring) with PTA (having the small [6]aneN$_3$ one) reveals the same environment at the phosphorus site, namely the occurrence of bridging carbon atoms between phosphorus and nitrogen sites. In the other words, stereochemically CAP can be considered either as "Verkade's ligand with the bridging P-**C**-N carbons" or as "macrocyclic counterpart of PTA".

At that point one could remind the known feature of PTA as stereochemical neighbor of CAP, namely that the PTA is regioselectively protonated at nitrogen rather than phosphorus site with the formation of quarternary (PTA-H)$^+$ cation.[21b−f] The latter property has profoundly enriched the coordination chemistry of PTA because the phosphorus atom, being located at sterically undemanding cage apex, retains electron-donating and hence metal-coordinating ability even in acidic solutions.[13c,d,22] However, it has also been reported that the successive protonation of the second and third nitrogen atoms of PTA is energetically unfavorable;[13c] hence, PTA is known as monoacidic base. In this respect, the distinctive feature of CAP is its polyamine function: contrary to PTA, CAP is triacidic amino base (Table 1). The selective protonation of all three

Table 1. Acidity Constants of CAP, PTA, and TACN[a]

	CAP	PTA	TACN
pK_{a1}	6.2	5.63−6.9	10.42
pK_{a2}	2.9		6.82
pK_{a3}	strong		strong

[a]This work (CAP); ref21b−f (PTA) 21g; (TACN).

nitrogen sites has been confirmed by the free refinement of hydrogen atoms in the solid-state structures of **2** and **3** (Figure 4). CAP is a weak base as compared to its direct precursor, TACN; the first dissociation constant of CAP falls in the range of pK_a values reported for PTA (Table 1). The pH of saturated aqueous CAP solution is 9.6. Acid−base titration curves of the free ligand **1** show two distinct inflections corresponding to the first and second protonation stages (Table 1), i.e., sequential formation of the cations (CAP-H)$^+$ and (CAP-H$_2$)$^{2+}$, respectively. The remaining third nitrogen site was found too weakly basic for an inflection to be observed. However, the existence of solid trihydrochloride **3** provides the evidence that the cation (CAP-H$_3$)$^{3+}$ does exist in highly acidic environment.

Herein one should point out the stereochemical peculiarity of CAP related to its polyamine function: the flexibility of nine-membered macrocycle embedded in the cage. The conformation of that ring in the structures of the free base **1** (Figure 1a) and triprotonated ion (CAP-H$_3$)$^{3+}$ (Figure 4b) can be designated as [333], according to the notation introduced by Dale.[23] Here the numbers in the brackets denote the three "sides" of nine-membered "triangular" polygon having three bonds per each side of the triangle. The [333] conformation of 9-membered ring in CAP is the same as that in 1,4,7-triazacyclononane (known as TACN or [9]aneN$_3$)[20,24] (see the TACN structure in the Supporting Information). Verkade's aminophosphine (Figure 1c), which has been previously synthesized based on TACN,[14] has somewhat different conformation of the triangle, perhaps due to the considerable steric strain in its molecule.[14] The [333] conformation is known as the most energetically favorable among nine-membered macrocycles.[23] However, those rings are also

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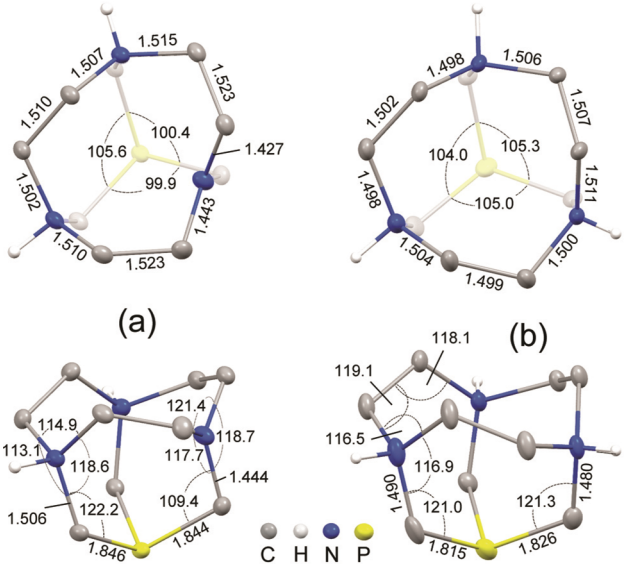

Figure 4. Conformations of di- and triprotonated CAP cage in the solid-state structures of hydrochlorides (a) $(CAP\text{-}H_2)^{2+}Cl_2$ **2** and (b) $(CAP\text{-}H_3)^{3+}Cl_3{\cdot}4/3H_2O$ **3**. Note that **3**, alike the free ligand **1** (Figure 1) exhibits highly symmetric [333] conformation of the nine-membered macrocycle, whereas **2** has distorted [1233] conformation and concave cage topology at the nonprotonated nitrogen. Displacement ellipsoids are shown at the 30% probability level. Projections approximately parallel (top row) and perpendicular (bottom row) to the (pseudo)3-fold axes. The back atoms at the top row are depth cued. Hydrogen atoms at the methylene groups and hydrate water molecules have been omitted for clarity. Drawing: CCDC Mercury 3.3 (ref 15).

known for high degree of conformational freedom affording a variety of distorted conformers.[23,25] That behavior is corroborated by CAP: protonation of the two nitrogen sites of CAP, being unsymmetric one, results in severe distortion of the macrocycle and the whole cage; thus, acquired conformation can be described as [1233][23b] with the concave cage topology at the nonprotonated nitrogen site (Figure 4a). The conformational flexibility of CAP can be regarded as the stereochemical highlight distinguishing it from PTA, the latter being known for cage rigidity.[13c,d,22]

2.3. CAP and Gold. Returning to the chemical behavior of CAP, we would like to explore its reactivity toward gold and gold compounds. The first feature which distinguishes CAP from other tertiary phosphines is its ability to reduce Au(III) to elemental gold. Addition of aqueous solution of **3** to the solution of $HAuCl_4$ results in immediate formation of cloudy deep-purple precipitate composed of gold nanoparticles with the dimensions between 5 and 10 nm (Figure 5). The partial formation of transparent dark-green "gold mirror" on the inner surface of reaction vial can also be observed (Figure 5c). The lattice parameter of thus obtained Au nanoparticles is 4.0722(6) Å, in agreement with the expected size-dependent decrease[26] of that value relative to compact metal gold, 4.07894(5) Å.[27]

It is known that the tertiary phosphines, in particular PPh_3, are good stabilizers for gold nanoparticles prepared by the reduction of Au(III) with hydrazine, borohydrides or organic agents such as ascorbic acid.[2,7,28] But, to the best of our knowledge, tertiary phosphines themselves are not capable of reducing Au(III) to Au(0). Instead, their reactions with Au(III) compounds afford (phosphine)gold(I) complexes: the classic

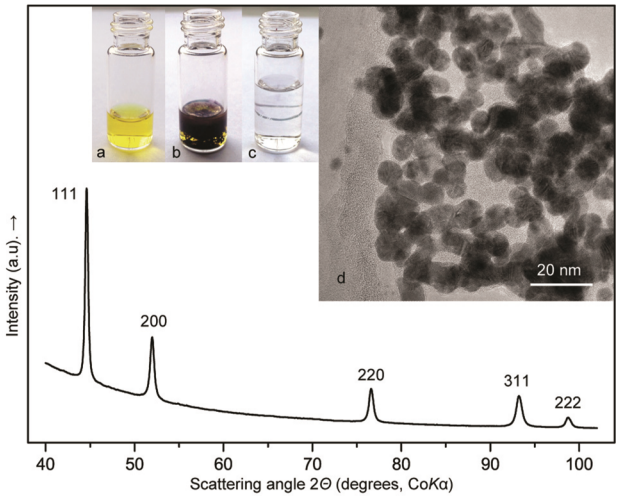

Figure 5. X-ray powder diffraction pattern of gold nanoparticles which were obtained by reduction of aqueous solution of $HAuCl_4$ with CAP trihydrochloride **3**. The insets show (a) the initial solution of $HAuCl_4$, (b) the deep-purple aggregate of Au nanoparticles formed upon addition of solution of **3** to the solution of $HAuCl_4$, (c) the nearly colorless solution containing gold(I) cation $[(CAP\text{-}H_2)_3Au]^{7+}$ (Figure 6a,b) formed upon addition of excess of **3** to the suspension of gold nanoparticles. Note the dark belt of undissolved "gold mirror" on the inner surface of the glass vial. The TEM image on the inset (d) illustrates the size and morphology of Au nanoparticles depicted on (b).

preparative route in the gold–phosphine chemistry.[8a] Note that because of the majority of the tertiary phosphines are poorly soluble in water, the reductions are typically carried out in the organic solvents.[29] Among the known water-soluble tertiary phosphine derivatives, tetrakis(hydroxymethyl)phosphonium chloride (THPC), $[P(CH_2OH)_4]Cl$, smoothly reduces Au(III) to Au(0) in aqueous solutions.[30] However, the reaction pathway involves the initial hydrolytic formation of formaldehyde: the latter is the moiety responsible for gold reduction, whereas tris(hydroxymethyl)phosphine itself does not reduce gold(III) to gold(0).[31] Therefore, CAP is likely the anomalous tertiary phosphine capable of reducing Au(III) to Au(0). The proposed reaction mechanism can be represented by the equation:

$$2(CAP\text{-}H_3)Cl_3 + AuCl_4^- + 2H_2O \rightarrow Au\downarrow + 2CAP{=}O + 10HCl \quad (1)$$

The reductive capability is not the only unusual feature of CAP with respect to its behavior toward gold compounds. We have found that further addition of an excess of aqueous solution of **3** to the precipitate of obtained gold nanoparticles (Figure 5b) under stirring results in fast (1–2 min) and complete dissolution of Au with formation of nearly colorless, very faint-yellowish solution (Figure 5c). At the same time, the "gold mirror" formed on the glass surface retains undissolved under the same conditions (Figure 5c).

Slow evaporation of the obtained solution (Figure 5c) at the room temperature affords very hydrosoluble, slightly yellowish transparent crystals of solvate **4** (Figure 6a,b) with the composition and structure corresponding to the formula $[(CAP\text{-}H_2)_3Au]Cl_7{\cdot}n HCl{\cdot}m H_2O$ ($n \approx 1.7$; $m \approx 18$). The analysis of the crystal structure of **4** reveals that it possesses layered topology and consists of perfect-triangular [(CAP-

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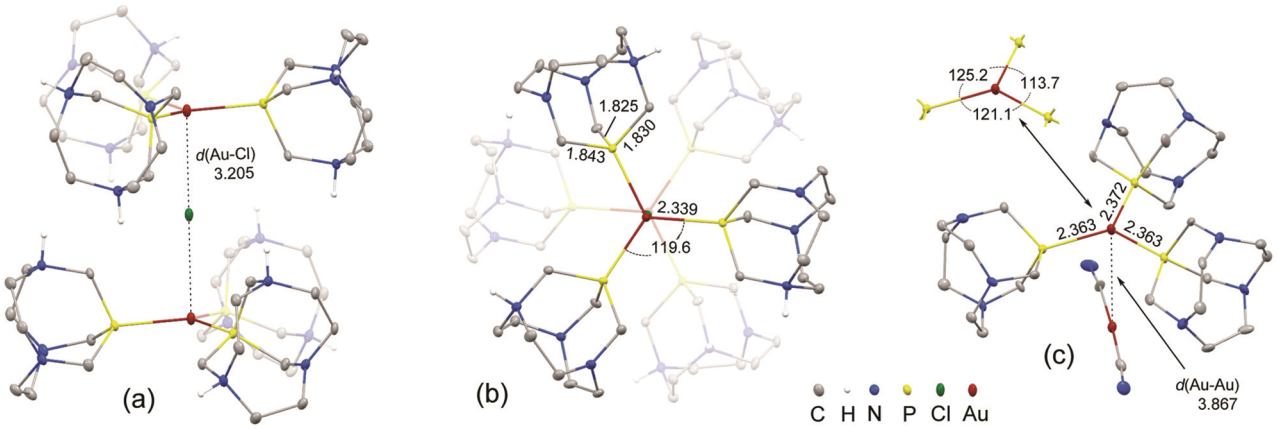

Figure 6. Solid-state structures of studied gold(I) complexes of CAP. (a and b) The two triangular $[(CAP\text{-}H_2)_3Au]^{7+}$ cations in **4** stacked in a pseudochloronium unit via pseudobridging chloride ion; projections approximately parallel (a) and perpendicular (b) to the 3-fold axis. (c) Triangular $[(CAP)_3Au]^{+}$ cation in $[(CAP)_3Au][Au(CN)_2]$ **5**. Note the long Au−Au bond which is outside of the range accepted for "aurophilic" interactions. Selected bond distances are given in Ångstroms and the angles in degrees. Displacement ellipsoids are shown at the 20% probability level. The back ligands are depth cued. Hydrogen atoms at the methylene groups and extra ions and molecules have been omitted for clarity. Drawing: CCDC Mercury 3.3 (ref 15).

$H_2)_3Au]^{7+}$ units (Figure 6a,b) where the central gold atom is *P*-coordinated by the three diprotonated $(CAP\text{-}H_2)^{2+}$ ligands. The latter have essentially the same cage conformation as in dihydrochloride **2** (Figure 4a). The (P_3Au) triangles are nearly planar (the sum of P−Au−P angles is 358.78°). The trigonal planar environment of gold(I) in cationic phosphine complexes is thoroughly studied; among them, water-soluble compounds of PTA and its derivatives have also been synthesized.[32] The distinctive feature of CAP complexes described herein is their polyprotic character arising from polyamine function of CAP ligand. The closer inspection of $[(CAP\text{-}H_2)_3Au]^{7+}$ units packing in the structure of **4** shows that these cations are pairwise stacked via bridging chlorine atoms (Figure 6a,b). The resulting binuclear construction topologically resembles those found in the reported gold(I) chloronium complexes.[33] However, the observed Au−Cl distance in **4** (3.203−3.205 Å) is too large: it exceeds the sum of covalent (2.33 Å)[34a] and even ionic radii of Au and Cl (3.18 Å);[34b] hence, the chloronium-like interactions in **4** are unlikely to occur.

On the basis of the available observations, one can conclude that CAP exhibits the capability toward complexation-promoted oxidative dissolution of elemental Au to Au(I). Gold is the noble metal, and aside from the several strong oxidizers such as aqua regia, hot H_2SeO_4, halogens, Me_3PI_2,[35] hypochlorite (ClO^-) and chlorate (ClO_3^-), there are very few classes of compounds capable of promoting oxidative dissolution of Au(0) under the mild conditions. The mechanisms underlying those reactions always imply complexation of Au with the ligands having strong affinity for gold, thereby shifting the redox potential of Au(0)/Au(I,III) pair toward negative values with the formation of Au(I) or Au(III) species. The oldest known example is the cyanide which oxidatively dissolves Au(0) yielding dicyanoaurate anion:[8,36]

$$4Au + 8CN^- + 2H_2O + O_2 \rightarrow 4[Au(CN)_2]^- + 4OH^- \quad (2)$$

Since the formation constant of $[Au(CN)_2]^-$ is very large (estimated value of 10^{-37} or 10^{-39}), the oxidation potential of Au(0) to Au(I) is shifted from +1.50 to −0.60 V allowing gold dissolution.[8a,c] Several other known complexants capable of dissolving gold(0) include sulfur-based ligands such as thiosulfate ion,[9] thiourea,[10] and thiols.[11]

The proposed reaction pathway between the nanogold and CAP hydrochloride solution can be described by the following equation, in the manner similar to the above-mentioned cyanide system:

$$4Au + 12(CAP\text{-}H_3)Cl_3 + O_2 \rightarrow 4[(CAP\text{-}H_2)_3Au]Cl_7 + 8HCl + 2H_2O \quad (3)$$

To check for the possible formation of intermediate Au(0) or mixed-valence Au(0)−Au(I) species, we carried out the EPR study of the solution freshly prepared by dissolving the nanogold in the solution of **3**. It is known that both Au(0) and ligand-stabilized Au(0)−Au(I) nanoclusters exhibit the distinct paramagnetic signature.[37] Our EPR experiments did not reveal any paramagnetic species other than dioxygen in the prepared solution; therefore, one can suppose that the reaction 3 does not involve hydrosoluble Au(0) or Au−nanocluster intermediates. The observed discrepancy in dissolution behavior of nanosized and thin-film gold (gold mirror) can likely be accounted for by kinetic reasons, owing to the high specific surface area of gold nanoparticles. The similar behavior toward nanogold has been recently reported in the thiol systems whereas compact gold does not dissolve in the thiol solutions.[11] The very rough estimation of particle size/dissolution rate dependence can be made via comparison with the best studied gold−cyanide systems where Au dissolution rate constant was determined as a decreasing cubic function of the particle diameter.[36]

Here we would like to make clear distinction between the oxidative chemical dissolution of Au(0) to Au(I) (as it is observed in the case of cyanide and CAP) and the well studied phenomenon of formation of colloidal phosphine-stabilized core−shell Au nanoparticles and Au_n (n = 4−55) nanoclusters bearing the metal−metal bonds.[2,7,37] Although phosphines possess strong affinity for Au, we could not find any literature reports on phosphine ligands capable of complexation-driven oxidative dissolution of the elemental gold. However, taking into account the enormous number of phosphine ligands, it is

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quite possible that the future studies can reveal the new phosphines with the chemical behavior similar to that of CAP.

Exploring the unusual chemical behavior of CAP toward Au, we have attempted to use the free ligand **1** for possible displacement of cyanide ion from $[Au(CN)_2]^-$, the latter being the strongest known gold(I) complex.[8a,c] It has been surprising that addition of aqueous solution of **1** to the solution of $KAu(CN)_2$ results in immediate formation of insoluble bright-yellow precipitate of compound **5**. The refinement of its crystal structure revealed that **5** is anhydrous salt $[(CAP)_3Au][Au(CN)_2]$ containing triangular $[(CAP)_3Au]^+$ cations charge-balanced with $[Au(CN)_2]^-$ anions (Figure 6c). From the structural point of view, **5** is a typical ionic salt without metal−metal bonding: the long Au−Au distance of 3.867 Å (Figure 6c) falls well beyond the ranges reported for "aurophilic" interactions.[38] Like many other tricoordinate Au(I) phosphine complexes,[5,13b,32e−g] **5** is luminescent (bright orange-yellow) under UV light.

The gold−triphenylphosphine complex similar to **5** of the formula $[(PPh_3)_3Au][Au(CN)_2]$ has previously been reported.[39] It can be prepared via reaction between PPh_3AuCN and excess of PPh_3 in ethanolic solution. It is likely that Au(I) in the $[(PPh_3)_3Au][Au(CN)_2]$ has trigonal coordination, but its crystal structure has not been determined.[39]

The chemical behavior of **5** is consistent with its salt-like ionic character: treatment of **5** with the diluted HCl results in immediate dissolution of the complex with the formation of nearly colorless solution which is, upon the air evaporation, affords colorless crystals of solvate **6**. The latter possesses the composition and crystal structure consistent with the formula $[(CAP\text{-}H_2)_3Au]Cl_7\cdot n HCl\cdot m H_2O$ ($n \approx 1.5$; $m \approx 8$). The basic structural unit of **6** is $[(CAP\text{-}H_2)_3Au]^{7+}$: identical to that found in solvate **4** (Figure 6a,b). Consequently, both compounds represent the two different crystal hydrates of the same gold(I)−CAP complex illustrated on Figure 6a,b. The dissolution of **5** with the formation of **6** can be represented as

$$([(CAP)_3Au][Au(CN)_2] + 6H^+ \rightarrow [(CAP\text{-}H_2)_3Au]^{7+} + [Au(CN)_2]^-) \quad (4)$$

The formation of **5** via displacement reaction of CAP with $KAu(CN)_2$ can be described as

$$[Au(CN)_2]^- + 3CAP \rightarrow [(CAP)_3Au]^+ + 2(CN)^- \quad (5)$$

The hypothetic formation of intermediate AuCN[8a] followed by its reaction with phosphine is ruled out because both starting solutions are highly alkaline (pH of the reaction mixture was 9.8) and thereby fall within the pH stability field of $[Au(CN)_2]^-$.[8a,c] Unfortunately, insolubility of **5** remained an open question: to what extent the displacement of cyanide is driven by that insolubility of $[(CAP)_3Au][Au(CN)_2]$. To clear that question, we tried to conduct the counterpart displacement pathway, i.e., the reaction between the trigonal CAP−Au complex and the free cyanide ion. The possibility of competitive CAP/CN displacement was checked up using ^{31}P NMR spectroscopy as those reactions would affect the phosphine coordination environment around the Au center leading to the splitting of ^{31}P NMR signal.[8c,40] It was found that adjustment of pD of $[(CAP\text{-}H_2)_3Au]^{7+}$ solution in D_2O to pD 6.8 using KCN resulted in the upfield shift of ^{31}P NMR resonance from 51 to 42 ppm but did not result in its splitting that evidence for the lack of ligand displacement or scrambling reactions.[8c,40] However, further addition of KCN resulted in the beginning of precipitation of the yellow powder; the latter was found to be $[(CAP)_3Au][Au(CN)_2]$ by the identity of its IR-spectrum and powder XRD pattern with those of **5** (see Supporting Information). Therefore, our results indicate that cyanide ion in the acid to nearly neutral environment is not capable of displacing CAP from $[(CAP\text{-}H_2)_3Au]^{7+}$, whereas in the alkaline solutions both CAP and cyanide exhibit roughly comparable level of affinity for gold; the insolubility of $[(CAP)_3Au][Au(CN)_2]$ precludes more precise estimations of displacement equilibria. The behavior of CAP relative to cyano-complexes of gold resembles that of thiolate ligands which are capable of competitive displacement of $(CN)^-$ for $(SH)^-$ in the acidic environment.[41]

2.4. Steric and Electronic Parameters of CAP. The existence of CAP Au(I) complexes having both [333] and [1233] conformers of the nine-membered ring (Figure 4) facilitates the determination of the respective Tolman cone angles (the steric parameter), the common measure for the steric bulk of phosphine ligands.[16a−d] Calculations using the method introduced by Müller and Mingos[42] gave the cone angle of 109° for the symmetric [333] cage conformation of CAP in the complex **5** (Figure 6c) and 111° for the distorted [1233] conformation in **4** (Figure 6a,b). Therefore, both conformers of CAP exhibit rather low steric demand, intermediate between that of PTA (102−103°)[21c,43] and PMe_3 (118°).[16b] The cone angle of Verkade's aminophosphine determined on the basis of the structural model of its *P*-oxide (Figure 1c) gave the value of 118°.

The electron-donating ability of phosphine ligands is conventionally estimated using Tolman's electronic parameter (TEP): the wavenumber of A1 carbonyl absorption band in the IR spectra of the respective $R_3PNi(CO)_3$ complexes.[16b,c,44] Although new computational approaches based on molecular electrostatic potential (MESP) have been developed[16d,45] and critically discussed[46] during the past decade, the TEP approach is still a basement for direct comparison of electron-donating power of phosphines.[16c−f] Moreover, it has been demonstrated that TEP value can be correctly determined using DFT computations, thereby eliminating the necessity of synthesizing $R_3PNi(CO)_3$ complexes.[16c,44] DFT computations of TEP for [333] conformation of CAP (Figure 1a) and for the cage of the Verkade's ligand (Figure 1c) have been performed at the B3LYP/6-31G(d,p) level of theory (with LANL2DZ basis set for Ni) using Gaussian 09 software suite;[47] the corrections were applied according to the equation reported by Starosta et al.[44] The accuracy of our computations can be confirmed by their consistency with the previous literature reports on PTA (selected as the reference ligand): the experimentally determined TEP of PTA[21c] is 2069 cm^{-1}; the previously calculated[44] TEP value is 2070.3 cm^{-1}, whereas our calculations gave TEP of PTA equal to 2070.2 cm^{-1}. The calculated TEP of Verkade's ligand is 2075.3 cm^{-1}, whereas the computations for CAP gave the value of 2056.8 cm^{-1}. The latter parameter implies that CAP possesses electron-donating ability at the level of the strongest known phosphine donors such as $P(t\text{-}Bu)_3$ and PCy_3 (Figure 7). The combination of low steric demand and strong electron-donating power is standing CAP outside of the general field for phosphine ligands (Figure 7). To explore the possible influence of the nitrogen lone pairs on the overall electron-donating power of CAP, we have conducted TEP computations for the hypothetic nitrogen-free counterpart of CAP, 9-phosphatricyclo[5.3.2.1^{4,9}]tridecane. The calculations gave the TEP value of 2059.6 cm^{-1} meaning that the electron

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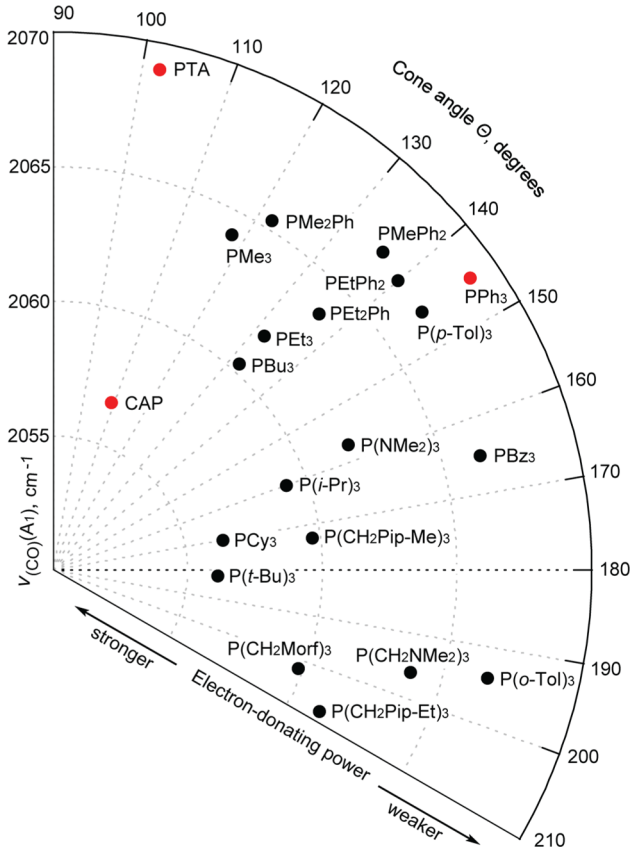

Figure 7. Polar stereoelectronic map of phosphine ligands with moderate to strong electron-donating power (Tolman's electronic parameter $\nu_{(CO)}(A_1)$ is less or equal to that of PPh_3). Note the unusual combination of low steric demand and strong electron-donating ability of CAP. Data: this work (CAP); ref 21c (PTA); ref 44 ($P(CH_2Pip\text{-}Me)_3$,0 $P(CH_2Pip\text{-}Et)_3$, $P(CH_2Morf)_3$); ref 16b (other phosphines).

donating ability of phosphorus in CAP is weakly related to the P−N lone pair interactions. It is likely that the cage conformation is the main factor governing the stereoelectronic properties of the new ligand.

2.5. ^{31}P NMR Spectroscopy. The phosphorus-31 chemical shifts for CAP and its studied compounds are given in Table 2,

Table 2. ^{31}P NMR Chemical Shifts δ (ppm) of CAP, Its Derivatives, and Some Related Compounds in Aqueous Solutions

compound (ion)	no.	δ	$\Delta\delta^a$	note
CAP	1	46.72[b]	-	[333][c]
$(CAP\text{-}H_2)^{2+}Cl_2$	2	12.81	−33.91	[1233][c]
$(CAP\text{-}H_3)^{3+}Cl_3$	3	12.34	−34.38	[333][c]
$[(CAP\text{-}H_2)_3Au]^{7+}$	4	50.99[d]	4.27	[1233][c]
PTA		−96.2	-	ref21b
$(PTA\text{-}H)^+Cl$		−89.9	6.3	ref21b
$(PTA)_2AuCl$		−36.1[e]	60.1	ref32f
$(PTA)_3AuCl$		−56.3[f]	39.9	ref32f
$(PTA)_4AuCl$		−58	38.2	ref48
Verkade's ligand		155[g]		ref14a

[a]Coordination chemical shift $\Delta\delta = \delta$(derivative) − δ(free ligand). [b]In $CDCl_3$: δ = 47.49 ppm. [c]Conformation of the nine-membered ring of CAP cage in the solid-state structure. [d]pD = 4. [e]CD_3CN. [f]MeOD. [g]Toluene-d_8.

in comparison with the data for PTA and Verkade's aminophosphine. It can be seen that the ^{31}P NMR shifts of CAP derivatives are extremely sensitive to the conformations of the nine-membered ring in CAP cage (Figure 1a, 4). It has also been found that ^{31}P NMR chemical shifts of CAP derivatives are pH-sensitive. The stereoelectronic properties of CAP discussed above seem to greatly affect the ^{31}P NMR chemical shifts (Table 2). The large downfield shift of the free ligand **1** is well outside of the general trend known for the tertiary phosphines where the large values of the chemical shift correlate with the increase of the Tolman cone angle[16b] (Figure 8). One can see that both CAP (Figure 1a) and its

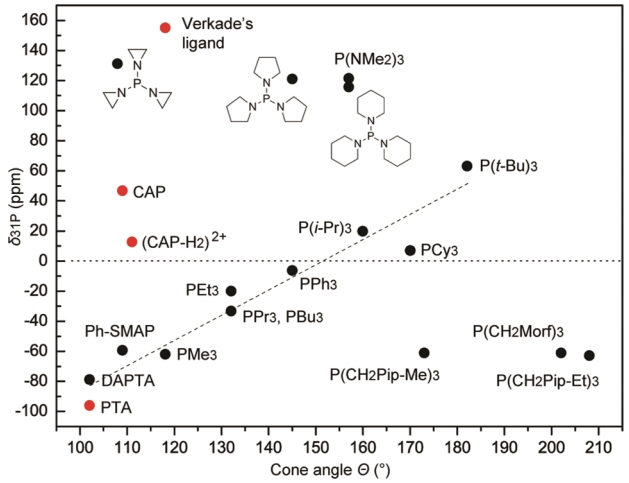

Figure 8. Relationships between the Tolman cone angles and ^{31}P NMR chemical shifts of CAP, $(CAP\text{-}H_2)^{2+}$ and a series of symmetric tertiary phosphines and aminophosphines. Linear fit for the reference phosphines (R^2 = 0.93) is shown as dashed line. Data: this work (CAP, $(CAP\text{-}H_2)^{2+}$); ref 14a (Verkade's ligand); ref 21b,c (PTA); ref 44 ($P(CH_2Pip\text{-}Me)_3$; $P(CH_2Pip\text{-}Et)_3$; $P(CH_2Morf)_3$); ref 49 (tris-(aziridinyl)phosphine, $P(NMe_2)_3$); ref 50 (Ph-SMAP); ref 51 (tris(pyrrolidinyl)phosphine, tris(piperidinyl)phosphine); refs 43,51 (DAPTA); ref 16b (other ligands).

diprotonated cation $(CAP\text{-}H_2)^{2+}$ (Figure 4a) populate the field between the classic tertiary phosphines and the extremely deshielded, sterically undemanding aminophosphines bearing direct phosphorus−nitrogen linkages, such as tris(aziridinyl)-phosphine[16b,49] and Verkades' ligand.[14a] Therefore, it is likely that CAP ^{31}P NMR downfield shift is indicative of substantial deshielding effect on ^{31}P nucleus due to nitrogen−phosphorus lone pair interactions governed by the CAP cage conformations.

The latter is well corroborated with the ^{31}P NMR data for the protonated derivatives **2** and **3**: since the protonation of the nitrogen sites eliminates the opportunity for the respective N−P lone pair interactions, one can observe the abrupt increase of ^{31}P nucleus shielding in **2** and **3** (Table 2).

The wide gap between ^{31}P NMR shifts of CAP and PTA Au(I) complexes (Table 2) provide the convenient opportunity for the observation of intermolecular phosphine exchange in their aqueous solutions. A room temperature experiment has been carried out in order to observe the possible equilibria between the protonated form of trigonal $(PTA)_3Au$ complex (the latter was prepared according to ref 32f) and the 3 equiv of CAP trihydrochloride **3**. The ligand exchange was expected to follow the scheme:

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J. Am. Chem. Soc. 2015, 137, 5526−5535

$$(PTA)_3Au + 3CAP \leftrightarrow (CAP)_3Au + 3PTA \quad (6)$$

with competitive formation of trigonal $[(CAP\text{-}H_2)_3Au]^{7+}$ ion (Table 2). However, the obtained results (Figure 9) were

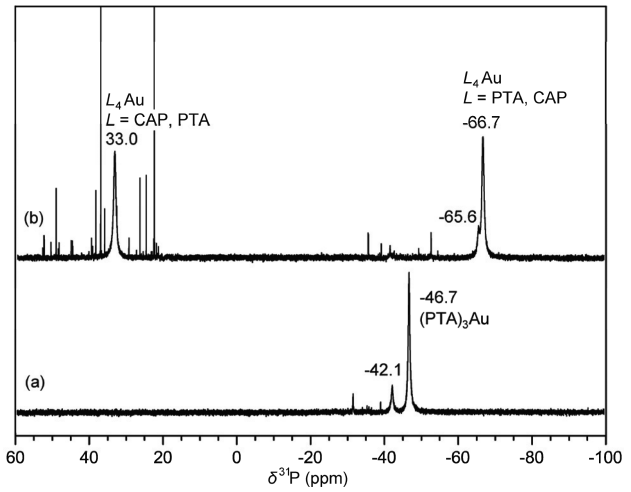

Figure 9. ^{31}P NMR spectra illustrating ligand-exchange equilibria between Au(I) complexes of PTA and CAP. (a) Solution of $(PTA)_3AuCl$ complex in 0.05 N DCl/D_2O. (b) The same solution after addition of 3 equiv of CAP trihydrochloride **3**.

completely different from the expected ones. The NMR resonances observed upon addition of **3** to $(PTA)_3Au$ complex do not correspond to either $[(CAP\text{-}H_2)_3Au]^{7+}$ or reported simple Au(I)−PTA complexes[32f,48] (Table 2). On the basis of the known general trend for the upfield ^{31}P shifts upon increase of Au coordination number in Au(I)−phosphine complexes, one can suppose that here we observe the complete rearrangement of the coordination environment around Au(I) centers, with the formation of the two types of (probably) tetrahedral Au(I) complexes: both CAP-dominant (δ = 33.0 ppm) and PTA-dominant (δ = −66.7) ones. The obtained results allow expecting that ligand-exchange reactions with CAP can substantially enrich the coordination chemistry of PTA.[13]

3. CONCLUSIONS

We have synthesized and characterized a symmetric tricyclic cage-like phosphine with the new parent ring architecture, a rare example of water-soluble, air- and thermally stable phosphine ligand. It exhibits unusual set of properties relative to gold and gold compounds: readily reduces Au(III) to Au(0); promotes oxidative dissolution of gold(0) and capable of displacing cyanide from dicyanoaurate ion. The new ligand can be ranked as one of the strongest phosphine electron donors with very low steric demand. Provided that its unusual chemical properties are likely related to the stereoelectronic profile, one could expect that several aminophosphines such as Verkade's ligand[14a] and tris(aziridinyl)phosphine[16b,49] would exhibit the similar but even more pronounced anomalies in their chemical behavior, as it is inferred by their low steric demand and high downfield ^{31}P NMR chemical shifts. Unfortunately, both latter ligands are extremely unstable as are the majority of other aminophosphines.[53] Therefore, our new ligand which populates the empty niche between the classic tertiary phosphines and aminophosphines could be regarded as an attractive compromise between these ligand classes, and could become a good supplement to a scarce number of stable water-soluble phosphines available in the chemist's toolbox.

■ ASSOCIATED CONTENT

Supporting Information

Procedures for the synthesis; characterization of **1**−**6**; summary of structural refinement details for **1**−**6**, PTA and TACN; Cartesian coordinates of DFT optimized geometries of $LNi(CO)_3$ complexes; crystallographic data for **1**−**6**, PTA, and TACN in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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