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Gold(I) and Silver(I) Metallocryptates Based on 2,9-Bis(diphenylphosphino)-1,8-naphthyridine

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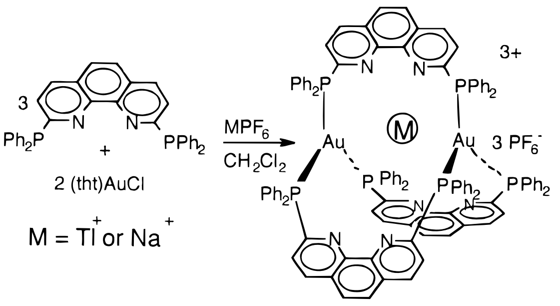
In acetonitrile the rigid diphosphine ligand 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn) reacts with (SMe_2)-AuCl in the presence of $NaPF_6$ to produce a pale-yellow material identified as $[Au_2Na(\mu\text{-dppn})_3](PF_6)_3$ (**1**). In acetonitrile dppn reacts with 2 equiv of $(SMe_2)AuCl$ to form the simple Au−Cl adduct of the ligand, Au_2Cl_2dppn (**2**). In a fashion analogous to that of the synthesis of **1**, the reaction of equimolar $AgNO_3$ with dppn produces the trimetallic species $[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3$ (**3**) as a bright-yellow material. **1**, **2**, and **3** were characterized by $^{31}P\{^1H\}$ NMR spectroscopy, electronic absorption spectroscopy, X-ray crystallography, emission spectroscopy, and elemental analysis. Additionally **1** was further characterized by cyclic voltammetry and mass spectrometry. $\mathbf{1}\cdot 4.5CH_3CN\cdot 0.5(C_2H_5)_2O$ $(C_{107}H_{72}Au_2F_{18}N_{10.5}NaO)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 15.408(3)$ Å, $b = 17.295(3)$ Å, $c = 22.425(5)$ Å, $\alpha = 73.68(1)°$, $\beta = 77.32(1)°$, $\gamma = 74.18(1)°$, $V = 5451.4(19)$ Å^3, and $Z = 2$. $C_{32}H_{24}Au_2Cl_2N_2P_2$ (**2**) crystallizes in the monoclinic space group Cc with $a = 10.936(2)$ Å, $b = 19.860(5)$ Å, $c = 20.864(2)$ Å, $\beta = 118.182(1)°$, $V = 3127.3(8)$ Å^3, and $Z = 4$. Compound **3** crystallizes as the bis-DMSO adduct $(C_{101}H_{84}Cl_2F_{18}N_6O_2P_9S_2)$ in the monoclinic space group $C2/c$ with $a = 28.825(7)$ Å, $b = 17.013(3)$ Å, $c = 23.916(7)$ Å, $\beta = 115.23(1)°$, $V = 10609.6(44)$ Å^3, and $Z = 4$. The structures of **1** and **3** contain a three-coordinate metal capping the metallocryptate with an encapsulated ion. The central Ag(I) ion in **3** is positioned off-center to form a short Ag···Ag interaction of 3.145(2) Å, while the central Na^+ ion of **1** is centrally positioned with long Au···Na interactions of ∼3.5 Å. The solution-state properties of **1** were probed. **1** is emissive, as are the Li, K, and Cs analogues.

Introduction

Recently, we reported the facile synthesis of gold(I) metallocryptates using a hybrid phosphine−phenanthroline ligand, 2,9-bis(diphenylphosphino)-1,10-phenanthroline (P_2phen).[1] The reaction of 3 equiv of P_2phen with 2 equiv of (tht)AuCl (tht is tetrahydrothiophene) in the presence of Na^+ ion generated an inorganic cage complex where two three-coordinate Au(I) centers encapsulate a Na^+ ion, forming a metallocryptate (Scheme 1). The X-ray structure revealed two long Au(I)−Na separations at ∼2.8 Å each and six long Na−N separations (3.26−3.47 Å), indicating that the Na^+ ion is loosely held and essentially “rattles” about the inside of this cage. Typical of trigonal Au(I)−phosphine complexes,[2] phosphine ligand dissociation is facile, and the two-coordinate metallomacrocycle is also observed in solution.

Interestingly, incorporation of Tl(I) ion in place of Na^+ ion produced a single species that was shown to possess two short Au(I)−Tl(I) interactions at ∼2.9 Å each and six long Tl(I)−N separations at ∼3.2 Å. Unlike the Na^+ analogue, $[Au_2(\mu\text{-}P_2\text{phen})_3Tl](PF_6)_3$ is not dynamic, and the phosphine ligands do not dissociate in solution. The attractive Au−Tl interactions are likely responsible for maintaining this assembly and “turning off” ligand dissociation. Typical of many Au−Tl complexes, this material is highly luminescent in both fluid solution and in the solid state.

Scheme 1



In 1994 Che and co-workers,[3] using the rigid ligand 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn), briefly reported a similar gold-based metallocryptate containing a central potassium ion. Unlike our P_2phen-based alkali metallocryptate, Che’s system is not labile, and the potassium ion appears to be responsible for maintaining this assembly. Also reported was the synthesis of the corresponding silver metallocryptate, but no structural data were presented. This report prompted us to study further the Au(I) and Ag(I) chemistry of the dppn ligand.

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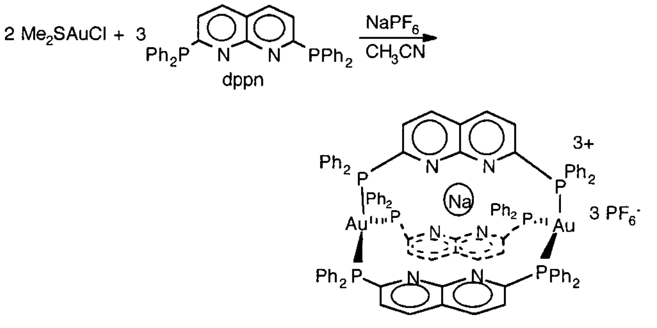
Scheme 2



1

Here, we report the synthesis and characterization of two dppn-supported metallocryptates and the simple Au−Cl adduct of dppn.

Results and Discussion

Synthesis. According to Scheme 2, $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$ (**1**) is synthesized by reaction of 3 equiv of dppn with excess $NaPF_6$ in acetonitrile followed by addition of 2 equiv of $(Me_2S)AuCl$. In this reaction it appears that the sodium ion acts as a template organizing the dppn ligands prior to addition of the Au centers. This is evidenced by the $^{31}P\{^1H\}$ NMR spectroscopy acquired during the reaction. In CD_3CN a single resonance at 0.7 ppm is observed for the free phosphine ligand. Addition of $NaPF_6$ changes the pale yellow solution to bright orange and produces a new resonance for the dppn ligand at +3.3 ppm along with a signal for the PF_6^- anion at −143.3 ppm. This dramatic color change indicates that the sodium ion is intimately interacting with the dppn ligand. The relatively minor shift of the phosphine resonance implies that sodium ion interacts more with the nitrogen bases than the phosphine moieties. Addition of $(Me_2S)AuCl$ to this solution produces a yellow solution and a new resonance at +43 ppm. This resonance is identical to the one obtained for crystals harvested from the sample used for single-crystal analysis. The order of addition may be reversed, indicating that the empty metallocryptand can be formed first without prior template formation followed by partitioning of the sodium ion into the cavity. In all of these experiments there is no evidence for the dissociation of a phosphine ligand, which is typical of many three-coordinate Au−phosphine complexes.

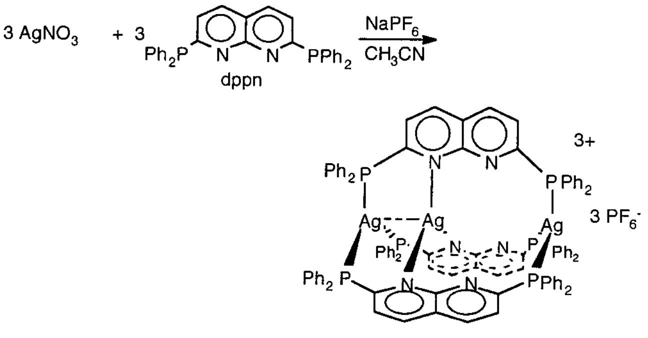
Under strict sodium-free conditions, the addition of 2/3 equiv of $(Me_2S)AuCl$ to dppn in acetonitrile produces a single, broad resonance at +29.82 ppm in the $^{31}P\{^1H\}$ NMR spectrum. This peak can be assigned to either the sodium-free metallocryptand or a two-coordinate metallomacrocycle that is in fast exchange with uncoordinated dppn ligand. Attempts to isolate either of these materials were unsuccessful and led only to isolation of compound **1**. This is not unexpected given the ubiquity of Na^+ ion.

The FAB mass spectrometry of $[Au_2Na(\mu\text{-dppn})_3](PF_6)_3$ in nitrobenzyl alcohol supports the inclusion of a sodium ion and is consistent with the formulation determined by X-ray crystallography (vide infra). The mass spectrum shows a moderately intense parent peak at 1912 amu consistent with the doubly-reduced species $[Au_2(\mu\text{-dppn})_3Na]^+$ along with the Na-free form at 1889 amu. The most intense peak (1028 amu) corresponds to dication $[Au_2(\mu\text{-dppn})_3Na](PF_6)^{2+}$. The limited mass range (2000 amu) of this instrument prevents detection of the monocation $[Au_2Na(\mu\text{-dppn})_3](PF_6)_2{}^+$. There are numerous other peaks that can be readily assigned to loss of one or more dppn ligands with and without the sodium ion.

The simple linear, two-coordinate Au−Cl adduct of the dppn ligand, Au_2Cl_2dppn (**2**), is readily synthesized upon addition of 2 equiv of Me_2SAuCl to the dppn ligand according to eq 1.

$$2Me_2SAuCl + dppn \rightarrow Au_2Cl_2dppn + 2Me_2S \qquad (1)$$

Addition of $AgNO_3$ to an acetonitrile solution of the dppn ligand also produces a metallocryptate; however, because Ag(I) has an affinity for both phosphorus and nitrogen, a Ag(I) ion is incorporated into the central cavity rather than Na^+ ion. Therefore, reaction of an equimolar methanolic solution of $AgNO_3$ with a dichloromethane solution of dppn followed by addition of $NaPF_6$ produces $[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3$ (**3**) as a bright-yellow material. The $^{31}P\{^1H\}$ NMR spectrum (1:1 $CDCl_3$/DMSO) shows two sets of deceptively simple non-first-order resonances (δ = 14.08 and 13.53 ppm) with resolvable $^1J_{P-^{109}Ag}$ and $^1J_{P-^{107}Ag}$ of 370 and 322 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum is very solvent dependent, indicating that coordinating solvents can bind to the exposed trigonal Ag(I) faces. In pure DMSO the resonances broaden significantly, masking the smaller coupling constants.



3

Structural Analyses. A single-crystal X-ray diffraction study of $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$ reveals the structures shown in Figure 1. The structure consists of two nearly trigonal Au(I) centers separated by 7.126(2) Å and spanned by the three dppn ligands (Table 2). The Au−P separations are typical for phosphine coordination to a Au(I) ion.[4] Each Au ion is puckered outward and resides slightly above the plane defined by its coordinated phosphorus atoms (0.20 and 0.21 Å for Au(1) and Au(2)). The average of the angles about the Au centers is 119°, close to the ideal 120° required for a trigonal planar geometry.

The sodium ion sits in the D_3 symmetric cavity formed by the naphthyridine ligands with long, nonbonding Na(1)−Au(1) and Na(1)−Au(2) separations of 3.544(6) and 3.584(6) Å, respectively. The Na(1)−N separations are very similar with an average Na(1)−N distance of 2.46 Å. This distance is significantly shorter than the corresponding distance (2.780 and 2.79 Å) observed in Lehn's $[Na(phenanthroline)_3]^+$ and $[Na(tris(bipyridine)cryptate)]^+$ complexes,[5] indicating both a smaller cavity and a more tightly held ion in **1**. As seen in Figure 1 the complex adopts a helical geometry with overall D_3 symmetry. Since the crystal is racemic as dictated by the centrosymmetric

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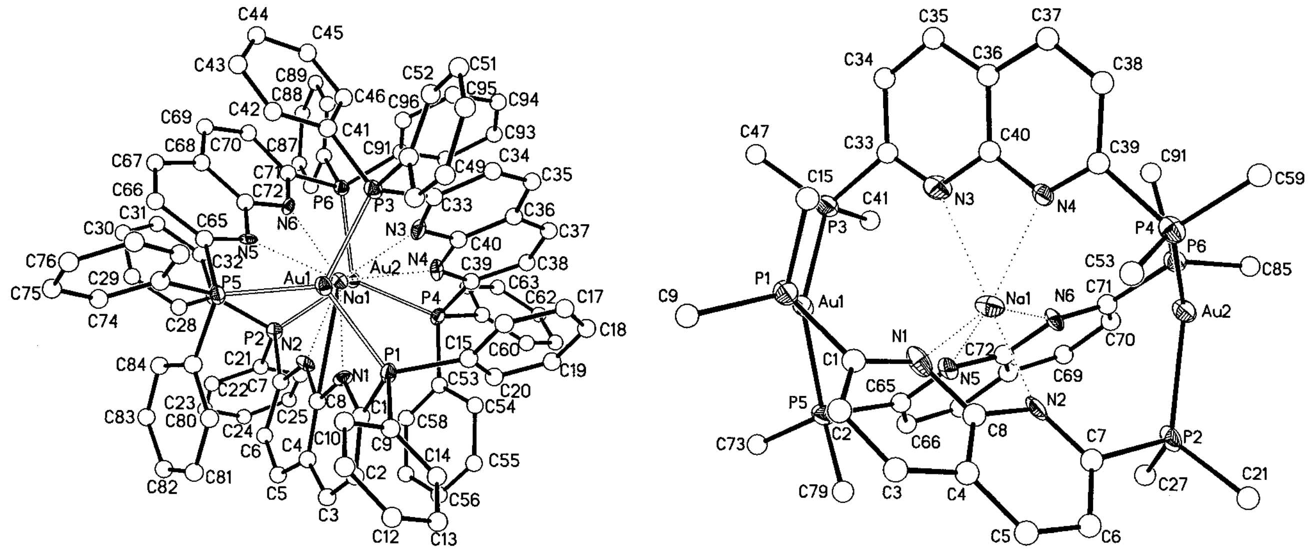

Figure 1. Thermal ellipsoid plot (40%) of **1** (left) and alternate view with phenyl rings and hydrogen atoms removed for clarity (right).

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1·4.5CH$_3$CN·0.5(C$_2$H$_5$)$_2$O	**2**	**3**·2DMSO·CH$_2$Cl$_2$
empirical formula	$C_{107}H_{72}Au_2F_{18}N_{10.5}NaO$	$C_{32}H_{24}Au_2Cl_2N_2P_2$	$C_{101}H_{84}Cl_2F_{18}N_6O_2P_9S_2$
fw	2550.40	963.31	2493.10
a, Å	15.408(3)	10.936(2)	28.825(7)
b, Å	17.295(3)	29.860(5)	17.013(3)
c, Å	22.425(5)	10.864(2)	23.916(7)
α, deg	73.69(1)		
β, deg	77.32(1)	118.18(1)	115.23(1)
γ, deg	74.18(1)		
V, Å^3	5451.4(19)	3127.3(8)	10609.6(44)
space group	$P\bar{1}$	*Cc*	*C*2/*c*
Z	2	4	4
D_{calcd}, g/cm^3	1.554	2.046	1.561
cryst size	0.40 × 0.24 × 0.24	0.06 × 0.40 × 0.60	0.18 × 0.42 × 0.26
μ(Mo Kα), mm^{-1}	2.907	9.669	0.865
radiation (λ, Å)	0.710 73	0.710 73	0.710 73
temp	293(2)	293(2)	293(2)
trans factors	0.88−0.83	0.99−0.26	0.86−0.81
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0549, 0.1128	0.0446, 0.1158	0.0797, 0.1835

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Au$_2$(μ-dppn)$_3$Na](PF$_6$)$_3$ (**1**)

	Distances (Å)		
Au(1)−Na(1)	3.544(6)	Au(2)−Na(1)	3.584(6)
Au(1)−P(1)	2.368(4)	Au(2)−P(2)	2.372(4)
Au(1)−P(3)	2.371(4)	Au(2)−P(4)	2.376(4)
Au(1)−P(5)	2.370(4)	Au(2)−P(6)	2.386(4)
Na(1)−N(1)	2.462(12)	Na(1)−N(4)	2.470(12)
Na(1)−N(2)	2.446(12)	Na(1)−N(5)	2.484(12)
Na(1)−N(3)	2.467(13)	Na(1)−N(6)	2.458(12)
Au(1)···Au(2)	7.126(2)		
	Angles (deg)		
Au(1)−Na(1)−Au(2)	178.5(2)	P(2)−Au(1)−P(4)	122.24(13)
P(1)−Au(1)−P(3)	116.99(14)	P(2)−Au(1)−P(6)	116.73(13)
P(1)−Au(1)−P(5)	120.30(14)	P(4)−Au(1)−P(6)	118.56(14)
P(3)−Au(1)−P(5)	120.77(14)		
P(1)−Au(1)−Au(2)−P(2)	92.1(1)	P(1)−Au(1)−Au(2)−P(4)	31.0(1)
P(3)−Au(1)−Au(2)−P(4)	86.5(1)	P(2)−Au(1)−Au(2)−P(5)	28.9(1)
P(5)−Au(1)−Au(2)−P(6)	88.6(1)	P(3)−Au(1)−Au(2)−P(6)	32.8(1)

space group $P\bar{1}$, both hands are present in the bulk material. The helical nature is manifested in the large torsion angles of 92.1°, 86.5°, and 88.6° for P(1)−Au(1)−Au(2)−P(2), P(3)−Au(1)−Au(2)−P(4), and P(5)−Au(1)−Au(2)−P(6), respectively.

For comparison, simple coordination of a Au−Cl unit to each phosphine moiety on the dppn ligand produces the Au$_2$Cl$_2$dppn structure depicted in Figure 2. The intramolecular Au(1)···Au(2) separation is long at 7.824(2) Å (Table 3). The P(1)−Au(1)−Cl(1) and P(2)−Au(2)−Cl(2) linkages are nearly linear at 175.2° and 175.3°, respectively. The linkages are canted away from each other as reflected by the P(1)−Au(1)−Au(2)−P(2) torsion angle of 42.7°. The Au$_2$Cl$_2$dppn molecules pack with a short intermolecular Au···Au separation of 3.212(2) Å. The orienta-

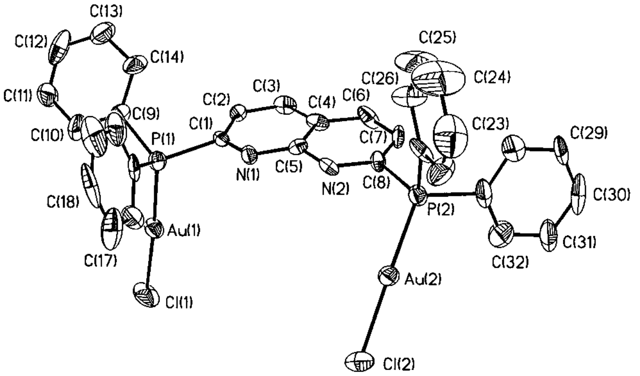

Figure 2. Perspective view of **2** with 40% thermal ellipsoids.

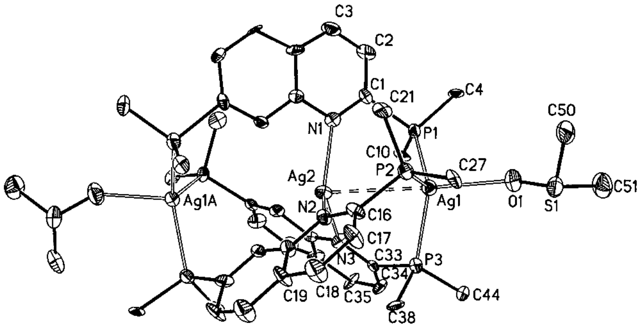

Figure 3. Thermal ellipsoid (40%) plot of **3**·2DMSO. Phenyl rings and hydrogen atoms are removed for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Au_2(dppn)Cl_2$ (**2**)

	Distances (Å)		
Au(1)···Au(2)	7.824(2)	Au(1)···Au(2a)	3.212(1)
Au(1)−P(1)	2.231(4)	Au(2)−P(2)	2.229(5)
Au(1)−Cl(1)	2.289(5)	Au(2)−Cl(2)	2.299(5)
	Angles (deg)		
P(1)−Au(1)−Cl(1)	175.2(2)	P(2)−Au(2)−Cl(2)	175.3(2)
P(1)−Au(1)−Au(2a)	93.01(11)	P(2)−Au(2)−Au(1a)	112.18(12)
Au(1a)−Au(2)−Cl(2)	72.51(13)	Au(2a)−Au(1)−Cl(1)	91.8(2)

tion of the P−Au−Cl units is twisted such that the two naphthyridine planes are nearly orthogonal to each other with a dihedral angle of 68°. This type of aggregation is fairly common for gold phosphines.[6]

The overall structure of $[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3$ (**3**) is similar to that of **1**. Crystallization from DMSO produces the bis-DMSO adduct depicted in Figure 3. Attempts to crystallize this material from noncoordinating solvents were not successful. The asymmetric unit contains half of the cation straddling a 2-fold rotational crystallographic symmetry element, with the central Ag(I) ions disordered across this element. As a result the molecule contains one short $d^{10}-d^{10}$ Ag(1)−Ag(2) distance of 3.145(2) Å and a longer Ag(2)−Ag(1a) separation of 4.628(2) Å (Table 4). Unlike **1**, the capping Ag(I) ions are distorted from trigonal toward tetrahedral geometry, with each ion residing 0.503 Å outward from the phosphine plane. This deviation is reflected in the P(1)−Ag(1)−P(2), P(1)−Ag(1)−P(3), and P(2)−Ag(1)−P(3) angles of 118.47(12)°, 114.75(13)°, and 114.98(13)°, respectively. The deviation from planarity for Ag(1) likely results from coordination of the weakly bound DMSO molecule. The Ag(1)−O(1) distance is 2.284(9) Å. The Ag(2) center adopts a more rigorous trigonal environment with N(1)−Ag(2)−N(2), N(1)−Ag(2)−N(3), and N(2)−Ag(2)−N(3) angles of 119.5(4)°, 117.9(9)°, and 118.8(4)°, respectively. This silver ion is strongly bonded to these nitrogen atoms with short[7] Ag(2)−N(1), Ag(2)−N(2), and Ag(2)−N(3) distances of 2.286(11), 2.278(11), and 2.286(10) Å, respectively. The Ag(1)−P(1), Ag(1)−P(2), and Ag(1)−P(3) distances at 2.506(4), 2.493(4), and 2.517(4) Å, respectively, are as expected[8] for a four-coordinate Ag(I) ion. Ag(2) resides 0.260 Å out of the plane formed by N(1), N(2), and N(3). Like **1**, $[Ag_2(DMSO)_2(\mu\text{-dppn})_3Ag](PF_6)_3$ is helical with P(1)−Ag(1)−Ag(1a)−P(3a), P(2)−Ag(1)−Ag(1a)−P(2a), and P(3)−Ag(1)−Ag(1a)−P(3a) torsion angles of 90.3(1)°, 87.1(1)°, and 90.3(1)°, respectively.

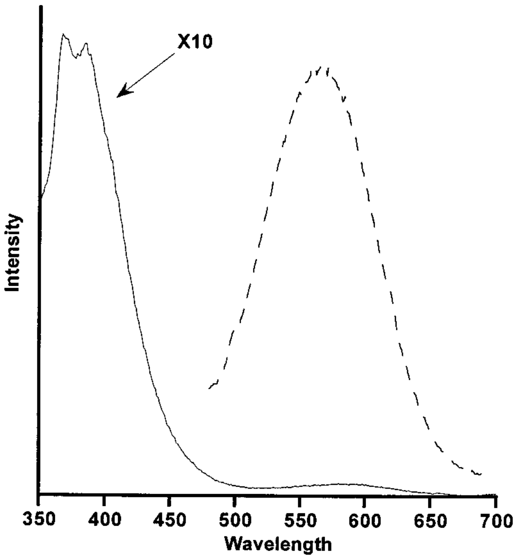

Figure 4. Emission spectra for **1** in acetonitrile solution (solid line, $\lambda_{exi} = 340$ nm) and in the solid state (dashed line, $\lambda_{exi} = 355$ nm). The solution spectrum was multiplied by a factor of 10 to bring it to the same scale as the solid-state spectrum.

Complex **1** is sparingly soluble in organic solvents including dichloromethane and is moderately soluble in acetonitrile and DMSO. The absorption spectrum of **1** in acetonitrile displays a shoulder at 315 nm and a broad band centered at 360 nm that tails into the visible. This 360 nm band is also observed in the absorption spectrum of the free ligand. The $d\sigma^*(d_{xy}, d_{x^2-y^2}) \rightarrow p_z$ transition associated with trigonal Au centers is likely buried in the low-energy portion of this band. As expected for three-coordinate gold centers,[9] **1** is highly luminescent both in solution and in the solid state. Figure 4 shows the emission spectra obtained for an acetonitrile solution of **1** (solid line) and for a

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3 \cdot 2DMSO$ (**3**)

Distances (Å)			
Ag(1)−Ag(2)	3.145(2)	Ag(2)···Ag(1a)	4.628(2)
Ag(1)−P(1)	2.506(4)	Ag(2)−N(1)	2.286(11)
Ag(1)−P(2)	2.493(4)	Ag(2)−N(2)	2.278(11)
Ag(1)−P(3)	2.517(4)	Ag(2)−N(3)	2.286(10)
Ag(1)−O(1)	2.284(9)	S(1)−O(1)	1.481(10)
S(1)−C(50)	1.78(2)	S(1)−C(51)	1.785(15)
Ag(1)···Ag(1a)	7.773(2)		
Angles (deg)			
Ag(1)−Ag(2)−Ag(1a)	179.4(1)	N(1)−Ag(1)−N(2)	119.5(4)
P(1)−Ag(1)−P(2)	118.47(12)	N(1)−Ag(1)−N(3)	117.9(4)
P(1)−Ag(1)−P(3)	114.75(13)	N(2)−Ag(1)−N(3)	118.8(4)
P(2)−Ag(1)−P(3)	114.98(13)	S(1)−O(1)−Ag(1)	134.9(7)
O(1)−Ag(1)−P(1)	93.9(3)	O(1)−Ag(1)−P(2)	108.4 (3)
O (1)−Ag(1)−P(3)	102.2(3)		
P(1)−Ag(1)−Ag(1a)−P(3a)	90.3(1)	P(1)−Ag(1)−Ag(1a)−P(1a)	28.4(1)
P(2)−Ag(1)−Ag(1a)−P(2a)	87.1(1)	P(2)−Ag(1)−Ag(1a)−P(3a)	31.9(1)
P(3)−Ag(1)−Ag(1a)−P(3a)	90.3(1)	P(3)−Ag(1)−Ag(1a)−P(2a)	31.9(1)

Table 5. Selected Spectroscopic and Electrochemical Properties

compound	$^{31}P\{^1H\}$ NMR[a] δ (ppm)	absorption spectra[c] λ_{max} (nm)	absorption spectra[c] ϵ (M^{-1} cm^{-1})	emission[c] λ_{max} (nm)	electrochemistry $E_{1/2}$ (ΔE) (mV)
$[Au_2(\mu\text{-dppn})_3Li](PF_6)_3$	40.79	315 (sh)	17 000	414	−900 (81)
		365	15 000	585	−1170 (60)
$[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$	43.48	310 (sh)	15 000	410	−910 (71)
		365	14 000	590	−1090 (83)
$[Au_2(\mu\text{-dppn})_3K](PF_6)_3$	43.48	323	17 000	413	−1160 (102)
		360 (sh)	13 000	577	−1360 (85)
$[Au_2(\mu\text{-dppn})_3Cs](PF_6)_3$	42.53[b]	324	18 000	419	−1060
		360 (sh)	19 000	575	−1420 (60)
					−1545 (64)

[a] CD_3CN, 25 °C. [b] Very broad resonance. [c] 5.6×10^{-5} M CH_3CN, 25 °C, under N_2.

thin film deposited on glass (dashed line). In the solid state an intense, long-lived (280 ms) emission is observed at 566 nm, while in solution two bands are resolved (410 and 590 nm). The excitation profile indicates that the 410 nm emission originates from a band at 340 nm while the 590 nm emission is effectively pumped by absorption ranging from 300 to 450 nm. In solution the lifetime of the low-energy band decreases to 50 ns, while the lifetime for the emission at 410 nm is less than the temporal resolution (∼30 ns) of our system. For comparison, McCleskey and Gray[10] reported a long-lived emission ($\lambda_{max} = 508$ nm, $\tau = 21$ ms, $\varphi = 0.8$) from the trigonal Au−phosphine complex $[Au_2(dcpe)_3](PF_6)_2$, where dcpe is 1,2-bis(dicyclohexylphosphino)ethane. The diminished intensity of the low-energy band and the shorter lifetime in **1** may be a reflection of the reduced steric congestion at the gold center imposed by the phenyl groups of **1** compared to cyclohexyl groups of dcpe.

The higher energy emission is likely a ligand-centered emission since, under identical conditions, the pure dppn ligand displays an identical emission as does an acetonitrile solution of **2**. The emission properties of **3** are consistent with those of a discrete d^{10}−d^{10} dimer[11] and were reported previously by Che.[3]

Solution Studies. The novelty of $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$ resides not only with the rare trigonal coordination mode of the Au centers in solution but also with its cryptand-like structure. The ability of molecules such as $[Au_2(\mu\text{-dppn})_3]^{2+}$ to bind alkali metal ions may be of interest as luminescent probes for alkali metals in solution. Using the same template methodology, a series of $[Au_2(\mu\text{-dppn})_3M](PF_6)_3$ complexes (M = Li, K, Cs) were prepared and compared to $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$. As seen in Table 5 all of these compounds have nearly identical $^{31}P\{^1H\}$ NMR (CD_3CN) resonances at ∼42 ppm and spectroscopic properties. All of the $^{31}P\{^1H\}$ NMR resonances are sharp except for the Cs^+ analogue, which shows a very broad signal. Under identical conditions, the emission spectra of this series are virtually superimposable, limiting the ability of the purported empty metallocryptand $[Au_2(\mu\text{-dppn})_3](PF_6)_2$ from acting as a luminescent reporter of encapsulated alkali metal ion.

The cyclic voltammetric data are also presented in Table 5. In acetonitrile none of the alkali metal complexes show reversible oxidation waves. However, cathodic sweeps reveal distinguishable reduction behavior. The best data were obtained for acetonitrile solutions of $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$, which exhibited two reversible waves at −0.91 and −1.09 V vs SCE. These processes likely correspond to ligand reductions.[12] The first wave shifts cathodically across the series $[Au_2(\mu\text{-dppn})_3M](PF_6)_3$ for M = Li, Na, and K. This order does not follow the $E°_{red}$ values for the free ions ($Na^+ < K^+ < Li^+$) and may better be attributed to the size and charge density of the alkali metal. The Cs analogue is anomalous. Its first reduction is not reversible, and the compound appears to decompose during successive sweeps.

To test whether the sodium ion can be removed from the cavity, we attempted to remove the Na^+ ion. The reaction of **1** with 1 equiv of 18-crown-6 does not remove the sodium ion after 24 h. However, using a traditional U-tube experiment,[13] sodium picrate is very slowly transported from the aqueous source layer, through a dichloromethane phase containing $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$, and into a receiving aqueous layer. In

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the absence of the metallocryptand or in the presence of tetrabutylammonium hexafluorophospate, no transport is observed.

Conclusions

The Au(I)-based metallocryptates described here represent another example in an expanding class of inorganic cage complexes. Although not a requirement for formation, these complexes are readily synthesized by a template reaction. Their ability to bind alkali metals in the gas, solution, and solid states was demonstrated. It appears that sodium-containing species $[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$ (**1**) is the most stable of the series likely due to size and charge considerations of the sodium ion. Using Ag(I) in place of Au(I) also produces a metallocryptate, but the harder nature of Ag(I) allows for this ion to partition into the central cavity.

Experimental Section

$(Me_2S)AuCl$[14] was prepared according to a published procedure. All other starting materials were commercially available and used without further purification. All solvents were used as received unless otherwise specified.

$^{31}P\{^1H\}$ NMR spectra were recorded at 121.65 MHz on a General Electric GN 300 FT-NMR spectrometer. Phosphorus chemical shifts are relative to external 85% $H_3PO_4(aq)$, with positive values being downfield of the reference. ^1H NMR spectra were recorded at 300 MHz on a General Electric QE 300 FT-NMR spectrometer. Proton chemical shifts are relative to TMS. The electrochemical apparatus and conditions were used as described elsewhere.[15]

2,7-Bis(diphenylphosphino)-1,8-naphthyridine (dppn). This compound was prepared by modification of a known procedure.[16] A 500 mL three-neck round-bottom flask was equipped with a stir bar, a N_2 inlet, an $NH_{3(g)}$ inlet, a powder addition funnel containing 4.0 g (0.020 mol) of 2,7-dichloro-1,8-naphthyridine,[17] and a coldfinger with an attached oil bubbler. The flask and the coldfinger were cooled to −78 °C with a dry ice/acetone bath. With both the N_2 and $NH_{3(g)}$ flowing, about 150 mL of $NH_{3(l)}$ was condensed. To this was added 4.4 equiv of Na° (2.0 g, 0.087 mol), turning the solution dark blue. After the sodium dissolved completely (~20 min), 2.2 equiv of PPh_2Cl (8.1 mL, 0.044 mol) was added via a syringe, causing the solution to turn bright orange. This mixture was allowed to stir for 30 min, and then the contents of the powder addition funnel were slowly added over 1 h, turning the mixture dark brown. Freshly distilled THF (Na°/benzphenone, 3 × 10 mL) was added to the powder addition funnel to wash any residual dichloronaphthyridine into the reaction flask. The solution was then allowed to stir overnight, slowly warming to room temperature. The reaction mixture was quenched with 20 mL of degassed methanol and then evaporated to dryness on a rotary evaporator. The residue was dissolved in dichloromethane and passed through a pad of Celite and then through a silica gel column (3 × 35 cm, eluent CH_2Cl_2). The eluted yellow liquid was evaporated to dryness. The resulting white solid was crystallized from dichloromethane and diethyl ether. ^1H NMR (300.52 MHz, 25 °C, $CDCl_3$): δ 7.95 (d, $^3J_{HH} = 8.3$ Hz, 2H) 7.47 (m, 8H) 7.36 (m, 12H) 7.20 (d, $^3J_{HH} = 8.3$ Hz, 2H). $^{31}P\{^1H\}$ NMR (121.0 MHz, 25 °C, $CDCl_3$): δ +1.96 ppm.

$[Au_2(\mu\text{-dppn})_3Na](PF_6)_3$ (1). To a dichloromethane solution (10 mL) containing dppn (212 mg, 0.43 mmol) was added a methanolic solution (10 mL) containing $NaPF_6$ (140 mg, 0.83 mmol). The mixture immediately turned orange. A dichloromethane solution (10 mL) of $(Me_2S)AuCl$ (84 mg, 0.28 mmol) was slowly added dropwise, producing a pale-yellow precipitate. This mixture was allowed to stir for 10 min, and the volatile components were removed under reduced pressure. The precipitate was suspended in methanol and collected by filtration. This powder was washed several times with methanol, affording 245 mg (73.5%) of a light-yellow solid. ^1H NMR (300.52 MHz, 25 °C, CD_3CN): δ 8.24 (d, $^3J_{HH} = 8.6$ Hz, 6H) 7.73 (m, 30H) 7.34 (d, $^3J_{HH} = 8.6$ Hz, 6H) 6.89 (m, 10H) 6.65 (m, 20H). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 43.48 (s), −143.4 (h, PF_6). Anal. Calcd for $C_{96}H_{72}Au_2F_{18}N_6NaP_9$: C, 49.1; H, 3.1; N, 3.6; Na, 1.0. Found: C, 49.21; H, 3.27; N, 3.56; Na, 0.89.

Au_2Cl_2dppn (2). An acetonitrile solution (10 mL) of $(Me_2S)AuCl$ (81.0 mg, 0.27 mmol) was added dropwise to an acetonitrile solution (10 mL) of dppn (68.5 mg, 0.14 mmol). Addition of the gold caused the pale-yellow dppn solution to slowly turn colorless. The volatile components were removed under vacuum, and the residue was suspended dichloromethane. The product was collected by filtration and dried under vacuum, affording 132.5 mg (72.5%) of the white solid. ^1H NMR (300.52 MHz, 25 °C, CD_3CN): δ 8.55 (d, $^3J_{HH} = 8.3$ Hz, 1H) 8.54 (d, $^3J_{HH} = 8.3$ Hz, 1H) 7.88 (d, $^3J_{HH} = 8.3$ Hz, 1H) 7.87 (d, $^3J_{HH} = 8.3$ Hz, 1H) 7.72−7.55 (m, 20H). $^{31}P\{^1H\}$ NMR (121.0 MHz, 1:1 CD_3CN/CH_3CN, 25 °C): δ +36.32 ppm (s). Anal. Calcd for $C_{32}H_{24}Au_2N_2P_2 \cdot CH_2Cl_2$: C, 37.8; H, 2.5; N, 2.7. Found: C, 38.14; H, 2.42; N, 2.56.

$[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3$ (3). To a stirred dichloromethane solution (20 mL) of dppn (220 mg, 0.44 mmol) was added a methanolic solution of $AgNO_3$ (75 mg, 0.44 mmol). The solution turned pale yellow. Addition of methanolic $NaPF_6$ (149 mg, 0.88 mmol) produced a bright-yellow precipitate. This mixture was evaporated to dryness under reduced pressure and resuspended in methanol. The yellow solid was collected by filtration and washed with methanol, affording 225 mg (76.8%) of a yellow solid. ^1H NMR (300.52 MHz, 25 °C, DMSO-d_6): δ 8.38 (d, $^3J_{HH} = 8.0$ Hz, 6H) 7.70 (m, 15H) 7.51 (m, 15H) 7.04 (d, $^3J_{HH} = 8.3$ Hz, 6H) 6.87 (m, 10H) 6.68 (m, 20H). $^{31}P\{^1H\}$ NMR (1:1 CD_3CN/DMSO): δ +14.08, +13.53, −143.4 (h, PF_6). Anal. Calcd for $C_{96}H_{72}Ag_3F_{18}N_6P_9 \cdot 2DMSO \cdot CH_3CN$: C, 50.0; H, 3.6; N, 4.00. Found: C, 50.04; H, 3.33; N, 4.00.

X-ray Crystallography. Yellow crystals of **1** were grown by slow diffusion of diethyl ether through a thin layer of methanol into an acetonitrile solution of the complex, while colorless crystals of **2** were grown by diffusing hexanes into an acetonitrile solution of **2**. X-ray-quality crystals of **3** were grown by slow diffusion of water into a DMSO/methanol/dichloromethane solution of **3**. Suitable crystals were coated with epoxy cement, mounted on a glass fiber, and placed on a Siemens P4 diffractometer. Unit cell parameters were determined by least-squares analysis of 46 reflections with $4.17° < \theta < 25.10°$ for **1**, 25 reflections with $5.04° < \theta < 12.52°$ for **2**, and 27 reflection with $1.55° < \theta < 12.71°$ for **3**. A total of 11 621 reflections were collected with $3.5° < 2\theta < 45°$, yielding 10 102 unique reflections ($R_{int} = 0.0533$) for **1**, while 3340 reflections were collected with $3.5° < 2\theta < 50.0°$, yielding 3207 unique reflections ($R_{int} = 0.0261$) for **2**. For **3** 8038 reflections were collected, generating 6939 unique ($R_{int} = 0.0887$) reflections with $3.5° < 2\theta < 45.0°$.

The data were corrected for Lorentz and polarization effects. Crystal data are given in Table 1. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[18]

Calculations were performed using the Siemens SHELXTL PLUS, version 5.03, system of programs refining on F^2. The structures were solved by direct methods. Complex **1** contained 4.5 acetonitrile solvates along with 0.5 diethyl ether molecule, while **3** contained a disordered dichloromethane molecule. Typical of room-temperature structures, there was also a minor amount of positional disorder for the fluorine atoms of two of the PF_6^- moieties in **1**. Simple models of all of this disorder provided satisfactory refinements. An absorption correction was applied using an empirical model derived from ψ scans. Hydrogen atom positions were calculated using a riding model with a C−H distance fixed at 0.96 Å and a thermal parameter 1.2 times that of the host carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters except for **1**, where the limited data-to-parameter ratio limited the carbon atoms to isotropic refinement. For **1** the largest peak in the final difference map corresponded to 1.77 $e^-/Å^3$ and was

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located 1.681 Å from N(6s). In **2** the largest peak in the final difference map corresponded to 3.68 $e^-/Å^3$ and was located 1.01 Å from Au(2), while in **3** the largest peak was equivalent to 1.05 $e^-/Å^3$ and was located close to the disordered dichloromethane molecule.

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Supporting Information Available: Three X-ray crystallographic files in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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