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Article

Coinage Metal Complexes of a Boron-Substituted Soft Scorpionate Ligand

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An improved synthesis of lithium phenyltris(methimazolyl)borate, Li[PhTm^{Me}], (methimazole = 1-methylimidazole-2-thione) is described, and the structure of the methanol-solvated [Li(OHMe)$_4$][PhTm^{Me}] has been determined. The syntheses and characterization of complexes [M(PhTm^{Me})(PR$_3$)] (M = Cu, Ag, Au; R = Et, Ph;) are reported, and the complexes [Cu(PhTm^{Me})(PPh$_3$)], [Ag(PhTm^{Me})(PEt$_3$)] and [Au(PhTm^{Me})(PEt$_3$)] are crystallographically characterized, showing a progression from pseudo-tetrahedral geometry (copper, S$_3$P coordination) to trigonal planar geometry (silver, S$_2$P coordination) to linear geometry (gold, SP coordination). In addition, the copper(I) and silver(I) triphenylphosphine complexes of the adventitiously formed phenylhydrobis(methimazolyl)borate ligand, [M(PhBm^{Me})-(PPh$_3$)], have been crystallographically characterized, showing both species to have a trigonal planar primary coordination sphere, with a secondary M···H–B interaction. Finally, reaction of copper(II) chloride with Li[PhTm^{Me}] results in formation of a compound analyzing as [Cu^{II}(PhTm^{Me})Cl], although its extreme insolubility and marked instability have precluded its complete characterization. Attempts to prepare this by ultra-slow diffusion of the reactants through solvent blanks has led to isolation of a mixed-valence copper(I/II) methimazolate cluster, [Cu$^I_{10}$-Cu$^{II}_2$(mt)$_{12}$Cl$_2$] and a copper(I) dimeric complex [Cu$_2$(PhTm^{Me})$_2$], indicating that copper(II) ions oxidatively decompose the phenyltris(methimazolyl)borate anion.

Introduction

The anionic soft tripodal ligand, hydrotris(methimazolyl)-borate (Tm^{Me}, Chart 1), was first reported[1] in 1996 and has since been extensively used in transition metal[2] and main group[3] chemistry. Subsequently, this ligand has been modified[4] by replacing the *N*-methyl group with a variety of alkyl and aryl groups (Tm^R, R = Ph, *o*-tolyl, mesityl, cumyl, benzyl, ethyl, *tert*-butyl, etc.), with the primary intention of altering the steric properties of the ligands. Although the Tm^R ligands are closely related to the now ubiquitous poly-
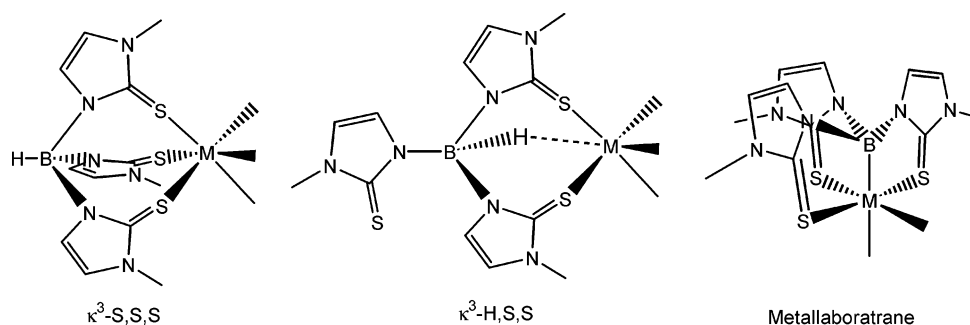
Chart 1

Tm^R
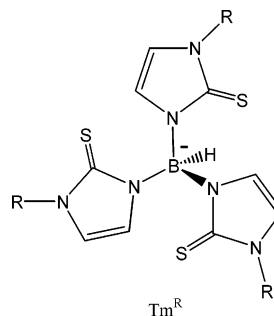
(pyrazolyl)borates (Tp),[5] they exhibit a number of characteristics which set them apart. In particular, they form eight-membered chelate rings on complexation with metals, resulting in a far greater flexibility. This is helpful in some respects, since in the standard tridentate coordination mode (κ^3-S,S,S; Chart 2, left) the ligands are able to twist to accommodate metals of disparate ionic radii. However, this flexibility also leads to a propensity to partial inversion leading to a bidentate coordination mode with an additional interaction of the borohydride with the metal center

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Chart 2

κ^3-S,S,S κ^3-H,S,S   Metallaboratrane

(κ^3-H,S,S; Chart 2, center).[6] In certain circumstances, this apparently leads to oxidative addition of the B−H bond to the metal center resulting in formation of metallaboratrane species (Chart 2, right),[7] but in the presence of oxidizing metals, this interaction often leads to ligand decomposition. Thus, while copper(II) complexes of Tp, e.g., Cu(Tp)$_2$, are readily prepared and characterized,[8] the reaction of copper-(II) salts with Tm^{Me} results in reduction of the metal and ligand decomposition. In the reaction of copper(II) chloride, formation of [CuCl(mtH)(μ-mtH)]$_2$ (mtH = 1-methylimidazole-2-thione) is observed.[9] Furthermore, attempts to oxidize metal Tm^R complexes often result in their decomposition.[2c]

In many applications of transition metal complexes, changes in metal oxidation state are essential features of the activity, and thus, the elimination of this decomposition pathway will necessarily be a key to realizing such applications. The most obvious ligand modification is replacement of the borohydride with other groups to render the ligand less reducing. Santos et al.[10] have recently reported the synthesis of PhTm^{Me} and MeTm^{Me} in which the borohydride is replaced with phenyl and methyl substituents, respectively. Subsequently, manganese[11] and rhenium[10] complexes of these

Chart 3

PhBm^{Me}
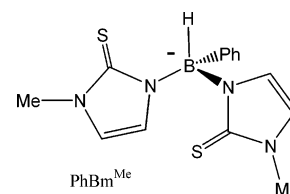
modified ligands have been prepared. However, the main concern in these studies was modification of solubility and a comparison of the bonding modes of the ligand variants; none of the examples to date are with oxidizing metals, and thus, this aspect still requires investigation.

Our interest in this modified ligand system is two-fold. First, the elusiveness of copper(II) complexes with the family of soft tripodal ligands has continued to be irksome, since the initial design concept envisaged the use of these ligands to model the active sites of copper(II) containing metalloproteins. Second, we have recently shown that Tm^{Me} is a good surface modifier for colloidal coinage metal nanoparticles.[12] To explore the mode of complexation to the metal surface, model compounds of copper, silver, and gold with these ligands are desirable. Thus, the present study concerns the preparation and characterization of complexes of the PhTm^{Me} ligand with the group 11 elements, copper, silver, and gold in the monovalent and higher oxidation states.

Results and Discussion

The lithium salt of the phenyl-substituted ligand, PhTm^{Me}, was initially prepared by the method of Santos et al.,[10] refluxing LiPhBH$_3$ and a slight excess of methimazole in toluene solution. It soon became clear to us (vide infra) that the product was contaminated with the incompletely substituted species LiPhBm^{Me} (Chart 3). Consequently, the use of the higher-boiling-point solvent xylene was adopted, resulting in complete conversion to the required product (Scheme 1). Recrystallization of the crude material from methanol/diethyl ether resulted in the isolation of a crystalline material suitable for X-ray crystallography. The structure determination revealed a solvent-separated ion pair in which the lithium ion is tetrahedrally coordinated by methanol and shows no interaction with the S atoms of the PhTm^{Me} anion (Figure

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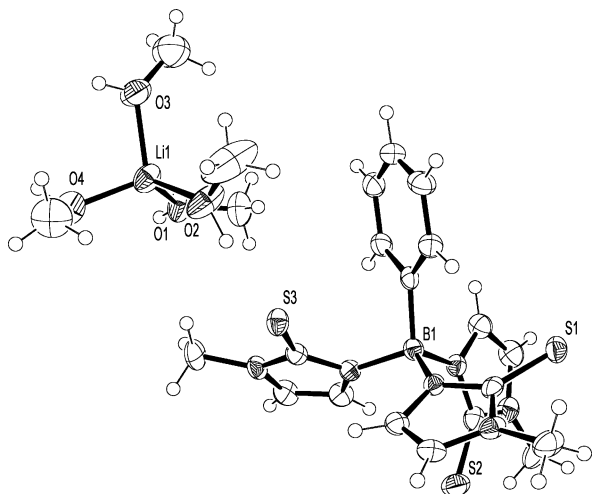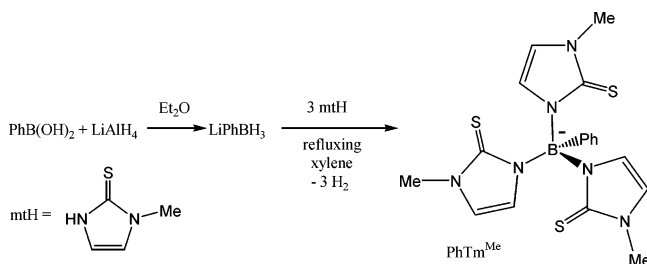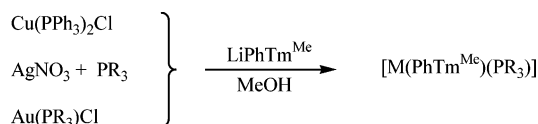
Figure 1. The X-ray structure of [Li(HOMe)$_4$]PhTm^{Me} with thermal ellipsoids shown at the 50% level.

Scheme 1

Scheme 2

1). This parallels the structure of NaTm^{Me} in which the sodium cation is hydrated and the Tm^{Me} anion does not coordinate to the metal.[1b] The conformation of the methimazolyl rings in PhTm^{Me} is somewhat different to that of the parent Tm^{Me} anion. In the latter species, the sulfur atoms of the rings adopt a "syn,syn,syn" orientation with respect to the B−H group, with H−B−N−C(=S) torsion angles of 26.8°, 38.5°, and 52.2°, while in the former, the rings adopt a "syn,syn,anti" arrangement relative to the Ph-B group (torsion angles 43.9°, 74.2°, and 173.2°). This is probably a reflection of the steric requirement of the phenyl substitutent, caused in part by the symmetry mismatch between the planar C_2-symmetric phenyl group and the C_3-symmetric B(mt)$_3$ unit. The methimazolyl rings are forced to rotate in such a way as to minimize the repulsive forces. This steric requirement also results in the boron atom lying some 0.041 Å out of the plane of the phenyl ring and in a distortion of the angles around boron (106.6−113.3°) from the ideal tetrahedral geometry.

The reaction of LiPhTm^{Me} in methanol with appropriate M^I precursors (M = Cu, Ag, Au; Scheme 2) results in the formation of colorless, diamagnetic complexes which analyze as [M(PhTm^{Me})(PR$_3$)] (M = Cu, Ag, Au; R = Ph, Et). The formulations are supported by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The NMR spectra indicate
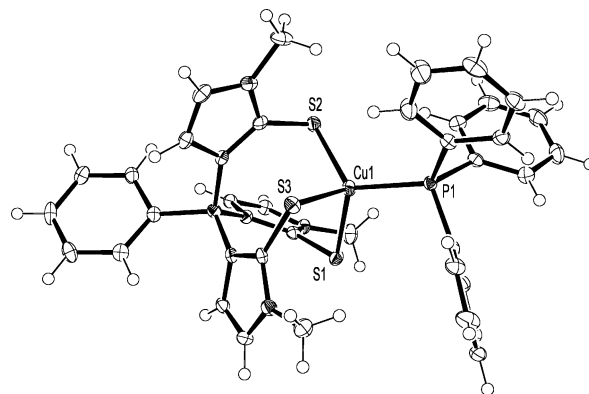

Figure 2. The X-ray structure of [Cu(PhTm^{Me})(PPh$_3$)] with thermal ellipsoids shown at the 50% level.

a degree of fluxionality but clearly show the presence of both phosphine and PhTm^{Me} ligands in a 1:1 ratio.

The copper(I) complex with triphenylphosphine as coligand was prepared by reaction of [Cu(PPh$_3$)$_2$Cl] with LiPhTm^{Me} in methanol. The X-ray crystal structure (Figure 2, Table 1) shows the expected κ^3-(S,S,S) coordination mode of the PhTm^{Me} ligand, resulting in a pseudo-tetrahedral S$_3$P coordination sphere at the metal center. Analogous copper-(I) complexes of the parent Tm^{Me} ligand have been reported,[13] and the structures of the complexes with P(o-tol)$_3$ and P(m-tol)$_3$ co-ligands reveal highly symmetrical molecules, with the boron, copper, and phosphorus atoms lying on a crystallographic C_3 axis. This results in equivalence of the methimazole rings. An identical situation also pertains in Bailey's [Cu(Tm^{Et})(PPh$_3$)][4d] and in Rabinovich's recently reported [Cu(Tm^{tBu})(PPh$_3$)].[14] However, in the case of the PhTm^{Me} complex, there is considerable asymmetry in both the ligand and the metal coordination sphere. As observed in the free ligand, there is substantial distortion of the angles about the boron atom (∠N−B−N in the range 105.93(18)− 112.3(2)°) and again the boron atom lies some 0.036(4) Å out of the plane of the phenyl ring. This is in turn reflected in the copper coordination sphere, where two of the Cu−S distances are essentially identical (2.3524(7) and 2.3542(6) Å), while the third, Cu−S(3), is distinctly inequivalent (2.4102(7) Å). The S−Cu−S and S−C−P bond angles also reflect this asymmetry. It would appear that the phenyl group influences the twist of the methimazole rings. In the symmetric [Cu(Tm^R)(PR′$_3$)] complexes, all three H−B−N−C torsion angles are all equal by symmetry (R = Me, PR′$_3$ = P(o-tol)$_3$, 144.6°; P(m-tol)$_3$, 148.0°; R = ^{t}Bu, PR′$_3$ = PPh$_3$, 145.9°; R = Et, PR′$_3$ = PPh$_3$, 148.4°), but in the PhTm^{Me} complex, there is a spread of torsion angles (132.8°, 145.4°, and 154.8°) presumably to minimize the repulsion between the phenyl group and the methimazole rings.

The silver(I) complexes are readily prepared by adding LiPhTm^{Me} to a mixture of AgNO$_3$ and the appropriate phosphine in a 1:1:1 ratio in methanol. The structure (Figure

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Table 1. Structural Parameters for [M(PhTm^{Me})(PR$_3$)] and [M(PhBm^{Me})(PPh$_3$)]

	[Cu(PhTm^{Me})(PPh$_3$)]	[Ag(PhTm^{Me})(PEt$_3$)]	[Au(PhTm^{Me})(PEt$_3$)]	[Cu(PhBm^{Me})(PPh$_3$)]	[Ag(PhBm^{Me})(PPh$_3$)]
d(M–S)/Å	2.3524(7)	2.4630(14)	2.3335(17)	2.2892(8)	2.5175(5)
	2.3542(6)	2.5868(13)	3.629(3)	2.3210(8)	2.5384(5)
	2.4102(7)				
d(M–P)/Å	2.1986(7)	2.3776(12)	2.2682(19)	2.2163(8)	2.4007(5)
d(M···H)/Å	–	–	–	1.831(2)	2.164(2)
∠S–M–S/°	100.95(2)	98.30(3)	–	115.94(3)	114.331(17)
	103.88(2)				
	109.20(2)				
∠S–M–P/°	111.06(3)	135.86(4)	171.55(7)	119.54(3)	121.204(17)
	120.31(3)	124.85(4)		120.23(3)	123.626(17)
	109.95(3)				
∠C=S–M/°	99.62(8)	88.91(10)	101.0(2)	98.27(10)	99.03(6)
	90.34(7)	102.09(9)		105.19(10)	107.19(6)
	93.92(8)				
∠N–B–N/°	112.3(2)	112.2(2)	106.6(5)	107.4(2)	107.06(14)
	105.93(18)	106.9(2)	110.0(5)		
	110.77(19)	108.1(2)	107.7(6)		
∠N–B–C$_{Ph}$/°	111.46(19)	103.7(2)	112.8(6)	112.6(2)	112.04(15)
	105.14(19)	111.9(2)	109.9(5)	111.0(2)	111.64(15)
	111.3(2)	113.9(2)	109.7(5)		

3, Table 1) of [Ag(PhTm^{Me})(PEt$_3$)] reveals distorted trigonal planar coordination at the silver ion, with an S$_2$P donor set. There is considerable distortion within the plane, with P–Ag–S angles of 124.85(4)° and 135.86(4)° and a S–Ag–S angle of 98.30(3)°. However, the overall degree of planarity is high, with the sum of the in-plane angles being 359.02°. The Ag–P distance (2.3776(12) Å) is typical of such species, while the two Ag–S bond distances are inequivalent (2.4630(14) and 2.5868(13) Å). The silver(I) complex with the parent ligand, [Ag(Tm^{Me})(PCy$_3$)][15] also has trigonal planar primary coordination geometry, but in this case, the borohydride also approaches the metal center at a distance of 2.41 Å. However, by contrast, the more recently reported complexes, [Ag(Tm^{Me})(P{^{i}Bu}$_3$)][16] and [Ag(Tm^{tBu})-(PPh$_3$)][14] have pseudo-tetrahedral geometries and are both situated on crystallographic C_3 axes. Inspection of space-filling representations of the structures suggests that in [Ag-(Tm^{Me})(PCy$_3$)] the PCy$_3$ ligand is sufficiently bulky to prevent the third sulfur atom from coordinating to the metal center. By contrast, the phenyl groups of the PPh$_3$ ligand in
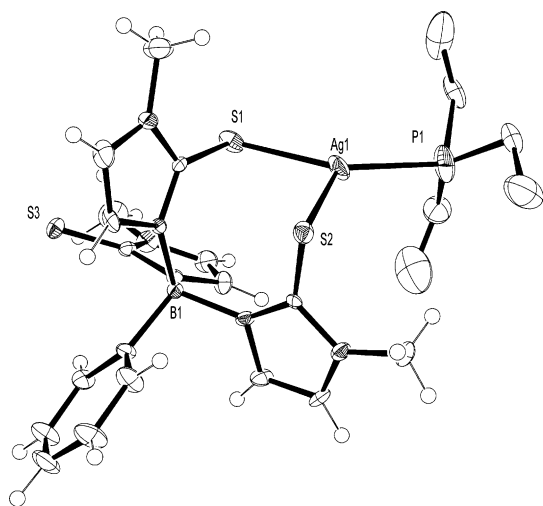

Figure 3. The X-ray structure of [Ag(PhTm^{Me})(PEt$_3$)] with thermal ellipsoids shown at the 50% level. The PEt$_3$ ligand is disordered and one conformation is shown. H atoms could not be placed with confidence and are omitted.

[Ag(Tm^{tBu})(PPh$_3$)] are able to twist in such a way that they "interlock" with the ^{t}Bu substituents on the scorpionate ligand allowing tridentate coordination. The ^{i}Bu groups in [Ag-(Tm^{Me})(P{^{i}Bu}$_3$)] do not prevent all three sulfur donors approaching the metal ion again leading to a κ^3-S,S,S coordination. Given the broad similarity between PEt$_3$ and P^{i}Bu$_3$, it is not certain why the PhTm^{Me} ligand does not also coordinate in a κ^3 mode. It may be that, since silver has a greater propensity to lower coordination numbers, the energy that would be gained by ligation of the third sulfur donor to silver is less than that required to induce the distortion in the ligand to enable this to occur. As further examples are reported it may become possible to rationalize these results with greater confidence.

Early in our studies, when using PhTm^{Me} prepared by the original literature method, we isolated small amounts of a second crystalline material from the reactions of copper and silver with PPh$_3$ and PhTm^{Me}. X-ray diffraction (Figures 4 and 5, Table 1) showed these to be the copper and silver complexes of the incompletely formed ligands, PhB(H)(mt)$_2^-$ (PhBm^{Me}, vide supra), [M(PhBm^{Me})(PPh$_3$)] (M = Cu, Ag). These complexes have only been prepared as byproducts in the reactions described above, and as yet, we have not attempted a rational synthesis of the PhBm^{Me} ligand, nor of its complexes. These complexes are not observed when PhTm^{Me} ligand prepared by our method is used. X-ray crystallography reveals that the metal centers exhibit nearly regular trigonal planar geometry, with the PhBm^{Me} ligands coordinating in a nominally κ^3 (H,S,S) mode. Given the presence of only two sulfur donors, this arrangement is as might be expected. The ligand bite angles are large at 115.94-(3)° (Cu) and 114.33(2)° (Ag) and are accommodated by an "inverted" conformation of the ligand, in which the H–B–N–C(=S) torsion angles are 36.4° and 3.8° (Cu) and 12.7° and 45.1° (Ag). The sums of the angles defining the trigonal

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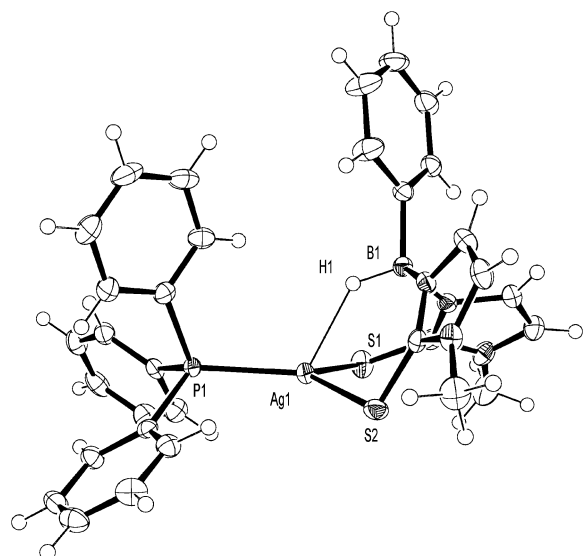
Figure 4. The X-ray structure of [Ag(PhBm^Me)(PPh₃)] with thermal ellipsoids shown at the 50% level.
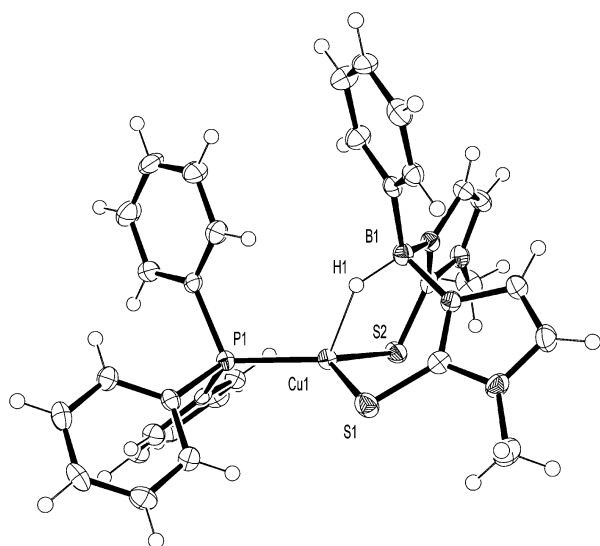

Figure 5. The X-ray structure of [Cu(PhBm^Me)(PPh₃)] with thermal ellipsoids shown at the 50% level.

plane are 355.5° (Cu) and 359.2° (Ag). The M···H−B interactions are much shorter than in other examples of inverted soft scorpionate complexes, though it should be noted that in each case the M···H(−B) distance is still greater than the sum of the covalent radii. In the copper complex, the Cu···H distance is 1.831(2) Å, compared to 2.22 and 2.29 Å in the only other soft scorpionate copper complex which shows this interaction, [Cu₂(Tt^Et)₂].[17] The distance is still slightly longer than in copper complexes with simple monodentate borohydride ligands such as [Cu(MeC{CH₂-PPh₂}₃)(HBH₃)] (1.605 Å)[18] and [Cu(PMePh₂)₃(HBH₃)] (1.698 Å).[19] In the silver complex [Ag(PhBm^Me)(PPh₃)], the Ag···H distance is 2.164(2) Å, some 0.2 Å shorter than in

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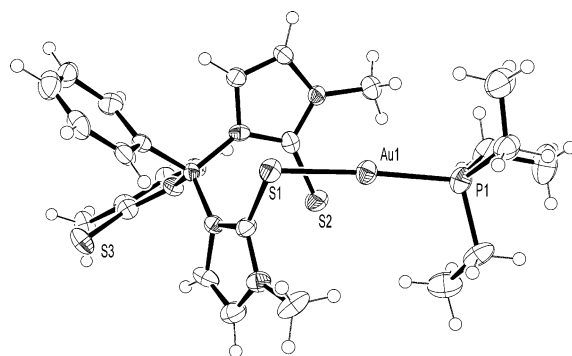
Figure 6. The X-ray structure of [Au(PhTm^Me)(PEt₃)] with thermal ellipsoids shown at the 50% level.

Table 2. Comparison of Structural Parameters for Linear Gold(I) Complexes with S,P-Donor Sets

compound[a]	d(Au−S)/Å	d(Au−P)/Å	S−Au−P/°	ref
[Au(PhTm^Me)(PEt₃)]	2.3335(17)	2.2682(19)	171.55(7)	this work
[Au(2-tur)(PEt₃)]	2.310	2.248	176.91	21a
[Au(mt)(PCy₃)]	2.331	2.291	171.99	21b
[Au(tu)(PCy₃)]	2.295	2.274	168.54	21c
[Au(tz)(PPh₃)]	2.324	2.260	170.11	21d

[a] 2-tur = 2-thiouracil; mtH = 1-methylimidazole-2-thione; tu = thiourea; tz = 1-methyl-5-thio-1,2,3,4-tetrazole.

[Ag(Tm^Me)(PCy₃)] (2.41 Å)[15] and 0.3 Å shorter than the shortest Ag···H distances in [Ag₂(Tm^Me)₂] (2.45 Å)[20] and [Ag₂(Tm^tBu)₂] (2.52 Å).[14]

Reaction of [Au^I(PR₃)Cl] (R = Et, Ph) with 1 equiv of LiPhTm^Me resulted in the formation of colorless complexes, whose analytical data are consistent with the expected formulation, [Au(PhTm^Me)(PR₃)]. The ¹H NMR spectra in solution are broad, indicative of a degree of fluxionality, but confirm the presence of both PhTm^Me and phosphine ligands. The complex [Au(PhTm^Me)(PEt₃)] yielded X-ray quality crystals. Analysis (Figure 6, Table 1) revealed a linear coordination geometry (Figure 4) with an S−Au−P bond angle of 171.55(7)° and showed the PhTm^Me ligand to be coordinated in a κ¹ mode via just one sulfur atom. The bond distances and angles are within the normal ranges observed in linear S,P-ligated Au^I complexes[21] (Table 2), and relatively little change in the metrical parameters is observed with different phosphine substituents. Two other mononuclear Au^I complexes of soft scorpionate ligands, [Au(Bm^Me)(PPh₃)][22] and [Au(Tm^tBu)(PPh₃)],[14] have been reported by Rabinovich, and on inspection, marked differences between these and our complex are observed. In [Au(PhTm^Me)(PEt₃)], there is a distant secondary Au···S(2) interaction at 3.629(3) Å. This contrasts sharply with the two complexes of Rabinovich, in which the Bm^Me and Tm^tBu ligands coordinate in an asymmetric κ² mode, with Au−S(2) = 2.3511(12) Å and Au−S(1) = 2.8155(13) Å for the Bm^Me complex, and Au−S(2)

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= 2.3488(11) Å and Au−S(1) = 2.8291(14) Å for the Tm^{tBu} complex. The overall molecular shape is close to T-shaped, although the stronger secondary Au−S interaction gives rise to a more marked deviation of the S−Au−P angle from linearity (159.74(4)° and 159.8 (av)°, respectively). In both cases, there are also Au···H−B contacts, at 2.56 and 2.47 Å, which by definition are not possible in our complex. It is not certain whether the different geometries adopted are driven by the presence of the borohydride interaction, or whether the more strongly electron donating PEt₃ ligand alters the electronic structure sufficiently to obviate the need for this secondary interaction. Unfortunately, it has not proved possible to grow crystals of the [Au(PhTm^{Me})(PPh₃)] complex to further investigate the origin of this phenomenon.

An initial hope for the Tm^R ligand system was to use the potentially less redox active thione donors to replace thiols or thiolates in models of copper proteins. However, this goal was not readily realized using the parent Tm^{Me} ligand, it is believed due to the presence of the reducing borohydride moiety. It was hoped that replacement of B−H with B−Ph would ameliorate this problem, and thus, attempts have been made to prepare copper(II) complexes of PhTm^{Me}. Reaction of copper(II) chloride in methanol with LiPhTm^{Me} results in the immediate precipitation of a blue powder, which analyzes as [Cu(PhTm^{Me})Cl]. The compound is insoluble in all common solvents, and thus, limited spectroscopic data are available. Attempts to recrystallize the product invariably led to decomposition, and on the basis that the insolubility indicated a polymeric structure, attempts were made to disrupt this using strong donors (e.g., pyridine). However, these were unsuccessful, resulting in decomposition to colorless solutions, presumably indicating reduction to copper(I). In an effort to obtain crystals suitable for structural determination, very slow diffusion of copper(II) chloride and the ligand through a solvent blank was also attempted. This resulted initially in the formation of very dark blue plates, and as the diffusion progressed, pale lilac crystals were also formed. Both were subjected to investigation by X-ray crystallography. The dark blue crystals were shown to be a neutral mixed-valence cluster compound [Cu^I₁₀Cu^{II}₂(mt)₁₂-Cl₂] (Figure 7). It is clear that the PhTm^{Me} ligand has decomposed and the resulting methimazolate ions act as bridging ligands between the various metal centers. The central core consists of copper(I) ions bridged by methimazole sulfur atoms, forming Cu₂S₂ squares, which in turn link by either trans or cis edges to form a distorted barrel-shaped Cu₈S₈ cluster. The copper atoms in the core are four-coordinate in S₄ or S₃N coordination environments. There are a further four copper atoms on the periphery of the structure. Each end of the cluster is capped by a square pyramidal copper(II) ion, coordinated to two methimazole sulfur atoms (S trans S) and two methimazole nitrogen atoms (N trans N), with a chloride anion in the apical position. Finally, two linear copper(I) ions are coordinated by two methimazole nitrogen atoms. If the slow diffusion is performed using Cu(BF₄)₂ instead of the chloride, then the structure obtained has water molecules replacing the apical chloride ions and noncoordinating BF₄ anions to balance the
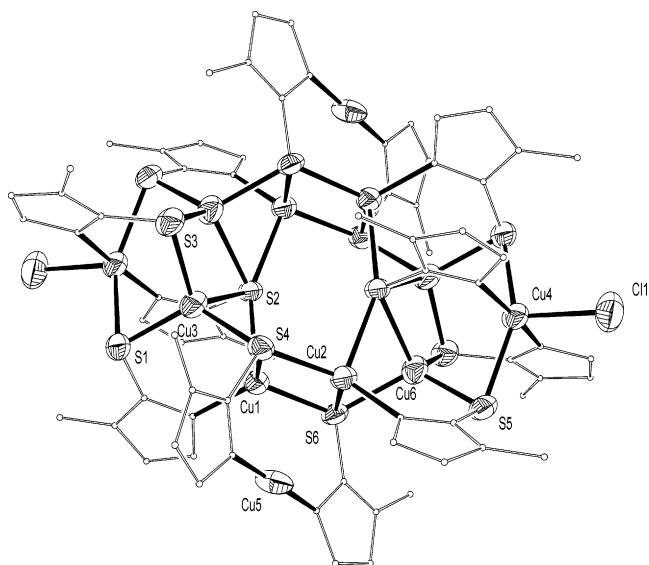

Figure 7. The X-ray structure of [Cu^I₁₀Cu^{II}₂(mt)₁₀Cl₂] with thermal ellipsoids shown at the 50% level. The core of the cluster is highlighted.
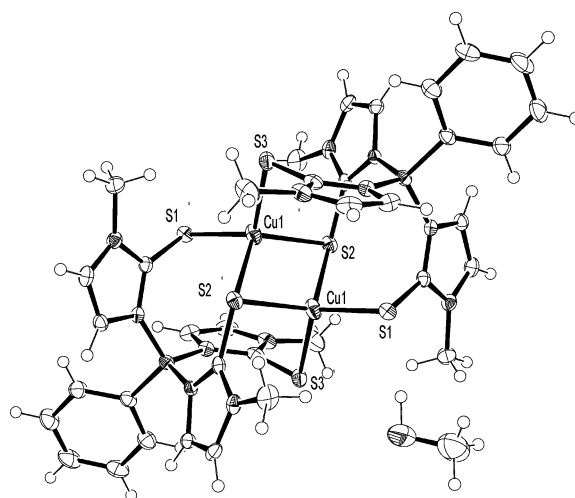

Figure 8. The X-ray structure of [Cu₂(PhTm^{Me})₂] with thermal ellipsoids shown at the 50% level.

charge. A similar compound has also been prepared from copper(II) nitrate, although in this case, the crystals were not sufficiently good for analysis by diffraction methods. A dicationic analogue of the methimazolate-supported copper core has previously been reported in which anionic chloride was replaced by neutral acetonitrile ligands.[23]

The pale lilac crystals were shown to be the simple dimeric copper(I) compound [Cu₂(PhTm^{Me})₂] (Figure 8). Both our group[1a] and Pettinari[13] have reported complexes with empirical formula [Cu(Tm^{Me})], which have not been structurally characterized. Marchio[17] has reported the structure of the dimeric complex of a closely related 2-thioxotriazole-based ligand, namely [Cu₂(Tt^{Et})₂]. This, however, differs markedly from our complex in a number of respects. In [Cu₂(PhTm^{Me})₂], the ligand spans the two copper centers with one sulfur atom coordinating to each copper atom and the third sulfur atom bridging between the two metal centers.

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The central Cu_2S_2 ring has a Cu···Cu distance of 2.59 Å. Searching the Cambridge Structural Database[24] reveals that this is one of the shortest known Cu···Cu distances in an Cu_2S_2 ring—the shortest in a dimeric species is in the $[Cu_2(\mu^2\text{-tu})_2(\text{tu})_4]^{2+}$ cation[25] (tu = thiourea) at 2.553 Å, while the mean is 2.99 Å. In the thiourea complex, the very short bond is ascribed to very strong intermolecular hydrogen-bonding interactions constraining the complex. In this case, it would seem that the ligand conformation adopted is the most likely driving force for such a short contact. Marchio's complex, $[Cu_2(Tt^{Et})_2]$, has an entirely different arrangement, with the ligand binding in a bidentate (S,S) coordination mode with a Cu···H interaction. The third, pendant S donor fills the coordination sphere of a neighboring copper atom to form a dimeric species, resulting in a much larger Cu···Cu separation of 4.28 Å. The structure of $[Cu_2(PhTm^{Me})_2]$ more closely parallels those seen in the related complexes $[Ag_2(Tm^{Me})_2]$ and $[Ag_2(Tm^{tBu})_2]$,[14] but the conformation of the $PhTm^{Me}$ ligand is quite different to that seen in the silver complexes, in which the borohydrides are directed toward the center of the Ag_2S_2 square, resulting in an "inverted" configuration of the ligand. In the case of the $PhTm^{Me}$ complex, the steric bulk of the phenyl group on the boron prevents ligand inversion, instead resulting in a more "normal" configuration.

It is clear from these results that, although the modified $PhTm^{Me}$ ligand is able to stabilize copper(II) if the complex is rapidly precipitated from solution, it is also still able to effect the reduction of copper(II) to copper(I), with concomitant ligand decomposition. Presumably the B−Ph group is still sufficiently redox active to drive the process, particularly in solution, where ligand exchange will be rapid, allowing the C−B bond to approach the metal center to facilitate the redox process. The formation of products in the slow diffusion reaction is interesting. The mixed-valence aggregate has previously been prepared directly by reaction of $[Cu(NCMe)_4]$ BF_4, $Cu(OAc)_2 \cdot H_2O$, and methimazole in acetonitrile. As the diffusion proceeds, it is this compound which forms first, suggesting that initially copper(II) is in excess at the point of mixing. Presumably, the small Cu^{2+} ion diffuses more rapidly than the bulky $PhTm^{Me}$ ion. The ligand reduces copper(II) to copper(I) and fragments to form methimazolate anions, but since there is an excess of copper(II) present, the mixed-valence cluster spontaneously self-assembles. As the reaction proceeds, all the copper(II) is reduced to copper(I) and the remaining $PhTm^{Me}$ reacts with the copper(I) ions to form the dimer, $[Cu^I_2(PhTm^{Me})_2]$.

Summary

Reaction of M^I precursors (M = Cu, Ag, Au) with $LiPhTm^{Me}$ in the presence of PPh_3 or PEt_3 leads to formation of complexes $[M^I(PhTm^{Me})(PR_3)]$. The structures of these reveal a progression from pseudo-tetrahedral (Cu) to trigonal planar (Ag) to linear (Au) with the ligand bonding mode correspondingly progressing from κ^3 through to κ^1. Reaction

with copper(II) salts results in ligand decomposition and the formation of a mixed-valence cluster supported by methimazolyl anions.

Experimental Section

$Li(PhBH_3)$ was prepared by modification of a literature method,[26] while all other reagents were commercially obtained and used as supplied. NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 400 MHz for ^1H, 100 MHz for ^{13}C, and 162 MHz for ^{31}P. The ^1H and ^{13}C spectra were referenced using internal solvent peaks to TMS. ^{31}P spectra were referenced externally to 85% H_3PO_4, using a $CDCl_3$ capillary as a lock. Mass spectra were recorded at the EPSRC facilities at University of Wales, Swansea, U.K., using a Finnegan MAT95 or MAT900.

Synthesis of LiPhTm^{Me}. A modification of the procedure of Santos et al. was used.[10] All operations were carried out under a N_2 atmosphere. Phenylboronic acid (0.8 g, 6.56 mmol) was dissolved in freshly distilled diethyl ether (15 mL). A 1.0 M solution of $LiAlH_4$ in diethyl ether (10 mL) was added via syringe to a Schlenk tube equipped with magnetic stirring bar and containing 2,2′-biquinoline (0.002 g). The solution of phenylboronic acid was slowly added until the solution changed from slate blue to colorless (ca. 14 mL). A granular precipitate formed. The mixture was filtered, and the solid washed with diethyl ether (2 × 10 mL). The washings were combined with the filtrate, and the solvent removed in vacuo to yield $Li(PhBH_3)$. The $Li(PhBH_3)$ formed was suspended in freshly distilled xylene (30 mL), and methimazole (2.4 g, 0.021 mol) was added. The mixture was refluxed for 5 h and then allowed to cool. The white solid formed was collected by filtration and washed first with chloroform and then hexane before drying. Yield 1.1 g, 36% (based on phenylboronic acid). X-ray quality crystals were obtained by vapor diffusion of diethyl ether into a methanol solution of the solid. Anal. Found: C, 48.61; H, 4.85; N, 19.10. Calcd for $C_{18}H_{20}N_6S_3BLi$: C, 49.79; H, 4.61; N, 19.36%. ^1H NMR (400 MHz, (d_6-dmso); δ): 3.37 (s, 9H, CH_3); 6.71 (s, 6H, CH); 6.95−6.99 (m, 3H, Ph); 7.18 (br, 2H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, (d_6-dmso); δ): 33.77 (s, CH_3, mt); 114.92 (s, CH, mt); 123.49 (s, CH, mt); 124.18 (s, $C_{o/m}$, Ph); 124.81 (s, $C_{o/m/p}$, Ph); 135.04 (s, C_i, Ph); 164.07 (s, C_{quat}, mt). MS (ESI; m/e): 427 (M − Li), 100%).

Synthesis of [Au(PhTm^{Me})(PEt$_3$)]. [Au(PEt$_3$)Cl] (0.250 g, 0.713 mmol) was suspended in methanol (10 mL), and a solution of $LiPhTm^{Me}$ (0.310 g, 0.713 mmol) in methanol (10 mL) was added. The mixture was stirred for 2 h, and the solvent removed in vacuo, resulting in a white solid. This solid was extracted with chloroform (14 mL), and the solution filtered to remove LiCl and unreacted $LiPhTm^{Me}$. The filtrate was taken to dryness in vacuo, and the resulting solid washed with diethyl ether and dried. Yield: 0.310 g; 59%. X-ray quality crystals were formed by vapor diffusion of hexane into a chloroform solution. Anal. Found: C, 38.07; H, 4.15; N, 10.86. Calcd for $C_{24}H_{35}N_6S_3PBAu$: C, 38.84; H, 4.72; N, 10.86%. ^1H NMR (400 MHz, $CDCl_3$; δ): 1.27 (dt, 9H, CH_3 (PEt_3)); 1.94 (dq, 6H, CH_2 (PEt_3)); 3.76 (s, 9H, CH_3 (mt)); 6.79 (d, 3H, CH (mt)); 7.24−7.36 (m, 8H, CH (mt, Ph)). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ): 8.81 (s, CH_3, PEt_3); 17.93 (d, CH_2, PEt_3, J_{C-P} 33.47 Hz); 35.06 (s, CH_3, mt); 109.50 (s, C_i, Ph); 117.61 (s, CH, mt); 124.46 (s, CH, mt); 126.11 (s, C_p, Ph); 126.70 (s, $C_{o/m}$, Ph); 134.19 (s, $C_{o/m}$, Ph); 159.56 (s, C_{quat}, mt). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$; δ): s, 34.77.

Synthesis of [Au(PhTm^{Me})(PPh$_3$)]. [Au(PPh$_3$)Cl] (0.228 g, 0.46 mmol) was suspended in methanol (8 mL), and a solution of

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Table 3. Crystallographic Parameters

complex	[Li(HOMe)₄] PhTm^Me	[Cu(PhTm^Me)(PPh₃)] CH₂Cl₂ solvate	[Ag(PhTm^Me)(PEt₃)]	[Au(PhTm^Me)(PEt₃)]
empirical formula	$C_{22}H_{24}BLiN_6O_4S_3$	$C_{37}H_{37}BCl_2CuN_6PS_3$	$C_{24}H_{35}AgBN_6PS_3$	$C_{24}H_{35}AuBN_6PS_3$
fw	550.23	838.13	638.29	742.54
T/K	173(2)	123(2)	123(3)	123(2)
cryst syst	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$Pbn2_1$	$P\bar{1}$	$P2_1/n$	$Pna2_1$
a/Å	14.6899(6)	11.9520(4)	10.180(5)	13.9270(4)
b/Å	14.7402(4)	12.9390(4)	29.852(5)	14.4549(4)
c/Å	13.7287(6)	13.5811(5)	10.498(5)	14.5183(3)
α/deg	90	82.507(2)	90	90
β/deg	90	70.210(2)	109.936(5)	90
γ/deg	90	74.053(2)	90	90
Z	4	2	4	4
V/Å³	2972.7(2)	1898.56(11)	2999(2)	2922.72(13)
μ_{calc}/mm⁻¹	0.286	0.960	0.957	5.328
$F(000)$	1192	864	1284	1472
cryst size/mm³	0.53 × 0.45 × 0.36	1.0 × 0.15 × 0.08	0.40 × 0.20 × 0.20	0.30 × 0.15 × 0.09
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
no. reflns measd	9823	15 133	21 701	44 450
no. unique reflns	5829(R_{int} = 0.0261)	8638(R_{int} = 0.0412)	6838(R_{int} = 0.0358)	6677(R_{int} = 0.0402)
no. of params	357	463	341	328
R^a ($I > 2\sigma(I)$)	0.0428	0.0412	0.0371	0.0426
R_w^b (all reflns)	0.0986	0.0800	0.1010	0.0966
GOF	1.068	1.014	1.056	1.025

complex	[Cu(PhBm^Me)(PPh₃)]	[Ag(PhBm^Me)(PPh₃)]	[Cu^I₁₀Cu^II₂(mt)₁₂Cl₂]	[Cu₂(PhTm^Me)₂] methanol solvate
empirical formula	$C_{32}H_{31}BCuN_4PS_2$	$C_{32}H_{31}BAgN_4PS_2$	$C_{48}H_{60}Cl_2Cu_{12}N_{24}S_{12}$	$C_{38}H_{48}B_2Cu_2N_{12}O_2S_6$
fw	641.05	685.38	2191.30	1045.94
T/K	123(2)	123(2)	123(2)	123(2)
cryst syst	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	10.4991(3)	10.6397(3)	10.9667(5)	10.1299(3)
b/Å	17.4448(4)	17.6269(4)	23.4584(12)	11.2001(5)
c/Å	16.6193(5)	16.8142(4)	15.5610(7)	11.4848(5)
α/deg	90	90	90	61.706
β/deg	97.3220(10)	98.5950(10)	93.432(3)	79.537
γ/deg	90	90	90	85.277
Z	4	4	2	1
V/Å³	3019.08(14)	3118.0(14)	3996.1(3)	1128.26
μ_{calc}/mm⁻¹	0.944	0.860	3.551	1.270
$F(000)$	1328	1400	2179	540
cryst size/mm³	0.35 × 0.25 × 0.10	0.70 × 0.50 × 0.20	0.40 × 0.15 × 0.03	0.40 × 0.15 × 0.10
radiation	MoKα	MoKα	MoKα	MoKα
no. reflns measd	19294	18874	24558	9118
no. unique reflns	5327(R_{int}=0.0580)	7103(R_{int}=0.0240)	7011(R_{int}=0.0918)	5110(R_{int}=0.0364)
no. of params	373	373	448	285
R^a ($I > 2\sigma(I)$)	0.0382	0.0263	0.0763	0.0430
R_w^b (all reflns)	0.0817	0.0633	0.1474	0.1000
GOF	1.052	1.048	1.064	1.024

$^a R = \sum||F_o| - |F_c||/\sum|F_o|.$ $^b R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}.$

LiPhTm^Me (0.2 g, 0.46 mmol) in methanol (5 mL) was added. The mixture was stirred for 1 h, after which time the solid formed was collected by filtration, washed with diethyl ether, and dried. Yield 0.319 g; 78%. Anal. Found: C, 48.26; H, 3.31; N, 9.39. Calcd for $C_{36}H_{35}N_6S_3PBAu$: C, 48.78; H, 3.95; N, 9.48%. ¹H NMR (400 MHz, (d_6-dmso); δ): 3.44 (s, 9H, CH₃); 6.82 (s, 3H, CH (mt)); 7.05 (m, 8H, CH (mt, Ph)); 7.53−7.65 (m, 15H, CH (PPh₃)). ¹³C-{¹H} NMR (100 MHz, (d_6-dmso); δ): 34.29 (s, CH₃); 118.15 (s, CH, mt); 123.18 (s, CH, mt); 125.41 (s, C_p, Ph); 125.94 (s, C_{o/m}, Ph); 129.02 (s, C_{o/m}, Ph); 129.32 (d, C_m, PPh₃, J_{C-P} 11.27 Hz); 131.74 (s, C_p, PPh₃); 133.63 (d, C_o, PPh₃, J_{C-P} 13.99 Hz); 133.89 (s, C_i, PPh₃). ³¹P{¹H} NMR (162 MHz, CDCl₃; δ): s(sh), 35.88.

Synthesis of [Ag(PhTm^Me)(PPh₃)]. AgNO₃ (0.08 g, 0.47 mmol) was suspended in methanol (5 mL). A solution of LiPhTm^Me (0.2 g, 0.46 mmol) and PPh₃ (0.123 g, 0.47 mmol) in methanol (10 mL) was added. The mixture was stirred for 2 h, after which time the solid was collected by filtration and washed sequentially with methanol and diethyl ether. Yield 0.260 g; 69%. Anal. Found: C, 52.15; H, 4.00; N, 10.30. Calcd for $C_{36}H_{35}N_6S_3PBAg$: C, 54.30;

H, 4.40; N, 10.55%. ¹H NMR (400 MHz, (d_6-dmso); δ): 3.42 (s, 9H, CH₃); 6.70 (d, 3H, CH (mt)); 7.07 (d, 3H, CH (mt)); 7.14−7.20 (m, 3H, CH (Ph)); 7.33−7.38 (m, 2H, CH (Ph)); 7.42−7.51 (m, 15H, CH (PPh₃)). ¹³C{¹H} NMR (100 MHz, (d_6-dmso); δ): 34.79 (s, CH₃); 120.36 (s, CH, mt); 126.76 (s, CH, mt); 129.12 (d, C_m, PPh₃, J_{C-P} 9.86 Hz); 130.71 (s, C_p, PPh₃); 131.42 (s, C_m, Ph); 131.70 (s, C_{o,p}, Ph); 133.31 (d, C_o, PPh₃, J_{C-P} 16.70 Hz); 133.54 (d, C_i, PPh₃, J_{C-P} 43.87 Hz); 157.12 (s, C_{quat}, mt). ³¹P{¹H} NMR (162 MHz, CDCl₃; δ): s(br), 3.87.

Synthesis of [Ag(PhTm^Me)(PEt₃)]. AgNO₃ (0.078 g, 0.46 mmol) was suspended in methanol (5 mL), and triethylphosphine (0.1 mL, 0.125 g, 1.06 mmol) was added via syringe. A solution of LiPhTm^Me (0.2 g, 0.46 mmol) in methanol (5 mL) was added and the mixture stirred for 1 h. The solvent was removed in vacuo, yielding a white powder which was purified by dissolution in dichloromethane, filtration through a Celite/glass wool plug, and removal of the solvent in vacuo. The crude product was suspended in diethyl ether to remove excess triethylphosphine, filtered, and dried. Yield 0.231 g; 77%. Anal. Found: C, 44.59; H, 6.50; N, 11.15. Calcd for

$C_{24}H_{35}N_6S_3PBAg$: C, 44.13; H, 5.36; N, 12.87%. ^{1}H NMR (400 MHz, (d_6-dmso); δ): 1.00−1.11 (dt, 9H, CH$_3$ (PEt$_3$)); 1.62−1.69 (dq, 6H, CH$_2$ (PEt$_3$)); 3.52 (s, 9H, CH$_3$ (mt)); 6.69 (d, 3H, CH (mt)) 7.07−7.20 (m, 8H, CH (mt, Ph)). ^{13}C{^{1}H} NMR (100 MHz, (d_6-dmso); δ): 5.45 (d, CH$_3$, PEt$_3$, J_{C-P} 4.83 Hz); 19.00 (d, CH$_2$, PEt$_3$, J_{C-P} 65.61 Hz); 34.37 (s, CH$_3$, mt); 118.01 (s, CH, mt); 122.41 (s, CH, mt); 125.45 (s, C$_p$, Ph); 125.97 (s, C$_m$, Ph); 131.34 (s, C$_i$, Ph); 134.00 (s, C$_o$, Ph); 160.79 (s, C$_{quat}$, mt).

Synthesis of [Cu(PhTm^{Me})(PPh$_3$)]. [Cu(PPh$_3$)$_2$Cl] (0.29 g, 0.46 mmol) was suspended in methanol (8 mL), and a solution of LiPhTm^{Me} (0.2 g, 0.46 mmol) in methanol (5 mL) was added. A white powder precipitated out immediately, and after being stirred for 2 h, the solid was collected by filtration and washed with methanol and then diethyl ether. Yield 0.272 g; 79%. X-ray quality crystals were grown by vapor diffusion of diethyl ether into a dichloromethane solution of the complex. Anal. Found: C, 56.78; H, 4.29; N, 10.28. Calcd for $C_{36}H_{35}N_6S_3PBCu$: C, 57.43; H, 4.65; N, 11.16%. ^{1}H NMR (400 MHz, CDCl$_3$; δ): 3.47 (s, 9H, CH$_3$); 6.66 (d, 3H, CH (mt)); 6.86 (d, 3H, CH (mt)); 7.17−7.68 (m, 20H, CH (Ph, PPh$_3$)). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$; δ): 34.73 (s, CH$_3$, mt); 117.61 (s, CH, mt); 123.27 (s, CH, mt); 126.63 (s, C$_m$, Ph); 127.04 (s, C$_{o/p}$, Ph); 128.12 (d, C$_m$, PPh$_3$, J_{C-P} 9.06 Hz); 129.15 (s, C$_p$, Ph); 134.00 (d, C$_o$, PPh$_3$, J_{C-P} 15.40 Hz); 134.83 (d, C$_i$, PPh$_3$, J_{C-P} 26.06 Hz); 163.47 (s, C$_{quat}$, mt). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$; δ): −5.29 (br). MS (ESI; m/e): 753 ([Cu(κ^3-PhTm^{Me})(PPh$_3$)], 100%).

[M(PhBm^{Me})(PPh$_3$)] (M = Cu, Ag). Crystals of these complexes were obtained during crystallization of the corresponding PhTm^{Me} complexes, leading to the conclusion that the LiPhTm^{Me} used was contaminated with LiPhBm^{Me}. Since these complexes were not obtained rationally and were difficult to separate in significant quantities, the only analyses performed were mass spectrometry and X-ray crystallography. MS (ESI; m/e): 685 ([Ag(κ^3-PhBm^{Me})-(PPh$_3$)], 100%). MS (ESI; m/e): 641 ([Cu(κ^3-PhBm^{Me})(PPh$_3$)], 60%).

Preparation of [Cu(PhTm^{Me})Cl]. Copper(II) chloride (0.037 g, 0.34 mmol) was dissolved in methanol (6 mL). To this was added LiPhTm^{Me} (0.15 g, 0.35 mmol). Almost immediately, a blue solid precipitated out of solution and this was collected by filtration. The crude powder was suspended in water to remove any LiCl before being thoroughly washed, first with methanol and then with diethyl ether before being dried. Yield 0.097 g; 54%. Anal. Found: C, 40.79; H, 3.96; N, 15.57. Calcd for $C_{18}H_{20}N_6S_3BCuCl$: C, 41.10; H, 3.80; N, 15.98%.

Synthesis of [Cu$^I_{10}$Cu$^{II}_2$(mt)$_{12}$Cl$_2$] and [Cu(PhTm^{Me})]$_2$. LiPhTm^{Me} (60 mg, 0.138 mmol) was dissolved in a small quantity of methanol in a small vial, and the vessel filled/layered slowly with blank methanol. In a larger vial, copper(II) chloride (0.0186 g, 0.138 mmol) was dissolved in the minimum volume of methanol. The small vial was then placed inside the large vial and methanol layered on top until the small vial was submerged. The vial was left in a vibration-free vicinity for approximately 1 month after which time very dark blue needles ([Cu$^I_{10}$Cu$^{II}_2$(mt)$_{12}$Cl$_2$]) and pale lilac blocks ([Cu(PhTm^{Me})]$_2$) had grown at the solvent interfaces. Similar results were obtained when copper(II) chloride was replaced with copper-(II) nitrate or tetrafluoroborate salts. Crystals of each compound suitable for X-ray diffraction were separated by hand. No further spectroscopic data were acquired.

X-ray Crystallography. Crystals were coated in mineral oil and mounted on glass fibers. Data were collected at 123 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. The heavy-atom positions were determined by Patterson methods and the remaining atoms located in difference electron density maps. Full matrix least-squares refinement was based on F^2, with all non-hydrogen atoms anisotropic. While hydrogen atoms were mostly observed in the difference maps, they were placed in calculated positions riding on the parent atoms. The structure solution and refinement used the program SHELX-97[27] and the graphical interface WinGX.[28] A summary of the crystallographic parameters is given in Table 3.

Supporting Information Available: X-ray Crystallographic data in CIF format. ^{1}H NMR spectra of [Ag(PhTm^{Me})(PR$_3$)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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