

Tris(mercaptoimidazolyl)borate complexes of the coinage metals: syntheses and molecular structures of the first gold compounds and related copper and silver derivatives

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The first tris(mercaptoimidazolyl)borate complexes of gold, Au(Tm^{tBu}) and (Tm^{tBu})Au(PPh₃), have been prepared and structurally characterized. Together with their copper and silver analogues M(Tm^{tBu}) and (Tm^{tBu})M(PPh₃) (M = Cu, Ag), these compounds constitute the first two complete series of Tm^R derivatives to be isolated for the coinage metals. In order to evaluate the steric and electronic effects of the bulky *tert*-butyl substituents in these species, comparative structural analyses with the known methyl-substituted analogue Ag(Tm^{Me}) and various (Tm^{Me})M(PR₃) derivatives (M = Cu, Ag) are also presented.

Introduction

The tris(2-mercapto-1-*tert*-butylimidazolyl)borate ligand (Fig. 1) is quickly becoming one of the most conspicuous members of the tris(mercaptoimidazolyl)borate (Tm^R) family of ligands.¹ Developed independently by the Vahrenkamp² and Rabinovich³ groups, alkali metal salts of [Tm^{tBu}]⁻ can be readily prepared in high yield and its complexes usually display good solubility, simple spectroscopic (*e.g.*, NMR) features in solution and good crystallinity in the solid state. The coordination chemistry of [Tm^{tBu}]⁻

ranges from the preparation of several well-defined sulfur-rich complexes of cobalt⁴ and the group 12 metals⁵ to the syntheses of the first organobismuth Tm^R compound⁶ and the first hydroselenido derivative of zinc.⁷ We have now extended these studies to the coinage metals and report in this paper the first two complete series of Tm^R derivatives of these elements, including the first such complexes of gold to be synthesized and structurally characterized. Although the silver complex Ag(Tm^{Me}) and a number of tertiary phosphine derivatives (Tm^{Me})M(PR₃) (M = Cu, Ag; R = alkyl, aryl) have been reported in recent years,⁸ these species are all circumscribed to the original [Tm^{Me}]⁻ ligand,¹ and our studies are thus also aimed at assessing the effect on bonding and structure of the bulkier borate ligand present in M(Tm^{tBu}) and (Tm^{tBu})M(PPh₃) (M = Cu, Ag, Au).

Results and discussion

Synthesis and structures of (Tm^{tBu})M(PPh₃) (M = Cu, Ag)

The tris(mercaptoimidazolyl)borate complexes (Tm^{tBu})M(PPh₃) (M = Cu, Ag) were easily prepared by allowing equimolar amounts of sodium tris(2-mercapto-1-*tert*-butylimidazolyl)borate, triphenylphosphine, and either copper(i) chloride or silver(i) nitrate to react in methanol (Scheme 1). The white, air- and light-stable products were isolated in *ca.* 75% yield after the appropriate work-up and are moderately soluble in chlorinated hydrocarbons (*e.g.*, CH₂Cl₂, CHCl₃) but essentially insoluble in other common organic solvents such as acetone, acetonitrile or benzene. They were characterized analytically

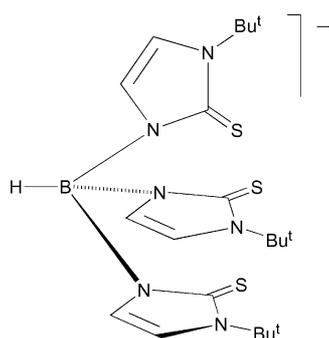
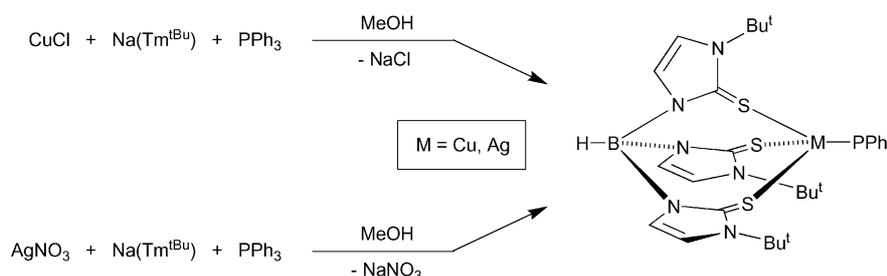


Fig. 1 The tris(2-mercapto-1-*tert*-butylimidazolyl)borate ligand, [Tm^{tBu}]⁻.



Scheme 1

and spectroscopically, including ^1H and ^{13}C NMR and IR spectroscopies, and all the data are consistent with the presence of mononuclear pseudo-tetrahedral species both in solution and in the solid state.

The molecular structures of both $(\text{Tm}^{\text{tBu}})\text{M}(\text{PPh}_3)$ ($\text{M} = \text{Cu}, \text{Ag}$) were confirmed by single-crystal X-ray diffraction (Figs. 2–3) and selected bond lengths (\AA) and angles ($^\circ$) are included in Table 1. The complexes are isostructural and present slightly distorted tetrahedral geometries, with crystallographically imposed three-fold rotation axes containing

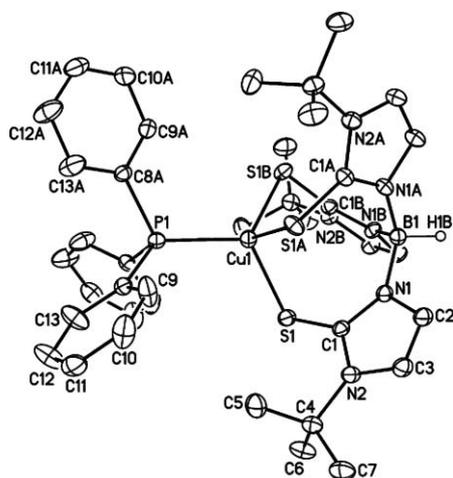


Fig. 2 Molecular structure of $(\text{Tm}^{\text{tBu}})\text{Cu}(\text{PPh}_3)$. Thermal ellipsoids are depicted at the 30% probability level and hydrogen atoms (except for the one directly attached to boron) are omitted for clarity. The equivalent positions $(1 - y, x - y, z)$ and $(1 - x + y, 1 - x, z)$ are indicated in the atomic labels by the use of the additional letters "A" and "B".

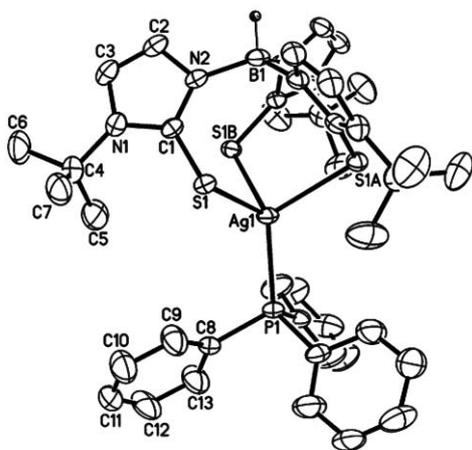


Fig. 3 Molecular structure of $(\text{Tm}^{\text{tBu}})\text{Ag}(\text{PPh}_3)$. Thermal ellipsoids are depicted at the 30% probability level. Hydrogen atoms (except for the one directly attached to boron) and solvent molecules are omitted for clarity. The equivalent positions $(1 - y, x - y, z)$ and $(1 - x + y, 1 - x, z)$ are indicated in the atomic labels by the use of the additional letters "A" and "B".

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) for $(\text{Tm}^{\text{tBu}})\text{M}(\text{PPh}_3)$ ($\text{M} = \text{Cu}, \text{Ag}$)

	M = Cu	M = Ag
M–S	2.3534(7)	2.5896(7)
M–P	2.2214(14)	2.4239(12)
S–C	1.707(3)	1.709(3)
S–M–S	104.56(2)	97.32(2)
S–M–P	114.02(2)	119.894(17)
M–S–C	99.78(9)	100.14(10)
M–P–C	115.04(10)	114.90(10)

the metal and phosphorus atoms. As such, they resemble Pettinari and Santini's $(\text{Tm}^{\text{Me}})\text{Cu}(\text{PAR}_3)$ ($\text{Ar} = m\text{-tolyl}, p\text{-tolyl}$)^{8d} and $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PBU}_3)$ ^{8e} complexes and display comparable metrical parameters. For example, the M–S bond lengths in $(\text{Tm}^{\text{tBu}})\text{M}(\text{PPh}_3)$ [2.353(1) \AA for $\text{M} = \text{Cu}$, 2.590(1) \AA for $\text{M} = \text{Ag}$] are virtually identical to those in $(\text{Tm}^{\text{Me}})\text{Cu}(\text{PAR}_3)$ [2.357(2) and 2.332(1) \AA for $\text{Ar} = m\text{-tolyl}$ and $p\text{-tolyl}$, respectively] and in $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PBU}_3)$ [2.595(1) \AA]. Similarly, the M–P bond lengths in $(\text{Tm}^{\text{tBu}})\text{M}(\text{PPh}_3)$ [2.221(1) \AA for $\text{M} = \text{Cu}$, 2.424(1) \AA for $\text{M} = \text{Ag}$] do not differ significantly from the corresponding values found in $(\text{Tm}^{\text{Me}})\text{Cu}(\text{PAR}_3)$ [2.217(3) and 2.226(1) \AA for $\text{Ar} = m\text{-tolyl}$ and $p\text{-tolyl}$, respectively] or in $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PBU}_3)$ [2.404(1) \AA]. Although the S–M–S angles in all these complexes are consistently smaller (and the S–M–P angles are consistently larger) than the ideal tetrahedral values, they tend to deviate more so in the silver complexes (by *ca.* 9–12 $^\circ$) than in the copper derivatives (by *ca.* 2–5 $^\circ$). It is also worth noting that the distorted tetrahedral silver atom in the related tricyclohexylphosphine complex $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PCy}_3)$ ^{8b} exhibits a distinctively different coordination environment, with a weak $\text{Ag} \cdots \text{H}-\text{B}$ interaction supplementing the binding of the phosphine and only two of the three thione groups of the $[\text{Tm}^{\text{Me}}]^-$ ligand to the metal center. Since $(\text{Tm}^{\text{tBu}})\text{Ag}(\text{PPh}_3)$ and $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PBU}_3)$ have very similar structures, the $\kappa^3\text{-S,S,H}$ coordination mode observed for the borate ligand in $(\text{Tm}^{\text{Me}})\text{Ag}(\text{PCy}_3)$ is likely to be a consequence of the larger cone angle of PCy_3 (170 $^\circ$) relative to those of either PPh_3 (145 $^\circ$) or PBU_3 (143 $^\circ$).⁹

Homoleptic $\text{M}(\text{Tm}^{\text{tBu}})$ complexes ($\text{M} = \text{Cu}, \text{Ag}$)

The base-free tris(mercaptoimidazolyl)borate complexes $\text{M}(\text{Tm}^{\text{tBu}})$ ($\text{M} = \text{Cu}, \text{Ag}$) were similarly obtained from the reaction of equimolar methanolic solutions of $\text{Na}(\text{Tm}^{\text{tBu}})$ and copper(i) chloride or silver(i) nitrate, respectively, and were isolated in 75–80% yield as white air- and light-stable solids. Unlike the triphenylphosphine derivatives $(\text{Tm}^{\text{tBu}})\text{M}(\text{PPh}_3)$ described above, they are both soluble in acetone, benzene and dimethyl sulfoxide (DMSO) in addition to chlorinated hydrocarbons. The observation of virtually identical spectroscopic (*e.g.*, NMR and IR) and physical properties for both compounds suggests that their structures, both in solution and in the solid state, are probably very similar.

The molecular structure of $\text{Ag}(\text{Tm}^{\text{tBu}})$ was established by single-crystal X-ray diffraction (Fig. 4) and selected bond lengths (\AA) and angles ($^\circ$) are shown in Table 2. Each of the two silver atoms in the centrosymmetric dimer is in a distorted tetrahedral environment, coordinated by two thione groups from each of the two $[\text{Tm}^{\text{tBu}}]^-$ ligands, which also partake in weak $\text{Ag} \cdots \text{H}-\text{B}$ interactions with the metal centers (Fig. 5).

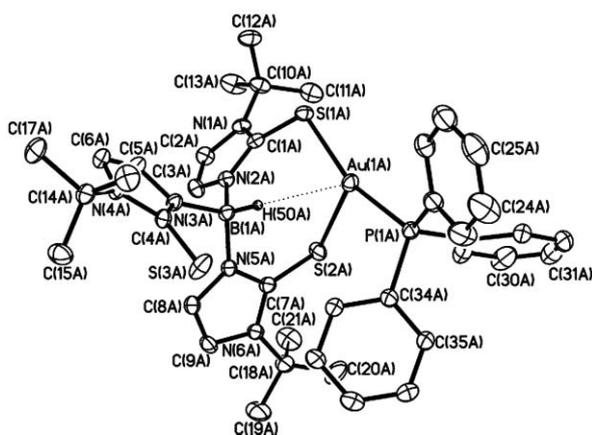
While the overall structure of $\text{Ag}(\text{Tm}^{\text{tBu}})$ is similar to that of the methyl-substituted analogue $\text{Ag}(\text{Tm}^{\text{Me}})$,^{8c} including the presence of a planar $[\text{Ag}_2\text{S}_2]$ core and the bridging bis(bidentate) coordination mode ($\mu\text{-}\kappa^2\text{-S,S}:\kappa^2\text{-S,S}$) exhibited by the borate ligands, there are some significant differences as well. For example, whereas the angles subtended at silver in $\text{Ag}(\text{Tm}^{\text{tBu}})$ are in the approximate range 90–126 $^\circ$, those in $\text{Ag}(\text{Tm}^{\text{Me}})$ deviate less from the ideal tetrahedral value (*ca.* 101–122 $^\circ$). The central $[\text{Ag}_2\text{S}_2]$ parallelogram in $\text{Ag}(\text{Tm}^{\text{tBu}})$ is somewhat more elongated than that in $\text{Ag}(\text{Tm}^{\text{Me}})$, with slightly more acute Ag–S–Ag and

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Ag}(\text{Tm}^{\text{tBu}})$

Ag(1)–S(1)	2.5952(6)	Ag(1) \cdots Ag(1A)	3.1578(4)
Ag(1)–S(1A)	2.8419(6)	S(1)–C(1)	1.715(2)
Ag(1)–S(2)	2.5492(7)	S(2)–C(8)	1.710(2)
Ag(1)–S(3A)	2.5691(6)	S(3)–C(15)	1.707(3)
S(1)–Ag(1)–S(1A)	109.153(16)	S(1)–Ag(1)–S(2)	126.09(2)
S(1)–Ag(1)–S(3A)	111.44(2)	S(1A)–Ag(1)–S(2)	89.80(2)
S(1A)–Ag(1)–S(3A)	105.21(2)	S(2)–Ag(1)–S(3A)	111.07(2)
Ag(1)–S(1)–Ag(1A)	70.847(16)		

Table 3 Selected bond lengths (Å) and angles (°) for the four independent molecules present in the unit cell of (Tm^{IBu})Au(PPh₃)

	Molecule A	Molecule B	Molecule C	Molecule D
Au(1)–S(1)	2.3488(11)	2.3488(11)	2.3400(11)	2.3442(11)
Au(1)–S(2)	2.8291(14)	2.8455(14)	2.8352(11)	2.8441(12)
Au(1)–P(1)	2.2535(11)	2.2474(11)	2.2492(11)	2.2492(11)
S(1)–C(1)	1.732(5)	1.721(5)	1.725(4)	1.730(4)
S(2)–C(7)	1.702(4)	1.699(5)	1.694(4)	1.698(4)
S(3)–C(4)	1.688(4)	1.681(4)	1.696(4)	1.688(4)
S(1)–Au(1)–S(2)	96.88(4)	96.91(4)	102.43(4)	100.87(4)
S(1)–Au(1)–P(1)	160.56(5)	159.30(5)	159.47(4)	159.75(4)
S(2)–Au(1)–P(1)	101.94(5)	102.98(5)	96.69(4)	97.21(4)

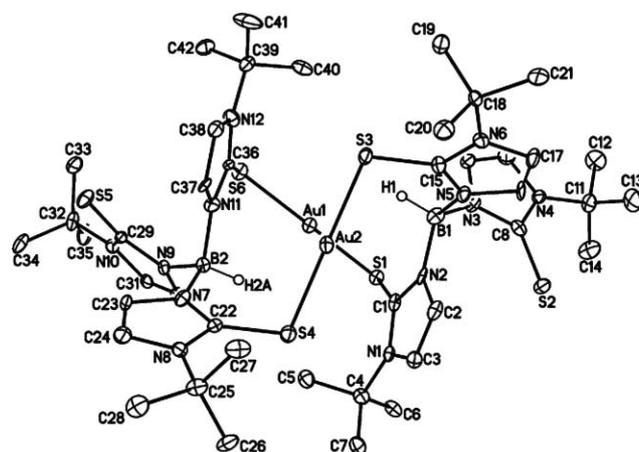
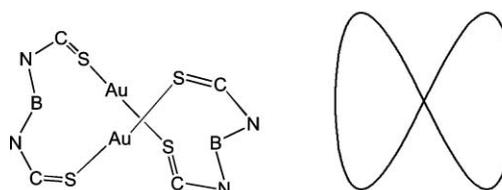
**Fig. 6** Molecular structure of one of the four independent but chemically identical molecules found in the unit cell of (Tm^{IBu})Au(PPh₃). Thermal ellipsoids are depicted at the 30% probability level. Hydrogen atoms (except for the one directly attached to boron) and solvent molecules are omitted for clarity.

with the third mercaptoimidazolyl group not coordinated to the metal. Accordingly, we note that: (i) the sum of angles subtended at the gold center is approximately 358.7°, (ii) the average S(1)–Au(1)–P(1) angle is 159.8°, and (iii) all the S(1)–Au–S(2) and S(2)–Au(1)–P(1) angles are in the relatively narrow range 96.7–103.0°. In addition, the degree of structural distortion from the ideal T-shape and regular trigonal planar geometries in this and other three-coordinate complexes could be estimated using a modified trigonality index $\tau = (\beta - \alpha)/90^\circ$ we introduce herein, where β and α are the largest and second-largest interligand angles.¹⁵ Thus, the value of $\tau = 0.64$ calculated for (Tm^{IBu})Au(PPh₃) is consistent with a distorted geometry in between the ideal T-shape ($\tau = 1$) and trigonal planar ($\tau = 0$) options. The [Tm^{IBu}][−] ligand in (Tm^{IBu})Au(PPh₃) exhibits a severely asymmetric bidentate (*i.e.*, anisobidentate) κ^2 -S,S coordination mode, with the two Au–S bond lengths differing by almost 0.50 Å, much like in the structure of (Bm^{Me})Au(PPh₃) mentioned above ($\Delta d = 0.46$ Å).¹⁴ More specifically, whereas the “short” Au–S bond lengths (average for the four independent molecules = 2.345 Å) are only slightly longer than the corresponding values found in a variety of thiourea and heterocyclic thione complexes of gold(I), all of which are in the relatively narrow range 2.25–2.33 Å,¹⁶ the “long” Au–S bond lengths (average = 2.838 Å) are clearly outside the norm. Despite the disparity in Au–S bond lengths, the Au–P bond distance (average = 2.250 Å) is very close to the mean value found in the CSD for three-coordinate gold phosphine complexes (2.295 Å).¹⁰ With regards to the Au...H bond distances in (Tm^{IBu})Au(PPh₃) (average = 2.47 Å), they are significantly weaker (*i.e.*, longer) than those in the only three compounds listed in the CSD that display such Au...H–B interactions (1.80–1.91 Å)¹⁷ and appear to have a negligible effect on the overall structure of the complexes.

Table 4 Selected bond lengths (Å) and angles (°) for Au(Tm^{IBu})

Au(1)–S(1)	2.291(2)	Au(2)–S(3)	2.291(2)
Au(1)–S(6)	2.295(2)	Au(2)–S(4)	2.299(2)
Au(1)...H(1)	2.96	Au(2)...H(1)	3.38
Au(1)...H(2)	2.96	Au(2)...H(2)	3.27
S(1)–Au(1)–S(6)	173.51(7)	S(3)–Au(2)–S(4)	176.94(8)
S(1)–Au(1)...H(1)	70.7	S(3)–Au(2)...H(1)	58.9
S(1)–Au(1)...H(2)	108.4	S(3)–Au(2)...H(2)	123.3
S(6)–Au(1)...H(1)	114.0	S(4)–Au(2)...H(1)	123.7
S(6)–Au(1)...H(2)	75.6	S(4)–Au(2)...H(2)	59.4
H(1)...Au(1)...H(2)	101.5	H(1)...Au(2)...H(2)	87.4

The molecular structure of Au(Tm^{IBu}) (Fig. 7, Table 4) also proved to be quite different from that of its silver analogue described above. The dinuclear complex displays a novel twisted 16-membered ring structure reminiscent of a bow-tie or a Lissajous curve (Fig. 8),¹⁸ with each gold center coordinated by a single thione group from a [Tm^{IBu}][−] ligand in an approximate linear fashion (S–Au–S \approx 173.5 and 176.9°). Significantly, the bridging bis(monodentate) coordination mode (μ - κ^1 -S: κ^1 -S) exhibited by the two borate ligands in [Au(Tm^{IBu})₂] is unprecedented in Tm^R chemistry, even though both monodentate

**Fig. 7** Molecular structure of Au(Tm^{IBu}). Thermal ellipsoids are depicted at 30% probability. Hydrogen atoms (except for those directly attached to boron) and solvent molecules are omitted for clarity.**Fig. 8** Schematic representation of the 16-membered ring in the molecular structure of [Au(Tm^{IBu})₂] and (to the right) a prototypical two-dimensional Lissajous curve described by the parametric equations $x(t) = A \sin(t + \pi/2)$ and $y(t) = B \sin(2t)$.

(κ^1 -S) and tris(monodentate) (μ - κ^1 -S: κ^1 -S: κ^1 -S) coordination modes have been previously identified in the main-group metal complexes ($\text{Tm}^{\text{Mc}}\text{SnR}_3$ (R = Ph, cyclohexyl)¹⁹ and $[(\text{Me}_2\text{Bi})_3(\text{Tm}^{\text{Bu}})]^+$,⁶ respectively. Although the two gold atoms in $[\text{Au}(\text{Tm}^{\text{Bu}})]_2$ are roughly facing each other halfway through the three-dimensional loop structure, their separation (Au...Au \approx 4.266 Å) precludes the existence of an aurophilic interaction²⁰ between them. The four unique Au–S bond lengths present in $[\text{Au}(\text{Tm}^{\text{Bu}})]_2$ are almost identical (2.291–2.299 Å) and fall within the range of values (2.25–2.33 Å) observed for such moieties in thione complexes of gold(I), as mentioned above.

Conclusions

The six tris(mercaptoimidazolyl)borate complexes ($\text{Tm}^{\text{Bu}}\text{M}(\text{PPh}_3)$ and $\text{M}(\text{Tm}^{\text{Bu}})$ (M = Cu, Ag, Au) comprise the first two complete series of Tm^{R} derivatives to be isolated for the coinage metals. Single-crystal X-ray diffraction studies have confirmed that whereas the triphenylphosphine derivatives are mononuclear in the solid state, the homoleptic compounds are dimeric. Significantly, $(\text{Tm}^{\text{Bu}})\text{Au}(\text{PPh}_3)$ and $\text{Au}(\text{Tm}^{\text{Bu}})$ are the first two Tm^{R} complexes of gold to be synthesized and structurally characterized and their structures have uncovered two new coordination modes for this ligand system: asymmetric bidentate (*i.e.*, anisobidentate) in the former and bridging bis(monodentate) in the latter. Our studies suggest that the presence of bulky tert-butyl substituents in the mercaptoimidazolyl rings tends to improve the solubility, stability, and crystallinity of $[\text{Tm}^{\text{Bu}}]^-$ complexes relative to those derived from $[\text{Tm}^{\text{Mc}}]^-$. However, the steric effect of the ring substituents on the overall structures and geometries of these types of complexes appears to be modest at best since analogous species such as $\text{Ag}(\text{Tm}^{\text{R}})$ and $(\text{Tm}^{\text{R}})\text{M}(\text{PR}_3)$ (M = Cu, Ag) (R = Me, Bu') exhibit comparable metrical parameters. This is in contrast to the related tris(pyrazolyl)borate family of ligands, for which the use of tert-butyl groups in the 3-position of the pyrazolyl rings has a profound effect on structure and reactivity and has earned ligands such as $[\text{Tp}^{\text{Bu}}]^-$ the reputation of “tetrahedral enforcers”.²¹

Experimental

1. General considerations

All reactions were performed under aerobic conditions unless otherwise noted, solvents were purified and degassed by standard procedures, and all commercially available reagents, including $(\text{Ph}_3\text{P})\text{AuCl}$ (Aldrich), were used as received. Whereas $\text{Na}(\text{Tm}^{\text{Bu}})$ was prepared as reported,³ the tetrahydrothiophene adduct $(\text{tht})\text{AuCl}$ was synthesized following a modified literature procedure,¹¹ starting from gold shot (99.99%, David H. Fell & Company, Inc.), which was dissolved in *aqua regia* [*i.e.*, a 3 : 1 mixture (v/v) of concentrated hydrochloric and nitric acids] to generate an aqueous solution of HAuCl_4 . ^1H and ^{13}C NMR spectra were obtained on Varian Gemini (300 MHz) or JEOL ECA-500 (500 MHz) FT spectrometers. Chemical shifts are reported in ppm relative to SiMe_4 ($\delta = 0$ ppm) for ^1H and ^{13}C and were referenced internally with respect to the solvent resonances (^1H : δ 7.24 for CHCl_3 ; ^{13}C : δ 77.0 for CDCl_3); coupling constants are given in hertz (Hz). IR spectra were recorded as KBr pellets on a Thermo Mattson Satellite 3000 FT-IR spectrophotometer and are reported in cm^{-1} ; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

2. Synthesis of $(\text{Tm}^{\text{Bu}})\text{Cu}(\text{PPh}_3)$

Methanol (8 mL) was added to a mixture of copper(I) chloride (0.020 g, 0.202 mmol), $\text{Na}(\text{Tm}^{\text{Bu}})$ (0.100 g, 0.200 mmol), and triphenylphosphine (0.052 g, 0.198 mmol), resulting in the immediate formation of a white suspension. After stirring for

45 min, a small amount of water (1 mL) was added to the reaction mixture and the product was isolated by filtration, washed with water (5 mL), and dried *in vacuo* for 18 h (0.118 g, 74%). Mp 248–251 °C. NMR data (in CDCl_3): ^1H δ 1.58 [s, 27H, $\text{C}(\text{CH}_3)_3$], 6.69 [br s, 3H, imidazole H], 6.79 [d, $^3J_{\text{H-H}} = 2.1$, 3H, imidazole H], 7.26 (br s, 6H, C_6H_5), 7.46 (br s, 9H, C_6H_5), BH not observed; ^{13}C δ 28.7 [q, $^1J_{\text{C-H}} = 127$, 9C, $\text{C}(\text{CH}_3)_3$], 58.3 [s, 3C, $\text{C}(\text{CH}_3)_3$], 114.7 [dd, $^1J_{\text{C-H}} = 192$, $^2J_{\text{C-H}} = 12$, 3C, imidazole C], 122.5 [br d, $^1J_{\text{C-H}} = 195$, 3C, imidazole C], 128.1 [dd, $^1J_{\text{C-H}} = 161$, $^3J_{\text{P-C}} = 9$, 6C, C_m], 128.8 [d, $^1J_{\text{C-H}} = 160$, 3C, C_p], 134.0 [dd, $^1J_{\text{C-H}} = 162$, $^2J_{\text{P-C}} = 16$, 6C, C_o], 161.4 [s, 3C, C = S], C_{ipso} not observed. IR data: 3186 (w), 3155 (w), 3047 (w), 2963 (w), 2921 (w), 2369 (w), 2292 (w), 2225 (w), 1645 (w), 1571 (w), 1539 (w), 1480 (w), 1435 (m), 1413 (m), 1394 (m), 1360 (s), 1291 (w), 1259 (w), 1222 (m), 1197 (s), 1175 (m), 1134 (w), 1094 (w), 1069 (w), 1029 (w), 928 (w), 821 (w), 760 (w), 743 (w), 718 (m), 692 (m), 682 (m), 591 (w), 558 (w), 519 (m), 497 (m), 458 (w), 431 (w). Anal. Calc. for $\text{C}_{39}\text{H}_{49}\text{BCuN}_6\text{PS}_3$: C, 58.3; H, 6.2; N, 10.5. Found: C, 58.6; H, 6.2; N, 10.4%.

3. Synthesis of $(\text{Tm}^{\text{Bu}})\text{Ag}(\text{PPh}_3)$

Methanol (10 mL) was added to a mixture of AgNO_3 (0.117 g, 0.600 mmol), $\text{Na}(\text{Tm}^{\text{Bu}})$ (0.300 g, 0.600 mmol), and triphenylphosphine (0.157 g, 0.599 mmol), resulting in the formation of a white suspension within 5 min. After stirring for 45 min, a small amount of water (1 mL) was added to the reaction mixture and the product was isolated by filtration, washed with water (5 mL), and dried *in vacuo* for 18 h (0.375 g, 74%). Mp 235–238 °C (decomp.). NMR data (in CDCl_3): ^1H δ 1.74 [s, 27H, $\text{C}(\text{CH}_3)_3$], 6.56 [br s, 3 H, imidazole H], 6.80 [br s, 3 H, imidazole H], 7.31 (br s, 6 H, C_6H_5), 7.49 (br s, 9 H, C_6H_5), BH not observed; ^{13}C δ 28.6 [q, $^1J_{\text{C-H}} = 128$, 9C, $\text{C}(\text{CH}_3)_3$], 58.3 [s, 3 C, $\text{C}(\text{CH}_3)_3$], 114.7 [dd, $^1J_{\text{C-H}} = 193$, $^2J_{\text{C-H}} = 11$, 3C, imidazole C], 119.9 [d, $^1J_{\text{C-H}} = 192$, 3 C, imidazole C], 128.5 [dd, $^1J_{\text{C-H}} = 161$, $^3J_{\text{P-C}} = 7$, 6C, C_m], 129.5 [d, $^1J_{\text{C-H}} = 160$, 3C, C_p], 134.1 [dd, $^1J_{\text{C-H}} = 162$, $^2J_{\text{P-C}} = 17$, 6C, C_o], 161.0 [s, 3C, C = S], C_{ipso} not observed. IR data: 3175 (w), 3144 (w), 3054 (w), 2953 (m), 2919 (m), 2381 (w), 2289 (w), 2233 (w), 1667 (w), 1586 (w), 1572 (w), 1479 (w), 1435 (m), 1412 (m), 1393 (m), 1353 (vs), 1294 (w), 1259 (w), 1221 (w), 1194 (s), 1173 (m), 1095 (w), 1066 (w), 1028 (w), 925 (w), 822 (w), 759 (w), 745 (m), 723 (w), 695 (m), 684 (w), 589 (w), 555 (w), 517 (m), 496 (m). Anal. Calc. for $\text{C}_{39}\text{H}_{49}\text{AgBN}_6\text{PS}_3$: C, 55.3; H, 5.8; N, 9.9. Found: C, 54.8; H, 5.8; N, 9.6%.

4. Synthesis of $(\text{Tm}^{\text{Bu}})\text{Au}(\text{PPh}_3)$

Methanol (15 mL) was added to a mixture of $\text{Na}(\text{Tm}^{\text{Bu}})$ (0.202 g, 0.404 mmol) and $(\text{Ph}_3\text{P})\text{AuCl}$ (0.200 g, 0.404 mmol), resulting in immediate formation of a brown solution and, within 5 min, an off-white precipitate. After stirring the suspension for 1 h and adding a small amount of water (*ca.* 2 mL), the product was isolated by filtration, washed with water (5 mL) and dried *in vacuo* for 16 h (0.321 g, 85%). Mp 222–224 °C (decomp.). NMR data (in CDCl_3): ^1H δ 1.72 [s, 27H, $\text{C}(\text{CH}_3)_3$], 6.07 [br s, 1H, BH], 6.73 [d, $^3J_{\text{H-H}} = 2.4$, 3 H, imidazole H], 6.79 [d, $^3J_{\text{H-H}} = 2.4$, 3H, imidazole H], 7.39 [br s, 9H, C_6H_5], 7.57 [m, 6H, C_6H_5]; ^{13}C δ 28.7 [q, $^1J_{\text{C-H}} = 127$, 9C, $\text{C}(\text{CH}_3)_3$], 58.2 [s, 3C, $\text{C}(\text{CH}_3)_3$], 114.7 [dd, $^1J_{\text{C-H}} = 193$, $^2J_{\text{C-H}} = 12$, 3C, imidazole C], 121.6 [dd, $^1J_{\text{C-H}} = 194$, $^2J_{\text{C-H}} = 10$, 3C, imidazole C], 128.8 [d, $^1J_{\text{C-H}} = 161$, $^3J_{\text{P-C}} = 11$, 6C, C_m], 130.9 [s, 3C, C_p], 134.5 [d, $^1J_{\text{C-H}} = 162$, $^2J_{\text{P-C}} = 14$, 6C, C_o], 159.3 [s, 3C, C = S], C_{ipso} not observed. IR data: 3154 (w), 3051 (w), 2974 (m), 2921 (w), 2411 (w), 1560 (w), 1479 (w), 1435 (m), 1397 (m), 1359 (s), 1304 (w), 1259 (m), 1199 (m), 1165 (m), 1099 (m), 821 (w), 750 (w), 708 (w), 694 (m), 535 (m), 510 (w). Anal. Calc. for $\text{C}_{39}\text{H}_{49}\text{AuBN}_6\text{PS}_3$: C, 50.0; H, 5.3; N, 9.0. Found: C, 49.8; H, 5.3; N, 8.8%.

5. Synthesis of $\text{Cu}(\text{Tm}^{\text{Bu}})$

Methanol (10 mL) was added to a mixture of $\text{Na}(\text{Tm}^{\text{Bu}})$ (0.200 g, 0.400 mmol) and copper(I) chloride (0.040 g, 0.404 mmol),

resulting in the formation of a slightly cloudy solution. After stirring for 1 h, the solution was filtered and the filtrate was concentrated under reduced pressure to *ca.* 2 mL. Addition of water (5 mL) resulted in the separation of the white solid, which was isolated by filtration and dried *in vacuo* for 18 h (0.168, 78%). Mp 207–209 °C. NMR data (in CDCl₃): ¹H δ 1.73 [s, 27H, C(CH₃)₃], 6.60 [br s, 3H, imidazole H], 6.75 [br s, 3H, imidazole H], BH not observed; ¹³C δ 28.8 [q, ¹J_{C-H} = 127, 9C, C(CH₃)₃], 58.5 [s, 3C, C(CH₃)₃], 114.7 [d, ¹J_{C-H} = 201, 3C, imidazole C], 119.9 [d, ¹J_{C-H} = 193, 3C, imidazole C], 159.6 [s, 3C, C=S]. IR data: 2975 (m), 2922 (w), 1638 (w), 1411 (m), 1361 (s), 1263 (w), 1198 (m), 1164 (m), 1103 (m), 821 (w), 715 (m), 681 (w). Anal. Calc. for C₂₁H₃₄BCuN₆S₃: C, 46.1; H, 6.3; N, 15.5. Found: C, 45.9; H, 6.3; N, 15.1%.

6. Synthesis of Ag(Tm^{IBu})

Methanol (25 mL) was added to a mixture of AgNO₃ (0.193 g, 0.991 mmol) and Na(Tm^{IBu}) (0.497 g, 0.993 mmol), resulting in the formation, within 5 min, of a white suspension. After stirring the suspension for an additional 1 h and adding a small amount of water (*ca.* 5 mL), the white product was isolated by filtration, washed with water (10 mL) and dried *in vacuo* for 18 h (0.468 g, 81%). Mp 245 °C (decomp.). NMR data (in CDCl₃): ¹H δ 1.75 [s, 27H, C(CH₃)₃], 6.46 (br s, 3H, imidazole H), 6.81 (br s, 3H, imidazole H), BH not observed; ¹³C δ 28.7 [q, ¹J_{C-H} = 127, 9C, C(CH₃)₃], 58.5 [s, 3C, C(CH₃)₃], 115.1 (d, ¹J_{C-H} = 198, 3C, imidazole C), 119.4 (d, ¹J_{C-H} = 188, 3C, imidazole C), 160.3 (s, 3C, C=S). IR data: 2976 (m), 2924 (w), 1638 (w), 1561 (w), 1481 (w), 1411 (m), 1397 (m), 1384 (m), 1359 (vs), 1277 (m), 1198 (m), 1163 (m), 1104 (m), 1060 (w), 820 (w), 722 (w), 683 (w), 559 (w), 478 (w). Anal. Calc. for C₂₁H₃₄AgBN₆S₃: C, 43.1; H, 5.9; N, 14.4. Found: C, 42.9; H, 6.0; N, 13.7%.

7. Synthesis of Au(Tm^{IBu})

Methanol (10 mL) was added to a mixture of Na(Tm^{IBu}) (0.300 g, 0.599 mmol) and (tht)AuCl (0.192 g, 0.599 mmol), resulting in the formation of a brown solution. After stirring for 1 h, the solution was filtered and the filtrate was concentrated under reduced pressure to *ca.* 5 mL. Addition of water (5 mL) resulted in the separation of a beige solid, which was isolated by filtration and dried *in vacuo* for 18 h (0.355, 88%). Mp 227–229 °C (decomp.). NMR data (in CDCl₃): ¹H δ 1.80 [s, 27H, C(CH₃)₃], 6.84 [br s, 6H, imidazole H], BH not observed; ¹³C δ 29.0 [q,

¹J_{C-H} = 127, 9C, C(CH₃)₃], 59.1 [s, 3C, C(CH₃)₃], 115.7 [d, ¹J_{C-H} = 195, 3C, imidazole C], 124.0 [d, ¹J_{C-H} = 196, 3C, imidazole C], 150.7 [s, 3C, C=S]. IR data: 3146 (w), 2975 (m), 2923 (w), 1655 (w), 1560 (w), 1480 (w), 1419 (w), 1398 (m), 1355 (s), 1303 (w), 1263 (w), 1200 (m), 1160 (m), 1102 (m), 1058 (w), 1002 (w), 982 (w), 823 (w), 720 (m), 682 (w). Anal. Calc. for C₂₁H₃₄AuBN₆S₃: C, 37.4; H, 5.1; N, 12.5. Found: C, 36.7; H, 5.1; N, 11.9%.

8. X-Ray structure determinations

A summary of crystal data collection and refinement parameters for (Tm^{IBu})Cu(PPh₃) (1), (Tm^{IBu})Ag(PPh₃)·H₂O (2), [Ag(Tm^{IBu})]₂·2CH₂Cl₂ (3), (Tm^{IBu})Au(PPh₃)·0.25C₆H₅Me (4), and [Au(Tm^{IBu})]₂·3.5C₆H₆ (5) is presented in Table 5. Suitable crystals were selected, mounted with viscous oil and cooled to the data collection temperatures. Data were collected either on Bruker AXS SMART or APEX CCD diffractometers using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Unit cell parameters were obtained from three sets of 20 frames using 0.3° scans from different sections of the Ewald sphere. Data sets were corrected for absorption using different versions of SADABS multiscan methods.²² No symmetry higher than triclinic was observed for Ag(Tm^{IBu}) nor (Tm^{IBu})Au(PPh₃). Systematic absences in the diffraction data and unit cell parameters are consistent for *Cc* and *C2/c* for Au(Tm^{IBu}), *R3*, *R3̄*, *R32*, *R3m*, and *R3m* for (Tm^{IBu})Cu(PPh₃), and *P3̄*, *P3̄*, *P321*, *P3m1*, *P3m1*, *P312*, *P31m*, and *P3̄1m* for (Tm^{IBu})Ag(PPh₃). The molecular symmetry and occupancy observed for (Tm^{IBu})Cu(PPh₃) is consistent only for *R3*. In a similar fashion, only *P3̄* and *P321* afford the proper symmetry and occupancy for (Tm^{IBu})Ag(PPh₃). In all the structures, except that of (Tm^{IBu})Cu(PPh₃), the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. Structures were solved using direct methods and refined with full-matrix least-squares methods based on *F*². The Flack parameter for (Tm^{IBu})Cu(PPh₃) refined to 0.46(1) suggesting a racemically twinned data crystal and the true hand of the data-set could not be determined. The dimeric molecule in Ag(Tm^{IBu}) is located on an inversion center. The structures of (Tm^{IBu})Cu(PPh₃) and (Tm^{IBu})Ag(PPh₃) are located on three-fold rotation axes. Four symmetry unique but chemically similar molecules of (Tm^{IBu})Au(PPh₃) are located in the asymmetric unit. Several structures display co-crystallized solvent molecules: Ag(Tm^{IBu}) has one CH₂Cl₂ disordered in two positions, (Tm^{IBu})Ag(PPh₃)

Table 5 Crystal, intensity collection, and refinement data

	(Tm ^{IBu})Cu(PPh ₃) (1)	(Tm ^{IBu})Ag(PPh ₃)·H ₂ O (2)	Ag(Tm ^{IBu}) ₂ ·2CH ₂ Cl ₂ (3)	(Tm ^{IBu})Au(PPh ₃)·0.25C ₆ H ₅ Me (4)	[Au(Tm ^{IBu})] ₂ ·3.5C ₆ H ₆ (5)
Formula	C ₃₉ H ₄₉ BCuN ₆ PS ₃	C ₃₉ H ₅₁ AgBN ₆ OPS ₃	C ₄₄ H ₇₂ Ag ₂ B ₂ Cl ₄ N ₁₂ S ₆	C _{40.75} H ₅₁ AuBN ₆ PS ₃	C ₆₃ H ₈₉ Au ₂ B ₂ N ₁₂ S ₆
Formula weight	803.34	865.69	1340.66	959.80	1622.38
Crystal system	Trigonal	Trigonal	Triclinic	Triclinic	Monoclinic
Space group	<i>R3</i> (no. 146)	<i>P3̄</i> (no. 147)	<i>P1̄</i> (no. 2)	<i>P1̄</i> (no. 2)	<i>C2/c</i> (no. 15)
<i>a</i> /Å	16.2864(7)	13.7388(6)	11.1232(6)	20.4526(17)	32.118(9)
<i>b</i> /Å	16.2864(7)	13.7388(6)	11.1843(6)	20.5057(18)	18.662(5)
<i>c</i> /Å	12.9249(11)	12.8691(11)	13.7964(8)	21.9610(19)	25.695(7)
<i>a</i> /°	90	90	95.443(1)	74.297(1)	90
<i>β</i> /°	90	90	112.811(1)	81.811(1)	114.016(3)
<i>γ</i> /°	120	120	106.636(1)	82.151(1)	90
<i>V</i> /Å ³	2969.0(3)	2103.7(2)	1474.14(14)	3212(3)	14068(7)
<i>Z</i>	3	2	1	8	8
<i>T</i> /K	213(2)	213(2)	100(2)	213(2)	120(2)
Radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D</i> _c /g cm ⁻³	1.348	1.367	1.510	1.461	1.531
μ(Mo-Kα)/mm ⁻¹	0.787	0.704	1.101	3.586	4.391
Reflections collected	6412	11327	11677	17720	28782
Independent reflections (<i>R</i> _{int})	2725 (0.0568)	3301 (0.0287)	6235 (0.0190)	39270 (0.0289)	10079 (0.0769)
No. of parameters	160	157	471	1900	784
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0427; 0.0992	0.0489; 0.1373	0.0331; 0.0785	0.0438; 0.1043	0.0445; 0.0786
<i>R</i> ₁ ; <i>wR</i> ₂ (all data) ^a	0.0440; 0.1000	0.0535; 0.1403	0.0383; 0.0808	0.0668; 0.1162	0.0712; 0.0891
GOF	1.036	1.141	1.095	1.022	1.013

^a Quantity minimized = $R(wF^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum (wF_o^2)^2 \}^{1/2}$; $R(F) = \sum |A| / \sum |F_o|$, $A = \|F_o\| - |F_c|$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$; $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$.

has one H₂O molecule located at a three-fold rotation axis, (Tm^{IBu})Au(PPh₃) has one toluene molecule in the asymmetric unit, and Au(Tm^{IBu}) displays four benzene molecules, one of which is located at a two-fold rotation axis yielding an equivalent of 3.5 benzene molecules per asymmetric unit. The hydrogen atoms in Ag(Tm^{IBu}) and the hydrogen atom attached to boron of (Tm^{IBu})Cu(PPh₃) were located from the electron density difference map with occupancies and isotropic displacement parameters based on the bonded non-hydrogen atom. All other hydrogen atoms were treated as idealized contributions except those on the disordered water molecule in (Tm^{IBu})Ag(PPh₃) which were ignored. All structure factors and anomalous displacement parameters are included in various versions of the SHELXTL program library.²²

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See <http://dx.doi.org/10.1039/b506046j> for crystallographic data in CIF or other electronic format.

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