

## Soft Scorpionates for surface Science: Supplementary material

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**Structural Analysis of  $[\text{Cu}(\kappa^3\text{-S,S,S-PhTm}^{\text{Me}})(\text{PCy}_3)]$ ,  $[\text{Ag}(\kappa^3\text{-S,S,S-PhTm}^{\text{Me}})(\text{PCy}_3)]$  and related compounds.**

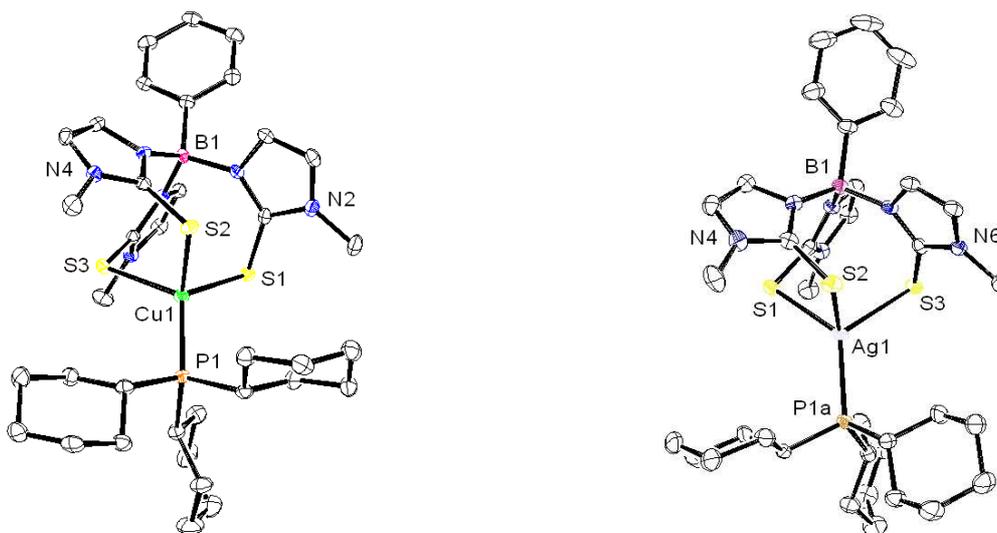


Figure S1. The X-ray crystal structures of  $[\text{Cu}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)]$  (left) and  $[\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)]$  (right, hydrogen atoms omitted for clarity). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for these complexes and the related  $\text{M}(\text{Tm})\text{PR}_3$  species can be found in table S1: Additional bond angles for copper: S(1)-Cu-S(2) 103.67(2), S(1)-Cu-S(3) 104.13(2), S(2)-Cu-S(3) 98.69(2) and silver; S(1)-Ag-S(2) 96.33(2), S(1)-Ag-S(3) 97.07(2), S(2)-Ag-S(3) 99.13(2).

X-ray crystallography analysis reveals that both  $\text{Cu}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)$  and  $\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)$  (Figure S1) have pseudo-tetrahedral geometry ( $\text{S}_3\text{P}$ ) with the ligand adopting a  $\kappa^3\text{-S,S,S}$  conformation. The analogous  $[\text{Cu}(\text{PhTm}^{\text{Me}})(\text{PPh}_3)]$  complex has been previously synthesised and also has pseudo-tetrahedral geometry [11d]. The  $[\text{Cu}(\text{PhTm}^{\text{Me}})(\text{PPh}_3)]$  complex exhibits a high degree of asymmetry which is reflected in the inequivalence of the Cu-S bond lengths (table S1). In comparison, the complex reported here is more symmetrical with all the Cu-S distances being essentially equal, a situation that is also observed in the analogous  $[\text{Cu}(\text{Tm}^{\text{Me}})(\text{PR}_3)]$  complexes (where  $\text{PR}_3 = \text{P}(o/m\text{-tolyl})_3$ ) [10d] along with Bailey's  $[\text{Cu}(\text{Tm}^{\text{Et}})(\text{PPh}_3)]$  [10c] and Patels's  $[\text{Cu}(\text{Tm}^{\text{tBu}})(\text{PPh}_3)]$  complexes [11a]. In contrast to  $\text{Cu}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)$ , the  $\kappa^3\text{-S,S,S}$  motif is somewhat unusual for silver. Both  $[\text{Ag}(\text{Tm}^{\text{Me}})(\text{PCy}_3)]$  [10b] and  $[\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PEt}_3)]$  [11d] have been previously synthesised

and exhibit the more common didentate coordination (table S1). The [Ag(Tm<sup>Me</sup>)(PCy<sub>3</sub>)] complex has an interaction from the hydride moiety which is attributed to the bulky PCy<sub>3</sub> ligand preventing the third sulfur atom from coordinating. Replacement of the BH moiety with a phenyl group in PhTm<sup>Me</sup> evidently eliminates the possibility for hydride interaction, however, the electronic and steric effect of the ligand alone do not impose κ<sup>3</sup> coordination, as is observed in the [Ag(PhTm<sup>Me</sup>)(PEt<sub>3</sub>)] complex [11d], where the ligand remains coordinated in κ<sup>2</sup> mode. Peculiarly, the complex reported here incorporates both the PhTm<sup>Me</sup> ligand and the bulky PCy<sub>3</sub> coligand, producing a complex with tridentate coordination, indicating that there is a subtle relationship between the RTm<sup>Me</sup> ligand and phosphine auxiliary ligand. The Ag-P bond length in the complex reported here (table S1) is typical of such complexes. As is seen in the analogous complexes there is a degree of asymmetry with the Ag-S distances of 2.5692(8), 2.6337(8) and 2.6381(7) Å being observed. However, these bond lengths are similar to those observed in the analogous [Ag(Tm<sup>Me</sup>)(PCy<sub>3</sub>)] and [Ag(PhTm<sup>Me</sup>)(PEt<sub>3</sub>)] complexes (table S1) [10b, 11d].

	Coord Mode	M-S (Å)	M-P (Å)	<S-M-P (°)	ref
Cu(Tm <sup>Me</sup> )P( <sup>m</sup> Tol) <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.357	2.217	114.00	10d
Cu(Tm <sup>Me</sup> )P( <sup>p</sup> Tol) <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.332	2.226	111.75	10d
Cu(Tm <sup>Et</sup> )PPh <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.387	2.229	115.83	10c
Cu(Tm <sup>tbu</sup> )PPh <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.353	2.221	114.02	11a
Ag(Tm <sup>Me</sup> )P <sup>i</sup> Pr <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.595	2.404	118.19	10a
Ag(Tm <sup>tbu</sup> )PPh <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.590	2.424	119.90	11a
Ag(Tm <sup>Me</sup> )PCy <sub>3</sub>	κ <sup>2</sup> -S,S-	2.603	2.420	126.37	10b
		2.581		119.67	
Au(Tm <sup>tbu</sup> )PPh <sub>3</sub>	κ <sup>2</sup> -S,S-	2.646	2.247	102.98	11a
		2.349		159.30	
Cu(PhTm <sup>Me</sup> )PPh <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.352	2.199	109.95	11d
		2.354		111.06	
		2.410		120.31	
Ag(PhTm <sup>Me</sup> )PEt <sub>3</sub>	κ <sup>2</sup> -S,S-	2.463	2.378	124.85	11d
		2.587		135.86	
Au(PhTm <sup>Me</sup> )PEt <sub>3</sub>	κ <sup>1</sup> -S-	2.333	2.268	171.54	11d
Cu(PhTm <sup>Me</sup> )PCy <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.3842(6)	2.2268(6)	118.98(2)	This work
		2.3762(6)		110.28(2)	
		2.3889(6),		118.34(2)	
Ag(PhTm <sup>Me</sup> )PCy <sub>3</sub>	κ <sup>3</sup> -S,S,S-	2.5692(8)	2.3959(8)	125.89(3)	This work
		2.6337(8)		119.39(3)	
		2.6381(7)		113.77(2)	

Table S1. The metrical parameters around the coinage metal centre for the family of complexes M(RTm<sup>R</sup>)PR<sub>3</sub>

## Computational Study

In order to make a more definitive assignment of the vibrational spectra of these species, a computational study was undertaken. The the structures of the  $\text{PhTm}^{\text{Me}}$  anion and two fragments,  $[\text{Ag}(\kappa^2\text{-S,S-PhTm}^{\text{Me}})]$  and  $[\text{Ag}(\kappa^3\text{-S,S,S-PhTm}^{\text{Me}})]$  were optimised and their vibrational spectra calculated. The structures of the optimised fragments are shown below (Figure S2) and the calculated Raman spectra are shown in Figure S3a-c, along with the observed solid state Raman spectra of structurally comparable complexes. The Raman vibrations from the calculated spectra, together with their assignment, are shown in Table S2. The vibrational modes are, on the whole, complex in nature and, although an attempt has been made to describe the major components, they are by no means complete descriptions. The Gaussian 03 output files can be requested from the authors if the reader wishes to inspect these in more detail.

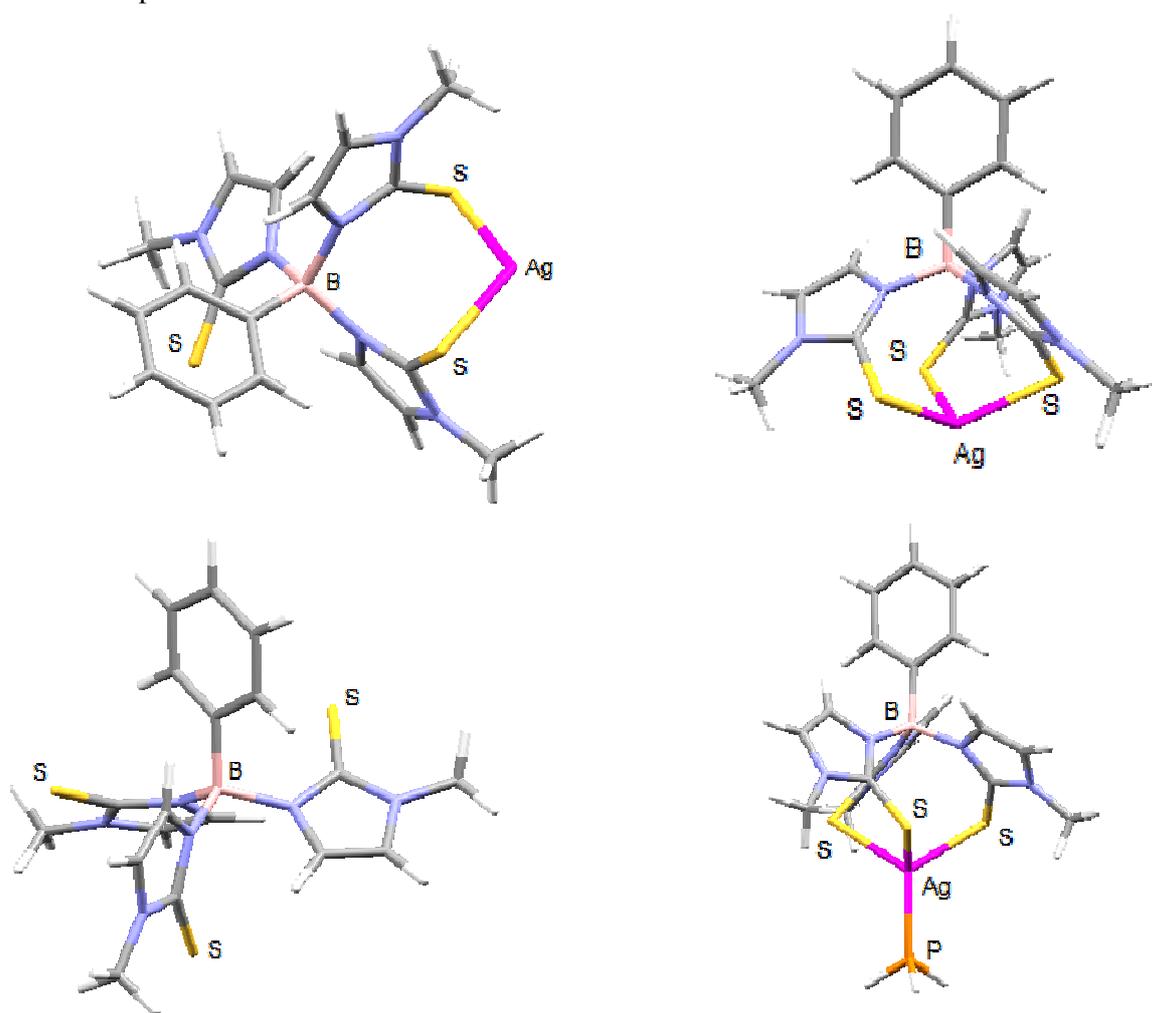


Figure S2: Calculated structures of the  $\text{PhTm}^{\text{Me}}$  anion (below, left),  $[\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PH}_3)]$  (below right) the  $[\text{Ag}(\kappa^2\text{-S,S-PhTm}^{\text{Me}})]$  fragment (above, left) and the  $[\text{Ag}(\kappa^3\text{-S,S,S-PhTm}^{\text{Me}})]$  fragment (above right).

Table S2: Calculated vibrational frequencies (cm<sup>-1</sup>), correlation with observed bands and assignments.

PhTm <sup>Me</sup> Calcd	LiPhTm <sup>Me</sup> Observed	[Ag( $\kappa^2$ -PhTm <sup>Me</sup> )] Calcd.	[Ag(PhTm <sup>Me</sup> )(PEt <sub>3</sub> )] Observed	[Ag( $\kappa^3$ -PhTm <sup>Me</sup> )] Calcd.	[Ag(PhTm <sup>Me</sup> )(PCy <sub>3</sub> )] Observed	[Ag(PhTm)(PH <sub>3</sub> )] Calcd	Assignment
523	535	491/495/526	532	509	530	515	$\nu(\text{C}=\text{S})$
579	613/618		622/636		607/616		mt out of plane ring deformation
620	635			645		645	mt out of plane ring deformation
699	712	687	690/714	691	677	692	$\nu(\text{N}-\text{CH}_3)$ / mt ring breathing
987	1001	988	1001	970/987	995	988	Ph ring breathing
1023	1032		1041	1015/1026	1028	1014/1026	Ph C-H rocking
1068	1090		1091	1070		1071	Ph C-H rocking
						1105	PH <sub>3</sub> P-H bending
1124	1152	1149/1160	1153	1113	1130	1154	mt C-H deformation + $\nu(\text{C}=\text{S})$
1202	1188	1192	1187	1201	1186/1201	1208	mt $\nu(\text{C}-\text{N})$
				1228	1268	1226	mt $\nu(\text{C}-\text{N})$
1265/1272	1283/1301	1261/1273	1309	1267	1290/1301/1314	1268	mt $\nu(\text{C}-\text{N})$
1325	1371	1319	1372	1322	1367	1324	mt $\nu(\text{C}-\text{N})$
1384	1406	1389	1411	1385	1405	1391	Me H-C-H bending/ mt C-C-H bending
1428	1453	1433/1442	1460	1436	1440	1437	Me H-C-H bending
1480	1471	1475		1477		1477	Me H-C-H bending/ Ph C-C-H bending
1547	1565	1535/1550	1567	1546	1567/1575	1549	Ph $\nu(\text{C}=\text{C})$ / mt $\nu(\text{C}=\text{C})$
1572	1592	1574	1595	1571	1591	1572	Ph $\nu(\text{C}=\text{C})$

mtH = methimazole

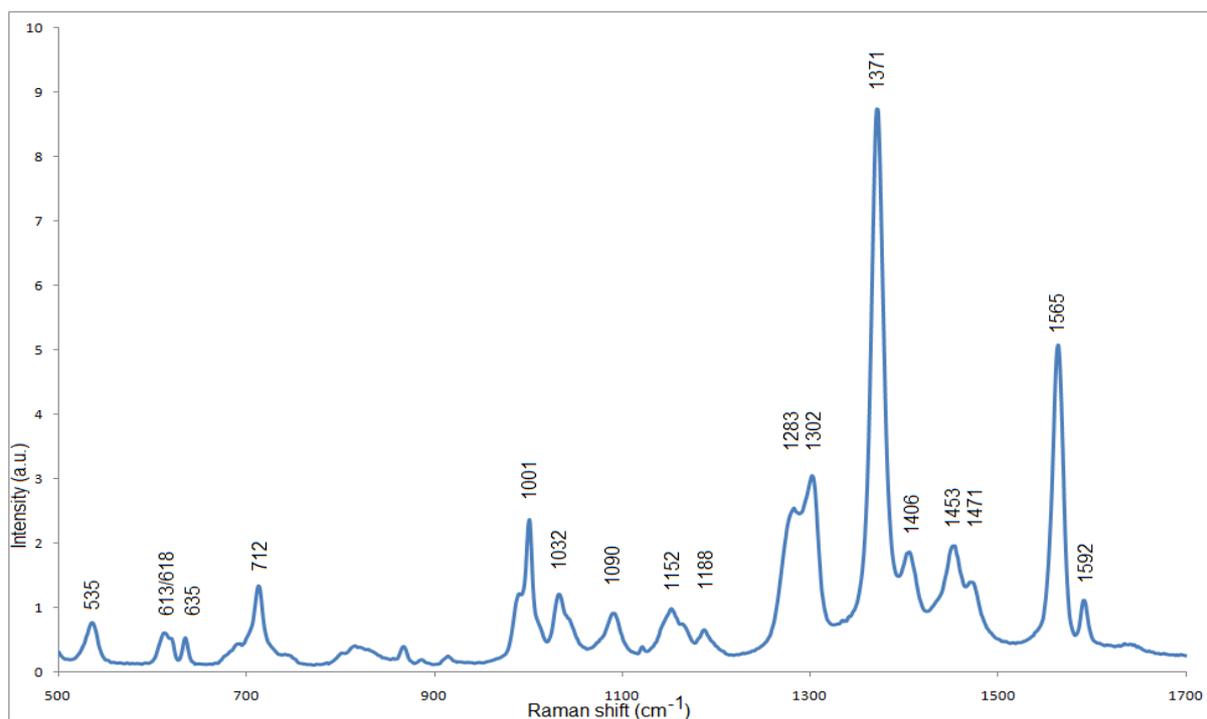
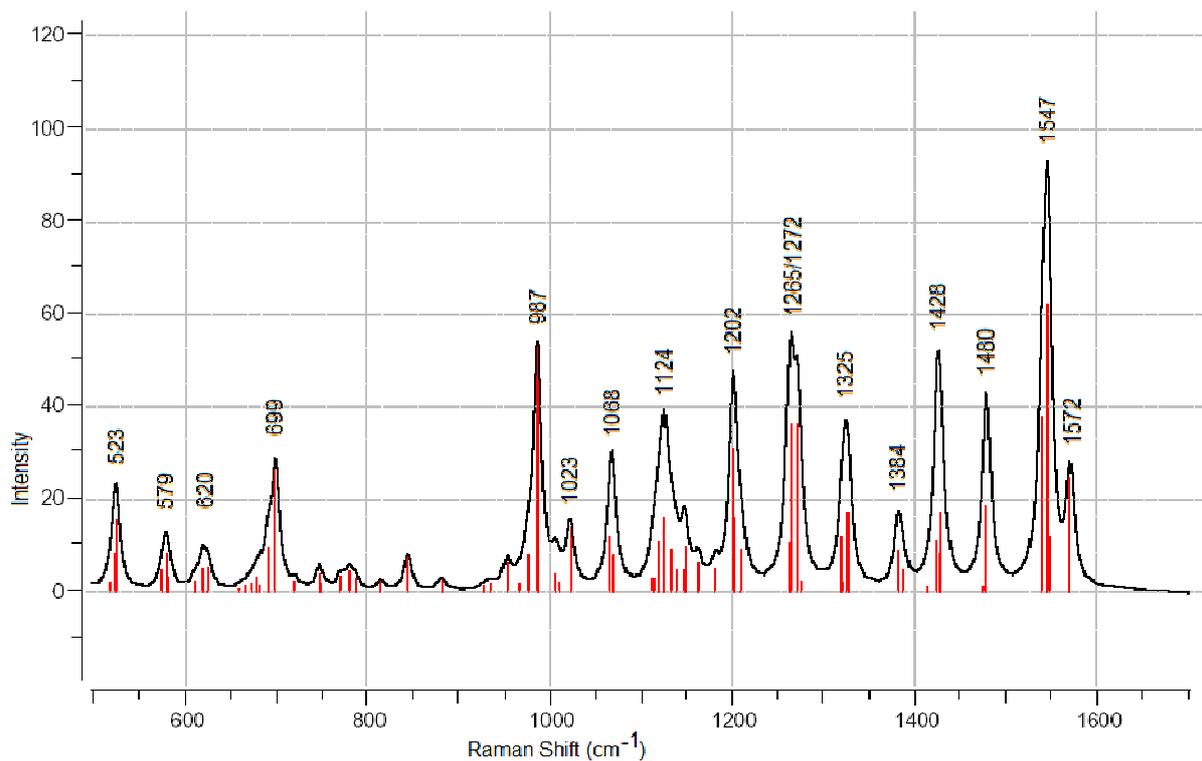


Figure S3a: Calculated (above) and Observed (below) Raman Spectra of  $\text{PhTm}^{\text{Me}}$ .

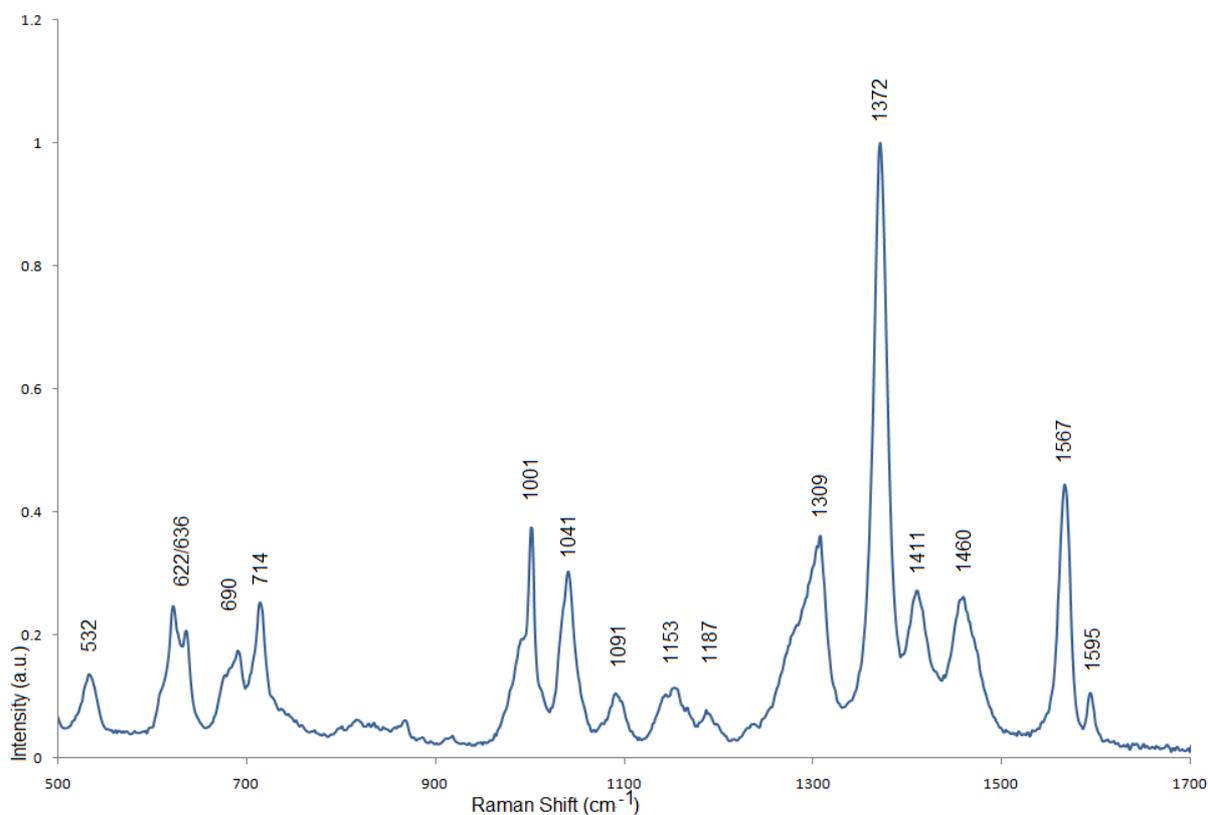
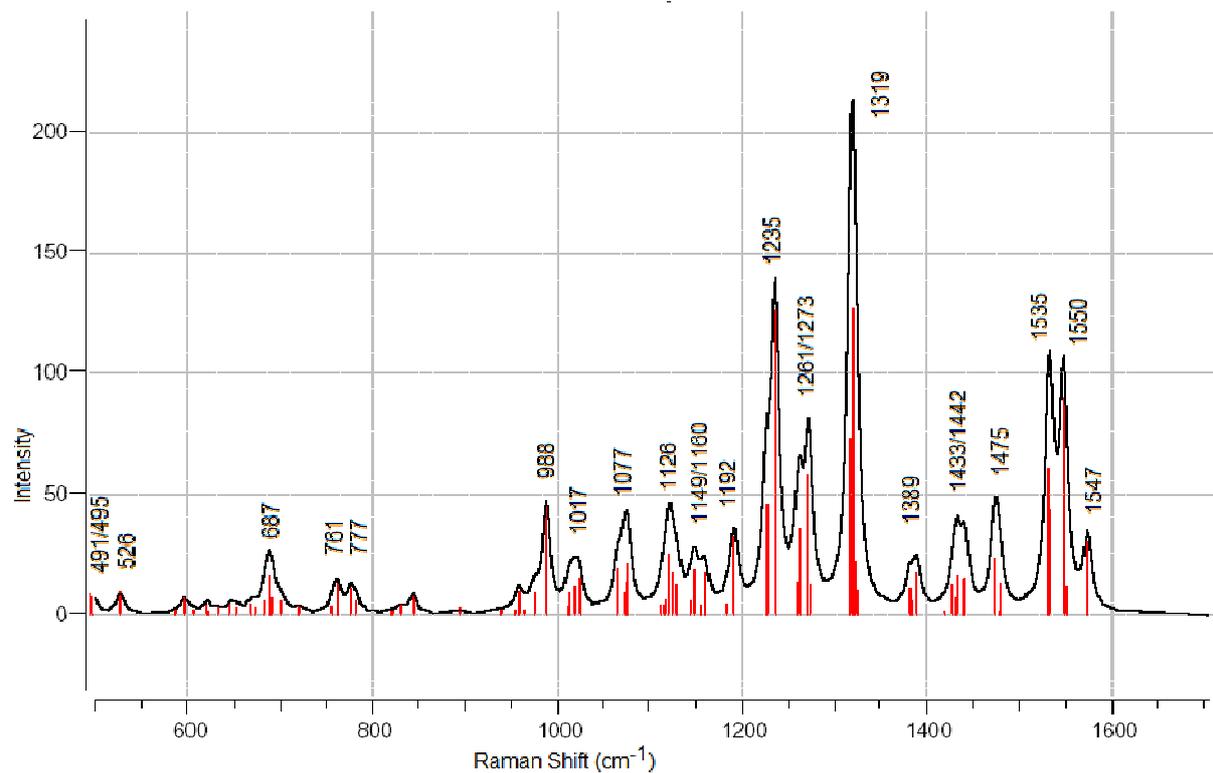


Figure S3b: Calculated Raman Spectrum of  $[\text{Ag}(\kappa^2\text{-S,S-PhTm}^{\text{Me}})]$  (above) and Observed Raman spectrum of  $[\text{Ag}(\kappa^2\text{-S,S-PhTm}^{\text{Me}})(\text{PEt}_3)]$ .

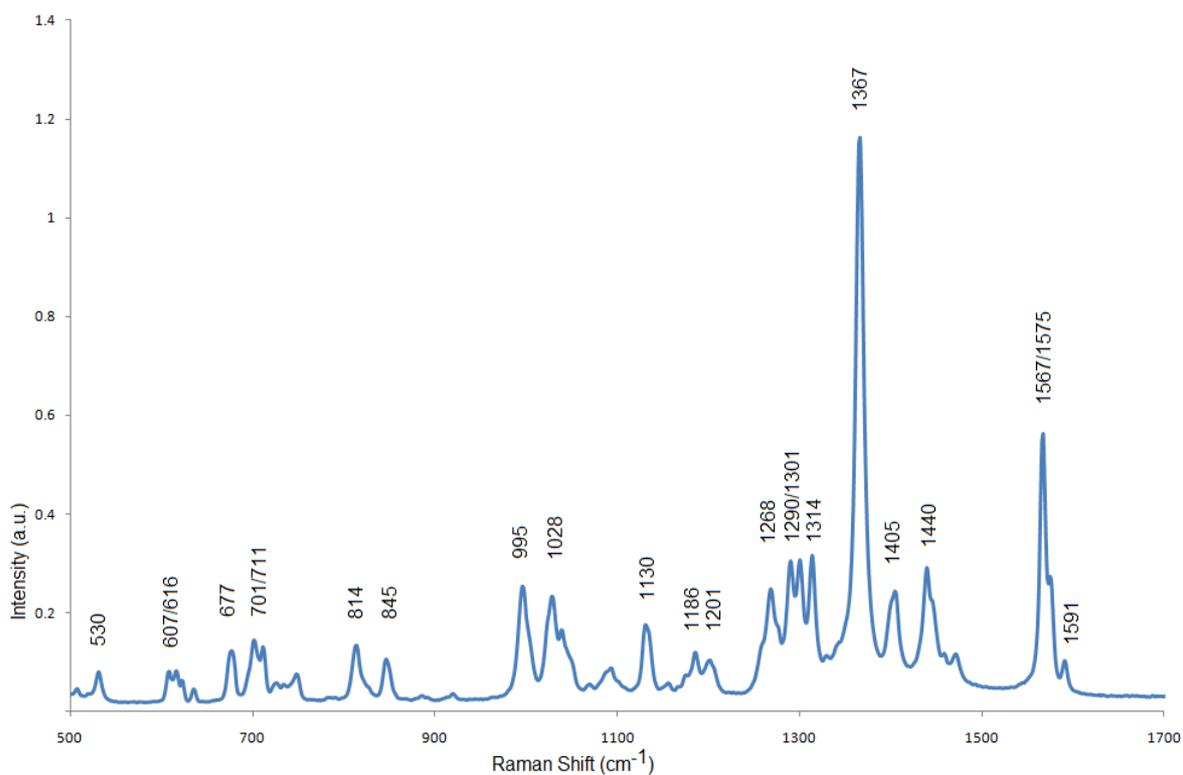
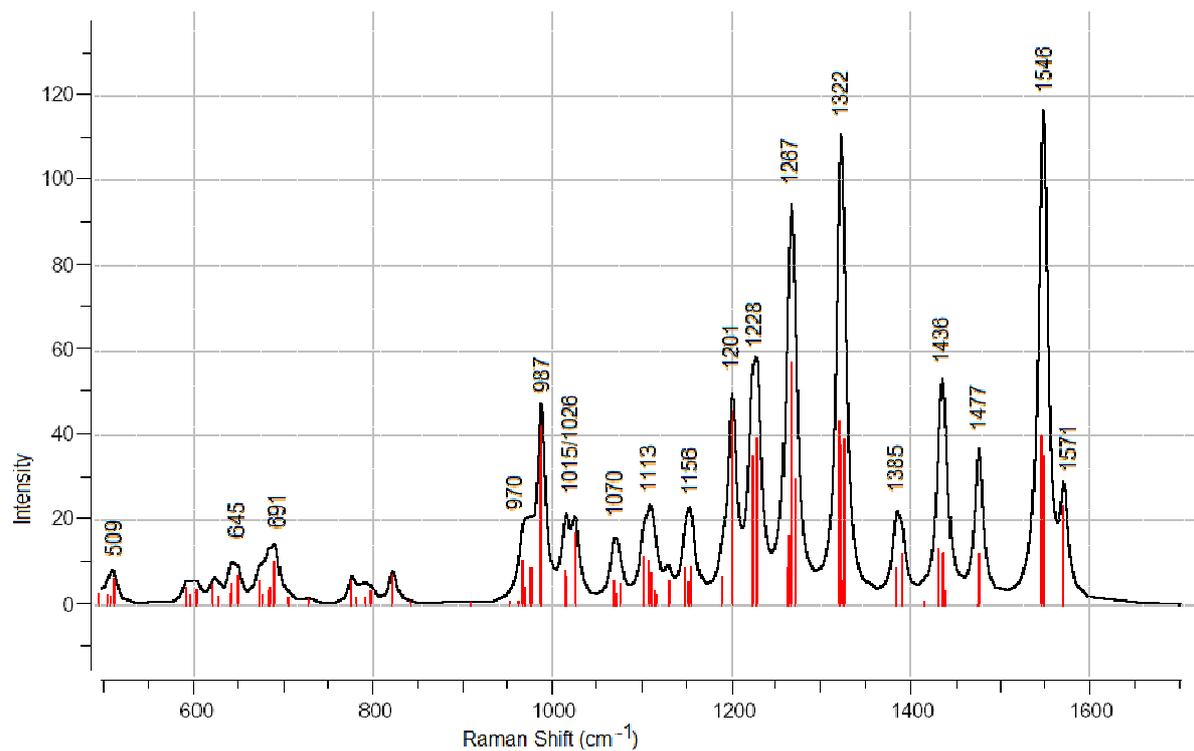


Figure S3c: Calculated Raman Spectrum of  $[\text{Ag}(\kappa^3\text{-S,S,S-PhTm}^{\text{Me}})]$  (above) and the observed Raman spectrum of  $[\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PCy}_3)]$  (below).

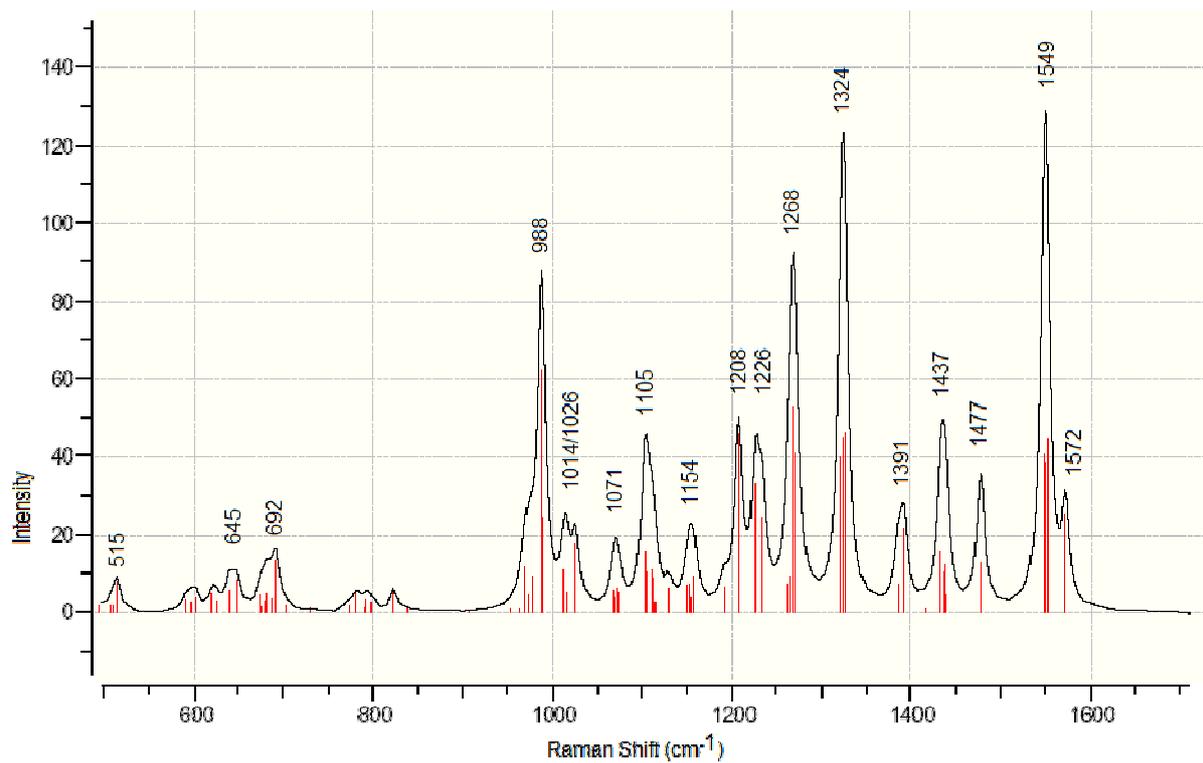


Figure S3d: Calculated Raman spectrum of  $[\text{Ag}(\text{PhTm}^{\text{Me}})(\text{PH}_3)]$ .