

SUPPORTING INFORMATION

Synthesis and Structural Characterization of *Bis* and *Tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato Complexes: Benzannulation Promotes κ^3 -Coordination

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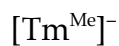
Table 1. Cartesian coordinates for geometry optimized structures of $[\text{Tm}^{\text{Me}}]^-$ anion (energies in parentheses are for the geometry optimization basis set, while those not in parentheses are for the single point basis set).

$[\text{Tm}^{\text{Me}}]^-$
(three sulfur donors in a plane on the same side of the molecule as the hydride)

-2015.37404686569 Hartrees
(-2015.02068193452 Hartrees)

| atom | x | y | z |
|------|--------------|-------------|-------------|
| B | 3.67415581 | 9.879062558 | 7.935441942 |
| H | 3.470140832 | 11.03491665 | 7.740480566 |
| S | 4.245685492 | 11.54650733 | 10.82650718 |
| S | 0.452667534 | 10.21946612 | 6.953401491 |
| S | 5.7839117 | 10.92428317 | 5.501988333 |
| N | 4.908432009 | 9.672193641 | 8.888098983 |
| N | 6.391061188 | 9.873347656 | 10.50240764 |
| N | 2.430888716 | 9.187457536 | 8.605950569 |
| N | 0.384718782 | 8.591240321 | 9.156133106 |
| N | 3.975895844 | 9.120128342 | 6.591486165 |
| N | 4.704351881 | 8.578187277 | 4.586525811 |
| C | 7.078080362 | 10.33073375 | 11.68834321 |
| H | 8.042017736 | 10.78535617 | 11.42981328 |
| H | 7.252431389 | 9.4985451 | 12.38144583 |
| H | 6.437080047 | 11.07753469 | 12.16242359 |
| C | 5.179357677 | 10.36610526 | 10.0426478 |
| C | 6.855822359 | 8.886923192 | 9.641789301 |
| C | 5.938068142 | 8.772128764 | 8.653893259 |
| C | -1.055756251 | 8.479608465 | 9.176199834 |
| H | -1.433986204 | 9.059448735 | 8.331142017 |

| | | | |
|---|--------------|-------------|-------------|
| H | -1.46453272 | 8.881964291 | 10.11085231 |
| H | -1.366349775 | 7.43239185 | 9.074514511 |
| C | 1.113442451 | 9.346390484 | 8.249901398 |
| C | 1.245488806 | 7.973645884 | 10.05456785 |
| C | 2.499199548 | 8.346921884 | 9.707647686 |
| C | 5.390190135 | 8.620392885 | 3.315548004 |
| H | 6.007413209 | 9.521717762 | 3.314063295 |
| H | 4.673021006 | 8.664222192 | 2.487103208 |
| H | 6.02682178 | 7.736175339 | 3.187587055 |
| C | 4.796160976 | 9.546292988 | 5.574888952 |
| C | 3.841418114 | 7.568793773 | 4.994088843 |
| C | 3.399519366 | 7.912164804 | 6.226222759 |
| H | 0.885099217 | 7.352697976 | 10.85976557 |
| H | 3.441721784 | 8.104471892 | 10.16779567 |
| H | 5.939254758 | 8.138717267 | 7.783379542 |
| H | 7.796381277 | 8.38318281 | 9.801179907 |
| H | 2.699938136 | 7.409295454 | 6.871755367 |
| H | 3.609696002 | 6.723568578 | 4.365019344 |



(two sulfur donors in a plane on the same side of the molecule as the hydride)

-2015.37916759418 Hartrees

(-2015.02634233218 Hartrees)

| atom | x | y | z |
|------|-------------|-------------|-------------|
| B | 3.555489456 | 9.783605934 | 8.000742496 |
| H | 3.410283628 | 10.96527093 | 7.906875581 |
| S | 4.446853904 | 11.6689539 | 10.64499747 |
| S | 0.45451563 | 10.4682087 | 6.970479917 |

| | | | |
|---|--------------|-------------|-------------|
| S | 3.655120079 | 6.477591382 | 6.72895048 |
| N | 4.788138767 | 9.506109167 | 8.926289587 |
| N | 6.373969575 | 9.735525151 | 10.43515384 |
| N | 2.274939899 | 9.139722397 | 8.593861248 |
| N | 0.174434253 | 8.674212981 | 9.028503708 |
| N | 3.836048338 | 9.258069131 | 6.538479532 |
| N | 4.005878417 | 8.189522262 | 4.623519774 |
| C | 7.168709181 | 10.24456634 | 11.52895834 |
| H | 8.140955513 | 10.60814265 | 11.1733671 |
| H | 7.336946347 | 9.462548175 | 12.27906648 |
| H | 6.612655193 | 11.07291873 | 11.97354074 |
| C | 5.192744369 | 10.29547306 | 9.978773084 |
| C | 6.690283074 | 8.615815757 | 9.673731217 |
| C | 5.710087469 | 8.480073924 | 8.750693556 |
| C | -1.26852115 | 8.655227275 | 8.974402352 |
| H | -1.570123619 | 9.348249819 | 8.185822808 |
| H | -1.697396039 | 8.976402296 | 9.931445883 |
| H | -1.636152643 | 7.648749619 | 8.739762143 |
| C | 0.992025162 | 9.424406875 | 8.204337249 |
| C | 0.950662509 | 7.936319687 | 9.915368615 |
| C | 2.241169354 | 8.228560272 | 9.635219865 |
| C | 4.03006358 | 7.13784158 | 3.631762608 |
| H | 3.996227426 | 6.185839374 | 4.16506842 |
| H | 4.946452971 | 7.197343146 | 3.032904906 |
| H | 3.163164977 | 7.211434716 | 2.964404828 |
| C | 3.819358684 | 8.005490153 | 5.979784643 |
| C | 4.130509275 | 9.545233879 | 4.345284062 |
| C | 4.018834893 | 10.19054825 | 5.528195046 |

| | | | |
|---|-------------|-------------|-------------|
| H | 0.512185635 | 7.273726355 | 10.64459874 |
| H | 3.148477877 | 7.860998354 | 10.08286733 |
| H | 5.554622371 | 7.715475109 | 8.004677972 |
| H | 7.570478286 | 8.022726919 | 9.867417667 |
| H | 4.020346252 | 11.24347513 | 5.75404834 |
| H | 4.258327937 | 9.912720925 | 3.339409616 |

[Tm^{Me}]⁻

(zero sulfur donor in a plane on the same side of the molecule as the hydride)

-2015.35581895299 Hartrees

(-2015.00069559300 Hartrees)

| atom | x | y | z |
|------|-------------|-------------|-------------|
| B | 3.647589232 | 9.623521589 | 8.039160692 |
| H | 3.48704959 | 10.82365563 | 7.882222642 |
| S | 6.53913706 | 7.529132524 | 7.969424456 |
| S | 2.9654314 | 7.432085878 | 10.77800913 |
| S | 2.395207515 | 6.756050099 | 6.312589829 |
| N | 4.857389925 | 9.503019476 | 9.011908768 |
| N | 6.632758249 | 9.057396961 | 10.22688141 |
| N | 2.306424076 | 9.112839575 | 8.64415898 |
| N | 0.59434616 | 8.177880402 | 9.654308901 |
| N | 3.939066451 | 9.066693766 | 6.614435403 |
| N | 4.211721879 | 8.008243199 | 4.708527549 |
| C | 7.849057569 | 8.448672605 | 10.71228107 |
| H | 7.683695333 | 7.985546873 | 11.69214662 |
| H | 8.651279168 | 9.192500989 | 10.79908207 |
| H | 8.134974434 | 7.683473734 | 9.9871686 |
| C | 5.966762968 | 8.693479099 | 9.065830843 |

| | | | |
|---|--------------|-------------|-------------|
| C | 5.949105165 | 10.079382 | 10.86953002 |
| C | 4.864035534 | 10.34868785 | 10.11313193 |
| C | -0.200018248 | 7.355041164 | 10.53595405 |
| H | 0.494214679 | 6.835620591 | 11.20028718 |
| H | -0.779156492 | 6.622393057 | 9.96161218 |
| H | -0.888884221 | 7.969662662 | 11.1292429 |
| C | 1.979953406 | 8.242708913 | 9.656525819 |
| C | 0.078885987 | 9.002281139 | 8.664569687 |
| C | 1.137655425 | 9.575197853 | 8.054144786 |
| C | 4.120156213 | 7.02043396 | 3.658992445 |
| H | 3.421417995 | 6.253945232 | 4.001395069 |
| H | 5.100974059 | 6.568761008 | 3.469450645 |
| H | 3.74757458 | 7.469414658 | 2.729447651 |
| C | 3.532482897 | 7.954229465 | 5.916958045 |
| C | 5.012478993 | 9.140133463 | 4.660523207 |
| C | 4.833821693 | 9.785100587 | 5.832671986 |
| H | 4.068428397 | 11.05955009 | 10.26627376 |
| H | 6.290680182 | 10.49977818 | 11.80230897 |
| H | -0.981039751 | 9.08684174 | 8.483216295 |
| H | 1.174232812 | 10.26404769 | 7.225932013 |
| H | 5.282930218 | 10.69235877 | 6.202758589 |
| H | 5.637604705 | 9.364818229 | 3.81064066 |

Table 2. Cartesian coordinates for geometry optimized structures of $[\text{Tm}^{\text{MeBenz}}]^-$ anion (energies in parentheses are for the geometry optimization basis set, while those not in parentheses are for the single point basis set).

$[\text{Tm}^{\text{MeBenz}}]^-$
(three sulfur donors in a plane on the same side of the molecule as the hydride)

-2476.46399494482 Hartrees
(-2475.98546502323 Hartrees)

| atom | x | y | z |
|------|-------------|-------------|-------------|
| B | 3.792939867 | 9.478591231 | 8.046239671 |
| H | 3.643803472 | 10.63723967 | 7.838015585 |
| S | 4.180519808 | 11.45404192 | 10.61269202 |
| S | 0.863949839 | 10.33689687 | 6.899988876 |
| S | 5.802928677 | 10.80576209 | 5.854844175 |
| N | 4.975871558 | 9.311871188 | 9.065888773 |
| N | 6.41950333 | 9.906983656 | 10.66005123 |
| N | 2.455820357 | 8.908924947 | 8.64389197 |
| N | 0.268057851 | 8.804554033 | 9.06888346 |
| N | 4.133341702 | 8.774053287 | 6.684368636 |
| N | 4.838629418 | 8.602849086 | 4.575273035 |
| C | 7.029232768 | 10.60996945 | 11.76392329 |
| H | 7.981783506 | 11.05902496 | 11.45809262 |
| H | 7.212819832 | 9.926077057 | 12.60177356 |
| H | 6.334593807 | 11.3939519 | 12.07156747 |
| C | 5.190135145 | 10.21915052 | 10.08387696 |
| C | 6.965094526 | 8.805372994 | 10.03258079 |
| C | 6.050351245 | 8.421470178 | 9.029737582 |
| C | 6.312849978 | 7.279142046 | 8.267772749 |
| H | 5.619987001 | 6.929671791 | 7.515626289 |

| | | | |
|---|--------------|-------------|-------------|
| C | 7.49836092 | 6.576800593 | 8.511130879 |
| H | 7.711022288 | 5.690103658 | 7.919768097 |
| C | 8.406845244 | 6.984467918 | 9.493583478 |
| H | 9.319449841 | 6.417037831 | 9.655623697 |
| C | 8.145948229 | 8.111569134 | 10.27877776 |
| H | 8.834525617 | 8.431745193 | 11.05469046 |
| C | -1.157415667 | 9.0122532 | 8.974323871 |
| H | -1.334559318 | 9.648618212 | 8.105141239 |
| H | -1.537787615 | 9.504943017 | 9.877173387 |
| H | -1.678189041 | 8.055220007 | 8.846784608 |
| C | 1.22230342 | 9.356170859 | 8.217089978 |
| C | 0.885185604 | 8.001130632 | 10.00656155 |
| C | 2.268413915 | 8.058889101 | 9.735318791 |
| C | 3.145610481 | 7.28108835 | 10.49671779 |
| H | 4.207723189 | 7.269135837 | 10.29882302 |
| C | 2.614663005 | 6.495052234 | 11.52475393 |
| H | 3.291491147 | 5.890468817 | 12.12265414 |
| C | 1.242669391 | 6.465987025 | 11.7958657 |
| H | 0.863464845 | 5.845214096 | 12.60333969 |
| C | 0.35090307 | 7.222040995 | 11.02842893 |
| H | -0.717969191 | 7.199109359 | 11.21730583 |
| C | 5.500884546 | 8.888264923 | 3.324339067 |
| H | 6.07041488 | 9.809361037 | 3.462502277 |
| H | 4.767653565 | 9.023510796 | 2.520213588 |
| H | 6.17836451 | 8.069917146 | 3.052130768 |
| C | 4.900132174 | 9.394353732 | 5.720342938 |
| C | 4.066629291 | 7.484477891 | 4.819138822 |
| C | 3.625707641 | 7.586403126 | 6.155425386 |

| | | | |
|---|-------------|-------------|-------------|
| C | 2.868707848 | 6.5473641 | 6.70506871 |
| H | 2.541820748 | 6.56867408 | 7.734795232 |
| C | 2.550219762 | 5.455061163 | 5.890658133 |
| H | 1.959420841 | 4.645035224 | 6.310313022 |
| C | 2.975417187 | 5.3800761 | 4.560030747 |
| H | 2.708826321 | 4.51782182 | 3.954526214 |
| C | 3.751714963 | 6.401437445 | 4.003765958 |
| H | 4.101140724 | 6.350787942 | 2.977100165 |



(two sulfur donors in a plane on the same side of the molecule as the hydride)

-2476.46840182634 Hartrees

(-2475.98939166979 Hartrees)

| atom | x | y | z |
|------|-------------|-------------|-------------|
| B | 3.700317264 | 9.543438487 | 8.137134278 |
| H | 3.526924912 | 10.71883697 | 8.064824003 |
| S | 4.477226991 | 11.60789468 | 10.58078246 |
| S | 0.78870542 | 10.4538576 | 7.068986485 |
| S | 2.867072355 | 6.558301742 | 6.462461924 |
| N | 4.9519895 | 9.334778786 | 9.073076206 |
| N | 6.563277251 | 9.865851746 | 10.52610177 |
| N | 2.400001927 | 8.910138169 | 8.699162008 |
| N | 0.212579941 | 8.659412807 | 9.034091625 |
| N | 4.038003337 | 9.064947687 | 6.672657357 |
| N | 4.045304943 | 8.182079303 | 4.626770609 |
| C | 7.305205867 | 10.54059038 | 11.56559064 |
| H | 8.260778391 | 10.91594938 | 11.17969511 |
| H | 7.505369743 | 9.855991628 | 12.39867594 |

| | | | |
|---|--------------|-------------|-------------|
| H | 6.694479428 | 11.3769297 | 11.91039397 |
| C | 5.318848929 | 10.25478006 | 10.03705386 |
| C | 6.980334467 | 8.713350474 | 9.887660037 |
| C | 5.960102019 | 8.368528027 | 8.980156677 |
| C | 6.070368761 | 7.195823497 | 8.229403042 |
| H | 5.269328453 | 6.861645256 | 7.581084806 |
| C | 7.22944384 | 6.427487277 | 8.381420217 |
| H | 7.327966156 | 5.512929563 | 7.802872051 |
| C | 8.251101972 | 6.797325509 | 9.264154987 |
| H | 9.138307178 | 6.176176285 | 9.355442364 |
| C | 8.135309624 | 7.951300576 | 10.04408266 |
| H | 8.910413583 | 8.240182851 | 10.74730038 |
| C | -1.218211345 | 8.792686109 | 8.90175483 |
| H | -1.404557358 | 9.510443917 | 8.100781122 |
| H | -1.660974617 | 9.158350053 | 9.836333844 |
| H | -1.671623937 | 7.826791576 | 8.648423621 |
| C | 1.159704295 | 9.336338322 | 8.27586441 |
| C | 0.843488575 | 7.810263044 | 9.921665761 |
| C | 2.227825161 | 7.960315254 | 9.705679407 |
| C | 3.12114946 | 7.194863718 | 10.45762862 |
| H | 4.187955727 | 7.256998586 | 10.30356099 |
| C | 2.602132839 | 6.315911615 | 11.41301239 |
| H | 3.292093833 | 5.715463551 | 12.00021219 |
| C | 1.22498164 | 6.186188728 | 11.62321676 |
| H | 0.854613509 | 5.492519345 | 12.37354991 |
| C | 0.318915715 | 6.937529923 | 10.87003707 |
| H | -0.752979117 | 6.84256454 | 11.01444918 |
| C | 3.812543665 | 7.281912052 | 3.521700621 |

| | | | |
|---|-------------|-------------|-------------|
| H | 3.294923472 | 6.406190577 | 3.917156154 |
| H | 4.763068896 | 6.976589643 | 3.067553371 |
| H | 3.192301729 | 7.763917751 | 2.756719395 |
| C | 3.6386289 | 7.971830178 | 5.942454194 |
| C | 4.712146446 | 9.388954251 | 4.528933134 |
| C | 4.703294661 | 9.946144356 | 5.818212888 |
| C | 5.307259893 | 11.18128702 | 6.053934029 |
| H | 5.292584506 | 11.62837365 | 7.040626764 |
| C | 5.915150446 | 11.82524213 | 4.972073234 |
| H | 6.390215729 | 12.78921473 | 5.133268477 |
| C | 5.922241248 | 11.26094943 | 3.689034133 |
| H | 6.403562938 | 11.78966966 | 2.870687781 |
| C | 5.313853098 | 10.02561391 | 3.446416157 |
| H | 5.307839729 | 9.582190275 | 2.45537254 |



(zero sulfur donor in a plane on the same side of the molecule as the hydride)

-2476.46058227102 Hartrees

(-2475.98056080269 Hartrees)

| atom | x | y | z |
|------|-------------|-------------|-------------|
| B | 3.644564721 | 9.671558143 | 8.029925584 |
| H | 3.484852666 | 10.86313474 | 7.87554086 |
| S | 6.425090389 | 7.520482646 | 8.031967199 |
| S | 2.980370951 | 7.388609295 | 10.61937027 |
| S | 2.532649502 | 6.764354944 | 6.401693037 |
| N | 4.825437588 | 9.554770557 | 9.03472656 |
| N | 6.624852284 | 9.070335363 | 10.24994542 |
| N | 2.289814143 | 9.160139148 | 8.597235866 |

| | | | |
|---|--------------|-------------|-------------|
| N | 0.580044829 | 8.190560797 | 9.641170943 |
| N | 3.973672564 | 9.126979811 | 6.611841202 |
| N | 4.23206366 | 8.019955438 | 4.698939356 |
| C | 7.833386818 | 8.43414747 | 10.71703575 |
| H | 7.675077758 | 7.993307181 | 11.70836911 |
| H | 8.654768783 | 9.159073033 | 10.77668066 |
| H | 8.085009739 | 7.650513052 | 10.00019866 |
| C | 5.918750113 | 8.718523606 | 9.097973157 |
| C | 5.992849373 | 10.11362107 | 10.8959734 |
| C | 4.857744548 | 10.4202514 | 10.12606965 |
| C | 4.00060618 | 11.44796485 | 10.5183722 |
| H | 3.113400695 | 11.68342952 | 9.943835535 |
| C | 4.31867609 | 12.15803607 | 11.68124888 |
| H | 3.663306741 | 12.96293967 | 12.00385056 |
| C | 5.454149846 | 11.84925568 | 12.43904161 |
| H | 5.670810097 | 12.41713342 | 13.34011492 |
| C | 6.313650623 | 10.8135381 | 12.05531758 |
| H | 7.193333477 | 10.56397681 | 12.64052902 |
| C | -0.184712901 | 7.345824975 | 10.52770693 |
| H | 0.527007024 | 6.797820084 | 11.14756322 |
| H | -0.795256027 | 6.640094038 | 9.952070847 |
| H | -0.843431138 | 7.949356371 | 11.16449814 |
| C | 1.973939841 | 8.255022346 | 9.587774523 |
| C | 0.027845054 | 9.044281312 | 8.707511186 |
| C | 1.108610343 | 9.658005921 | 8.050553564 |
| C | 0.876792365 | 10.59112251 | 7.04015153 |
| H | 1.699573017 | 11.05878421 | 6.513898717 |
| C | -0.451293505 | 10.89658413 | 6.72272123 |

| | | | |
|---|--------------|-------------|-------------|
| H | -0.652965638 | 11.62155794 | 5.938362743 |
| C | -1.520995124 | 10.28469436 | 7.385920342 |
| H | -2.541257108 | 10.54108116 | 7.11263739 |
| C | -1.295376009 | 9.341288536 | 8.394748879 |
| H | -2.119796316 | 8.858290002 | 8.910156157 |
| C | 4.133233637 | 7.003608289 | 3.678936492 |
| H | 3.47475099 | 6.222105139 | 4.062158427 |
| H | 5.122259488 | 6.583247874 | 3.461920147 |
| H | 3.712966559 | 7.42072223 | 2.755572496 |
| C | 3.591529258 | 7.986125612 | 5.939177464 |
| C | 4.994535721 | 9.16523837 | 4.587541613 |
| C | 4.828811605 | 9.864793659 | 5.795445189 |
| C | 5.477521444 | 11.08317323 | 5.994429892 |
| H | 5.372921043 | 11.62427238 | 6.926461397 |
| C | 6.273819627 | 11.57876039 | 4.956178533 |
| H | 6.787511635 | 12.52697565 | 5.091887893 |
| C | 6.428075378 | 10.87844487 | 3.754418615 |
| H | 7.05686748 | 11.2890708 | 2.968691523 |
| C | 5.786757543 | 9.651295608 | 3.551468375 |
| H | 5.904826548 | 9.099321693 | 2.624129512 |