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Toward charge-neutral 'soft scorpionates': Coordination chemistry and Lewis acid promoted isomerization of tris(1-organo-imidazol-2-ylthio)methanes

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Abstract

Two tris(1-organo-imidazol-2-ylthio)methanes, HC(S-tim^R)$_3$ (R = organo = methyl, tert-butyl), have been prepared by a triphasic reaction between chloroform, the appropriate heterocycle, and saturated aqueous solutions of Na$_2$CO$_3$, in the presence of a phase transfer agent, (NBu$_4$)(Br). These ligands have been characterized both spectroscopically and by single crystal X-ray diffraction. The reaction chemistry of these potentially N,N,N-tripodal ligands with AgBF$_4$ was also explored where simple 1:1 coordination complexes could be isolated from reactions performed in THF solution at room temperature. The derivative {Ag[HC(S-tim^{Me})$_3$]}(BF$_4$) was structurally characterized which showed that the ligand binds in a μ–$\kappa^2 N,\kappa^1 N$-mode to give a coordination polymer with an interesting layered supramolecular structure. Surprisingly, heating CH$_3$CN solutions of the silver complexes at reflux resulted in decomposition of the complex and concomitant isomerization of the ligands to give metal-free tris(3-organo-1-imidazole-2-thione)methane, HC(N-imt^R)$_3$; the heretofore elusive charge-neutral analogues of the well-studied 'soft scorpionate' Tm^{R-} anions. The solution isomerization of HC(S-tim^R)$_3$ to HC(N-imt^R)$_3$ was found to be general, occurring in a variety of solvents with any of a host of different Lewis acids [*para*-toluenesulfonic acid, KPF$_6$, and M(CO)$_5$Br (M = Mn, Re)] but did not occur by heating in the absence of Lewis acid. The compound HC(N-imt^{Me})$_3$ exhibited unusually low solubility in common organic solvents. Single crystal X-ray diffraction of HC(N-imt^{Me})$_3$ revealed a remarkable honeycomb supramolecular structure with ca. 5 Å channels filled with solvent. The robust nature of this solid is a result of strong dipolar stacking interactions of molecules into polymer chains bolstered by concerted π–π and CH–π interactions involving the heterocycles, holding the chains together in the remaining two dimensions.

Graphical abstract

The preparation and coordination chemistry of potentially tripodal N,N,N-ligands, HC(S-tim^R)$_3$ (R = Me, tBu), has been investigated. The isomerization of these ligands to the heretofore elusive class of charge-neutral 'soft scorpionates' HC(N-imt^R)$_3$ was found to be promoted by a variety of Lewis acids. In the case of R = Me, the C$_3$-symmetric dipolar molecule has surprising properties due to its robust, porous honeycomb supramolecular structure.
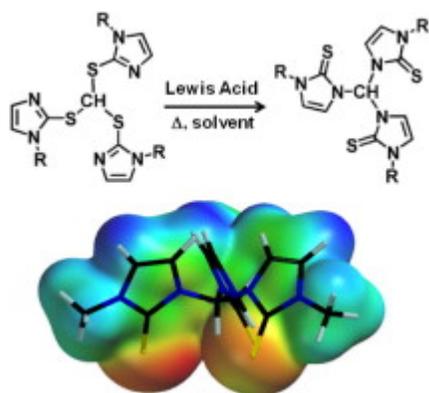
Keywords

1. Introduction

There is continued interest in the development of facially-coordinating tripodal ligands that incorporate nitrogen- and sulfur-containing heterocycles ('soft scorpionates') owing to the ability of metal complexes of these ligands to serve as structural and reactive models of metalloenzymes.[1–4] Much of the traditional investigations of 'soft scorpionate' chemistry has centered on metal complexes of poly(3-organo-imidazoline-2-thione)borate complexes (such as Bm^{R-} or Tm^{R-}, Fig. 1A and B, respectively), where variations in ligand designs have lead to important advances in understanding the coordination and reaction chemistry. Moreover, suitably designed systems have been found to promote remarkable new chemical transformations[5] or can serve as tectons for the deliberate construction of interesting supramolecular assemblies.[6]
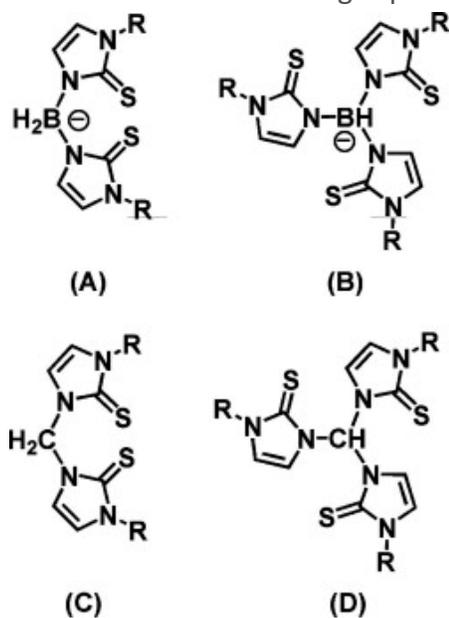

Fig. 1. Known 'soft' scorpionates (A) Bm−, (B) Tm−, and their charge-neutral counterparts (C) H2C(N-imtR)2 and (D) HC(N-imtR)3.

We became interested in developing compounds of the type $H_{4-x}C(N\text{-imt}^R)_x$ (x = 2 or 3, N-imt^R = 3-organo-N-imidazole-2-thione; Fig. 1C and D) which would be the charge-neutral counterparts to the Bm^{R-} or Tm^{R-} anions. It was anticipated that such species should exhibit different coordination behavior than the anionic derivatives and might also easily modified at the methylene (x = 2) or methine position (x = 3) (by deprotonation of the acidic methylene or methine followed by reaction with 'linked' electrophiles) to permit access to scaffolds capable of forming multimetallic complexes of interest in catalysis or in supramolecular chemistry. During the course of these studies rather unexpected results were obtained that had no reported counterparts in analogous borate chemistries. That is, we previously reported[7] that the reaction between 2-mercapto-1-methylimidazole and dichloromethane under biphasic conditions lead to the formation of easily separable mixtures of sulfur-bonded kinetic products ClCH$_2$(S-tim^{Me})$_2$ and CH$_2$(S-tim^{Me})$_2$ where 'S-tim^{Me}' refers to the thioimidazoline form of the heterocycle (Scheme 1). The ratios of each product in the mixture could be varied by changing the time of reaction. Each of these products could be converted to thermodynamically-more stable nitrogen-bonded forms on heating: the former converts to a cyclic anionic derivative [CH$_2$(μ-C$_4$H$_5$N$_2$S)$_2$CH$_2$](Cl)$_2$(above ca 40 °C) whereas heating the latter above 120 °C causes stepwise isomerization first to CH$_2$(S-tim^{Me})(N-imt^{Me}) then to CH$_2$(N-imt^{Me})$_2$ again where 'N-imt^{Me}' refers to the imidazoline-thione form of the heterocycle. Work by our group[8] and others[9] have shown that each isomeric CH$_2$(S-tim)$_2$ or CH$_2$(N-imt^{Me})$_2$ exhibits rich coordination chemistry. Of particular interest to this work, is that numerous binding modes are possible (and have been observed in) metal complexes of the CH$_2$(S-tim^R)$_2$ ligands that take advantage of metal–nitrogen, metal–sulfur, or both types of interactions as in Scheme 2.
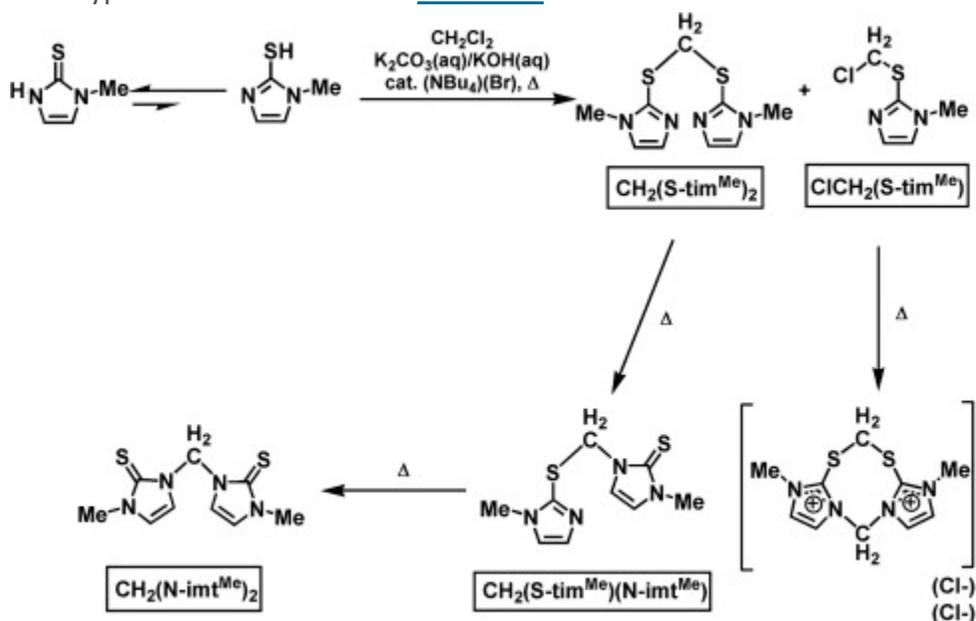
Scheme 1.
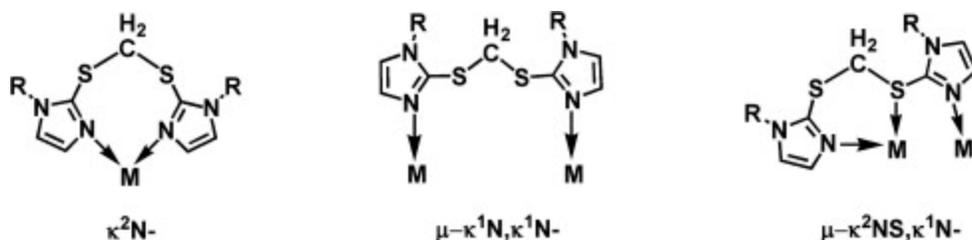
Scheme 2. Representative binding modes in metal complexes of $CH_2(S\text{-}tim^R)_2$.

Despite the success in obtaining and studying the coordination chemistry of the $CH_2(S\text{-}tim^R)_2$ or $CH_2(N\text{-}imt^R)_2$ ligands, the corresponding tripodal derivatives $HC(S\text{-}tim^R)_3$ or $HC(N\text{-}imt^R)_3$ remain unknown. Herein, we report on the successful endeavors to prepare the former and in the course of studying the coordination chemistry of this species, the unexpected transformation that led to the latter.

2. Experimental

2.1. Materials

The heterocycle 2-mercapto-1-tert-butyl-imidazole was prepared according to the literature procedure,[10] while the all other chemicals were commercially available and were used as received. The solvents used in the preparations were dried by conventional methods and distilled prior to use, except were indicated (i.e. aqueous biphasic conditions). The syntheses of the silver complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques and in foil-covered apparatus to protect $AgBF_4$ from light. After complex formation, no special precautions to avoid light were necessary.

2.2. Physical measurements

Midwest MicroLab, LLC, Indianapolis, Indiana 45250, performed all elemental analyses. IR spectra were recorded in the 4000–500 cm^{-1} region (KBr disc) on a Nicolet Magna-IR 560 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer. Chemical shifts were referenced to solvent resonances at δ_H 2.50 and δ_C 39.51 for DMSO, δ_H 7.26 and δ_C 77.23 for $CDCl_3$, δ_H 1.94 and δ_C 118.9 for CD_3CN. ^{19}F NMR spectra were recorded on a Varian 400 MHz spectrometer and were referenced to external samples of CF_3CO_2H δ_F = 0.00 ppm. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. Mass spectrometric measurements recorded in ESI(+) mode were obtained on a Micromass Q-TOF spectrometer whereas those performed by using direct-probe analyses were made on a VG 70S instrument. For the ESI(+) experiments formic acid (approximately 0.1% v/v) was added to the mobile phase (CH_3CN).

2.3. Synthesis of ligands

2.3.1. Synthesis of HC(S-timMe)3

A triphasic mixture of 5.03 g (44.1 mmol) 2-mercapto-1-methyl-imidazole, 0.499 g (3.06 mmol) (NBu$_4$)(Br), and 47.7 g (441 mmol) Na$_2$CO$_3$ in 50 mL each CHCl$_3$ and water was heated at reflux 3 d. During this time, the mixture turned blue after 1 h, peach after 2 h, orange after 4 h, and finally deep red after one day. After 3 d, the mixture was allowed to cool to room temperature and the excess solid Na$_2$CO$_3$ was removed by filtration. The aqueous phase was separated from the dark red–orange organic phase and was extracted with three 100 mL portions of CH$_2$Cl$_2$. It is important that the collected organic fractions were washed with sufficient amounts of water to remove the phase transfer catalyst (three 100 mL portions were used here) as this catalyst is very difficult to separate from the product(s). The collected organic phases were then dried over MgSO$_4$, filtered, and solvent was removed by rotary evaporation leaving a red oily mixture that was separated by column chromatography on silica gel. The column was eluted first with 1:2 acetone–hexane mixture (R_f = 0.89, silica plate) to give 1.15 g (13% based on 2-mercapto-1-methylimidazole) of (1-methyl-2-thioimidazolyl)dichloromethane as a dark orange oil. Mp, above 5 °C but below 20 °C. *Anal.* Calc. for C$_5$H$_6$Cl$_2$N$_2$S: C, 30.47; H, 3.07; N, 14.21. Found: C, 30.09; H, 3.48; N, 13.94%. ^{1}H NMR (CDCl$_3$) δ_H = 7.22 (d, J = 1 Hz, 1H, N═CH), 7.09 (d, J = 1 Hz, 1H, MeNCH═), 6.83 (s, 1H, HCCl$_2$), 3.80 (s, 3H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$) δ_C = 136.07 (SCN), 131.33 (NCH═CH), 124.55 (MeNCH═CH), 75.71 (HCCl$_2$), 34.35 (CH$_3$) ppm. IR (KBr, cm^{-1}) 3164, 3086, 2958, 2933, 2858, 1728 (s, C═C), 1573 (m, C═N), 916 (m, C–S), 732 (s, C–Cl). HRMS [Direct Probe, m/z] *Anal.* Calc. (Obs) for C$_5$H$_6$Cl$_2$N$_2$S, [M], 195.9629 (195.9626). LRMS (Direct Probe) m/z(Int.) [assign.]: 196 (20) [M$^.$]$^+$, 161 (100) [M–Cl]$^+$, 125 (23) [M–Cl–HCl]$^+$, 113 (82) [tim^{Me}]$^+$. The column was next eluted with ethyl acetate to recover 0.627 g (5.47 mmol, 12%) of unreacted 2-mercapto-1-methyl-imidazole (R_f = 0.45, SiO$_2$ same solvent). ^{1}H NMR (CDCl$_3$) δ_H 11.55 (br s, 1H, NH) 6.71 (d, J = 2 Hz, 1H, ═CH), 6.67 (d, J = 2 Hz, 1 H, ═CH), 3.61 (s, 3H, CH$_3$). Finally, after flushing the column with copious MeOH, and evaporating solvent 3.21 g (9.11 mmol, 62%) of HC(S-tim^{Me})$_3$ was obtained as an amber oil that solidified on standing. Mp, 105–106 °C. *Anal.* Calc. for C$_{13}$H$_{16}$N$_6$S$_3$: C, 44.29; H, 4.58; N, 23.84. Found: C, 43.81; H, 4.67; N, 23.34%. ^{1}H NMR (CDCl$_3$) δ_H = 7.07 (d, J = 1 Hz, 1H, HC═N), 6.95 (d, J = 1 Hz, 1H, HCNMe), 5.80 (s, 1H, HCS$_3$), 3.59 (s, 9H, CH$_3$) ppm. ^{1}H NMR (CD$_3$CN) δ_H = 7.13 (d, J = 1 Hz, 1H, HC═N), 7.04 (d, J = 1 Hz, 1H, HCNMe), 5.78 (s, 1H, HCS$_3$), 3.59 (s, 9H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$) δ_C = 138.00 (SCN), 130.49 (NCH═CH), 123.89 (MeNCH═CH), 64.15 (HCS$_3$), 34.21 (CH$_3$) ppm. ^{1}H NMR (acetone-d$_6$) δ = 7.25 (d, J = 1 Hz, 3H, ═CH), 7.03 (d, J = 1 Hz, 3H, ═CH), 5.92 (s, 1H, CH), 3.68 (s, CH$_3$) ppm. ^{13}C NMR (acetone-d$_6$) δ = 138.4 (SCN), 130.6 (═CH), 124.9 (═CH), 64.7 (CH), 34.1 (CH$_3$) ppm. HRMS [Direct Probe, m/z] Calc. (Obs) for C$_{13}$H$_{16}$N$_6$S$_3$, [M]$^+$, 352.0599 (352.0603). LRMS (Direct Probe) m/z (Int.) [assign.]: 352 (53) [M$^.$]$^+$, 239 (37) [M-tim^{Me}]$^+$, 125 (100) [M-2tim^{Me}]$^+$, 113 (82) [tim^{Me}]$^+$. IR (KBr, cm^{-1}) 3099, 2941, 2846, 1651 (C═C), 1502 (C═N), 913 (C–S). Large amber crystals of HC(S-tim)$_3$ are obtained by layering an ethyl acetate solution with dry Et$_2$O and

allowing the solvents to slowly diffuse. Single crystals of a water solvate could be obtained using wet solvent.

2.3.2. Synthesis of HC(S-timtBu)3

In a manner similar to above, a mixture of 2.79 g (17.9 mmol) 2-mercapto-1-*tert*-butylimidazole, 0.404 g (1.25 mmol) of (NBu$_4$)(Br), and 19.0 g (179 mmol) of Na$_2$CO$_3$ in 50 mL each CHCl$_3$ and water were heated at reflux 3d. The red oil obtained after work up described above was subjected to purification by column chromatography on silica gel. Elution first with a 1:2 acetone–hexane mixture (R_f = 0.96, silica plate) gave 0.540 g, (6% based on 2-mercapto-1-tert-butylimidazole) Cl$_2$CH(S-tim^{tBu}) as an orange oil. ^{1}H NMR (CDCl$_3$) δ_H = 7.29 (s, 1H, HCCl$_2$), 7.10 (d, J = 2 Hz, 1H, N=CH), 7.09 (d, J = 2 Hz, 1H, tBuNCH), 1.65 (s, 9H, (CH$_3$)$_3$C) ppm. ^{13}C NMR (CDCl$_3$) δ_C = 136.13 (SCN), 129.24 (NCH=CH), 120.03 (tBuNCH=CH), 75.84 (HCCl$_2$), 57.51 (NC(CH$_3$)$_3$), 30.81 ((CH$_3$)$_3$C) ppm. IR (KBr, cm^{-1}) 3147, 3118, 3095, 2981, 2939, 2883, 1728 (s, C=C), 1573 (m, C=N), 916 (m, C–S), 750 (s, C–Cl). HRMS [Direct Probe, m/z] Calc. (Obs) for C$_8$H$_{12}$Cl$_2$N$_2$S, [M]$^+$, 238.0098 (238.0095). LRMS (Direct Probe) m/z (Int.) [assign.]: 238 (19) [M]$^+$, 203 (4) [M–Cl]$^+$, 182 (24) [M–tBu] $^+$, 147 (79) [M–tBu–Cl]$^+$, 111 (23) [M–tBu–CHCl$_2$]$^+$, 57 (100) [tBu]$^+$. The starting material, 2-mercapto-1-tert-butylimidazole, 0.404 g (1.25 mmol, 14%) was eluted next (R_f = 0.83). Mp, 185–187 °C. ^{1}H NMR (CDCl$_3$) δ_H 11.70 (s, 1H, NH), 6.83(d, J = 3 Hz, 1H, NCH=), 6.66 (d, J = 3 Hz, 1H, tBuNCH=), 1.79 (s, 9H, (CH$_3$)$_3$C). ^{13}C NMR (CDCl$_3$) δ_C = 159.43 (C=S), 116.12 (HNCH=CH), 113.66 (tbuNCH=CH), 58.92 [C(CH$_3$)$_3$], 28.41 (CH$_3$)$_3$C) ppm. Finally, elution with 100% acetone (R_f = 0.39) afforded 1.81 g (3.68 mmol, 62% yield) HC(S-tim^{tBu})$_3$ after evaporating the solvent. Mp 179–181 °C. *Anal.* Calc. for C$_{22}$H$_{34}$N$_6$S$_3$: C, 55.19; H, 7.16; N, 17.55. Found: C, 55.34; H, 6.82; N, 17.13%. ^{1}H NMR (CDCl$_3$) δ_H = 7.06 (d, J = 1 Hz, 3H, HC=N), 7.01 (d, J = 1 Hz, HC–NtBu, 3H), 6.98 (s, 1H, HCS$_3$), 1.57 (s, 27 H, (CH$_3$)$_3$C) ppm. ^{1}H NMR (CD$_3$CN) δ_H = 7.26 (s, HCS$_3$, 1H), 7.18 (d, J = 1 Hz, 3H, HC=N), 6.97 (d, J = 1 Hz, 3H, HCNtBu), 1.56 (s, 27 H, (CH$_3$)$_3$C) ppm. ^{13}C NMR (CDCl$_3$) δ_C = 138.36 (SCN), 128.57 (NCH=CH), 119.16 (tBuNCH=CH), 63.22 (HCS$_3$), 56.70 [NC(CH$_3$)$_3$], 30.57 [C(CH$_3$)$_3$] ppm. HRMS [Direct Probe, m/z] Calc. (Obs) for C$_{22}$H$_{34}$N$_6$S$_3$, [M]$^+$, 478.2007 (478.2009). LRMS (Direct Probe) m/z (Int.) [assign.]: 478 (72) [M$^+$], 323 (100) [M-tim^{tBu}]$^+$, 157 (89) [H$_2$tim^{tBu}]$^+$. IR (KBr, cm^{-1}) 3101, 3018, 2962, 2926, 2866, 1628 (s, C=C), 1497 (m, C=N), 914 (m, C–S). X-ray quality crystals of HC(S-tim^{tBu})$_3$ were obtained by vapor diffusion of Et$_2$O into a dichloromethane solution.

2.3.3. Synthesis of HC(N-imtMe)₃

2.3.3.1. Method A

A mixture of 2.88 g (8.16 mmol) HC(S-tim^{Me})$_3$ and 0.0281 g (0.163 mmol) para-toluenesulfonic acid in 20 mL of a 1:1 toluene–THF solution was heated at reflux for 36 h. After cooling to room temperature, the solvent was removed by rotary evaporation and the product was washed with two 20 mL portions of THF followed by 20 mL portions of diethyl ether. The remaining colorless residue was recrystallized by allowing a boiling acetonitrile solution (ca. 200 mL) to cool to room temperature, thereby affording 2.65 g (93%) of HC(N-imt^{Me})$_3$ as colorless needles after filtration and drying under vacuum. Mp, 218–

220 °C. *Anal.* Calc. for $C_{13}H_{16}N_6S_3$: C, 44.29; H, 4.58; N, 23.84. Found: C, 44.40; H, 4.44; N, 23.51%. ^1H NMR (CD$_3$CN) δ_H = 8.56 (s, HCN$_3$, 1H); 6.94 (d, J = 3 Hz, HC═N), 6.48 (d, J = 3 Hz, HCNMe), 3.52 (s, 9H, CH$_3$) ppm. ^{13}C NMR: low solubility prevented resolution of signals in reasonable acquisition time. IR (KBr, cm^{-1}) 3145, 3097, 3020, 2929, 2860, 1570 (C═C), 1234 (s, C═S). HRMS [Direct Probe, m/z] Calc. (Obs) for $C_{13}H_{16}N_6S_3$, [M]$^+$, 352.0599 (352.0591). LRMS (Direct Probe) m/z (Int.) [assign.]: 352 (48) [M$^-$]$^+$, 239 (35) [M-imt^{Me}]$^+$, 125 (100) [M-2imt^{Me}]$^+$, 113 (21) [imt^{Me}]$^+$. X-ray quality crystals of HC(N-imt^{Me})$_3$ were obtained by vapor diffusion of Et$_2$O into a DMF solution at 4 °C.

2.3.3.2. Method B

A mixture of 0.46 g (1.30 mmol) HC(S-tim^{Me})$_3$ and 0.240 g (1.30 mmol) KPF$_6$ in 20 mL of 1:1 toluene:THF solution was heated at reflux for 12 h. After cooling to room temperature, the colorless precipitate was washed with two 10 mL portions of THF followed by two 10 mL portions of diethyl ether. The product was recrystallized from CH$_3$CN, as described above to give 0.390 g (85%) HC(N-imt^{Me})$_3$ as colorless needles.

Alternatively, a catalytic amount of KPF$_6$ can be used. In one case, 0.213 g (0.604 mmol) HC(S-tim^{Me})$_3$ and 0.0111 g (0.0604 mmol) KPF$_6$ in 20 mL of 1:1 toluene:THF solution was heated at reflux for 16 h to give 0.168 g (79%) HC(N-imt^{Me})$_3$ after purification as above.

2.3.3.3. Method C

A mixture of 0.337 g (0.956 mmol) HC(S-tim^{Me})$_3$ and 0.00370 g (0.0191 mmol) AgBF$_4$ in 15 mL each toluene and THF were heated at reflux 12 h, then solvent was removed from the insoluble portion of the product mixture by cannula filtration. The solid was washed with two 10 mL portions of acetonitrile (to remove any residual AgBF$_4$) followed by two 10 mL portions of diethyl ether, and was dried under vacuum to give 0.256 g (76%) of HC(N-imt^{Me})$_3$ as a colorless solid.

2.3.3.4. Method D

A mixture of 0.130 g (0.240 mmol) HC(S-tim^{Me})$_3$ and 0.0960 g (0.240 mmol) Re(CO)$_5$Br in 15 mL toluene was heated at reflux 12 h. The solvent was removed by vacuum distillation. The residue was extracted three times with 25 mL boiling CH$_3$CN, which filtration (to remove unidentified decomposition products) and cooling to room temperature, afforded 0.0850 g (57%) HC(N-imt^{Me})$_3$ as colorless needles.

2.3.4. Synthesis of HC(N-imt^{tBu})$_3$

2.3.4.1. Method A

A mixture of 0.440 g (0.920 mmol) HC(S-tim^{tBu})$_3$ and 0.0040 g (0.0230 mmol) *para*-toluenesulfonic acid in 10 mL toluene was heated at reflux for 24 h. After cooling to room temperature, solvent was removed by rotary evaporation and the residual sticky solid was washed with CH$_2$Cl$_2$ to remove unreacted starting material (0.0396 g, 0.0827 mmol, 9%), acid catalyst, and 1-tert-butyl-2-mercaptoimidazole (0.170 g, 1.09 mmol, 39%). The remaining colorless precipitate was washed with two 20 mL portions of Et$_2$O, two 20 mL portions hexanes and was dried under vacuum to yield 0.210 g (48%) HC(N-imt^{tBu})$_3$ as a colorless solid. Mp 203–205 °C. *Anal.* Calc. for C$_{22}$H$_{34}$N$_6$S$_3$: C, 55.19; H, 7.16; N, 17.55. Found: C, 54.95; H, 7.02; N, 17.69%. ^{1}H NMR (CD$_3$CN) δ_H = 8.70 (s, 1H, HCN$_3$), 7.05 (d, J = 3 Hz, 3H, HC═N), 6.34 (d, J = 3 Hz, 3H, HCNtBu), 1.75 (s, 27H, C(CH$_3$)$_3$) ppm. ^{13}C NMR (CD$_3$CN) δ_C = 163.39, 128.69, 119.47, 63.40, 57.32, 30.66 ppm. IR (KBr, cm^{-1}) 3188, 3155, 3080, 2980, 2918, 2887, 1578 (s, C═C), 1236 (s, C═S). ESI(+) MS (CH$_3$CN) *m/z* (Int.) [assign.]: 479 (100) [M+H]$^+$, 389 (18) [M-tBu]$^+$, 367 (9) [[M-2tBu]$^+$, 323 (8) [M-imt^{tBu}]$^+$.

2.3.4.2. Method B

A mixture of 0.0820 g (0.171 mmol) HC(S-tim^{tBu})$_3$ and 0.0032 g (0.017 mmol) KPF$_6$ in 10 mL each toluene and THF was heated at reflux for 16 h. After cooling to room temperature, the colorless solution was separated from KPF$_6$ by cannula filtration. After removing the organic solvents, by vacuum distillation, the pale yellow residue was washed with two 10 mL portions Et$_2$O and two 10 mL portions hexanes. The colorless solid was dried under vacuum to give 0.062 g (75%) of HC(N-imt^{tBu})$_3$ as identified by its mp and ^{1}H NMR spectrum.

2.3.4.3. Method C

A mixture of 0.107 g (0.224 mmol) HC(S-tim^{tBu})$_3$ and 0.0062 g (0.0224 mmol) Mn(CO)$_5$Br in 15 mL toluene was heated at reflux for 16 h. After removing the organic solvents, by vacuum distillation, the sticky orange residue was washed with two 10 mL portions Et$_2$O and two 10 mL portions hexanes. The colorless solid was dried under vacuum to give 0.0589 g (55%) of HC(N-imt^{tBu})$_3$ as identified by its mp and ^{1}H NMR spectrum.

2.4. Preparation of the silver complexes

2.4.1. Synthesis of {Ag[HC(S-timMe)3]}(BF4). (1a)

A solution of 0.410 g (1.16 mmol) HC(S-tim^{Me})$_3$ in 10 mL THF was added dropwise to a solution of 0.227 g (1.16 mmol) AgBF$_4$ in 10 mL THF to immediately produce a colorless precipitate. After the mixture had been stirred at room temperature for 4 h, the solid was separated by cannula filtration and was washed with two 20 mL portions of THF, two 20 mL portions of Et$_2$O, and was dried under

vacuum to give 0.592 g (76%) of **1a** as a colorless solid. Mp 185 °C, brown, 228–230 °C dec. to brown oil. *Anal.* Calc. for $C_{13}H_{16}AgBF_4N_6S_3$: C, 28.54; H, 2.95; N, 15.36. Found: C, 28.58; H, 2.94; N, 15.07%. ^1H NMR (CD_3CN) δ_H = 7.60 (br, 3H, HC=N), 7.19 (br, 3H, HCNMe), 6.15 (br, 1H, HCS_3), 3.68 (s, 9H, CH_3) ppm. ^{13}C NMR (CD_3CN) δ_C = 137.99 (SCN), 131.30 (HC=N, 126.90 (C–NMe), 64.12 (HCS_3), 35.67 (CH_3) ppm. ^{19}F NMR (CD_3CN) δ_F = −152.10 ppm. ^1H NMR (DMSO) δ = 7.64 (b, NCH=CH), 7.28 (b, NCH=CH), 6.16(s, CH), 3.68(s, CH_3) ppm. ^{13}C NMR (DMSO) δ = 136.72 (SCN), 130.35 (NCH=CH), 126.91 (NCH=CH), 63.14 (HCS_3), 39.42 (CH_3) ppm. IR (KBr, cm^{-1}) 3132, 2941, 2850, 1620 (C=C), 1518 (C=N), 1053 (B–F), 933 (C–S). HRMS [ESI(+), *m/z*] Calc. (Obs) for $C_{13}H_{16}Ag_2N_6S_3$, $[AgL]^+$, 458.9650 (458.9654). ESI(+) MS (CH_3CN) *m/z* (Int.) [assign.]: 811 (10) $[AgL_2]^+$, 459 (25) $[AgL]^+$, 353 (100) $[HL]^+$, 271 (13) $[Ag(CH_3CN)_4]^+$, 239 (9) $[L\text{-}tim^{Me}]^+$, 189 (78) $[Ag(CH_3CN)_2]^+$, 148 (8) $[Ag(CH_3CN)]^+$, 126 (54) $[L\text{-}2tim^{Me}]^+$, 115 (78) $[Htim^{Me}]^+$. Colorless crystals suitable for X-ray diffraction were obtained at −20 °C by layering Et_2O onto a CH_3CN solution of **1a** and allowing solvents to slowly diffuse.

2.4.2. Synthesis of {Ag[HC(S-timtBu)3]}(BF4) (1b)

A solution of 0.230 g (0.480 mmol) $HC(S\text{-}tim^{tBu})_3$ in 5 mL CH_2Cl_2 was added dropwise to a solution of 0.0900 g (0.480 mmol) $AgBF_4$ in 5 mL THF. A colorless precipitate formed after a few minutes and after 4 h of stirring at room temperature, the solid was separated by cannula filtration, was washed with two 20 mL portions of THF, two 20 mL portions of diethyl ether, and was dried under vacuum to give 0.270 g (84%) **1b** as a colorless solid. Mp 189–190 °C dec. to brown liq. *Anal.* Calc. for $C_{22}H_{34}AgBF_4N_6S_3$: C, 39.24; H, 5.09; N, 12.48. Found: C, 38.88; H, 5.23; N, 12.61%. ^1H NMR (CD_3CN) δ_H = 7.29 (d, 2 Hz, 3H, HC=N), 6.99 (d, *J* = 2 Hz, 3H, HC–NtBu), 5.45 (s, 1H, HCS_3), 1.60 (s, 27H, $C(CH_3)_3$) ppm. ^{13}C NMR (CD_3CN) δ_C = 137.50 (C–S), 127.58 (HC=N), 120.93 (HC–NtBu), 59.99 (HCS_3), 59.01 ($C(CH_3)_3$), 30.31 ($C(CH_3)_3$) ppm. ^{19}F NMR (CD_3CN) δ_F = −152.8 ppm. IR (KBr, cm^{-1}) 3159, 2978, 2929, 2873, 1612 (C=C), 1473 (C=N), 1053 (B–F), 918 (C–S). HRMS [ESI(+), *m/z*] Calc. (Obs) for $C_{22}H_{34}AgN_6S_3$, $[AgL]^+$, 585.1058 (585.1063). ESI(+) MS (CH_3CN) *m/z* (Int.) [assign.]: 485 (4) $[AgL]^+$, 479 (100) $[HL]^+$, 423 (34) $[L\text{-}tBu]^+$, 367 (19) $[L\text{-}2tBu]^+$, 323 (27) $[L\text{-}tim^{tBu}]^+$, 189 (12) $[Ag(CH_3CN)_2]^+$, 157 (9) $[H_2tim^{tBu}]^+$.

3. Single crystal X-ray crystallography

X-ray intensity data from a colorless plate of $HC(S\text{-}tim^{Me})_3$, a colorless block of $HC(S\text{-}tim^{Me})_3 \cdot H_2O$, a colorless block of $HC(S\text{-}tim^{tBu})_3$, were collected at 100(2) K with a Bruker AXS 3-circle diffractometer equipped with a SMART2[11] CCD detector (Mo Kα radiation, λ = 1.54178 Å) while those for a pale yellow needle of $HC(N\text{-}imt^{Me})_3 \cdot$solvate, and a colorless plate of {Ag[HC(S-tim^{Me})3]}(BF4) (**1a**) were collected at 150(1) K on a Bruker SMARTAPEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[11] Raw data frame integration and Lp corrections were performed with SAINT+.[11] Final unit cell parameters were determined by least-squares refinement of 5167 reflections from the data set of $HC(S\text{-}tim^{Me})_3$, 7259 reflections from the data set of $HC(S\text{-}tim^{Me})_3 \cdot H_2O$, 9202 reflections from that of $HC(S\text{-}tim^{tBu})_3$, 1770 reflections from that of $HC(N\text{-}imt^{Me})_3 \cdot$solvate, and 5693 reflections of **1a**, each with *I* > 2σ(*I*) for each.

Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions, difference Fourier calculations and full-matrix least-squares refinements against F^2 were performed with SHELXTL.[12] Semi-empirical absorption correction based on the multiple measurement of equivalent reflections was applied to the data of each with SADABS[11] with the exception of the data from HC(N-imt^{Me})$_3$·solvate where no absorption correction was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The X-ray crystallographic parameters and further details of data collection and structure refinements are presented in Table 1. Special details regarding the structure solutions for HC(N-imt^{Me})$_3$·solvate and for **1a** are given below.

Table 1. Crystallographic data collection and structure refinement for HC(S-timMe)3, HC(S-timMe)3·H2O, HC(S-timtBu)3, HC(N-imtMe)3·solvate, and for {Ag[HC(S-timMe)3]}(BF4) (1a).

Compound	HC(S-tim^{Me})$_3$	HC(S-tim^{Me})$_3$·H$_2$O	HC(S-tim^{tBu})$_3$	HC(N-imt^{Me})$_3$-solvate[b]	1a
Formula	C$_{13}$H$_{16}$N$_6$S$_3$	C$_{26}$H$_{36}$N$_{12}$O$_2$S$_6$	C$_{22}$H$_{34}$N$_6$S$_3$	C$_{13}$H$_{16}$N$_6$S$_3$	C$_{13}$H$_{16}$AgBF$_4$N$_6$S$_3$
Formula weight	352.50	741.03	478.73	352.50	547.18
Crystal system	triclinic	monoclinic	orthorhombic	trigonal	monoclinic
Space group	P1$^-$	$P\,2_1/c$	$P\,na2_1$	$P3^-c1$	$P\,2_1$
Temperature [K]	100(2)	100(2)	100(2)	150(1)	150(1)
a [Å]	7.3387(2)	26.2111(3)	12.4426(2)	13.1403(4)	7.0698(5)
b [Å]	8.7234(2)	10.68740(10)	11.7503(2)	13.1403(4)	11.4049(8)
c [Å]	12.8763(3)	12.8551(2)	16.9669(3)	12.3722(9)	12.6773(9)
α [°]	97.7660(10)	90	90	90	90
β [°]	93.1890(10)	103.8390(10)	90	90	99.0380(10)
γ [°]	94.9050(10)	90	90	120	90
V [Å^3]	811.88(3)	3496.55(8)	2480.63(7)	1850.07(16)	1009.48(12)
Z	2	4	4	4	2
$D_{calc.}$ [g cm^{-3}]	1.442	1.408	1.282	1.266	1.800
λ [Å] (Cu Kα)	1.54178	1.54178	1.54178	0.71073[c]	0.71073[c]
μ [mm^{-1}]	4.219	3.989	2.894	0.405	1.356

Compound	HC(S-tim^{Me})$_3$	HC(S-tim^{Me})$_3$·H$_2$O	HC(S-tim^{tBu})$_3$	HC(N-imt^{Me})$_3$-solvate[b]	1a
Abs. correction	multi-scan	multi-scan	multi-scan	none	Semi-empirical
$F(0\,0\,0)$	368	1552	1024	736	544
ϑ range [°]	3.47–66.47	3.47–67.33	4.58–67.24	1.79–24.10	1.63–26.39
Reflections collected	6452	6056	20 792	15 090	10 686
Independent reflections	2625 (R_{int} 0.0164)	6056 (R_{int} 0.0392)	3936 (R_{int} 0.0146)	990 (R_{int} 0.0827)	4122 (R_{int} 0.0274)
Temperature at min/max	0.3280/0.7026	0.2728/0.6461	0.3906/0.5315		0.8249/1.000
Data/restraints/parameters	2625/0/263	6056/0/438	3936/1/280	990/1/74	4122/1/256
Goodness-of-fit on F^2	1.054	1.029	0.956	0.998	1.032
$R_1/wR_2[I > 2\sigma(I)]$[a]	0.0280/0.0730	0.0314/0.0768	0.0214/0.0567	0.0353/0.0780	0.0310/0.0773
R_1/wR_2 (all data)[a]	0.0287/0.0734	0.0400/0.0803	0.0214/0.0567	0.0538/0.0854	0.0321/0.0779

[a]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ $wR_2 = [\Sigma w(|Fo| - |Fc|)2/\Sigma w|Fo|2]^{1/2}$.
[b]Known unit cell contents only, see text.
[c]Mo Kα.

HC(N-imt^{Me})$_3$ crystallizes in the trigonal system. The space group $P\bar{3}c1$ was indicated by the pattern of systematic absences in the intensity data and eventually confirmed. The asymmetric unit consists of ⅓ of a C$_{13}$H$_{16}$N$_6$S$_3$ molecule located on a three-fold axis of rotation and a columnar region of unidentifiable electron density, assumed to be disordered solvent molecules. These electron density peaks are distributed continuously along the crystallographic c axis at $(x, y) = (0, 0)$. The program Squeeze (Platon)[13] was used to remove the contribution of these disordered species from the structure factor calculations. There is a solvent-accessible void volume of 323.2 Å^3 in the unit cell, corresponding to 58 electrons per cell. Note that the reported M.W., $F(0\,0\,0)$ and d(Calc.) reflect known unit cell contents only.

{Ag[HC(S-tim^{Me})$_3$]}(BF$_4$) (**1a**) crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data were consistent with the space groups $P2_1$ and $P2_1/m$. Intensity statistics strongly indicated an acentric structure. The space group $P2_1$ was eventually confirmed by successful solution,

refinement and examination of the structure, and also by the ADDSYM program in PLATON.[13] There is one complete formula unit in the asymmetric unit. The final Flack parameter of −0.01(2) confirms the correct absolute structure.

4. Results and discussion

4.1. Syntheses

Our initial strategy to obtaining the charge-neutral tripodal $HC(N\text{-}imt^R)_3$ compounds was to exploit reactions analogous to those previously reported by our group for $H_2C(N\text{-}imt^{Me})_2$. That is, the reaction between in situ generated aqueous sodium salts of the heterocycle and chloroform in the presence of a phase transfer catalyst should give a tripodal sulfur-derivatized species that could subsequently undergo thermal isomerization reactions to give the desired $HC(N\text{-}imt^R)_3$: the first part of the strategy was successful but not the latter. Thus, the triphasic reaction in Scheme 1a produced a mixture of the unreacted 2-mercapto-alkyl-imidazole (ca. 15%), the monosubstituted derivative $Cl_2CH(S\text{-}tim^R)$ (ca. 12%), and the desired compound $HC(S\text{-}tim^R)_3$ (ca. 62%). It is remarkable that about 90% of the starting heterocycle could be accounted for after working up the reaction but no di-substituted $ClCH(S\text{-}tim^R)_2$ could be identified as a discrete species in the crude product mixture; the reason for this observation remains unclear. All attempts to obtain $HC(N\text{-}imt^R)_3$ by thermal isomerization of $HC(S\text{-}tim^R)_3$ as neat liquids or as solutions only resulted in re-isolation of the starting material or to decomposition, especially in the case of the neat reactions with the *tert*-butyl derivative $HC(S\text{-}tim^{tBu})_3$. Instead, in a manner similar to those reactions observed in *tris*(3-organo-pyrazolyl)methane chemistry,[14] isomerization to the desired $HC(N\text{-}imt^R)_3$ species was accomplished in good to excellent yields by heating solutions in the presence of a Lewis acid (Scheme 3b). Thus, heating a mixture of the $HC(S\text{-}tim^R)_3$ and a catalytic amount of either *para*-toluenesulfonic acid at reflux in toluene for 12 h was found to be a good method for obtaining the desired $HC(N\text{-}imt^R)_3$, giving 93% for R = Me and 48% for R = tBu. The lower yield of the latter is likely due to both the slower isomerization reaction and due to the lower stability of this species, as both unreacted starting material can be recovered and free 2-mercapto-1-tert-butyl-imidazole was also found to be a byproduct of this reaction. To further explore the generality of this reaction, isomerization reactions of $HC(S\text{-}tim^R)_3$ were also successfully carried out in the presence of other potential Lewis acids, KPF_6, $AgBF_4$, and $M(CO)_5Br$ (M = Mn or Re) and other solvent systems. For $HC(S\text{-}tim^{tBu})_3$, reactions with catalytic amount of KPF_6 in 1:1 toluene:THF was found to be the optimal providing 75% conversion. Interestingly, the room-temperature reactions between $Ag(BF_4)$ and the appropriate $HC(S\text{-}tim^R)_3$ in THF afforded $\{Ag[HC(S\text{-}tim^R)_3]\}(BF_4)$ (R = Me (**1a**), R = tBu (**1b**)) as thermally unstable compounds. These complexes decompose in CH_3CN solution on heating to give solvated silver salts and metal-free $HC(N\text{-}imt^R)_3$ on heating. It is also noteworthy that in the cases where isomerization reactions were carried out with other metal-based Lewis acids, no $\{M[HC(N\text{-}imt^R)_3]\}^{n+}$ complexes could be obtained (vide infra). While the properties of $HC(N\text{-}imt^{tBu})_3$ are rather unexceptional for an organic molecule, $HC(N\text{-}imt^{Me})_3$ is soluble in DMSO, only modestly soluble in DMF, can be crystallized by cooling boiling acetonitrile solutions to room temperature, but is

insoluble in most nonpolar solvents including toluene and halocarbons. The unusual solubility properties of HC(N-imt^{Me})$_3$ likely reflects its remarkable solid state structure (vide infra).
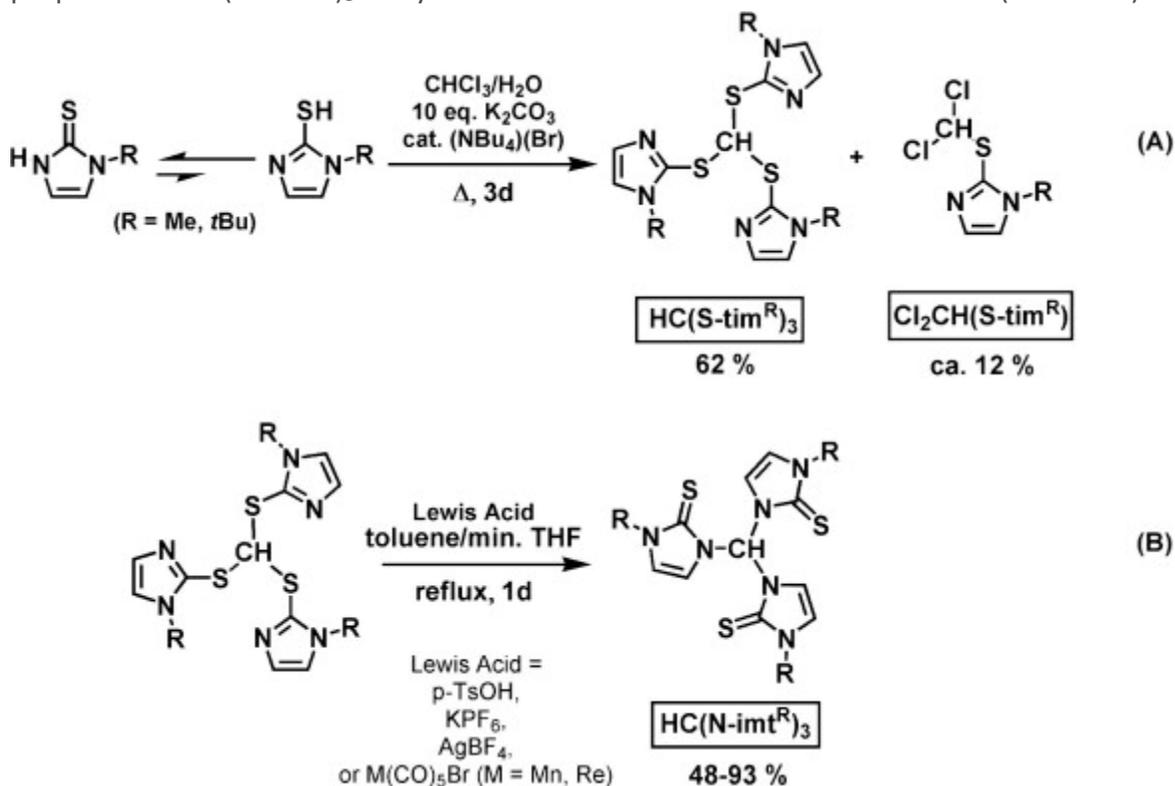
Scheme 3. Preparative routes to the tripodal compounds HC(S-tim^R)$_3$ and HC(N-imt^R)$_3$.

4.2. Description of crystal structures

Single crystals of HC(S-tim^R)$_3$ (R = Me, tBu), HC(S-tim^{Me})$_3$·H$_2$O, HC(N-imt^{Me})$_3$·solvate, and {Ag[HC(S-tim^R)$_3$]}(BF$_4$) (R = Me, **1a**) suitable for X-ray diffraction were obtained where the structures of a representative series (for R = Me) are given in Figs. 2–4 while the remaining structures are given in the Supporting Information. The ligand structures verify the proposed connectivity depicted in Scheme 3b and as anticipated from spectroscopic studies. For HC(S-tim^{Me})$_3$, the bond distances within the ligand framework are rather unremarkable. It is noted that the three imidazoline rings of the molecule are each directed toward the central methine hydrogen but are disposed such that only two rings have the N-methyl groups (C9 and C13) directed toward the methine hydrogen vector and one N-methyl (C5) is directed away from the vector, thereby reducing the overall symmetry of the molecule from C$_3$ to C$_1$. In contrast, the water solvate HC(S-tim^{Me})$_3$·H$_2$O and *tert*-butyl derivative HC(S-tim^{tBu})$_3$ have near C$_3$ symmetry with all three N-organyl groups oriented toward the C$_{methine}$–H vector. The differences in crystal packing (Supporting Information) are likely responsible for the conformational arrangement in the solid. Hydrogen bonding interactions in the water solvate modify the pi-stacking of heterocycles in HC(S-tim^{Me})$_3$ and intermolecular pi-pi stacking interactions are absent in HC(S-tim^{tBu})$_3$. Moreover, the *tert*-butyl groups are large enough to support intramolecular CH-pi interactions (two interactions at ~ 2.8 Å and one at ~2.9 Å).
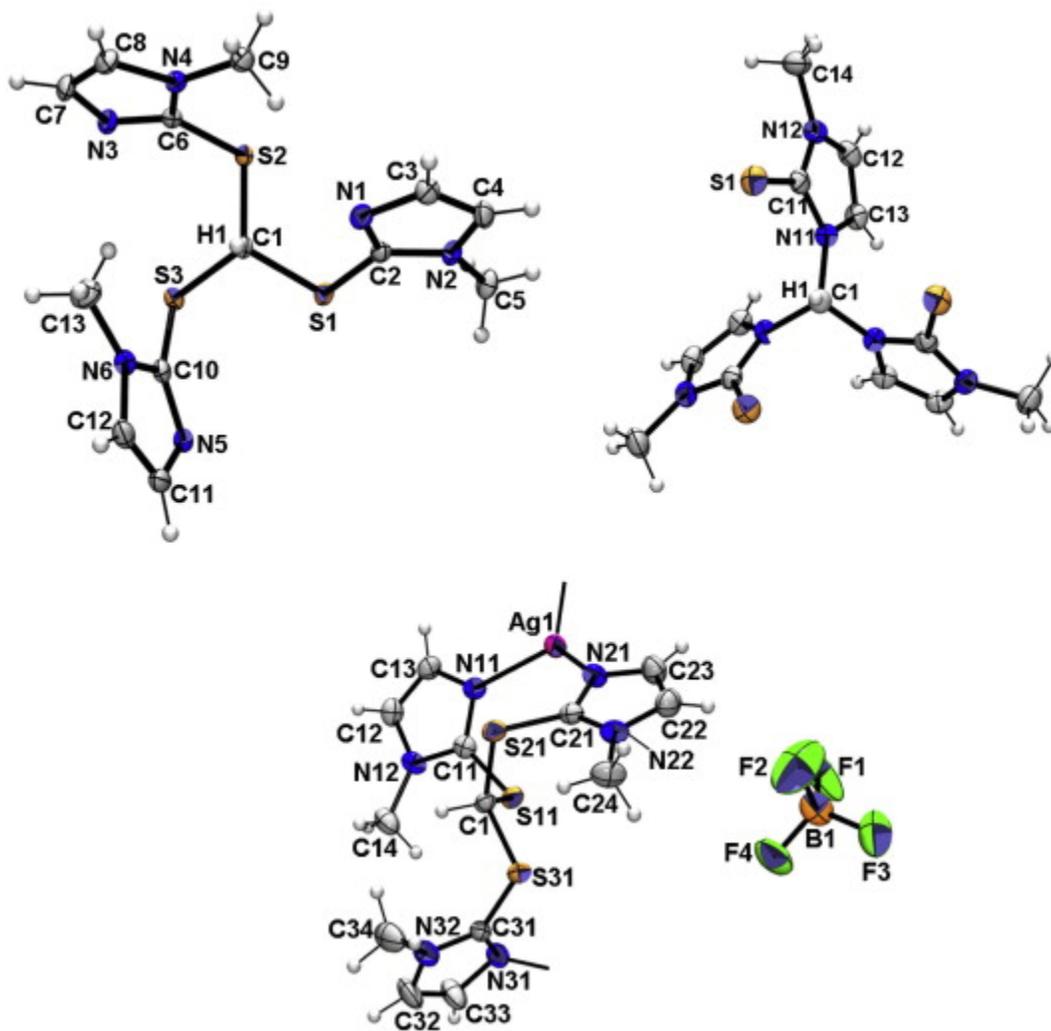
Fig. 2. Structures of HC(S-tim^R)$_3$ (top left), HC(N-imt^{Me})$_3$·solvate (top right), and asymmetric unit of {Ag[HC(S-tim^R)$_3$]}(BF$_4$) (bottom) with thermal ellipsoids shown at 50% probability level.
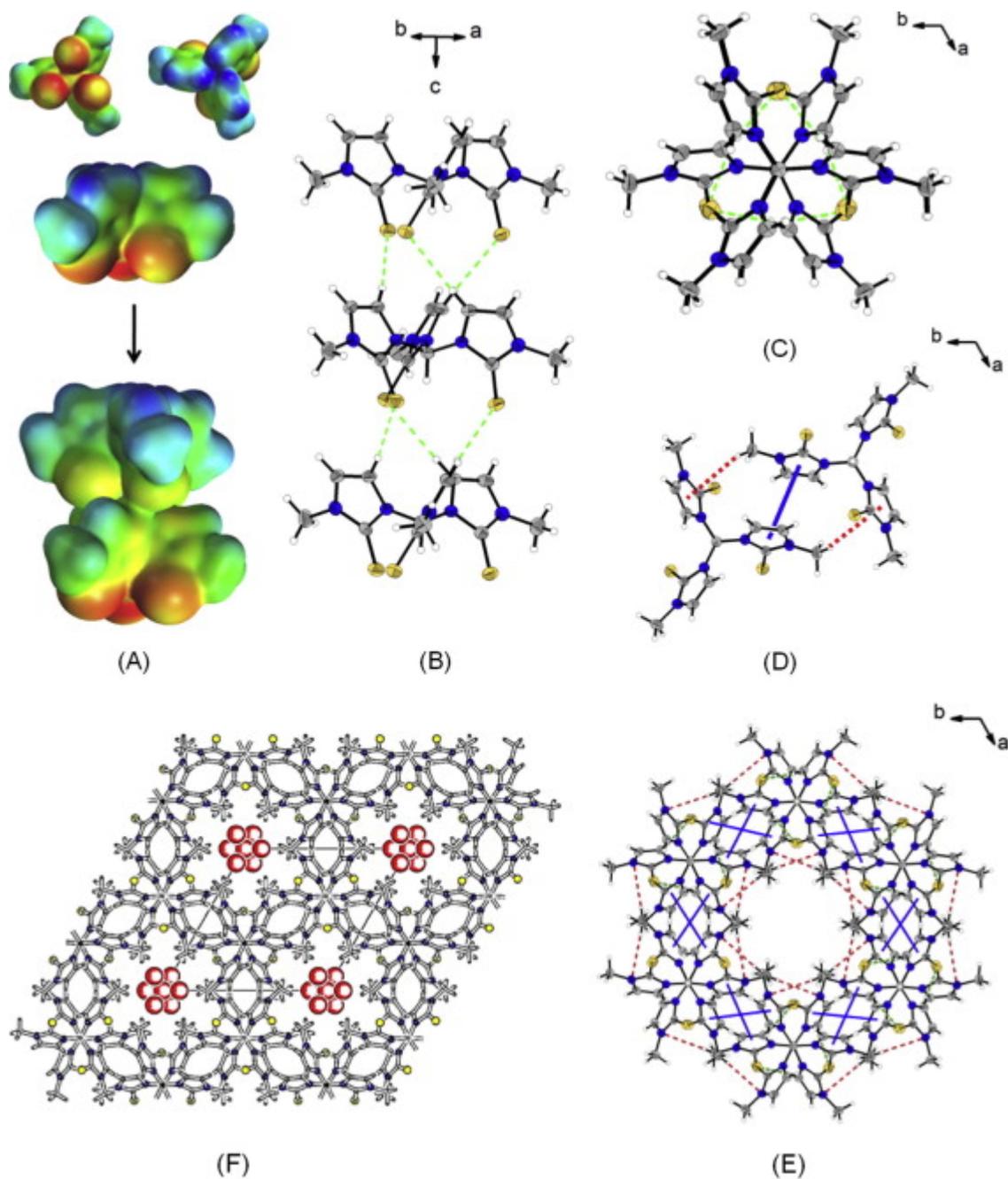
Fig. 3. Supramolecular organization of HC(N-imt^{Me})_3 with (A) Three views of electrostatic potential energy surface density plots for a molecule (red, negative; blue, positive) and for a dimer. (B) view along polymer chain along *c* with CH–S interactions (C) view down the *c*-axis (D) concerted CH-π and π–π interactions organizing adjacent chains (E) six chains forming hexagonal tube (F) view of crystal packing with unidentified solvent molecules filling channels along *c*. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
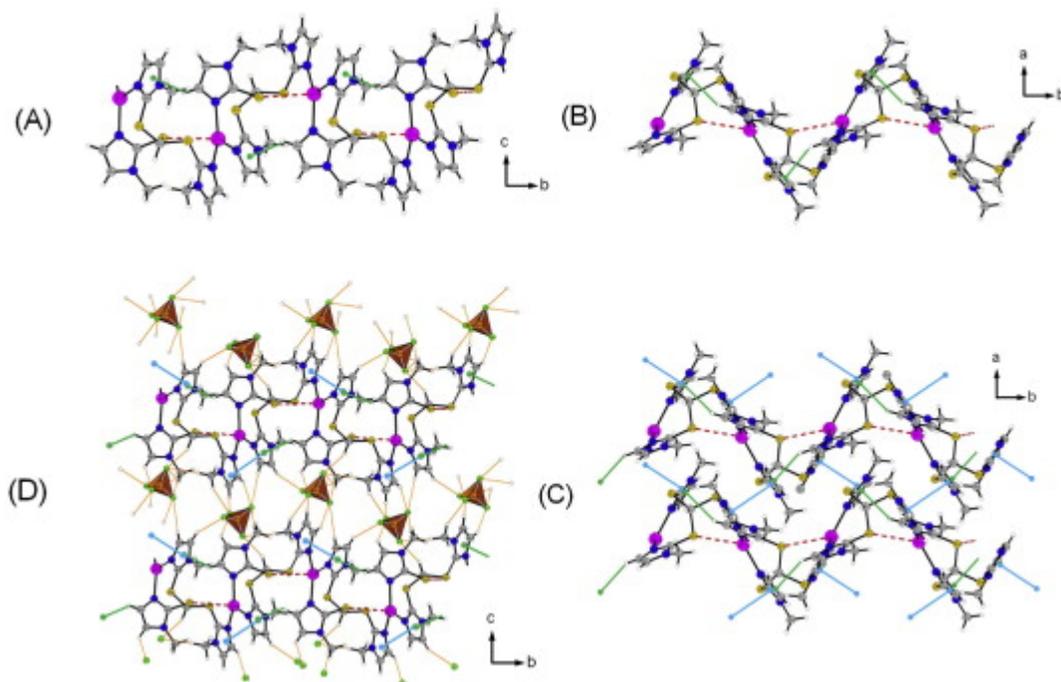
Fig. 4. Extended and supramolecular structure of {Ag[HC(S-tim^R)$_3$]}(BF$_4$). (A) View down a-axis of polymer chain with CH-π interactions (green lines) and Ag(pink)–S(yellow) contacts (red dashed line). (B) View down c-axis of polymer chain. (C) View down c-axis of tacking of polymer chain along the a-direction via π-π stacking (cyan lines). (D) View down a-axis showing layered structure with CH–F interactions (thin orange lines) involving BF4- anions (tetrahedra). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The compound HC(N-imt^{Me})$_3$ resides on a crystallographic three-fold rotation axis and, hence, has precise C$_3$ symmetry. Here, each of the heterocycles is bound to the central methine via one of the nitrogen atoms such that the thione group (C═S, 1.677 Å) is oriented toward the face of the molecule coinciding with the methine C1–H1 vector such that the three sulfur atoms encapsulate the central hydrogen with a rather short intramolecular contact distance (C1H1–S1) of 2.694 Å which is much shorter than the sum of the van der Waals radii of sulfur and hydrogen (3.00 Å).[15] The low solubility of HC(N-imt^{Me})$_3$ may be due to the rather remarkable supramolecular organization of the crystalline solid (Fig. 3). Likely driven by the large dipole moment of HC(N-imt^{Me})$_3$ (Calc. 9.44 D; PM3//B3LYP/6-31G∗, Fig. 3A) directed along the methine C–H vector, molecules of this compound are organized into polymer chains that run along the c-direction (Fig. 3A–C). The stacking is such that a given enantiomer (of C$_3$ symmetry) is sandwiched between molecules of opposite chirality (the enantiomers are related via the c-glide operation) such that there appears to be a concerted set of shorter CH–S contacts that occurs between imidazoline ring hydrogens and the sulfurs of adjacent molecules (C13H13–S1 2.895 Å, 172.9°). Another set of concerted set of noncovalent interactions (Fig. 3D) reminiscent of a quadruple phenyl embrace[16] or quadruple pyrazolyl embrace[17] serves to organize adjacent polymers in to a honeycomb network (Fig. 3F). These non-covalent interactions include a set of π–π stacking interactions between heterocycles on neighboring chains that have a centroid-to-centroid(Ct) distance

of 3.88 Å, a perpendicular distance between mean heterocyclic planes of 3.35 Å (with α = 0.0° and β = γ = 30.4°) and a set of CH-π interaction occurring between an N-methyl hydrogen and the thione (C=S) group [C14H14c–Ct(C=S) 2.77 Å, 157.9°] where the closest contact occurs between (C14)H14 and C11 (2.76 Å, 147.5°). As a result, adjacent polymer chains have opposite polarity, with the thione groups and methine hydrogens of one chain oriented in the +c direction while those groups of an adjacent chain are oriented in the −c direction. The channels formed via supramolecular aggregation of the honeycomb network have a diameter of approximately 5 Å and the void-space would account for 17.6% of the total volume of the unit cell. In the crystal, these channels are filled with unidentified solvent molecules whose electron density runs continuously down the channel. These solvent molecules are held only loosely, as elemental analyses of vacuum-dried samples were consistent with the solvent-free compound.

The solid state structure of {Ag[HC(S-tim^{Me})$_3$]}(BF$_4$) (**1a**) is that of a coordination polymer that propagates along the crystallographic b-axis where the ligand bridges silver centers binding in a μ-κ^2N,κ^1N-fashion (Fig. 4A). As such, silver resides in a nearly ideal trigonal planar AgN$_3$ coordination environment (Σ $\angle$'s about Ag = 358°) with Ag–N distances in the range 2.21–2.27 Å, typical of three-coordinate silver and, as expected, slightly longer than the average Ag–N distance of 2.10 Å found in {Ag[μ-H$_2$C(S-tim^{Me})$_2$]}$_2$(BF$_4$)$_2$ with a linear AgN$_2$ coordination environment.[8b] The small deviation from planarity of the silver coordination sphere in **1a** is likely due to a short Ag–S contact (Ag1–S11 3.295 Å) that is between the values of 2.62 and 4.19 Å which are the sums of the covalent and van der Waals radii of the atoms, respectively. From our previous analysis of the Cambridge structural database concerning the silver–sulfur interaction, the current value (Ag1–S11 3.295 Å) is outside the acceptable ranges for Ag–S bonding for either three-(2.29–2.69 Å) or four-coordinate silver (2.40–2.80 Å),[8b] and probably represents a weak (noncovalent) ion-dipole interaction. This interaction is bolstered by a set of intra-chain CH-π interactions occurring between C13H13 and the centroid of an imidazoline ring containing N21 [green lines, Fig. 4A and B; C13H13–Ct(N21) = 2.72 Å, 140o, γ = 6.04o]. A set of π–π interactions (cyan lines Fig. 4C and D) and multiple CH–F interactions (orange lines, Fig. 4D and Table 2) serve to organize the overall supramolecular structure into discrete layers of cationic polymer sheets (in the ab-plane) alternating between layers of tetrafluoroborate anions where stacking occurs along the c-direction. Specifically, the set of π–π interactions (cyan lines, Fig. 4C) occurs between the heterocyclic ring containing N21 of one chain with that containing N31 of a neighboring chain with a centroid–centroid distance of 3.603 Å, dihedral angle a of 7.4° and slip angles β of 11.4° and γ of 18.7°. The weak CH–F interactions (Table 2)[18] involve the anion as the hydrogen acceptor and the various acidic hydrogen donors decorating the ligand including the methine hydrogen, those hydrogens on the imidazoline portion of the heterocycle and the N-methyl hydrogens.

Table 2. Summary of weak CH-F interactions in **1a**.

Donor–H–Acceptor	D–H (A)	H–A(A)	DH–A (°)
C12H12–F1	0.95	2.39	130
C32H23–F1	0.95	2.49	128
C34H34b–F1	0.98	2.25	151
C14H14a–F3	0.98	2.50	169
C33H33–F3	0.95	2.43	153
C1H1–F4	1.00	2.23	149
C34H34c–F4	0.98	2.54	163

5. Solution characterization of the ligands and silver complexes

5.1. IR and NMR spectroscopy

One of the simplest means to distinguish between linkage isomers HC(S-tim^{Me})$_3$ and HC(N-imt^{Me})$_3$ is by examination of the characteristic C–S stretching bands in the IR spectra. The thione (C═S) group exhibits a stretch in the 1230–1280 cm^{-1} region whereas a thioether (C–S–C) linkage affords weak but sharp bands in the range of 910–925 cm^{-1}; findings consistent with our previous observations for CH$_2$(S-tim^{Me})$_2$ and CH$_2$(N-imt^{Me})$_2$. We have also shown previously for CH$_2$(S-tim^{Me})$_2$ and CH$_2$(N-imt^{Me})$_2$that the coupling constants of the hydrogens on the imidazoline rings and the chemical shifts of methylene hydrogens are useful for distinguishing carbon–sulfur versus carbon-nitrogen bonded linkage isomers. The coupling constants for imidazoline hydrogens are about 2 Hz for CH$_2$(N-imt^{Me})$_2$ whereas they are only about 1 Hz in CH$_2$(S-tim)$_2$. Moreover, the chemical shift of the central methylene shifts considerably downfield for CH$_2$(N-imt^{Me})$_2$versus CH$_2$(S-tim)$_2$. This spectroscopic differentiation was also preserved in CH$_2$(S-tim)(N-imt), ClCH$_2$(S-tim) and [CH$_2$(μ-tim)$_2$CH$_2$](X)$_2$ (X = Cl, PF$_6$) and the current tripodal ligands. A 1 Hz coupling constant was observed for the imidazoline hydrogens in Cl$_2$CH(S-tim^R) and for those in HC(S-tim^R)$_3$ while a 2 Hz coupling was observed for those in HC(N-imt^R)$_3$. The chemical shift of the methine hydrogen of δ_H 5.92 ppm for HC(S-tim^R)$_3$ occurs considerably upfield from that found in HC(N-imt^R)$_3$ (δ_H 8.56 ppm) and related compounds with local HCN$_3$ environments such as the tris(pyrazolyl)methanes (which typically occur above δ_H 8.1 ppm) [14]. In addition, the chemical shifts for the thioether sp^2-carbon was in the range of δ_C 136–138 ppm in the cases of CD$_3$CN solutions of HC(S-tim^R)$_3$ (R = Me, tBu) but was δ_C 163 ppm for the thione C═S group in CD$_3$CN solutions of HC(N-imt^{tBu})$_3$. Note that the very low solubility of HC(N-imt^{Me})$_3$ in CD$_3$CN at room temperature precluded obtaining its ^{13}C NMR spectra in reasonable acquisition times. The ^{1}H NMR spectrum of each {Ag[HC(S-tim^R)$_3$]}(BF$_4$) (R = Me, **1a** or R = tBu, **1b**) in CD$_3$CN exhibited only one set of signals for the thioimidazolyl ring hydrogens at δ_H = 7.60, 7.19 ppm for **1a** and δ_H = 7.29, 6.99 ppm for **1b** (d, J = 2 Hz) which are shifted downfield with respect to the free ligands in the same solvent. The

appearance of only one set of thioimidazolyl ring hydrogens indicates that the solid state structure of **1a** is not retained in solution; the thioimidazolyl rings are either symmetrically bound to silver in each of the complexes or are undergoing rapid exchange in solution. Cooling CD_3CN solutions of **1a** or **1b** to −30 °C was insufficient to slow down any dynamic processes, if such processes occur at all.

5.2. Mass spectrometry

The ESI(+) mass spectra of silver(I) coordination complexes are thought to be representative of the solution structures.[19] In the case of **1a**, fragmentation patterns consistent with $[AgL_2]^+$, $[AgL]^+$ (monomer), free ligand $[HL]^+$ (100% ion), its decomposition fragments $[L-tim^{Me}]^+$, $[H_2tim^{Me}]^+$, and solvated silver cations $[Ag(CH_3CN)_n]^+$ (n = 1,2,4) are consistent with the dissociation of coordination polymers in CH_3CN, similar to that seen in silver coordination polymers of poly(pyrazolyl)methane chemistry. In the case of **1b**, $[AgL_2]^+$ was not observed but many of the remaining fragment ions were observed including those for the loss of *tert*-butyl radicals, an observation shared for the free ligands $HC(S-tim^{tBu})_3$ or $HC(N-imt^{tBu})_3$. Thus, the corresponding spectra of $HC(S-tim^{Me})_3$ or $HC(N-imt^{Me})_3$ were much simpler than their *tert*-butyl counterparts, as the loss of methyl radicals appears much less favorable than *tert*-butyls, as expected.

6. Concluding remarks

Two members of the tripodal compounds $HC(S-tim^R)_3$ or $HC(N-imt^R)_3$ (R = Me, tBu) have been successfully prepared by first using a triphasic reaction between aqueous $Na(S-tim^R)$ (prepared in situ using a saturated Na_2CO_3 solution) and chloroform in the presence of a phase transfer agent to obtain $HC(S-tim^R)_3$ with thioether linkages. Silver(I) complexes of $HC(S-tim^R)_3$ could be obtained at room temperature and the structural characterization of $\{Ag[HC(S-tim^{Me})_3]\}(BF_4)$ (**1a**) shows a coordination polymer in the solid state where the ligand binds metal centers in a μ-$\kappa^2 N,\kappa^1 N$-fashion. Both **1a** and its *tert*-butyl relative $\{Ag[HC(S-tim^{tBu})_3]\}(BF_4)$ (**1b**) is likely dissociated in CH_3CN solution from NMR and mass spectral data. Interestingly, simply heating CH_3CN solutions of this complex or heating solutions of $HC(S-tim^R)_3$ with various Lewis acids, lead to the isolation of the metal-free linkage isomer $HC(N-imt^R)_3$ with three carbon-nitrogen bonds and free thione (C═S) groups, corresponding to the charge-neutral analogues of the Tm^{R-} soft scorpionates. Although it has not yet been possible to obtain metal complexes of $HC(N-imt^R)_3$, the remarkable properties and robust honeycomb structure of $HC(N-imt^{Me})_3$ (with channels of ca. 5 Å in diameter) suggest that appropriately modified variants of these polar C_3-symmetric molecules may be exciting new supramolecular tectons for the construction of porous materials or for other self-assembly studies.

Acknowledgements

Appendix A. Supplementary material

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References

[1]M.D. Spicer, J. Reglinski, *Eur. J. Inorg. Chem*., in press, doi:10.1002/ejic.200801240.

[2]S. Trofimenko **The Coordination Chemistry of Polypyrazolylborate Ligands.** Imperial College Press, London (1999)

[3]C. Pettinari **Scorpionates II: Chelating Borate Ligands.** Imperial College Press, London (2008)

[4]G. Parkin. Chem. Rev., 104 (2004), p. 699

[5](a) J.M. Tanski, G. Parkin. *Chem. Commun*. (2008), p. 1008. (b) K. Pang, S.M. Quan, G. Parkin. *Chem Commun.* (2006), p. 5015. (c) J.S. Figueroa, J.G. Melnick, G. Parkin. *Inorg. Chem*., 45 (2006), p. 7056. (d) V.K. Landry, J.G. Melnick, D. Buccella, K. Pang, G. Parkin. *Inorg. Chem*., 45 (2006), p. 2588

[6](a) R.M. Silva, C. Gwengo, S.V. Lindeman, M.D. Smith, G.J. Long, F. Grandjean, J.R. Gardinier. *Inorg. Chem*., 47 (2008), p. 7233. (b) J.R. Gardinier, R.M. Silva, C. Gwengo, S.V. Lindeman. *Chem. Commun*. (2007), p. 1524. (c) R.M. Silva, C. Gwengo, S.V. Lindeman, M.D. Smith, J.R. Gardinier. *Inorg. Chem*., 45 (2006), p. 10998

[7]R.M. Silva, M.D. Smith, J.R. Gardinier. *J. Org. Chem*., 70 (2005), p. 8755

[8](a) R.M. Silva, B.J. Liddle, S.V. Lindeman, M.D. Smith, J.R. Gardinier. *Inorg. Chem*., 45 (2006), p. 6794. (b) R.M. Silva, M.D. Smith, J.R. Gardinier. *Inorg. Chem*., 45 (2006), p. 2132

[9](a) J.S. Casas, A. Castiñeiras, E. García Martínez, P. Rodríguez Rodríguez, U. Russo, A. Sánchez, A. Sánchez González, J.Sordo. *Appl. Organomet. Chem*., 13 (1999), p. 69. (b) F. Bigoli, P. Deplano, F.A. Devillanova, V. Lippolis, M.L. Mercuri, M.A. Pellinghelli, E.F. Trogu. *Inorg. Chim. Acta*, 267 (1998), p. 115 (c) F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghelli, A. Sabatini, E.F. Trogu, A. Vacca. *J. Chem. Soc*., Dalton Trans. (1996), p. 3583 (d) D.J. Williams, A. Shilatifard, D. VanDerveer, L.A. Lipscomb, R.L. Jones. *Inorg. Chim. Acta*, 202 (1992), p. 53. (e) L.S. Bark, N. Chadwick, O. Meth-Cohn. *Tetrahedron*, 48 (1992), p. 7863 (f) D.J. Williams, D. VanDerveer, R.L. Jones, D.S. Menaldino. *Inorg. Chim. Acta*, 165 (1989), p. 173

[10]R.G. Jones, E.C. Kornfeld, K.C. Mclaughlin, R.C. Anderson. *J. Am. Chem. Soc*., 71 (1949), p. 4000

[11]SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

[12]G.M. Sheldrick, SHELXTL Version 6.14, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

[13]A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.

[14](a) D.L. Reger, T.C. Grattan, K.J. Brown, C.A. Little, J.J.S. Lamba, A.L. Rheingold, R.D. Sommer. *J. Organomet. Chem.*, 607 (2000), p. 120. (b) D.L. Jameson, R.K. Castellano. *Inorg. Synth.*, 32 (1998), p. 51. (c) D.L. Reger, J.E. Collins, D.L. Jameson, R.K. Castellano. *Inorg. Synth.*, 32 (1998), p. 63

[15]A. Bondi. *J. Phys. Chem.*, 68 (1964), p. 441

[16]I. Dance, M. Scudder. Chem. Eur. J., 2 (1996), p. 481

[17]D.L. Reger, J.R. Gardinier, R.F. Semeniuc, M.D. Smith. *Dalton Trans*. (2003), p. 1712

[18]F. Grepioni, G. Cojazzi, S.M. Draper, N. Scully, D. Braga. *Organometallics*, 17 (1998), p. 296

[19](a) D.L. Reger, R.F. Semeniuc, M.D. Smith*. Inorg. Chem. Commun.*, 5 (2002), p. 278. (b) D.L. Reger, R.F. Semeniuc, M.D. Smith. *Eur. J. Inorg. Chem*. (2002), p. 543. (c) D.L. Reger, T.D. Wright, R.F. Semeniuc, T.C. Grattan, M.D. Smith. *Inorg. Chem*., 40 (2001), p. 6212