Synthesis and structural characterization of tris(2-seleno-1-mesitylimidazolyl) hydroborato complexes: A new type of strongly electron donating tripodal selenium ligand†‡

Mao Minoura, Victoria K. Landry, Jonathan G. Melnick, Keliang Pang, Luciano Marchiò and Gerard Parkin*

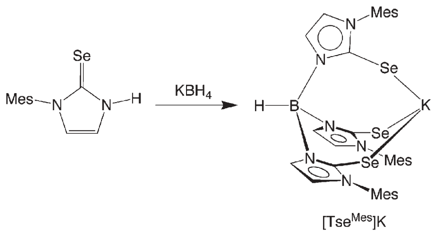
Received (in Berkeley, CA, USA) 6th June 2006, Accepted 19th July 2006
First published as an Advance Article on the web 10th August 2006
DOI: 10.1039/b608078b

A new tripodal ligand that features three selenium donors, namely the tris(2-seleno-1-mesitylimidazolyl)hydroborato ligand, [Tse^{Mes}], has been constructed *via* the reaction of KBH_4 with 1-mesitylimidazole-2-selone; comparison of the IR spectroscopic data of [Tse^{Mes}]Re(CO)$_3$ with those of a variety of related LRe(CO)$_3$ complexes demonstrates that the [Tse^{Mes}] ligand is more strongly electron donating than Cp, Cp*, [Tp], [Tp^{Me_2}] and [Tm^{Mes}] ligands.

Tripodal ligands, a prominent feature in coordination chemistry, provide three donor atoms for facial coordination to a metal center. The widespread use of this ligand system derives mainly from the ability to manipulate both steric and electronic properties. For example, electronic properties are strongly influenced by whether the tripod ligand is a neutral L_3 donor or "anionic" L_2X or X_3 donor,[1] as illustrated by the series of [N_3]-donors: tris(pyrazolyl)methane (L_3),[2] tris(pyrazolyl)hydroborato (L_2X),[3] and tris[(amido)methyl]ethane (X_3).[4,5] Tripodal ligands belonging to the L_2X class, in particular, have found widespread applications because of the large variety of donor atoms that have been incorporated. Thus, the donor set of the L_2X class of ligands may be comprised of either a homonuclear or heteronuclear array, with examples of the former including [C_3],[6] [N_3],[3] [P_3],[7] and [S_3][8,9] donors. In this paper, we introduce a new class of tripodal L_2X ligand that features an [Se_3] donor array.

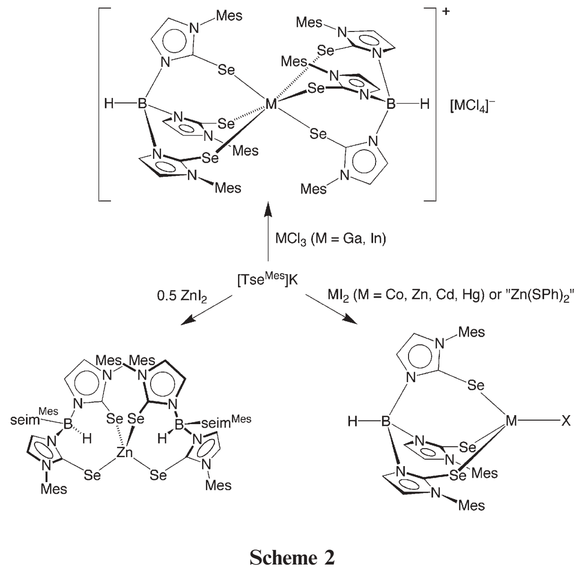
Whereas [S_3] tripodal ligands are ubiquitous,[8–10] analogous ligands that feature an [Se_3] donor array are uncommon, and the only examples of which we are aware belong to the neutral L_3 tris(selenoether) $MeC(CH_2SeR)_3$ (R = Me, Ph) system.[11,12] Since the tris(2-mercapto-1-R-imidazolyl)hydroborato ligand, [Tm^R], introduced by Reglinski and Spicer[8a] has proven to be versatile,[13] with a large variety of [Tm^R] derivatives having been prepared,[8] we envisioned that a similar series of tripodal ligands that feature an L_2X [Se_3] donor array should be accessible and thereby provide a set of ligands with modified electronic properties.

Indeed, the tris(2-seleno-1-mesitylimidazolyl)hydroborato ligand may be obtained as its potassium derivative, [Tse^{Mes}]K, *via* the reaction of KBH_4 with 1-mesitylimidazole-2-selone,[14] as illustrated in Scheme 1.[15] [Tse^{Mes}]K is a convenient reagent for a variety of derivatives of both the main group metals and transition metals (Scheme 2).[16] For example, [Tse^{Mes}]K reacts with 1 equivalent of MI_2 (M = Co, Zn, Cd, Hg) to give the corresponding [Tse^{Mes}]MX derivative, with the structure of the cobalt complex being illustrated in Fig. 1. Similarly, [Tse^{Mes}]K reacts with "Zn(SPh)$_2$" to give [Tse^{Mes}]ZnSPh. In addition to these 1 : 1 complexes, the 2 : 1 complex [Tse^{Mes}]$_2$Zn may be obtained by treatment of ZnI_2 with 2 equivalents of [Tse^{Mes}]K. The molecular structure of [Tse^{Mes}]$_2$Zn has been determined by X-ray diffraction, thereby demonstrating that the [Tse^{Mes}] ligands coordinate in a κ^2-*Se*,*Se* manner such that the zinc is effectively tetrahedral.[17]



Scheme 1

Treatment of the trivalent metal halides $GaCl_3$ and $InCl_3$ with [Tse^{Mes}]K yields {[Tse^{Mes}]$_2$M}[MCl$_4$] (M = Ga, In). Despite the fact that the cations {[Tse^{Mes}]$_2$M}$^+$ (M = Ga, In) have a similar 2 : 1 composition to that of the zinc complex, [Tse^{Mes}]$_2$Zn, a significant difference resides with the fact that the [Tse^{Mes}] ligands



Scheme 2

Department of Chemistry, Columbia University, New York, New York 10027, USA. E-mail: parkin@columbia.edu

† Electronic supplementary information (ESI) available: experimental details and crystallographic data. See DOI: 10.1039/b608078b

‡ The HTML version of this article has been enhanced with colour images.

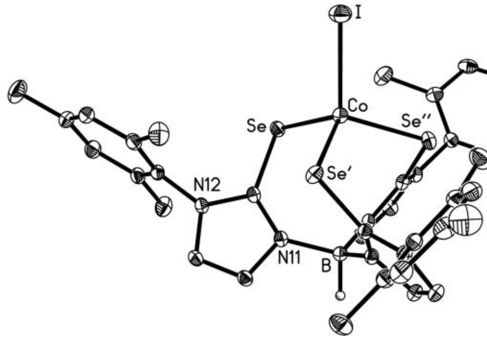


Fig. 1 Molecular structure of [Tse^{Mes}]CoI.

of $\{[Tse^{Mes}]_2M\}^+$ (M = Ga, In) coordinate in a κ^3-*Se*,*Se*,*Se* manner such that the metal centers are octahedral.[16]

In addition to κ^2-*Se*,*Se* and κ^3-*Se*,*Se*,*Se* coordination modes to a single metal center, the [Tse^{Mes}] can also bridge two metals. Thus, the [Tse^{Mes}] ligand in $\{[Tse^{Mes}]Cu\}_2$, obtained from the reaction of [Tse^{Mes}]K with CuCl (Scheme 3), bridges the two metals such that each ligand coordinates in a κ^2-*Se*,*Se* mode to one copper and a κ^1-*Se* mode to the other, with the result that each copper is trigonally coordinated (Fig. 2). This type of motif is also observed in the structure of the sulfur counterpart $\{[Tm^{Mes}]Cu\}_2$ and the related tris(thioxotriazolyl)hydroborato complexes $\{[Tr^{Et,Me}]Cu\}_2$,[18] $\{[Tr^{Me,o\text{-}Py}]Cu\}_2$,[19] and $\{[Tr^{Mes,Me}]Cu\}_2$.[19]

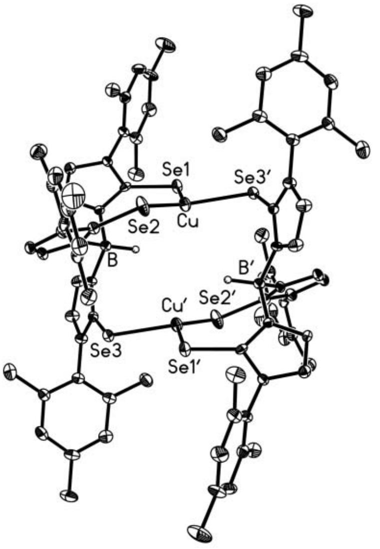
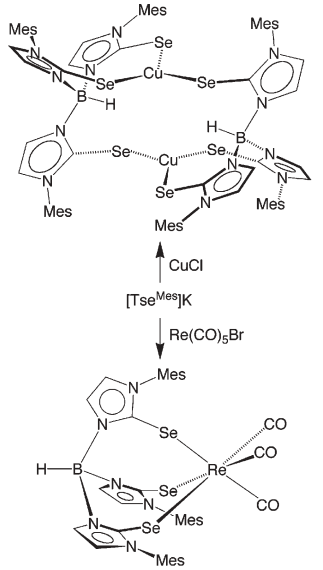


Fig. 2 Structure of $\{[Tse^{Mes}]Cu\}_2$.

An important issue concerned with the application of the [Tse^{Mes}] ligand relates to its steric and electronic properties and, in particular, how they compare with those of the [Tm^{Mes}] sulfur counterpart. In this regard, the first comprehensive evaluation of the steric and electronic properties of ligands was provided by Tolman, who obtained data for PR_3 ligands by analyzing a large series of nickel carbonyl complexes of the type $Ni(PR_3)_3(CO)$.[20] Nickel, however, is not an ideal choice of metal for the evaluation of the steric and electronic properties of multidentate ligands such as [Tse^R], [Tm^R], [Tp$^{RR'}$] and [Cp^R], because a corresponding series of nickel carbonyl complexes is unknown. Fortunately, a large number of [Tp$^{RR'}$]Re(CO)$_3$ and [Cp^R]Re(CO)$_3$ complexes are known and provide a good basis for evaluating the steric and electronic properties of such ligands.[21] For this reason, we have synthesized and structurally characterized the rhenium tricarbonyl compounds, [Tse^{Mes}]Re(CO)$_3$ (Fig. 3 and Scheme 3)[22] and [Tm^{Mes}]Re(CO)$_3$.[23]



Scheme 3

With respect to the steric properties, X-ray diffraction studies indicate that the average Re–Se bond length (2.64 Å) is 0.11 Å longer than the corresponding Re–S bond length (2.53 Å),[24] thereby causing the mesityl substituents to be displaced further from the metal center. Consequently, the [Tse^{Mes}] ligand is less sterically demanding than the [Tm^{Mes}] ligand, as quantified by their respective cone angles: [Tse^{Mes}] (211°) and [Tm^{Mes}] (219°); see Table 1.[25]

A convenient means of assessing the electron donating ability of a ligand is *via* measurement of the ν_{CO} stretching frequency of a metal carbonyl derivative.[26] On this basis, the lower ν_{CO} stretching frequencies of [Tse^{Mes}]Re(CO)$_3$ (1999 and 1886 cm^{-1}) compared to [Tm^{Mes}]Re(CO)$_3$ (2007 and 1890 cm^{-1}) indicate that the [Tse^{Mes}] ligand is more electron donating than the [Tm^{Mes}] ligand.[27,28] In addition to [Tse^{Mes}] being more electron donating than [Tm^{Mes}], it is important to note that it is also more electron donating than Cp, Cp*, [Tp] and [Tp^{Me_2}] ligands (Table 1).[29] Thus, [Tse^{Mes}] belongs to a new class of strongly electron donating tripodal ligand.

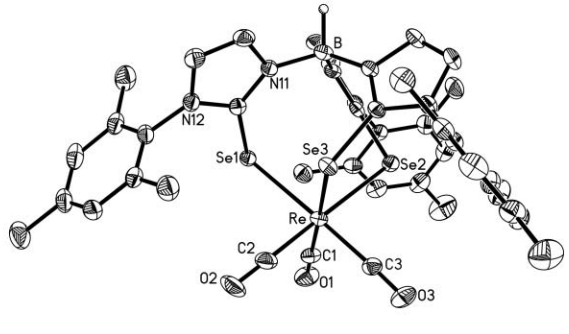


Fig. 3 Molecular structure of [Tse^{Mes}]Re(CO)$_3$.

Table 1 Electron donating and steric properties of various ligands as evaluated by ν_{CO} values and cone angles (Θ)

LRe(CO)$_3$	ν_{CO} (cm^{-1})[c]	$\nu_{CO(av)}$ (cm^{-1})	Θ (°)
[Tp][a]	2020, 1896	1958	211
Cp[a]	2019, 1897	1958	141
[Tp^{Me_2}][a]	2017, 1893	1955	255
[Tm^{Mes}][b]	2007, 1890	1949	219
Cp*[a]	1999, 1892	1946	170
[Tse^{Mes}][b]	1999, 1886	1943	211

[a] Reference 21*a*. [b] This work. [c] KBr disk.

In summary, a new tripodal ligand that features three selenium donors, namely [Tse^{Mes}], has been constructed *via* the reaction of KBH$_4$ with 1-mesitylimidazole-2-selone. Reactivity studies indicate that [Tse^{Mes}] is an effective ligand for both main group metals and transition metals, while a comparison of [Tse^{Mes}]Re(CO)$_3$ and a variety of related LRe(CO)$_3$ complexes demonstrates that the [Tse^{Mes}] ligand is more strongly electron donating than Cp, Cp*, [Tp], [Tp^{Me_2}] and [Tm^{Mes}] ligands. As such, [Tse^{R}] ligands offer considerable potential in coordination chemistry.

We thank the National Science Foundation (CHE-03-50498) for support of this research.

Notes and references

1 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127.

2 (*a*) H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635; (*b*) D. L. Reger, *Comments Inorg. Chem.*, 1999, **21**, 1.

3 Tris(pyrazolyl)hydroborato ligands are commonly abbreviated as [Tp$^{RR'}$]. See: S. Trofimenko, *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.

4 L. H. Gade, *Acc. Chem. Res.*, 2002, **35**, 575.

5 An important related class of LX$_3$ are tris(amidoethyl)amine and its various derivatives, *i.e.* [N(CH$_2$CH$_2$NR)$_3$]. See, for example: (*a*) R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 9; (*b*) R. R. Schrock, *Pure Appl. Chem.*, 1997, **69**, 2197; (*c*) J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483; (*d*) J. G. Verkade, *Coord. Chem. Rev.*, 1994, **137**, 233.

6 See, for example: (*a*) R. Fränkel, U. Kernbach, M. Bakola-Christianopoulou, U. Plaia, M. Suter, H. Ponikwar, H. Nöth, C. Moinet and W. P. Fehlhammer, *J. Organomet. Chem.*, 2001, **617–618**, 530; (*b*) R. Fränkel, C. Birg, U. Kernbach, T. Habereder, H. Nöth and W. P. Fehlhammer, *Angew. Chem., Int. Ed.*, 2001, **40**, 1907; (*c*) I. Nieto, F. Cervantes-Lee and J. M. Smith, *Chem. Commun.*, 2005, 3811.

7 For example, [PhB(CH$_2$PR$_2$)$_3$] ligands. See: (*a*) I. R. Shapiro, D. M. Jenkins, J. C. Thomas, M. W. Day and J. C. Peters, *Chem. Commun.*, 2001, 2152; (*b*) A. A. Barney, A. F. Heyduk and D. G. Nocera, *Chem. Commun.*, 1999, 2379; (*c*) J. C. Peters, J. D. Feldman and T. D. Tilley, *J. Am. Chem. Soc.*, 1999, **121**, 9871.

8 For example, [Tm^{R}] ligands. See: (*a*) M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 1975; (*b*) J. Reglinski, M. Garner, I. D. Cassidy, P. A. Slavin, M. D. Spicer and D. R. Armstrong, *J. Chem. Soc., Dalton Trans.*, 1999, 2119; (*c*) C. Santini, G. G. Lobbia, C. Pettinari, M. Pellei, G. Valle and S. Calogero, *Inorg. Chem.*, 1998, **37**, 890; (*d*) C. Kimblin, B. M. Bridgewater, D. G. Churchill and G. Parkin, *Chem. Commun.*, 1999, 2301; (*e*) M. Tesmer, M. Shu and H. Vahrenkamp, *Inorg. Chem.*, 2001, **40**, 4022; (*f*) S. Bakbak, V. K. Bhatia, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, *Polyhedron*, 2001, **20**, 3343.

9 For example, [Tt^{R}] ligands. See: (*a*) P. J. Schebler, C. G. Riordan, I. A. Guzei and A. L. Rheingold, *Inorg. Chem.*, 1998, **37**, 4754; (*b*) K. Fujita, A. L. Rheingold and C. G. Riordan, *Dalton Trans.*, 2003, 2004.

10 W. Levason and G. Reid, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, New York, 2004, ch. 1.17 and 1.18.

11 D. J. Gulliver, E. G. Hope, W. Levason, G. L. Marshall, S. G. Murray and D. M. Potter, *J. Chem. Soc., Perkin Trans. 2*, 1984, 429.

12 (*a*) A. J. Barton, A. R. J. Genge, N. J. Hill, W. Levason, S. D. Orchard, B. Patel, G. Reid and A. J. Ward, *Heteroat. Chem.*, 2002, **13**, 550; (*b*) W. Levason, S. D. Orchard and G. Reid, *Coord. Chem. Rev.*, 2002, **225**, 159.

13 For example, we have employed the [Tm^{R}] system to mimic aspects of the sulfur-rich active sites in zinc enzymes and proteins. See, for example: M. M. Morlok, K. E. Janak, G. Zhu, D. A. Quarless and G. Parkin, *J. Am. Chem. Soc.*, 2005, **127**, 14039.

14 1-Mesitylimidazole-2-selone is obtained using a method analogous to that for the methyl derivative. See: L. J. Guziec and F. S. Guziec, Jr., *J. Org. Chem.*, 1994, **59**, 4691.

15 The nature of [Tse^{Mes}]K has not been determined by X-ray diffraction and the connectivity shown in Scheme 1 is only intended to be illustrative.

16 The molecular structures of [Tse^{Mes}]MI (M = Co, Zn, Cd, Hg), [Tse^{Mes}]ZnSPh, [Tse^{Mes}]$_2$Zn, {[Tse^{Mes}]$_2$M}[MCl$_4$] (M = Ga, In), {[Tse^{Mes}]Cu}$_2$, [Tse^{Mes}]Re(CO)$_3$ and [Tm^{Mes}]Re(CO)$_3$ have been determined by X-ray diffraction (see Electronic Supplementary Information†). Thermal parameters for the structures illustrated in Fig. 1–3 are at the 20% probability level.

17 As expected for a tetrahedral zinc center, the 3-center-2-electron Zn–H–B interaction is largely insignificant. See, for example, reference 8e and (*a*) C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 891; (*b*) H. M. Alvarez, T. B. Tran, M. A. Richter, D. M. Alyounes, D. Rabinovich, J. M. Tanski and M. Krawiec, *Inorg. Chem.*, 2003, **42**, 2149; (*c*) C. Kimblin, B. M. Bridgewater, D. G. Churchill, T. Hascall and G. Parkin, *Inorg. Chem.*, 2000, **39**, 4240.

18 M. Careri, L. Elviri, M. Lanfranchi, L. Marchiò, C. Mora and M. A. Pellinghelli, *Inorg. Chem.*, 2003, **42**, 2109.

19 R. Cammi, M. Gennari, M. Giannetto, M. Lanfranchi, L. Marchiò, G. Mori, C. Paiola and M. A. Pellinghelli, *Inorg. Chem.*, 2005, **44**, 4333.

20 (*a*) C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956; (*b*) C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

21 (*a*) D. M. Tellers, S. J. Skoog, R. G. Bergman, T. B. Gunnoe and W. D. Harman, *Organometallics*, 2000, **19**, 2428; (*b*) R. G. Bergman, T. R. Cundari, A. M. Gillespie, T. B. Gunnoe, W. D. Harman, T. R. Klinckman, M. D. Temple and D. P. White, *Organometallics*, 2003, **22**, 2331.

22 For comparison with a cationic analogue, [{MeC(CH$_2$SeMe)$_3$}Re(CO)$_3$]$^{+}$, see: J. Connolly, A. R. J. Genge, W. Levason, S. D. Orchard, S. J. A. Pope and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1999, 2343.

23 For some [RTm^{Me}]Re(CO)$_3$ derivatives, see: (*a*) R. Garcia, A. Paulo, A. Domingos and I. Santos, *J. Organomet. Chem.*, 2001, **632**, 41; (*b*) R. Garcia, A. Paulo, A. Domingos and I. Santos, *Dalton Trans.*, 2003, 2757.

24 This difference is comparable to the difference in covalent radii of sulfur (1.03 Å) and selenium (1.19 Å). See: S. S. Batsanov, *Russ. Chem. Bull.*, 1995, **44**, 2245.

25 Note that these cone angles refer specifically for coordination to Re.

26 See, for example, reference 21*a* and C. E. Zachmanoglou, A. Docrat, B. M. Bridgewater, G. Parkin, C. G. Brandow, J. E. Bercaw, C. N. Jardine, M. Lyall, J. C. Green and J. B. Keister, *J. Am. Chem. Soc.*, 2002, **124**, 9525.

27 Methyl substituted [RTm^{Me}] ligands are more electron donating than the mesityl derivative as judged by the ν_{CO} frequencies of [Tm^{Me}]Re(CO)$_3$ (1987 & 1863 cm^{-1}),[23a] [PhTm^{Me}]Re(CO)$_3$ (1895 & 1865 cm^{-1})[23b] and [MeTm^{Me}]Re(CO)$_3$ (1895 & 1860 cm^{-1})[23b].

28 This observation is in accord with comparisons between thioethers and selenoethers which indicate that the selenoether is a better donor because of a reduced electronegativity (references 11 and 12) Furthermore, selenolate ligands are also more electron donating than thiolate ligands, as illustrated by lower energy ν_{CO} stretching frequency of Ru(SeC$_6$Me$_4$H)$_4$(CO) (2019 cm^{-1}) compared to Ru(SC$_6$Me$_4$H)$_4$(CO) (2040 cm^{-1}). See: M. M. Millar, T. O'Sullivan, N. de Vries and S. A. Koch, *J. Am. Chem. Soc.*, 1985, **107**, 3714.

29 For other studies which indicate that [Tm^{R}] ligands are more strongly electron donating than [Tp$^{RR'}$] ligands, see: (*a*) L. A. Graham, A. R. Fout, K. R. Kuehne, J. L. White, B. Mookherji, F. M. Marks, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2005, 171; (*b*) M. Garner, M.-A. Lehmann, J. Reglinski and M. D. Spicer, *Organometallics*, 2001, **20**, 5233.