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Rational Synthesis and Complexation Behavior of the Bidentate Lewis Acid 1,2-Bis(chloromercury)ferrocene

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1,2-Disubstituted ferrocenes represent an interesting, yet underdeveloped class of redox-active bidentate Lewis acids. We describe here a new rational synthesis of 1,2-bis(trimethylstannyl)ferrocene (**2**) and its high yield conversion to 1,2-bis(chloromercury)ferrocene (**3**). X-ray crystal structures for complexes of the bidentate Lewis acid **3** with DMSO, [Bu_4N]Cl, and [PPh_4]Cl were obtained. In all cases the two Hg atoms form reverse chelates with the nucleophile. With DMSO a 1:1 complex is formed, in which DMSO is coordinated from the *endo* side of ferrocene. Two molecules of **3** are used in the binding to the chloride anion. Different modes are realized with the two different counterions. In the complex with [Bu_4N]Cl the chloride ion is coordinated from the *exo* side of both ferrocenes, while with [PPh_4]Cl the chloride ion is *endo* with respect to one and *exo* with respect to the other ferrocene moiety. Layered and channel-like supramolecular structures are realized with [Bu_4N] and [Ph_4P] counterions, respectively.

Introduction

Arylmercury compounds have long been known to serve as highly selective precursors to other organometallic compounds through transmetalation reactions.[1] More recently, multifunctional arylmercury species have attracted much interest with regard to their ability to act as Lewis acid receptors in the recognition of anions and neutral Lewis basic species[2−8] and to serve as building blocks for supramolecular chemistry.[8−10] They have also proven useful as chemo- and stereoselective Lewis acid catalysts,[11,12] phase transfer catalysts,[13] sensors,[14] luminescence enhancing materials,[15] and membrane components.[16]

Over the past about 20 years Wuest and co-workers have done extensive work on the complexation behavior and catalytic activity of 1,2-phenylenedimercury dichloride **A**.[4a−d] The respective fluorinated species **B** has been explored by Gabbaï,[5h−k,10,11] and the naphthalene derivative **C** has been studied by Schmidbaur and Oh.[6,7] However, although the related 1,2-dimercurated ferrocene derivative has been reported by Rausch and co-workers as early as 1974,[17] a lack of binding studies using this metallocene-based bidentate Lewis acid is noticeable. The latter may be attributed to difficulties

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(1) Elschenbroich, C.; Salzer, A. *Organometallics, A Concise Introduction*, 2nd, revised ed.; VCH: Weinheim, New York, 1992.

(2) Recent reviews: (a) Kaufmann, D. E.; Otten, A. *Angew. Chem.* **1994**, *106*, 1917. (b) Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55. (c) Beer, P. D.; Smith, D. K. *Prog. Inorg. Chem.* **1997**, *46*, 1. (d) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267. (e) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81. (f) Wedge, T. J.; Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111. (g) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486.

(3) (a) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1507. (b) Yang, X. G.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142. (c) Zheng, Z.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 12338. (d) Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 5105. (e) Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 432. (f) Zinn, A. A.; Knobler, C. B.; Harwell, D. E.; Hawthorne, M. F. *Inorg. Chem.* **1999**, *38*, 2227. (g) Lee, H.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 776. (h) Lee, H.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 8543. (i) Bayer, M. J.; Jalisatgi, S. S.; Smart, B.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1854.

(4) (a) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410. (b) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931. (c) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73. (d) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153. (e) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1987**, *109*, 4714. (f) Nadeau, F.; Simard, M.; Wuest, J. D. *Organometallics* **1990**, *9*, 1311. (g) Simard, M.; Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 370. (h) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1215. (i) Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 13016.

(5) (a) Tschinkl, M.; Schier, A.; Riede, J.; Mehltretter, G.; Gabbaï, F. P. *Organometallics* **1998**, *17*, 2921. (b) King, J. B.; Tsunoda, M.; Gabbaï, F. P. *Organometallics* **2002**, *21*, 4201. (c) Haneline, M. R.; King, J. B.; Gabbaï, F. P. *Dalton Trans.* **2003**, 2686. (d) Tschinkl, M.; Gabbaï, F. P. *J. Chem. Cryst.* **2003**, *33*, 595. (e) Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2003**, *125*, 10492. (f) Haneline, M. R.; Gabbaï, F. P. *C. R. Chim.* **2004**, *7*, 871. (g) Haneline, M. R.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 5471. (h) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **1999**, *38*, 3547. (i) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Organometallics* **1999**, *18*, 1747. (j) Tschinkl, M.; Bachman, R. E.; Gabbaï, F. P. *Organometallics* **2000**, *19*, 2633. (k) Beckwith, J. D.; Tschinkl, M.; Picot, A.; Tsunoda, M.; Bachman, R.; Gabbaï, F. P. *Organometallics* **2001**, *20*, 3169.

(6) (a) Lopez, P.; Reilly, M.; Oh, T. *Recent Res. Dev. Org. Chem.* **1999**, *3*, 297. (b) Lopez, P.; Oh, T. *Tetrahedron Lett.* **2000**, *41*, 2313.

(7) Schmidbaur, H.; Öller, H. J.; Wilkinson, D. L.; Huber, B.; Müller, G. *Chem. Ber.* **1989**, *122*, 31.

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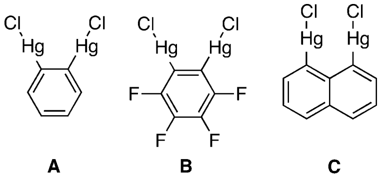
in preparing this compound in high yield. Direct mercuration of ferrocene with $Hg(OAc)_2$ leads primarily to monomercurated and 1,1′-dimercurated ferrocene,[18−20] and the crude 1,2-dimercurated species is obtained only in a very low yield of ca. 2% after tedious workup procedures including column chromatographic separation of the different isomers. On the other hand, ferrocene-based bidentate Lewis acids of this type[21−23] are particularly intriguing due to the unique three-dimensional geometry and, maybe even more importantly, the opportunity to influence the binding strength through the oxidation state of the central metal ion.[23i,j,24] We have previously demonstrated that heteronuclear bidentate ferrocene-based Lewis acids comprised of boron and/or tin groups can readily be prepared through a rearrangement reaction from 1,1′-bis(trimethylstannyl)ferrocene and boron halides.[22] Here we report a new synthetic route to 1,2-bis(chloromercury)ferrocene and the first studies on the complexation behavior of this ferrocene-based bidentate Lewis acid with neutral and anionic substrates.

Chart 1



Results and Discussion

For the preparation of 1,2-dimetalated ferrocenes we have chosen a new modular approach that is outlined in Scheme 1. This method involves initial preparation of a 1,2-distannylated ferrocene, which in itself is an interesting molecule that may serve as a versatile precursor to other bidentate Lewis acids. The related compound 1,2-bis(tributylstannyl)ferrocene had been mentioned previously by Butler and co-workers to form upon lithiation of 1,2-dibromoferrocene and subsequent treatment with tributyltin chloride.[25] However, this intriguing distannylated ferrocene had not been ob-

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(8) (a) Shur, V. B.; Tikhonova, I. A.; Yanovskii, A. I.; Struchkov, Y. T.; Petrovskii, P. V.; Panov, S. Y.; Furin, G. G.; Vol'pin, M. E. *Dokl. Akad. Nauk* **1991**, *321*, 1002. (b) Shur, V. B.; Tikhonova, I. A.; Yanovskii, A. I.; Struchkov, Y. T.; Petrovskii, P. V.; Panov, S. Y.; Furin, G. G.; Vol'pin, M. E. *J. Organomet. Chem.* **1991**, *418*, C29. (c) Shur, V. B.; Tikhonova, I. A.; Yanovskii, A. I.; Struchkov, Y. T.; Petrovskii, P. V.; Panov, S. Y.; Furin, G. G.; Vol'pin, M. E. *Izv. Akad. Nauk, Ser. Khim.* **1991**, 1466. (d) Shur, V. B.; Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T.; Volkonsky, A. Y.; Solodova, E. V.; Panov, S. Y.; Petrovskii, P. V.; et al. *J. Organomet. Chem.* **1993**, *443*, C19. (e) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Struchkov, Y. T.; Yanovsky, A. I.; Tikhonova, I. A.; Shur, V. B. *J. Organomet. Chem.* **1997**, *536*, 413. (f) Saitkulova, L. N.; Bakhmutova, E. V.; Shubina, E. S.; Tikhonova, I. A.; Furin, G. G.; Bakhmutov, V. I.; Gambaryan, N. P.; Chistyakov, A. L.; Stankevich, I. V.; Shur, V. B.; Epstein, L. M. *J. Organomet. Chem.* **1999**, *585*, 201. (g) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Starikova, Z. A.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2000**, *613*, 60. (h) Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2002**, *654*, 123. (i) Tikhonova, I. A.; Shubina, E. S.; Dolgushin, F. M.; Tugashov, K. I.; Teplitskaya, L. N.; Filin, A. M.; Sivaev, I. B.; Petrovskii, P. V.; Furin, G. G.; Bregadze, V. I.; Epstein, L. M.; Shur, V. B. *Russ. Chem. Bull. (Transl. of Izv. Akad. Nauk, Ser. Khim.)* **2003**, *52*, 594. (j) Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Ellert, O. G.; Novotortsev, V. M.; Furin, G. G.; Antipin, M. Y.; Shur, V. B. *J. Organomet. Chem.* **2004**, *689*, 82. (k) Tikhonova, I. A.; Dolgushin, F. M.; Yakovenko, A. A.; Tugashov, K. I.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *Organometallics* **2005**, *24*, 3395.

(9) (a) Tschinkl, M.; Bachman, R. E.; Gabbaï, F. P. *J. Organomet. Chem.* **1999**, *582*, 40. (b) Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 8335. (c) King, J. B.; Haneline, M. R.; Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 9350.

(10) Gardinier, J. R.; Gabbaï, F. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2861.

(11) King, J. B.; Gabbaï, F. P. *Organometallics* **2003**, *22*, 1275.

(12) (a) Oh, T.; Lopez, P.; Reilly, M. *Eur. J. Org. Chem.* **2000**, *16*, 2901. (b) Lee, H.; Diaz, M.; Hawthorne, M. F. *Tetrahedron Lett.* **1999**, *40*, 7651.

(13) (a) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1985**, *107*, 6121. (b) Zaraisky, A. P.; Kachurin, O. I.; Velichko, L. I.; Tikhonova, I. A.; Volkonsky, A. Y.; Shur, V. B. *Izv. Akad. Nauk, Ser. Khim.* **1994**, 2047. (c) Zaraisky, A. P.; Kachurin, O. I.; Velichko, L. I.; Tikhonova, I. A.; Furin, G. G.; Shur, V. B. *J. Mol. Catal. A* **2005**, *231*, 103. (d) Shur, V. B.; Tikhonova, I. A. *Russ. Chem. Bull. (Transl. of Izv. Akad. Nauk, Ser. Khim.)* **2003**, *52*, 2539.

(14) Badr, I. H. A.; Johnson, R. D.; Diaz, M.; Hawthorne, M. F.; Bachas, L. G. *Anal. Chem.* **2000**, *72*, 4249.

(15) (a) Zander, M. *Z. Naturforsch.* **1971**, *26a*, 1371. (b) Haneline, M. R.; Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 3737. (c) Omary, M. A.; Kassab, R. M.; Haneline, M. R.; Elbjeirami, O.; Gabbaï, F. P. *Inorg. Chem.* **2003**, *42*, 2176.

(16) (a) Badr, I. H. A.; Diaz, M.; Hawthorne, M. F.; Bachas, L. G. *Anal. Chem.* **1999**, *71*, 1371. (b) Johnson, R. D.; Badr, I. H. A.; Diaz, M.; Wedge, T. J.; Hawthorne, M. F.; Bachas, L. G. *Electroanalysis* **2003**, *15*, 1244. (c) Yan, Z.; Zhou, Z.; Wu, Y.; Tikhonova, I. A.; Shur, V. B. *Anal. Lett.* **2005**, *38*, 377.

(17) Roling, P. V.; Rausch, M. D. *J. Org. Chem.* **1974**, *39*, 1420.

(18) (a) Nesmeyanov, A. N.; Perevalova, E. G.; Golovnya, R. V.; Newmeyanova, O. A. *Dokl. Akad. Nauk.* **1954**, *97*, 459. (b) Rausch, M.; Vogel, M.; Rosenberg, H. *J. Org. Chem.* **1957**, *22*, 900. (c) Rausch, M. D. *J. Org. Chem.* **1963**, *28*, 3337. (d) Nefedov, V. A. *Zh. Obshch. Khim.* **1966**, *36*, 1954. (e) Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1955. (f) Fung, C. W.; Roberts, R. M. G. *Tetrahedron* **1980**, *36*, 3289. (g) Lemonovskii, D. A.; Urazovskii, I. F.; Baukova, T. V.; Arkhipov, I. L.; Stukan, R. A.; Perevalova, E. G. *J. Organomet. Chem.* **1984**, *264*, 283. (h) Cui, X. L.; Wu, Y. J.; Zou, D. P.; He, C. H.; Chai, J. J. *Polyhedron* **1999**, *18*, 1023. (i) Xu, X.; Fong, S.-W. A.; Li, Z.; Loh, Z.-H.; Zhao, F.; Vittal, J. J.; Henderson, W.; Khoo, S.-B.; Hor, T. S. A. *Inorg. Chem.* **2002**, *41*, 6838.

(19) For polymercuration of metallocenes see: (a) Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* **1992**, *11*, 3169. (b) Winter, C. H.; Han, Y.-H.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1161. (c) Han, Y.-H.; Heeg, M. J.; Winter, C. H. *Organometallics* **1994**, *13*, 3009. (d) Kur, S. A.; Heeg, M. J.; Winter, C. H. *Organometallics* **1994**, *13*, 1865. (e) Kur, S. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1995**, *34*, 414. (f) Kur, S. A.; Winter, C. H. *J. Organomet. Chem.* **1996**, *512*, 39. (g) Seneviratne, K. N.; Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 5506.

(20) For mechanistic studies see: (a) Cunningham, A. F. *Organometallics* **1997**, *16*, 1114. (b) Mayor-Lopez, M. J.; Weber, J.; Mannfors, B.; Cunningham, A. F. *Organometallics* **1998**, *17*, 4983.

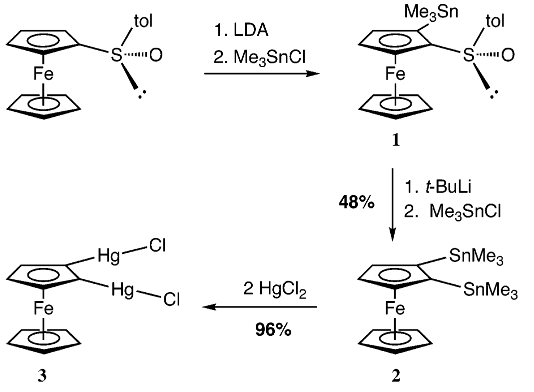
(21) Atwood, J. L.; Shoemaker, A. L. *Chem. Commun.* **1976**, 536.

(22) (a) Gamboa, J. A.; Sundararaman, A.; Kakalis, L.; Lough, A. J.; Jäkle, F. *Organometallics* **2002**, *21*, 4169. (b) Boshra, R.; Sundararaman, A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L.; Jäkle, F. *Chem. Eur. J.* **2005**, *11*, 2810. (c) Venkatasubbaiah, K.; Zakharov, L. N.; Kassel, W. S.; Rheingold, A. L.; Jäkle, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5428.

(23) The respective 1,1′-disubstituted metallocenes are generally more readily accessible and thus more common: (a) Herdtweck, E.; Jäkle, F.; Wagner, M. *Organometallics* **1997**, *16*, 4737. (b) Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453. (c) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669. (d) Ma, K.; Scheibitz, M.; Scholz, S.; Wagner, M. *J. Organomet. Chem.* **2002**, *652*, 11. (e) Ding, L.; Ma, K. B.; Durner, G.; Bolte, M.; de Biani, F. F.; Zanello, P.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **2002**, 1566. (f) Herberich, G. E.; Fischer, A.; Wiebelhaus, D. *Organometallics* **1996**, *15*, 3106. (g) Jutzi, P.; Lenze, N.; Neumann, B.; Stammler, H.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1423. (h) Carpenter, B. E.; Piers, W. E.; McDonald, R. *Can. J. Chem.* **2001**, *79*, 291. (i) Aldridge, S.; Bresner, C.; Fallis, I. A.; Coles, S. J.; Hursthouse, M. B. *Chem. Commun.* **2002**, 740. (j) Bresner, C.; Aldridge, S.; Fallis, I. A.; Jones, C.; Ooi, L.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3606.

(24) (a) Dusemund, C.; Sandanayake, K. R. A. S.; Shinkai, S. *Chem. Commun.* **1995**, 333. (b) Takeuchi, M.; Mizuno, T.; Shinkai, S.; Shirakami, S.; Itoh, T. *Tetrahedron: Asymmetry* **2000**, *11*, 3311. (c) Norrild, J. C.; Sotofte, I. *J. Chem. Soc., Perkin Trans. 2* **2001**, 727. (d) Norrild, J. C.; Sotofte, I. *J. Chem. Soc., Perkin Trans. 2* **2002**, 303. (e) Arimori, S.; Ushiroda, S.; Peter, L. M.; Jenkins, A. T. A.; James, T. D. *Chem. Commun.* **2002**, 2368. (f) Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 924. (g) Scheibitz, M.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Nowik, I.; Herber, R. H.; Krapp, A.; Lein, M.; Holthausen, M.; Wagner, M. *Chem. Eur. J.* **2005**, *11*, 584.

Scheme 1. Synthesis of 1,2-Bis(chloromercury)ferrocene



tained in pure form and was only characterized by ^{1}H NMR spectroscopy. We chose a slightly different synthetic method, where *p*-tolylsulfinylferrocene serves as the starting material. The 1,2-functionalized ferrocene species 1-trimethylstannyl-2-*p*-tolylsulfinylferrocene (**1**) was prepared through directed lithiation followed by treatment with trimethyltin chloride according to a literature procedure.[26,27] Subsequent reaction of **1** with *tert*-butyllithium (1.1 equiv) followed by addition of trimethyltin chloride (1.2 equiv) led to the formation of the desired 1,2-bis(trimethylstannyl)ferrocene (**2**) together with a small amount of the monostannylated species 1-trimethylstannylferrocene (Scheme 1). Removal of trimethylstannylferrocene by vacuum distillation gave pure **2** in 48% isolated yield. Formation of **2** was confirmed by multinuclear NMR spectroscopy and mass spectrometry. For instance, the ^{1}H NMR spectrum of **2** shows a triplet at δ 4.41 (1H) and a doublet at δ 4.20 (2H) with a coupling constant of $^3J = 2.5$ Hz, which is characteristic of 1,2-disubstituted ferrocenes.[17,22,28] Moreover, a single signal at δ −4.2 in the ^{119}Sn NMR spectrum is consistent with the symmetry of **2**. The molecular ion peak is found at $m/z = 512$ in the mass spectrum, further confirming the identity of **2**.

Aryltriorganotin compounds are known to react with mercuric halides with high selectivity and under mild conditions to give the respective arylmercury species.[29] Thus, treatment of **2** with 2 equiv of $HgCl_2$ in acetone led to formation of 1,2-bis(chloromercury)ferrocene (**3**) as a yellow solid in 96% isolated yield. Comparison of the ^{1}H NMR spectrum of the product with literature data for **3** confirmed the 1,2-substitution pattern;[17] compound **3** was further characterized by ^{13}C NMR spectroscopy and elemental analysis. We also studied the redox properties of **3** by cyclic voltammetry in DMF, which reveals a reversible one-electron oxidation wave at $E_{1/2} = -96$ mV with respect to FcH/FcH$^+$.[30] The latter confirms that **3** may indeed act as a redox-active bidentate Lewis acid in the recognition of anions and neutral Lewis basic substrates.

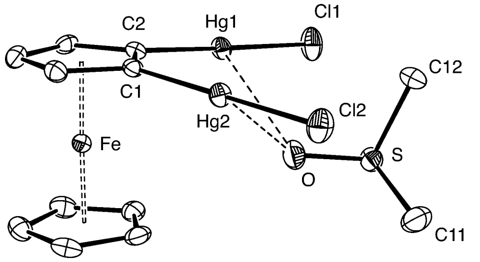


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Hg1−C2 2.028(4), Hg2−C1 2.021(4), Hg1−Cl1 2.3195(12), Hg2−Cl2 2.3341(13), Hg2−O 2.771(3), Hg1−O 2.955(4), C2−Hg1−Cl1 178.68(12), C1−Hg2−Cl2 173.74(12), Cl1−Hg1−O 90.63(8), Cl2−Hg2−O 92.47(8), C2−Hg1−O 90.68(13), C1−Hg2−O 93.64(14).

To investigate the ability of **3** to serve as a bifunctional Lewis acid, we have performed binding studies of **3** with the neutral substrate DMSO and with chloride as an anionic nucleophile. Recrystallization of **3** from hot acetone in the presence of DMSO led to X-ray quality single crystals of the DMSO adduct **4**. The incorporation of DMSO in the product was confirmed by IR spectroscopy, which shows the expected S=O stretching band at 1018 cm^{-1}. Elemental analysis of **4** is consistent with incorporation of only one molecule of DMSO. To further examine the binding of DMSO to the bidentate Lewis acid **3**, we performed a single-crystal X-ray diffraction study.

The molecular structure of **4** confirms the formation of a 1:1 complex, in which the oxygen atom coordinates to both Hg atoms (Figure 1). Interestingly, the DMSO molecule is coordinating from the *endo* side of the ferrocene, which stands in contrast to what we have previously observed for the binding of pyridine to the heteronuclear bifunctional Lewis acid 1,2-fc($SnMe_2Cl$)(BMeCl) comprising organotin and organoboron moieties in the 1,2-positions of the same Cp ring.[22b] The lower steric demand of the DMSO molecule is probably in part responsible for the preference for the *endo* side in **4**, and packing effects likely also play an important role. The Hg···O distances of 2.955(4) and 2.771(3) Å significantly differ from one another, although both are shorter than the sum of the van der Waals radii (for O, 1.54 Å;[31] for Hg, 1.73−2.00 Å[32]). In comparison, the Hg···O contacts in the related complexes 1,8-bis(chloromercurio)naphthalene·DMSO,[7] 1,2-bis(chloromercurio)benzene·DMF,[4d] and 1,2-bis(chloromercurio)tetrafluorobenzene·$(DMSO)_2$[5h] are all in the range from 2.681 to 2.804 Å. The larger distortion from linearity for C1−Hg2−Cl2 (173.7(1)°) relative to C2−Hg1−Cl1 (178.7(1)°) is associated with the shorter Hg···O contact and is tentatively attributed to a combination of electronic effects due to nucleophile

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(25) Butler, I. R.; Drew, M. G. B. *Inorg. Chem. Commun.* **1999**, *2*, 234.

(26) (a) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. (b) Riant, O.; Argouarch, G.; Guillaneux, D.; Samuel, O.; Kagan, H. B. *J. Org. Chem.* **1998**, *63*, 3511.

(27) See also related work: (a) Hua, D. H.; Lagneau, N. M.; Chen, Y.; Robben, P. M.; Clapham, G.; Robinson, P. D. *J. Org. Chem.* **1996**, *61*, 4508. (b) Lagneau, N. M.; Chen, Y.; Robben, P. M.; Sin, H.-S.; Takasu, K.; Chen, J.-S.; Robinson, P. D.; Hua, D. H. *Tetrahedron* **1998**, *54*, 7301. (c) Bolm, C.; Kesselgruber, M.; Muñiz, K.; Raabe, G. *Organometallics* **2000**, *19*, 1648.

(28) Pickett, T. E.; Richards, C. J. *Tetrahedron Lett.* **1999**, *40*, 5251.

(29) See for example: (a) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43. (b) Roberts, R. M. G.; Silver, J.; Azizian, J. *J. Organomet. Chem.* **1986**, *303*, 387. (c) Rot, N.; de Kanter, F. J. F.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **2000**, *593−594*, 369.

(30) See also: Fernandes, J. C.; de Lima, G. M.; Filgueiras, C. A. L. *Quim. Nova* **1994**, *17*, 17.

(31) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr. Sect. B* **1985**, *41*, 274.

(32) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225.

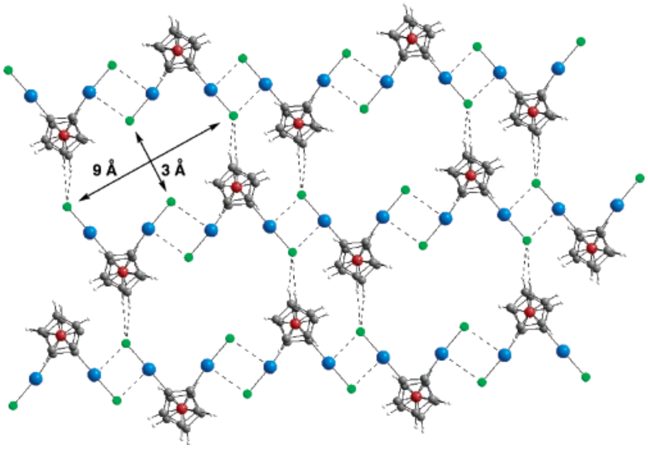

Figure 2. View of the extended structure of **4** (one layer). The DMSO molecules that are located inside the channels are omitted for clarity.

binding to Hg and steric distortions that result from interference between the chloro substituent and one of the DMSO methyl groups. A slight tilting of the HgCl substituents relative to the Cp planes ($Cp_{Centroid}$−C2−Hg1 = 174.7(1)° and $Cp_{Centroid}$−C1−Hg2 = 174.8(1)°) toward the Fe atoms may also be associated with binding of the DMSO ligand, although a comparison with the elusive structure of the free acid **3** would be needed to confirm this feature. The Hg−C bond lengths of 2.021(4) and 2.028(4) Å as well as the Hg−Cl bond distances of 2.319(1) and 2.334(1) Å are comparable to those found in other chloromercuryferrocene derivatives.[33]

The packing diagram of **4** shown in Figure 2 reveals an interesting sheet-like supramolecular structure. Infinite chains arise due to weak intermolecular Hg⋯Cl contacts (Hg1⋯Cl1* 3.31(2) and Hg2⋯Cl2* 3.46(3) Å), which fall within the limit of the sum of the van der Waals radii of chlorine (1.58−1.78 Å)[31] and mercury (1.73−2.00 Å).[32] Weak hydrogen-bonding interactions (Cl⋯H = 3.07(3) and 3.14(2) Å) between these chains lead to the formation of an extended sheet structure. The sheets in turn are further interlinked by hydrogen-bonding interactions that lead to formation of a 3D network containing channels with effective diagonals of ca. 9 and 3 Å (Figure 2). The channels are occupied by the coordinated DMSO molecules, which can be removed at elevated temperature, as shown by thermogravimetric analysis (TGA). The TGA trace shows a 9% weight loss at 151 °C (onset), corresponding to evaporation of DMSO from the solid. A microporous solid with channels (effective diagonals of ca. 10 and 7 Å), in which the walls consist of four dimercuriobenzene species, was reported previously for the structure of 1,2-bis(chloromercurio)-tetrafluorobenzene by Gabbaï.[5h] While in Gabbaï's system assembly into a three-dimensional structure is promoted by π-stacking interactions, in our case hydrogen bonding results in formation of extended channels.

The chloride complexes $[Bu_4N][(C_5H_5FeC_5H_3Hg_2Cl_2)_2Cl]$ (**5a**) and $[Ph_4P][(C_5H_5FeC_5H_3Hg_2Cl_2)_2Cl]$ (**5b**) were prepared by treatment of **3** with $[Bu_4N]Cl$ and $[Ph_4P]Cl$, respectively. Slow solvent evaporation gave **5a** (from CH_2Cl_2) and **5b** (from $CHCl_3$) as orange crystalline compounds. The ^1H NMR spectra of the crystals indicated in both cases the formation of a 2:1 complex with Cl^-, which was further confirmed by X-ray crystallography and elemental analysis.

The structures of **5a** and **5b** are shown in Figure 3a and Figure 3b, respectively. In both species, formation of the complex anion $[(C_5H_5FeC_5H_3Hg_2Cl_2)_2Cl]^-$ is evident, which consists of a chloride ion (Cl5) that is bridged by four Lewis acidic mercury atoms from two molecules of 1,2-bis(chloromercurio)ferrocene. Thus the chloride anion (Cl5) is coordinated by each ferrocene unit in a bidentate manner. This structural feature has also been found by Wuest et al. for the chloride complex of 1,2-phenylenedimercurydichloride.[4c] However, an interesting observation is made in that the coordination mode with respect to the central iron atom is different for the two complexes **5a** and **5b**. While for the $[Bu_4N]^+$ complex **5a** the chloride anion occupies positions on the *exo* side with respect to both ferrocene moieties (Figure 3a), in **5b** the chloride anion is bound from the *exo* side of one ferrocene, but from the *endo* side of the other ferrocene moiety (Figure 3b). This observation suggests again that, in contrast to our previous work on the pyridine binding to heteronuclear bidentate ferrocene Lewis acids,[22b] there is no strong preference for the binding mode with respect to the iron center in these chloride complexes and that packing and counterion effects play a decisive role. While the bond lengths and angles for **5a** and **5b** are overall fairly similar, closer inspection reveals some subtle differences. The Cl(5)−Hg distances vary from 2.889(2) to 3.144(2) Å for **5a** and from 2.934(3) to 3.141(3) Å for **5b**. However, for **5a** three relatively long and one shorter Hg4⋯Cl5 contact of 2.889(2) Å are formed, whereas three short and one longer contact of Hg1⋯Cl5 = 3.141(3) Å are present in **5b**. In comparison, Wuest et al. observed similar Hg⋯Cl distances of 2.857−3.335 Å for the complex ion $[(1,2\text{-}C_6H_4(HgCl)_2)_2Cl]^-$, although with two short and two longer contacts.[4c] Interestingly, the short Hg4⋯Cl5 distance in **5a** can be related to a significant deviation from linearity of the C12−Hg4−Cl4 moiety (170.0(3)°) and a relatively long Hg4−Cl4 bond of 2.346(3) Å. The long contact in **5b** on the other hand is associated with a more modest deviation from linearity for C10−Hg1−Cl1 (175.1(4) Å) and a shorter Hg−Cl bond of 2.310(3) Å. Overall, however, the Hg−C distances for **5a** (2.032(10) to 2.051(10) Å) and **5b** (2.047(12) to 2.071(12) Å) and the Hg−Cl distances for **5a** (2.315(3) to 2.346(3) Å) and **5b** (2.310(3) to 2.359(3) Å) are in the same range as those reported in the literature. A slight tilting of the HgCl substituents in **5a** toward Fe ($Cp_{Centroid}$−C−Hg of 174.4° to 177.7°) that is similar to though less pronounced than in **4** is observed. However, especially distortions for Hg2 and Hg4 are to a large extent due to displacement within the plane, as evident from comparison of the angles C13−C12−Hg4 and C11−C12−Hg4 (129.8(8)° and 123.8(8)°) as well as C3−C2−Hg2 and C1−C2−Hg2 (128.6(7)° and 122.8(8)°) with the expected angle of 126° in an undistorted system. In **5b** only one of the HgCl substituents for each ferrocene moiety is tilted toward Fe ($Cp_{Centroid}$−C19−Hg3 = 173.2(1)° and

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[33] (a) Sünkel, K.; Kiessling, T. *J. Organomet. Chem.* **2001**, *637−639*, 796. (b) Huo, S. Q.; Zhu, Y.; Wu, Y. J. *J. Organomet. Chem.* **1995**, *490*, 243. (c) Wu, Y. J.; Cui, X. L.; Liu, Y. H.; Yuan, H. Z.; Mao, X. A. *J. Organomet. Chem.* **1997**, *543*, 63. (d) Lin, K.; Song, M.; Zhu, Y.; Wu, Y. *J. Organomet. Chem.* **2002**, *660*, 139.

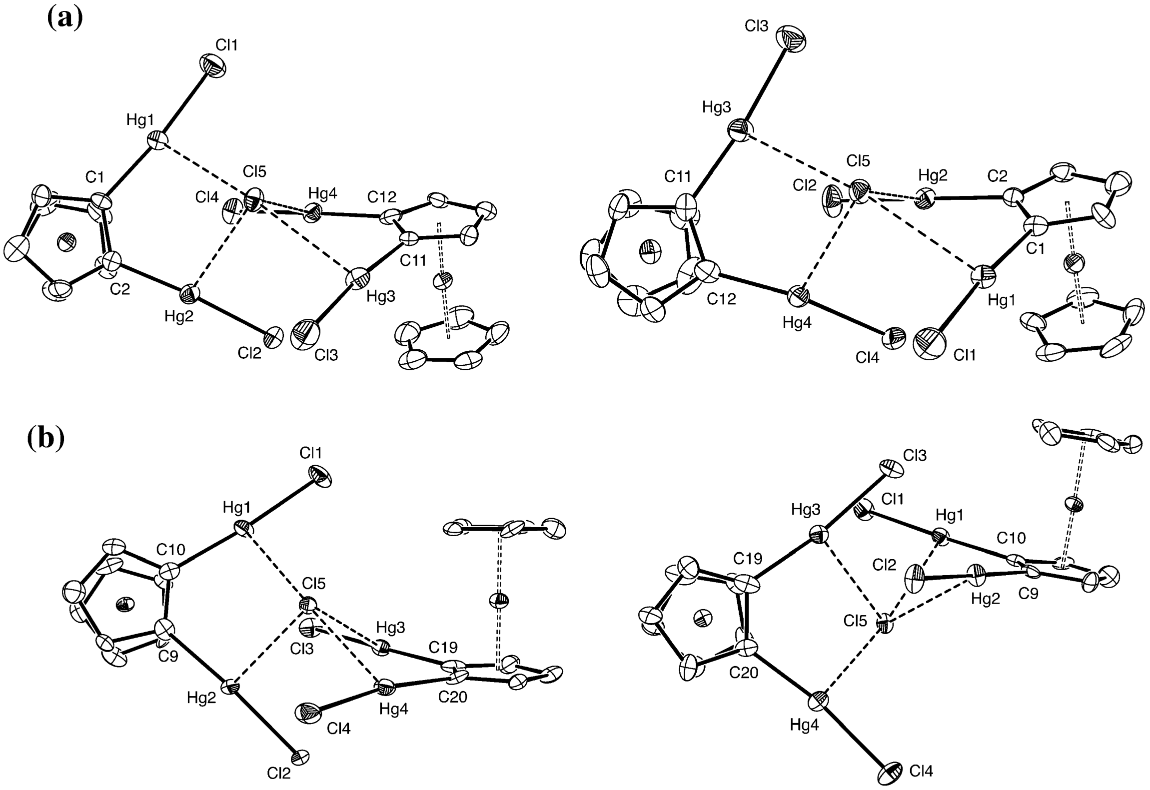

Figure 3. (a) Two different views of the molecular structure of **5a** with thermal ellipsoids at the 50% probability level showing the chloride ion above the Cp plane of both ferrocene moieties. Hydrogen atoms and the countercation are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Hg1−C1 2.032(10), Hg2−C2 2.051(10), Hg3−C11 2.044(11), Hg4−C12, 2.037(11), Hg1−Cl1 2.315(3), Hg2−Cl2 2.335(3), Hg3−Cl3 2.325(3), Hg4−Cl4 2.346(3), Hg1−Cl5 3.144(2), Hg2−Cl5 3.043(3), Hg3−Cl5 3.129(2), Hg4−Cl5 2.889(2); C1−Hg1−Cl1 173.8(3), C2−Hg2−Cl2 174.6(3), C11−Hg3−Cl3 173.2(3), C12−Hg4−Cl4 170.0(3), C12−Hg4−Cl5 99.6(3), C11−Hg3−Cl5 92.8(3), C1−Hg1−Cl5 94.2(3), C2−Hg2−Cl5 97.5(3), Hg1−Cl5−Hg2 76.10(6), Hg3−Cl5−Hg4 77.94(6). (b) Two different views of the molecular structure of **5b** with thermal ellipsoids at the 50% probability level showing the chloride ion (i) below the plane of the Cp ring of one of the ferrocene moieties and (ii) above the plane of the Cp ring of the adjacent ferrocene. Hydrogen atoms and the countercation are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Hg1−C10 2.071(12), Hg2−C9 2.053(13), Hg3−C19 2.053(12), Hg4−C20 2.047(12), Hg1−Cl1 2.310(3), Hg2−Cl2 2.343(3), Hg3−Cl3 2.359(3), Hg4−Cl4 2.322(3), Hg1−Cl5 3.141(3), Hg2−Cl5 2.985(3), Hg3−Cl5 2.934(3), Hg4−Cl5 2.957(3); C10−Hg1−Cl1 175.1(4), C9−Hg2−Cl2 175.8(4), C19−Hg3−Cl3 172.5(4), C20−Hg4−Cl4 169.3(3), C9−Hg2−Cl5 92.7(3), C10−Hg1−Cl5 88.8(3), C19−Hg3−Cl5 97.6(4), C20−Hg4−Cl5 95.4(3), Hg1−Cl5−Hg2 77.16(7), Hg3−Cl5−Hg4 81.91(7).

$Cp_{Centroid}$−C10−Hg1 = 175.4(1)°), whereas the other one is slightly bent away ($Cp_{Centroid}$−C20−Hg4 = 179.0(1)° and $Cp_{Centroid}$−C9−Hg2 = 178.4(1)°).

While the structural parameters are quite similar for **5a** and **5b** on the molecular level, considerable differences are apparent in the supramolecular structures. The packing diagram of compound **5a** reveals the formation of a sheet-like structure with layers of the complex anion $[(1,2\text{-fc}(HgCl)_2)_2Cl]^-$ alternating with layers of $[Bu_4N]^+$ counterions (Figure 4). Relatively short intermolecular Hg···Cl contacts (3.543(17) and 3.546(9) Å) result in chains of complex anions, which in turn are interconnected by C−H···Cl hydrogen-bonding interactions (2.97(1) to 3.06(2) Å) to form the layered structure of anions (Figure 5).

In contrast to the layered structure of **5a**, a channel-like structure is realized in the case of the phosphonium complex **5b** (Figure 6). The $[(1,2\text{-fc}(HgCl)_2)_2Cl]^-$ anions form zigzag chains, in which the individual units are connected by weak intermolecular Hg···Cl contacts (3.623(3) Å). Hydrogen-bonding interactions between ferrocene H atoms and the chlorine atoms of cocrystallized $CHCl_3$ molecules (C−H···Cl = 2.764(4) to 2.987(4)

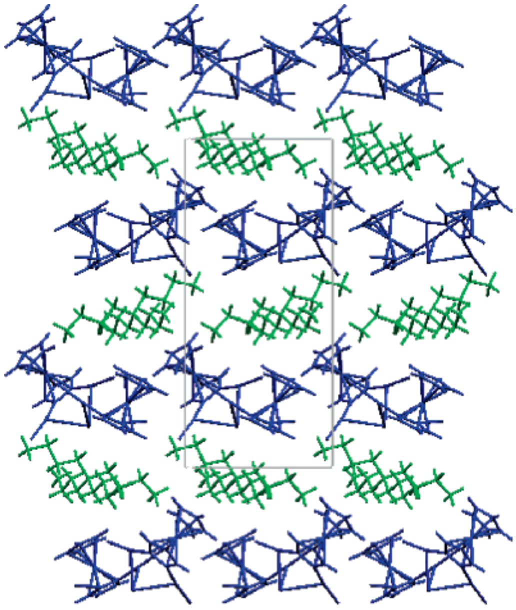

Figure 4. Packing diagram of **5a** showing the layered structure; green = cations, blue = complex anions.

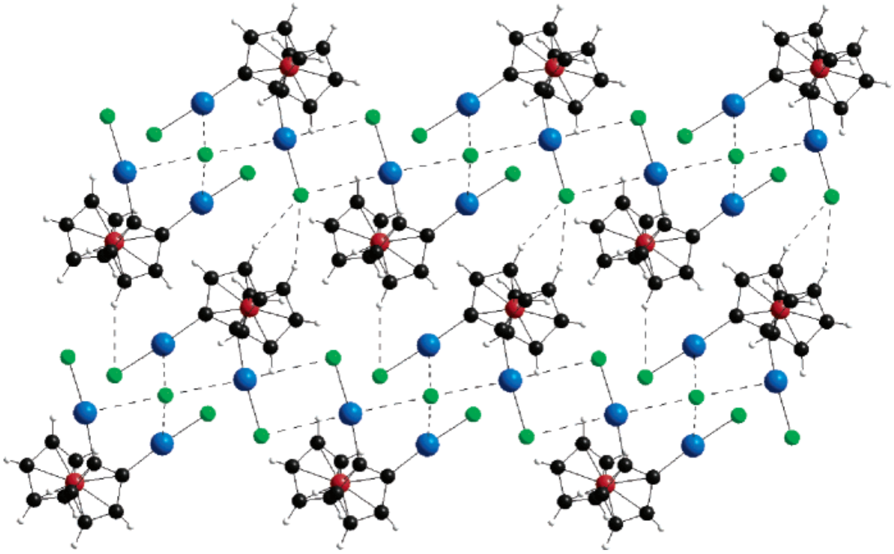

Figure 5. View of the sheet-like network in **5a** formed through Hg···Cl contacts within the anion layer.

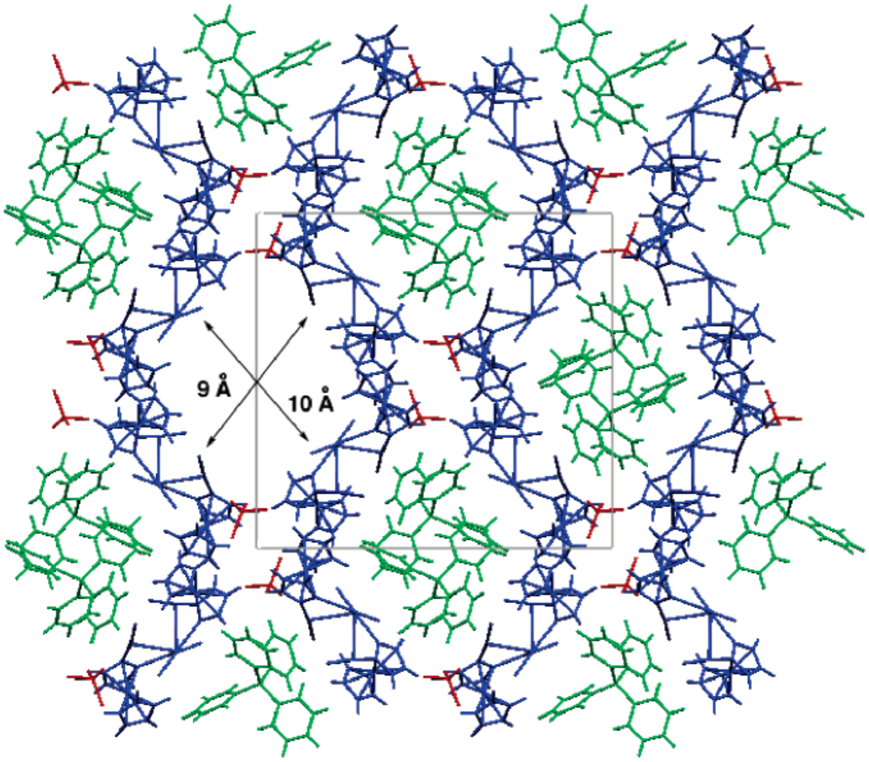

Figure 6. Packing diagram of **5b** showing the presence of cation-directed channels; green = cations, blue = complex anions, and red = solvent ($CHCl_3$). One of the cations was removed to illustrate the channel diagonals.

Å) lead to the formation of channels that consist of four $[(fc(HgCl)_2)_2Cl]^-$ units and two $CHCl_3$ molecules. The $CHCl_3$ molecules are released only at fairly high temperatures as shown by TGA analysis.[34] A 6% weight loss at 163 °C (onset) corresponds to evaporation of $CHCl_3$ from the solid. The $[Ph_4P]^+$ cations are located inside these channels, which have effective diagonals of ca. 10 and 9 Å.

In conclusion, we have developed a new method for the preparation of the redox-active bidentate Lewis acid 1,2-bis(chloromercurio)ferrocene (**3**). Different binding modes are realized, where the nucleophiles are coordinated from either the *exo* or the *endo* side of ferrocene. The fact that both binding modes can be observed in the very same structure (**5b**) and that different geometries are realized with different counterions (**5a** vs **5b**) indicate that packing effects dominate the individual complex geometries in the case of the relatively small nucleophiles studied here. Interestingly, the observation that **3** undergoes reversible one-electron oxidation opens up new possibilities for further fine-tuning of the Lewis acid–Lewis base interactions through changes in the oxidation state of iron. The reported 1,2-dimetalated

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[34] A reviewer kindly pointed out that the observation that $CHCl_3$ is released only at relatively high temperatures may be due to the fact that the lattice is ionic, making the distortions needed for the loss of guests in the solid state more difficult. It is also interesting to note that the $CHCl_3$ molecules are part of the channel framework in **5b** with the PPh_4 cations inside the channels, while in the extended structure of **4** the coordinated DMSO molecules are located inside the channels.

Table 1. Details of X-ray Structure Determinations

	4	**5a**	**5b**
empirical formula	$C_{12}H_{14}Cl_2FeHg_2OS$	$C_{36}H_{52}Cl_5Fe_2Hg_4N$	$C_{45}H_{37}Cl_8Fe_2Hg_4P$
MW	734.22	1590.10	1806.38
T, K	162(2)	161(2)	100(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/c$
a, Å	7.4804(13)	9.8089(18)	10.1136(13)
b, Å	7.7155(13)	22.226(4)	22.411(3)
c, Å	13.743(3)	10.107(2)	21.073(3)
α, deg	85.591(12)		
β, deg	88.926(15)	99.354(19)	90.195(2)
γ, deg	80.568(18)		
V, Å^3	780.1(2)	2174.2(7)	4776.4(11)
Z	2	2	4
ρ_{calc}, g cm^{-3}	3.126	2.429	2.512
μ(Mo Kα), mm^{-1}	21.011	15.052	13.915
F(000)	660	1464	3320
cryst size, mm	0.20 × 0.12 × 0.06	0.22 × 0.20 × 0.05	0.40 × 0.30 × 0.20
θ range, deg	2.68−32.68	1.83−30.10	1.82−26.00
limiting indices	$-11 \le h \le 11$	$-13 \le h \le 13$	$-12 \le h \le 12$
	$-11 \le k \le 11$	$-29 \le k \le 30$	$-27 \le k \le 27$
	$-20 \le l \le 20$	$-14 \le l \le 13$	$-25 \le l \le 25$
no. of reflns collected	13 959	32 673	20 774
no. of indepe reflns	5086 [R(int) = 0.0581]	11 103 [R(int) = 0.0852]	6045 [R(int) = 0.0449]
absorption correction	numerical, SHELXTL	numerical, SHELXTL	SADABS
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	5086/0/175	11 103/1/434	6045/0/541
goodness-of-fit on F^2	1.240	1.303	1.055
final R indices [$I > 2\sigma(I)$]	R1 = 0.0295	R1 = 0.0483	R1 = 0.0444
	wR2 = 0.0602	wR2 = 0.0871	wR2 = 0.1029
R indices (all data)	R1 = 0.0398	R1 = 0.0625	R1 = 0.0607
	wR2 = 0.0631	wR2 = 0.0923	wR2 = 0.1065
peak$_{max}$/hole$_{min}$ (e Å^{-3})	2.412 and −1.285	2.089 and −2.555	5.666 and −1.099

ferrocenes **2** and **3** represent potentially useful precursors to various other bidentate Lewis acids through transmetalation reactions with other main group and transition metal complexes, an area of research that we are currently further pursuing.

Experimental Section

General Procedures. *tert*-Butyllithium (1.5 M in hexanes), mercuric chloride, $[Bu_4N]Cl$, and $[Ph_4P]Cl$ were purchased from Acros, and trimethyltin chloride was purchased from Strem. 1-Trimethylstannyl-2-*p*-tolylsulfinylferrocene was prepared according to a literature procedure.[26] All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies). THF was distilled from sodium/benzophenone. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies), and the chlorinated solvents were subsequently degassed via several freeze−pump−thaw cycles. All 499.9 MHz ^1H NMR, 125.7 MHz ^{13}C NMR, and 186.4 MHz ^{119}Sn NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). All solution ^1H and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{119}Sn NMR spectra were referenced externally to $SnMe_4$ ($\delta = 0$) in C_6D_6. Infrared spectra of KBr pellets were recorded on a Nicolet IR-200 spectrometer. Cyclic voltammetry was carried out on a CV-50W analyzer from BAS. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode, and an Ag wire as the reference electrode. The voltammogram was recorded in DMF containing $[Bu_4N][PF_6]$ (0.1 M) as the supporting electrolyte and referenced relative to decamethylferrocene as an internal standard. The redox potential is reported relative to ferrocene (+480 mV vs decamethylferrocene). Thermogravimetric analyses were performed on a Perkin-Elmer Pyris 1 analyzer under N_2 atmosphere at a scan rate of 20 °C/min. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of 1,2-Bis(trimethylstannyl)ferrocene (2). A solution of *t*-BuLi (0.7 mL, 1.5 M in hexanes, 1.05 mmol) was added dropwise via syringe to a solution of **1** (0.48 g, 0.98 mmol) in freshly distilled THF (20 mL) at −78 °C. The solution was stirred for 5 min before adding Me_3SnCl (0.24 g, 1.20 mmol) in THF (10 mL). The solution was stirred at the same temperature for 1 h and subsequently quenched with a small amount of distilled water. Standard workup and flash column chromatography on silica gel with hexanes as the eluent gave a mixture of 1,2-bis(trimethylstannyl)ferrocene and 1-trimethylstannylferrocene. Distillation under high vacuum (135 °C) yielded spectrocopically pure 1,2-bis(trimethylstannyl)-ferrocene as an orange oil. Yield: 0.26 g (48%). ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 4.41 (t, J = 2.5 Hz, 1H, Cp-4), 4.20 (d, J = 2.5 Hz, 2H, Cp-3,5), 4.07 (s, 5H, C_5H_5), 0.29 (s/d, $J(^{117/119}Sn, H)$ = 52/54 Hz, 18H, Sn-Me). ^{13}C NMR (125.69 MHz, C_6D_6, 25 °C): δ 78.6 (s/dd, $^2J(^{117/119}Sn, C)$ = 62 Hz, $^3J(^{117/119}Sn, C)$ = 51 Hz, Cp-3,5), 76.5 (*ipso*-CpSn), 73.0 (s/d, $J(^{117/119}Sn, ^{13}C)$ = 38 Hz, Cp-4), 68.6 (C_5H_5), −7.3 (s/d, $J(^{117/119}Sn, C)$ = 333/349 Hz, Sn-Me). ^{119}Sn NMR (149.1 MHz, C_6D_6, 25 °C): δ −4.2. GC-MS (*m/z*, (%)): 512 [M$^+$] (86), 497 [M$^+$ − Me] (91), 467 [M$^+$ − 3Me] (100).

Synthesis of 1,2-Bis(chloromercury)ferrocene. A solution of **2** (0.98 g, 1.90 mmol) in acetone (20 mL) was added dropwise to a solution of $HgCl_2$ in acetone (30 mL). The mixture was stirred for 30 min before adding it to water. A yellow solid precipitated, which was collected on a frit and washed first with water and then with hexanes. The product was dried under high vacuum at 60 °C for 6 h. Yield: 1.20 g (96%). For **3**: ^1H NMR (500 MHz, DMSO-d_6, 25 °C): δ 4.52 (t, J = 2.0 Hz, 1H, Cp-4), 4.29 (d, J = 2.0 Hz, 2H, Cp-3,5), 4.21 (s, 5H, C_5H_5). ^{13}C NMR (125.69 MHz, DMSO-d_6, 25 °C): δ 90.7 (Cp-1,2), 74.5 (Cp-3,5), 70.2 (Cp-4), 68.8 (C_5H_5). IR (cm^{-1}): 3087, 2920, 2850, 2372, 1654, 1106, 1026, 1001, 816, 497. Anal.

Calcd for $C_{10}H_8FeHg_2Cl_2$: C 18.31, H 1.23. Found: C 18.50, H 1.00.

Complexation of 1,2-Bis(chloromercury)ferrocene with DMSO. DMSO (0.2 mL) was added to a suspension of 1,2-bis(chloromercury)ferrocene (25.1 mg, 38 μmol) in acetone (3 mL). The mixture was heated gently to give a homogeneous solution, from which yellow single crystals of the DMSO complex **4** formed upon cooling to room temperature. Yield: 24.9 mg (89%). For **4**: IR (cm^{-1}): 3087, 2920, 2850, 2372, 1654, 1018, 996, 951, 822, 499. TGA analysis (20 °C/min): 9% weight loss at 151 °C (onset) corresponding to loss of DMSO. Anal. Calcd for $C_{12}H_{14}FeHg_2Cl_2OS$: C 19.63, H 1.92. Found: C 19.82, H 1.58.

Complexation of 1,2-Bis(chloromercury)ferrocene with [Bu$_4$N]Cl. To a suspension of 1,2-bis(chloromercury)ferrocene (34.2 mg, 52 μmol) in dichloromethane was added [Bu$_4$N]Cl (7.2 mg, 26 μmol) in chloroform. 1,2-Bis(chloromercury)ferrocene is insoluble in dichloromethane, but forms a homogeneous solution after the addition of [Bu$_4$N]Cl. Slow evaporation of dichloromethane gave yellow single crystals of the 2:1 complex **5a**. Yield: 30.9 mg (75%). For **5a**: ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ 4.52 (t, J = 2.5 Hz, 2H, Cp-4), 4.28 (d, J = 2.5 Hz, 4H, Cp-3,5), 4.21 (s, 10H, C_5H_5), 3.16 (t, J = 8.5 Hz, 8H, Bu), 1.56 (m, 8H, Bu), 1.31 (m, 8H, Bu), 0.93 (t, J = 7.5 Hz, 12H, Bu). ^{13}C NMR (125.69 MHz, DMSO-d_6, 25 °C): δ 90.7 (Cp-1,2), 74.6 (Cp-3,5), 70.3 (Cp-4), 68.7 (C_5H_5), 57.5, 29.0, 19.2, 13.4 (Bu). IR (cm^{-1}): 3083, 2953, 2929, 2871, 1637, 1487, 1458, 1102, 998, 826, 816, 736, 501. Anal. Calcd for $C_{36}H_{52}Cl_5Fe_2Hg_4N$: C 27.19, H 3.30, N 0.88. Found: C 28.54, H 3.56, N 0.98.

Complexation of 1,2-Bis(chloromercury)ferrocene with [PPh$_4$]Cl. To a suspension of 1,2-bis(chloromercury)ferrocene (42.5 mg, 65 μmol) in chloroform was added [PPh$_4$]Cl (12.1 mg, 32 μmol) in chloroform. 1,2-Bis(chloromercury)ferrocene is insoluble in chloroform, but forms a homogeneous solution after the addition of [PPh$_4$]Cl. Slow evaporation of chloroform gave yellow single crystals of the 2:1 complex **5a**. Yield: 44.3 mg (81%). For **5b**: ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ 7.98−7.20 (m, 20H, PPh$_4$), 4.51 (t, J = 2.5 Hz, 2H, Cp-4), 4.28 (d, J = 2.5 Hz, 4H, Cp-3,5), 4.20 (s, 10H, C_5H_5). ^{13}C NMR (125.69 MHz, DMSO-d_6, 25 °C): δ 135.4 (Ph), 134.5 (m, Ph), 130.4 (m, Ph), 118.8 (d, J(P,C) = 89 Hz, *ipso*-Ph), 90.7 (Cp-1,2), 74.6 (Cp-3,5), 70.3 (Cp-4), 68.7 (C_5H_5). IR (cm^{-1}): 3087, 3048, 2919, 2850, 2372, 1654, 1436, 1106, 995, 814, 722, 688, 526, 500, 484. Anal. Calcd for $C_{44}H_{36}Cl_5Fe_2Hg_4P$: C 31.33, H 2.15. Found: C 31.36, H 1.92.

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Supporting Information Available: Crystallographic data for compounds **4**, **5a**, and **5b** including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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