are currently in progress and will be reported in a future publication.

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Registry No. $C_6H_5\bar{C}HCH_3$, 13822-53-2; HCO_2^-, 71-47-6; $(CH_3)_2C^-CN$, 42117-14-6; CH_3C^-HCN, 42117-12-4; $Fe(CO)_5$, 13463-40-6; $(C_6H_6CHCH_3)Fe(CO)_5^-$, 93473-87-1; $(C_6H_5CHCH_3)$-$Fe(CO)_4^-$, 93473-88-2; $HFe(CO)_4^-$, 18716-80-8; $(HCO_2)Fe(CO)_5^-$, 93473-89-3; $((CH_3)_2CCN)Fe(CO)_5^-$, 93473-90-6; $((CH_3)_2CCN)Fe$-$(CO)_4^-$, 93473-91-7; $(CH_3CHCN)Fe(CO)_5^-$, 93473-92-8; $(CH_3CH$-$CN)Fe(CO)_4^-$, 93473-93-9; $(CH_3CHCOCH_3)Fe(CO)_5^-$, 93473-94-0; $(CO)_4FeCHO^-$, 48055-09-0; $CH_3C^-HCOCH_3$, 64723-99-5.

Multidentate Lewis Acids. Halide Complexes of 1,2-Phenylenedimercury Dihalides[1]

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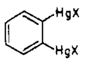
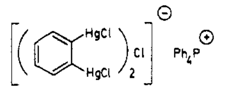
Summary: The bidentate Lewis acids dichloro-1,2-phenylenedimercury (**1**) and dibromo-1,2-phenylenedimercury (**2**) form complexes with halides. These are the first anionic complexes of organomercury compounds which have been isolated and characterized.

The coordination chemistry of multidentate Lewis bases is a subject of great theoretical and practical importance, and the study of analogous Lewis acids promises to be equally interesting.[2] In this paper, we describe the coordination chemistry of three bidentate Lewis acids, 1,2-phenylenedimercury dihalides **1–3**,[3] and we report the first isolation and structural characterization of anionic complexes of organomercury compounds.



1 (X=Cl)
2 (X=Br)
3 (X = I)



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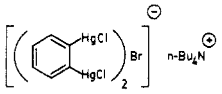

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Although inorganic halomercurate anions are well-known, analogous complexes of organomercury compounds have been remarkably elusive.[4,5] Since halogen bridges are a typical structural feature of inorganic halomercurate anions,[6] we suspected that the bidentate organomercury compounds **1–3** might form halide complexes stable enough to be isolated. Dichloro-1,2-phenylenedimercury (**1**) is nearly insoluble in dichloromethane, but the addition of an approximately equimolar amount of tetraphenylphosphonium chloride at 25 °C rapidly produced a homogeneous solution. Addition of hexane precipitated crystals of the 2:1 complex **4** (mp 205–207 °C) in 75% yield.[7] The reactions of other phosphonium and ammonium halides with compounds **1** and **2** yielded similar complexes.[8] However, an analogous experiment with chlorophenylmercury and tetraphenylphosphonium chloride yielded only diphenylmercury and tetraphenylphosphonium tetrachloromercurate, the products of a re-

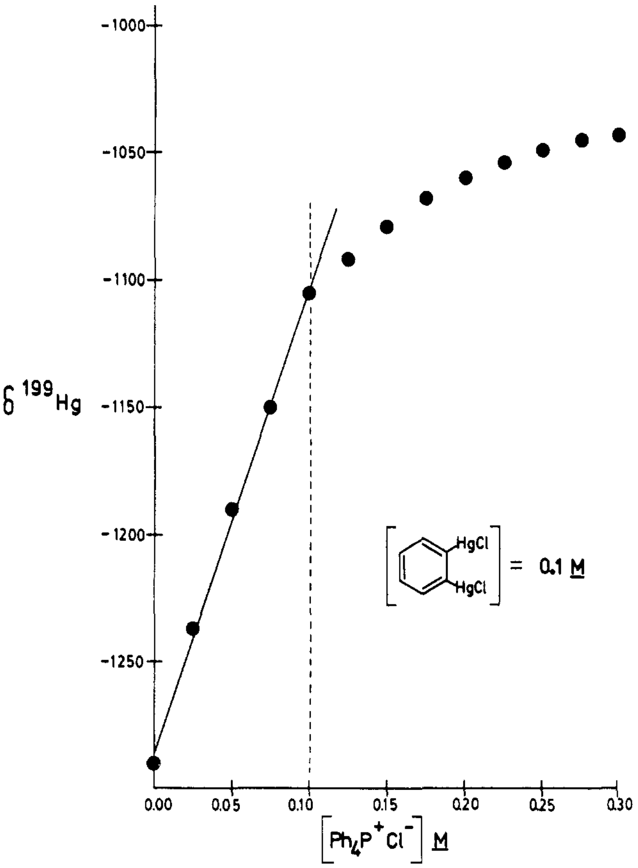

Figure 1. Relationship between the ^{199}Hg chemical shift of dichloro-1,2-phenylenedimercury (**1**; 0.1 M in Me_2SO) and the molar concentration of added tetraphenylphosphonium chloride.[11]

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(1) Presented in part at the 67th Conference of the Canadian Institute of Chemists, Montréal, June 4, 1984.

(2) Newcomb, M.; Azuma, Y.; Courtney, A. R. *Organometallics* **1983**, *2*, 175–177. Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Ibid.* **1983**, *2*, 106–114. Hosseini, M. W.; Lehn, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3525–3527. Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *Ibid.* **1981**, *103*, 1282–1283. Schmidtchen, F. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 466–468. Vögtle, F.; Sieger, H.; Müller, W. M. *Fortschr. Chem. Forsch.* **1981**, *98*, 107–161. Seetz, J. W. F. L.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1981**, *22*, 4857–4860. Gladfelter, W. L.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 5909–5910. Park, C. H.; Simmons, H. E. *Ibid.* **1968**, *90*, 2431–2432. Shriver, D. F.; Biallas, M. J. *Ibid.* **1967**, *89*, 1078–1081.

(3) Prepared by modifications of the methods of: Wittig, G.; Ebel, H. F. *Justus Liebigs Ann. Chem.* **1961**, *650*, 20–34. Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 883–894.

(4) For a useful introduction, see: Wardell, J. L. in "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 863–978.

(5) (a) Studies of coordination in solution are reported by: Goggin, P. L.; Goodfellow, R. J.; Hurst, N. W. *J. Chem. Soc., Dalton Trans.* **1978**, 561–566. Lucchini, V.; Wells, P. R. *J. Organomet. Chem.* **1975**, *92*, 283–290. Beletskaya, I. P.; Butin, K. P.; Ryabtsev, A. N.; Reutov, O. A. *Ibid.* **1973**, *59*, 1–44. Relf, J.; Cooney, R. P.; Henneike, H. F. *Ibid.* **1972**, *39*, 75–86. Plazzogna, G.; Zanella, P.; Doretti, L. *Ibid.* **1971**, *29*, 169–173. (b) The isolation and elemental analysis of halide complexes of perfluoroalkylmercury compounds have been reported by: Emeléus, H. J.; Lagowski, J. J. *J. Chem. Soc.* **1959**, 1497–1501. However, this work has been criticized by: Downs, A. J. *Ibid.* **1963**, 5273–5278.

(6) For recent references, see: (a) Bats, J. W.; Fuess, H.; Daoud, A. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2150–2152. (b) Sandström, M.; Liem, D. H. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 509–514. Biscarini, P.; Fusina, L.; Nivellini, G.; Pelizzi, G. *J. Chem. Soc. Dalton Trans.* **1977**, 664–668. Barr, R. M.; Goldstein, M. *Ibid.* **1976**, 1593–1596.

(7) The structure assigned to this new compound is consistent with its elemental analysis and its IR, far-IR, Raman, ^1H NMR, ^{199}Hg NMR, and mass spectra.

(8) With a variety of phosphonium and ammonium halides, dichloro-1,2-phenylenedimercury (**1**) yielded 2:1 complexes analogous to **4**. In contrast, elemental analysis suggests that dibromo-1,2-phenylenedimercury (**2**) favors 5:3 complexes. Diiodo-1,2-phenylenedimercury (**3**) and 1,8-naphthalenedimercury dihalides appeared to form related complexes, but these compounds were too unstable to be isolated.

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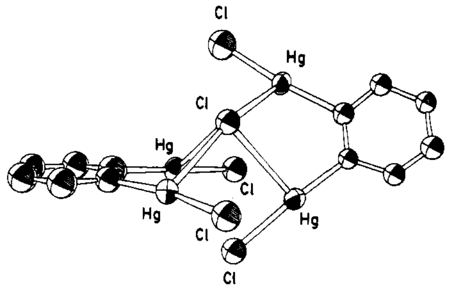

Figure 2. Crystal structure of the 2:1 complex 4 of dichloro-1,2-phenylenedimercury (1) and tetraphenylphosphonium chloride with tetraphenylphosphonium and all hydrogen atoms omitted for clarity.

distribution reaction. This result confirms that the formation of a stable halide complex requires a multidentate Lewis acid.

The far-infrared spectra of these halide complexes are similar to those of the uncomplexed 1,2-phenylenedimercury dihalides 1 and 2. For example, the strong band at 335 cm^{-1} in dichloride 1 (solid dispersed in polyethylene film), due predominantly to mercury–chlorine stretching, is shifted to 327 cm^{-1} in the 2:1 complex with tetrabutylammonium chloride. This shift to lower frequency indicates that additional coordination of chloride to mercury has occurred,[9] but the small magnitude of the shift suggests that the complex incorporates dichloro-1,2-phenylenedimercury units which are only slightly perturbed.[10]

The ^{199}Hg NMR spectra of the halide complexes also confirm that additional coordination of halide to mercury has taken place. For example, the ^{199}Hg chemical shift of dichloro-1,2-phenylenedimercury (1) is −1291 ppm in Me_2SO (0.1 M),[11] whereas the chemical shift of the 2:1 complex 4 with tetrabutylammonium chloride is −1220 ppm. The direction of this shift is persuasive evidence that additional chloride is complexed to mercury,[12] but its magnitude is small, presumably because the additional chloride is shared by four atoms of mercury. Figure 1 shows in detail how the ^{199}Hg chemical shift of dichloride 1 in Me_2SO increases as tetraphenylphosphonium chloride is added. The increase is steep and linear until a 1:1 ratio is reached, and subsequent changes are much smaller. This result suggests that although 2:1 complexes are isolated by precipitation, 1:1 complexes may be preferred in solution.

Study of complex 4 by X-ray crystallography,[13] summarized in Figure 2, confirms that the added chloride bridges two dichloro-1,2-phenylenedimercury units and is strongly coordinated to all four atoms of mercury. The four bonds from mercury to the central chloride average 3.02 Å in length, similar to the separation of mercury and the bridging chloride in $Hg_2Cl_5^-$.[6a]

The complexation of halides by 1,2-phenylenedimercury dihalides shows interesting selectivity. Initial tests of this selectivity have involved the competition of two 1,2-phenylenedimercury dihalides for an insufficient amount of halide, and the reaction of one 1,2-phenylenedimercury dihalide with two competing halides. For example, when dichloride 1, dibromide 2, and tetraphenylphosphonium chloride are mixed in the ratio 2:2:1, compound 2 can be recovered quantitatively by filtration, and complex 4 can be isolated in 73% yield after crystallization. These and similar results suggest that dichloride 1 is a stronger Lewis acid than bromide 2.[14] In addition, a 2:1:1 mixture of dichloride 1 and tetrabutylammonium chloride and bromide yielded complex 5 (mp 144–146 °C) in 72% yield after crystallization.[7] For a given 1,2-phenylenedimercury dihalide, the stabilities of complexes formed from added halide therefore appear to increase in the order $Cl^- < Br^- < I^-$.[15]

We are now studying the ability of 1,2-phenylenedimercury dihalides and related compounds to bind and activate organic substrates like thiocarbonyl compounds.

Acknowledgment. This work was financially supported by Research Corp., the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Education du Québec. We are grateful to Dr. Jeffrey C. Hayes, who performed some preliminary experiments, and to Mr. Robert Mayer and Mr. Jean-Claude Bolduc, who skilfully recorded our ^{199}Hg NMR and far-infrared spectra.

Registry No. 1, 35099-05-9; 2, 89280-87-5; 3, 89487-90-1; 4, 93605-04-0; 5, 93605-06-2; $[(ClHgC_6H_4\text{-}o\text{-}HgCl)_2Cl]Bu_4N$, 93605-08-4; $[(ClHgC_6H_4\text{-}o\text{-}HgCl)Cl]PPh_4$, 93644-89-4; tetraphenylphosphonium tetrachloromercurate, 93605-07-3; diphenylmercury, 587-85-9; chlorophenylmercury, 100-56-1.

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[9] Clark, R. J. H. *Spectrochim. Acta* **1965**, *21*, 955–963.

[10] Such comparisons are deceptive if the mercury–halogen stretching frequencies in the solid dihalides 1–3 are themselves lowered by intermolecular interactions. Goggin, P. L.; Kemeny, G.; Mink, J. *J. Chem. Soc., Faraday Trans. 2* **1976**, 1025–1035.

[11] All $\delta(^{199}Hg)$ are reported in parts per million relative to external neat dimethylmercury. Negative values indicate upfield shifts.

[12] Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; pp 195–278.

[13] (a) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B., manuscript in preparation. (b) Crystals of complex 4, solvated with dichloromethane, belong to the triclinic space group $P\bar{1}$, with $a = 13.35$ (1) Å, $b = 16.42$ (1) Å, $c = 20.20$ (2) Å, $\alpha = 108.43$ (6)°, $\beta = 94.48$ (6)°, and $\gamma = 105.41$ (6)°. An Enraf-Nonius CAD4 diffractometer was used to collect a limited set of intensity data ($2\theta \leq 70°$, Cu Kα, 3057 nonzero reflections). The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R = 0.041$, $R_w = 0.056$, and goodness-of-fit ratio = 2.21. A complete set of three-dimensional intensity data is now being collected.

[14] Because the solubilities of compounds 1–3 are low, competitive complexation could not be studied conveniently in homogeneous solution. As a result, we cannot exclude the possibility that differential solubilities or rates of crystallization have important effects.

[15] For related observations, see: Ahrland, S.; Persson, I.; Portanova, R. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 49–60. Giuashvili, I. I.; Katsman, L. A.; Vargaftik, M. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 80–83. Schwarzenbach, G.; Schellenberg, M. *Helv. Chim. Acta* **1965**, *48*, 28–46. Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265–276.

Synthesis and Reactions of Bridging (Vinylcarbyne)diiron Complexes

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Summary: Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(CH_2)_2CH_3]$ (**4**) with the hydride abstracting reagent $(C_6H_5)_3C^+PF_6^-$ leads to the vinylcarbyne complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH{=}CHCH_2CH_3)\}^+PF_6^-$ (**5**). Conjugate addition of $P(CH_3)_3$ to **5** leads to $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH[P(CH_3)_3]CH_2CH_3)\}^+PF_6^-$ (**13**). Deprotonation of **5** with $Li^+[(CH_3)_3Si]_2N^-$ leads to the dienylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH{=}CHCH_3)$ (**14**).

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