for the other methyl groups. γ-CH interactions would be expected to dampen the thermal motion of these atoms. A definitive explanation for these close methyl–metal contacts will have to wait for further, accurate structural (e.g. neutron diffraction) studies.

## Conclusions

$Ce(OAr)_3$ is a convenient precursor for the preparation of neutral monopentamethylcyclopentadienyl organocerium(III) complexes containing Ce–O, Ce–N, and Ce–C bonds. Disproportionation with the formation of $(C_5Me_5)_2CeX$ and $CeX_3$ compounds is observed frequently and seems a general feature of this class of compounds. This lability of ancillary ligands hampers detailed reactivity and mechanistic studies. The molecular structures of **2**, **4**, and **5** display interesting secondary interactions that relieve the electron deficiency of the highly unsaturated cerium center. Some indication for β-SiC agostic interaction is obtained from the slightly longer Si–C bonds.

**Acknowledgment.** Shell Research B.V. is acknowledged for financial support. We thank Dr. P. Pasman for providing details about the synthesis of (1,3-diphenyl-2-methylindenyl)lithium and Dr. E. J. M. de Boer, Dr. C. J. Schaverien, Dr. P. W. N. M. van Leeuwen, and Mr. H. van der Heijden for stimulating discussions.

**Registry No.** **1**, 113034-77-8; **2**, 121934-76-7; **3**, 122923-71-1; **4**, 122923-72-2; **5**, 121934-77-8; **6**, 122923-73-3; $CeCl_3$, 7790-86-5; Li(OAr), 55894-67-2; (Ind*)Li, 122875-95-0; $KCH(SiMe_3)_2$, 118111-55-0; $LiCH(SiMe_3)_2$, 41823-71-6; $NaN(SiMe_3)_2$, 1070-89-9; $(C_5Me_5)_2CCH(SiMe_3)_2$, 106333-13-5; HC≡C(*t*-Bu), 917-92-0; $[(C_5Me_5)Ce(C{\equiv}C(t\text{-Bu}))_2]_n$, 122923-74-4; 1,3-diphenyl-2-methylidene, 51310-26-0; ethylene, 74-85-1; propylene, 115-07-1; 2,4-di-*tert*-butyl-1-buten-3-yne, 59474-22-5.

**Supplementary Material Available:** Tables of all atomic coordinates, thermal parameters, bond distances, and bond angles for **2**, **5**, and **6** and a table of least-squares planes for **6** (18 pages); listings of observed and calculated structure factors for **2**, **5**, and **6** (41 pages). Ordering information is given on any current masthead page.

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# Mono-, Poly-, and Permercuration in the Acetone–Mercury(II) System†

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Mercuration occurs spontaneously, if slowly, in acidic aqueous solutions of acetone and free mercuric ion to produce at least nine organomercury species, all of which can exist in equilibrium simultaneously. The reaction sequence was followed by $^1H$ and $^{199}Hg$ NMR; the order of appearance of the $^1H$ and $^{199}Hg$ spectra and the spin-coupling interactions therein suffice to distinguish a monomercury, two dimercury (symmetrical and unsymmetrical), two trimercury, two tetramercury (symmetrical and unsymmetrical), one pentamercury, and one hexamercury species. The $^2J_{HgCH}$ coupling in the previously unreported $-CHHg_2$ moiety is 190–200 Hz.

Polymercuration of aromatic systems is well-known, and many such investigations have been reported in an extensive series of papers by Deacon[1a] et al.; a comprehensive review has been given by Wardell.[1b] While many monomercury derivatives of nonaromatic compounds have been prepared of the types RHgX or $R_2Hg$, including the monoacetone[2] $[(CH_3COCH_2)Hg]I$ and diacetone[3] $(CH_3COCH_2)_2Hg$ compounds, few polymercury derivatives have been described. Some dimercury derivatives of doubly activated methylene groups (i.e., diketones) have been reported,[4] and some compounds have been characterized by X-ray diffraction.[5,6] The first permercurated alkyl compounds were synthesized and identified by Matteson[8] as $C(HgI)_4$ and $C(HgC_2H_3O_2)_4$. A number of "mercarbides" prepared by Hoffmann[7] around 1900 have been elucidated in part as monomeric $[CHg_4{}^{4+}]$ and polymeric $[CHg_4O^{2+}]_n$ species by Grdenic[9] et al.

The present work uses $^1H$ and $^{199}Hg$ NMR spectra to investigate the mercuration of acetone in acidic aqueous solution where stepwise replacement of $H^+$ by $Hg^{2+}$ is observed without C–C bond cleavage or other redox complications.

## Results and Discussion

Table I. $^1H$ and $^{199}Hg$ NMR of the Nine Hg–Acetone Species

| symbol | structure | $^1H$ shift[a] | $^{199}Hg$ shift[b] |
|---|---|---|---|
| I | $[(CH_3COCH_2)Hg]^+$ | 0.07, 0.86 | 571 t |
| IIA | $[Hg(CH_2COCH_2Hg]^{2+}$ | 0.94 | 567 t |
| IIB | $[(CH_3COCH)Hg_2]^{2+}$ | 0.17, 1.41 | 720 d of d |
| IIIA | $[Hg(CH_2COCH)Hg_2]^{3+}$ | 1.03, 1.64 | 562 t, 700 d of d |
| IIIB | $[(CH_3COC)Hg_3]^{3+}$ | 0.28 | 792 s |
| IVA | $[Hg_2(CHCOCH)Hg_2]^{4+}$ | 1.78 | 686 d |
| IVB | $[Hg(CH_2COC)Hg_3]^{4+}$ | 1.12 | 557 t, 785 s |
| V | $[Hg_2(CHCOC)Hg_3]^{5+}$ | 2.07 | 673 d, 773 s |
| VI | $[Hg_3(CCOC)Hg_3]^{6+}$ |  | 762 s |

[a] In units from internal free acetone; shifts are given in order of position in structure. [b] In units from "free" mercuric ion. Abbreviations: s, singlet: d, doublet: t, triplet.

**Qualitative Interpretation of Spectra.** When acetone (e.g., 0.5 mL, 7 mmol) was added to aqueous mercuric nitrate solution (e.g., 10 mL of 1.4 M $Hg(NO_3)_2$—14 mmol—in 1 M $HNO_3$), a complex set of sequential reactions occurred over a period of about 50 h. The resulting

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† This work is dedicated to the memory of Dr. Charles B. Colburn, who died on August 2, 1988.

(1) (a) Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1977**, *30*, 293. (b) Wardell, J. L. *Comprehensive Organometallic Chemistry*: Pergamon Press: Oxford, 1982; Vol. 2, Chapter 17, pp 863–977.

(2) Morton, A. A.; Penner, H. P. *J. Am. Chem. Soc.* **1951**, *73*, 3300.

(3) Fedot'eva, I. B.; Kruglaya, O. A.; Fedot'ev, B. V.; Vyazankin, N. S. *Zh. Obskch. Khim.* **1978**, *48*, 2387.

(4) Seyferth, D.; Marmor, R. S. *J. Organomet. Chem.* **1973**, *59*, 231.

(5) (a) Allman, R.; Fatau, K.; Musso, H. *Chem. Ber.* **1972**, *105*, 3067. (b) Dietrich, K.; Musso, H.; Allman, R. *J. Organomet. Chem.* **1975**, *93*, 15. (c) Allman, R.; Musso, H. *Chem. Ber.* **1973**, *106*, 3001.

(6) McCandlish, L. E.; Macklıln, J. W. *J. Organomet. Chem.* **1975**, *99*, 31.

(7) Hoffmann, K. A. *Ber. Deutsch. Chem. Ges.* **1898**, *31*, 1904; **1899**, *32*, 870; **1900**, *33*, 1328; **1905**, *38*, 3654.

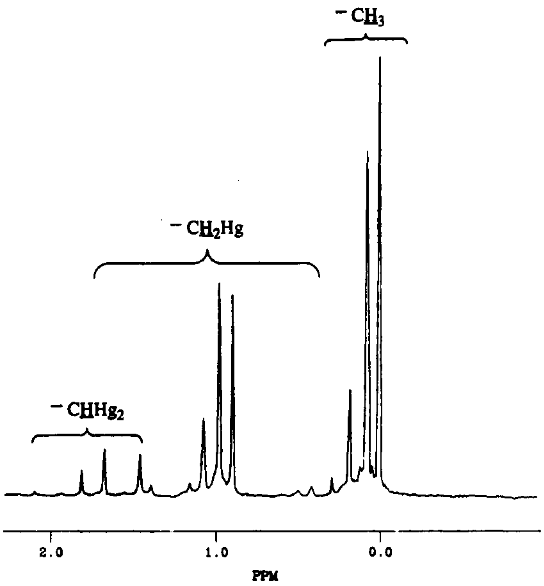

**Figure 1.** 400-MHz $^1$H NMR spectrum of an equilibrium mixture of mercurated acetone species (Hg/acetone = 2.02; final [H$^+$] = 2.3 M). Free acetone is the peak at highest field and was used as an internal standard.

solution was metastable toward precipitation for a few days—proton and mercury NMR spectra reveal nine mercurated acetone species in equilibrium. The nine species have been identified by their spectra and the sequence of their appearance and are listed in Table I along with their $^1$H and $^{199}$Hg chemical shifts.

Figure 1 shows a 400-MHz $^1$H spectrum of the equilibrium mixture specified above (Hg/acetone = 2.02; final [H$^+$] = 2.3M). Free acetone is the peak at highest field and was used as an internal standard—identification of this peak was accomplished in other samples by addition of acetone, whereupon an instant increase in peak height was followed by a very slow decrease as further reaction occurred. The various other $CH_3$ moieties appear within 0.3 ppm of free acetone; increasing mercury substitution at the distant carbon atom shifts the CH$_3$ resonances downfield, so that four positions are observed (corresponding to zero, one, two, and three Hg at the distant carbon). The various $-CH_2$Hg proton resonances are grouped near 1 ppm downfield of acetone; again there are four positions (zero, one, two, and three Hg on the distant carbon), and again increasing substitution produces greater downfield shifts. The $-CH$Hg$_2$ proton resonances occur 1.6–2.1 ppm downfield from free acetone; as with the CH$_3$ and CH$_2$ moieties, the CH resonance positions are shifted to lower field with increasing Hg substitution at the distant carbon. These consistent downfield proton shifts are presumed to result primarily from deshielding by the increase in positive charge on replacement of H$^+$ by Hg$^{2+}$.

Figure 2 shows a $^{199}$Hg spectrum of a different equilibrium solution (Hg/acetone = 3.23; [H$^+$] = 0.76 M; NO$_3^-$ counterion) which has a greater extent of substitution than the system of Figure 1. The chemical shifts are given relative to the original position of mercuric nitrate. Three groups of $^{199}$Hg peaks appear. The group near 660 ppm is assigned to four kinds of $-$CH$_2$*Hg* moieties on the basis of the 1:2:1 triplets resulting from a large two-bond mercury–proton coupling constant of 400 Hz; the four kinds of $-$CH$_2$*Hg* have zero, one, two, or three mercuric ions at the distant carbon. In Figure 2 and other spectra of nitrate solutions, the chemical shifts of the four kinds of $-$CH$_2$*Hg* are awkwardly close to the coupling constant, resulting in extensive overlapping of the triplet systems to display only six peaks of a possible 12; however, shift differences in the fluoroborate system are greater, and all 12 peaks of four triplets are easily distinguished. A second group of peaks near 700 ppm downfield of "free" Hg$^{2+}$ results from Hg nuclei in the $-$CH*Hg*$_2$ environment; low-resolution spectra (e.g., in the nitrate system, especially when a large line-broadening instrumental parameter is used to enhance spectral signal-to-noise) appear to show four doublet patterns with a $^2J_{\mathrm{HgCH}}$ of about 200 Hz. Each doublet results from a dimercury methine $-$CH*Hg*$_2$ moiety with zero, one, two, or three mercuric ions on the distant carbon. In higher resolution spectra, especially in the perchlorate and fluoroborate systems, additional details appear (vide infra) as the presumed result of conformational effects. Four singlets near 770 ppm are assigned to *Hg*$_3$C moities with zero, one, two, or three mercuric ions substituted at the distant carbon; as for the monomercury and dimercury groups, increasing mercury substitution at the other methyl carbon brings about small upfield shifts—this interpretation is based on the sequence in which peaks appear (described below) and cannot necessarily be extracted from the equilibrium spectra of Figure 2, even with the aid of available details of four-bond H–Hg spin coupling. The regular trend of upfield shift with increasing mercuric substitution at the distant carbon may be a result of increasing anion coordination resulting from increasing positive charge on the whole species.

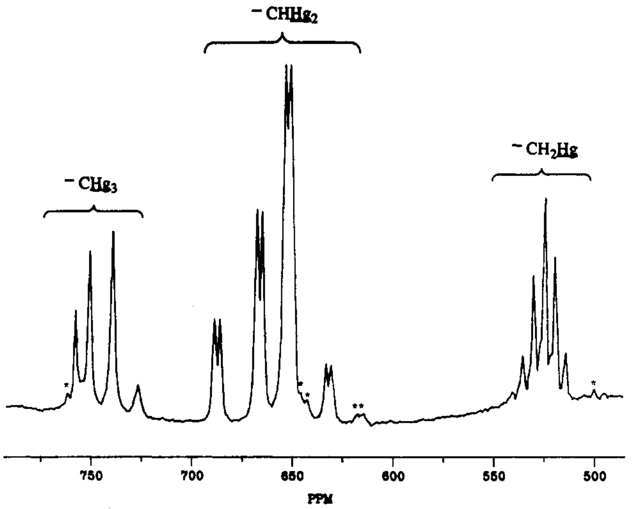

**Figure 2.** $^{199}$Hg NMR spectrum of an equilibrium mixture of mercurated acetone species (Hg/acetone = 3.23; final [H$^+$] = 0.76 M; NO$_3^-$ counterion). The chemical shifts are relative to the original position of aqueous mercuric nitrate. Impurity peaks are indicated with an asterisk.

**Sequence of Appearance with Increasing Substitution.** The sequence of peak appearance during the reaction process allows the assignment of peaks to species. Figure 3 shows relative abundances of species based on integration of the proton spectra, scaled to the known initial concentration of acetone. The acetone peak is the only *H*–C resonance visible initially, but it decreases rapidly and merges with the base-line noise after about 180 min. The 0.075 and 0.868 ppm proton peaks of I grow in a 3:2 area ratio prior to the appearance of any other CH peaks; the triplet that appears first in the Hg spectrum is at 571 ppm, downfield of the other triplets that appear later in the sequence. Species I increases in relative

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(8) Matteson, D. S.; Castle, R. B.; Larson, G. L. *J. Am. Chem. Soc.* **1970**, *92*, 231.

(9) (a) Grdenic, D.; Sikirica, M.; Koper-Colig, B. *J. Organomet. Chem.* **1978**, *153*, 1. (b) Grdenic, D.; Kamenar, B.; Korpar-Colig, B.; Sikirica, M.; Jovanovski, G.; *J. Chem. Soc., Chem. Commun.* **1974**, 646. (c) Grdenic, D.; Sirikicia, M. *Z. Kristallogr.* **1979**, *150*, 107.

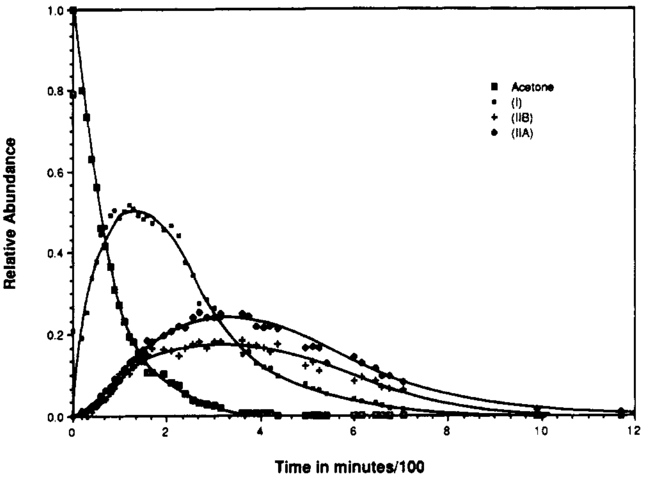

**Figure 3.** Relative abundances of mercurated species based on integration of proton spectra. Values are scaled to the known initial concentration of acetone. The symbols refer to the complexes in Scheme I.

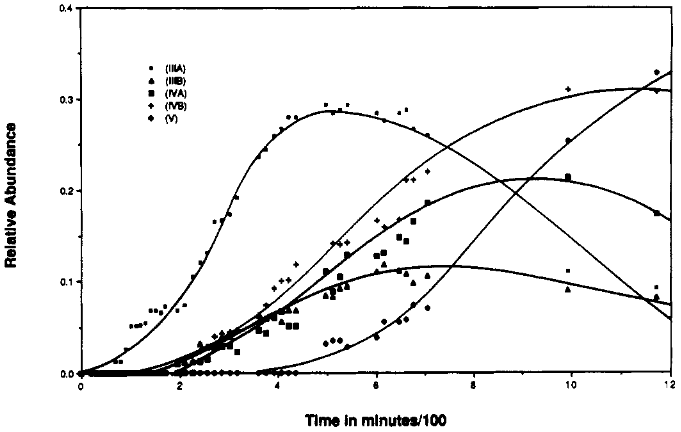

**Figure 4.** Relative abundances of mercurated species based on integration of proton spectra. This figure shows the growth curves for the more highly substituted species. The symbols refer to the complexes in Scheme I.

abundance until about 120 min and decreases thereafter as it is replaced by more highly substituted homologues. Disubstituted species IIA and IIB grow in simultaneously, reaching a maximum abundance at about 360 min and declining thereafter. Symmetrical IIA has a single proton resonance at 0.94 ppm in the region characteristic of $-C\mathit{H}_2Hg$, while unsymmetrical IIB has one resonance due to the unsubstituted methyl group at 0.17 ppm and another at 1.41 ppm which ultimately appears as the upfield $-C\mathit{H}Hg_2$ resonance. Species IIA is responsible for the second triplet to appear in the $^{199}Hg$ spectrum near 567 ppm, while IIB is responsible for the first doublet to appear in the $-CH\mathit{Hg}_2$ region at 720 ppm.

The growth curves for the more highly substituted species are shown in Figure 4. It should be noted that both Figures 3 and 4 are based solely on proton integrals and that Figure 4 gives a somewhat distorted view of relative abundances because the hexasubstituted species VI is not detectable in the proton spectrum—the result is an overestimate of the abundance of those species which are detectable. This problem is negligible in Figure 3 since species VI is still not present in significant amount.

The "symmetrical" trisubstituted IIIA grows at 1.03 and 1.64 ppm in the proton spectrum before the unsymmetrical IIIB at 0.28 ppm. The triplet at 562 ppm due to $-CH_2\mathit{Hg}$ and the apparent doublet at 700 ppm due to $-CH\mathit{Hg}_2$ belong to the more nearly symmetrical IIIA, while the unsymmetrical IIIB has only the singlet at 792 ppm, the first peak to appear in the permercurymethyl region. These two species reach their maximum abundances at about 500 and 600 min, respectively—well after the disubstituted entities but distinctly before the tetrasubstituted members.

The symmetrical tetramercury IVA has its single proton peak at 1.78 ppm downfield from acetone, and its only trace in the Hg spectrum is a characteristic doublet at 686 ppm in the $-CH\mathit{Hg}_2$ region. The unsymmetrical IVB has its only proton peak at 1.12 ppm; the two kinds of mercury nuclei contribute both a typical $-CH_2\mathit{Hg}$ triplet at 557 ppm (the last and farthest upfield set of peaks to occur in this region) and a singlet at 785 ppm (the second of the $-C\mathit{Hg}_3$ type to appear). The trace of the relative abundance of IVA reaches a maximum about 1000 min after the initial mixing, while IVB has already begun to decline at that time.

The pentamercury species V has the last proton peak to appear, which does not emerge cleanly from the base line until 400 min—well after the mono- and both disubstituted ions have begun to decrease in concentration—and still has not reached its maximum at the 1200-min limit of the experiment. Mercury peaks at 673 (the last doublet to appear) and 773 ppm (the third of the downfield singlets) have a time-dependent behavior similar to the lone proton peak of this, the next-to-last of the compounds in the sequence.

Hexasubstituted species VI does not appear in the proton spectrum at all but was significant in size at 762 ppm in the mercury spectrum taken just after 1000 min and appeared still to be increasing in abundance when the final spectrum of the sample was taken some 50 h after mixing.

**Detailed Interpretation of Spectra.** It should be recognized that the assignment of $^1H$ and $^{199}Hg$ spectra given above is incomplete, providing only approximate explanation of the most obvious features of each spectrum. The major features of the proton spectra are derived from species with no NMR-active mercury nuclei, but there are some traces of the large number of isotopomers present. Some 54 permutations (supplementary material) of the nine species exist with all possible numbers and positions of the NMR-active $^{199}Hg$ nucleus which is 16.86% abundant in ordinary mercury. A two-bond coupling between $^1H$ and $^{199}Hg$ of approximately 400 Hz is noted in all $-C\mathit{H}_2Hg$ spectra; this large value is outside the range of values previously reported for $-CH_2Hg$. The value appears not to have been measured by others who have prepared mercury–acetone compounds.[2,3] For $CH_3HgX$ compounds in water the two-bond $^1H-^{199}Hg$ coupling appears to increase for less coordinating X and to increase as pH decreases ranging[11] from 174 to 260 Hz, but no methyl ketone systems appear to be available for comparison. A four-bond coupling is visible in the $CH_3$ region of the proton spectrum of I in the form of satellite peaks which are 15 Hz from the center resonance resulting from isotopomers of species I which contain no $^{199}Hg$. There appear to be no analogous couplings reported previously.

Species IIB has one isotopomer with a single $^{199}Hg$ which is 28.03% abundant—both a 15 Hz four-bond proton–mercury coupling and another four-bond coupling of about 25 Hz are seen, presumably as the result of conformational effects (next paragraph). The proton spectrum of IIA shows satellite peaks from a 400 Hz coupling to mercury.

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[10] Waki, H.; Fritz, J. S. *J. Inorg. Nucl. Chem.* **1966**, 577.

[11] Brown, J. A.; Howarth, O. W.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1589.

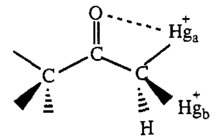
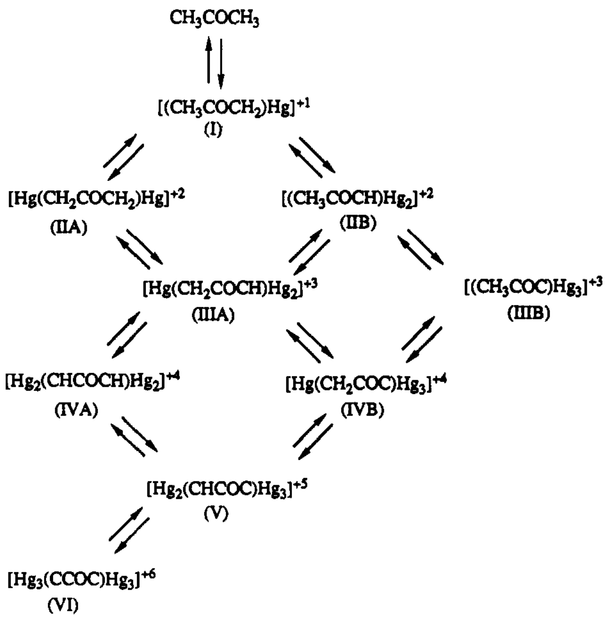


**Figure 5.** Representation of the different environments of $\mathrm{Hg_a}$ and $\mathrm{Hg_b}$ in a disubstituted species.

**Scheme I**



The $^{199}\mathrm{Hg}$ spectra of IIB and IIIA are more complex than expected. The $-\mathrm{CH}\mathit{Hg}_2$ patterns in the 673 to 720 ppm region of the spectrum appear to be doublets of doublets for IIIA and IIB. The larger spacing of the apparent doublet-of-doublet spectra corresponds to the 200 Hz coupling of the $-\mathrm{CHHg_2}$ group obtainable from the proton spectrum and the apparent doublet Hg spectra near 700 ppm for IVA and V. The smaller spacing in the doublet-of-doublet patterns does not correspond to any coupling constant in the proton spectrum and varies somewhat from spectrum-to-spectrum and sample-to-sample, being greatest in the perchlorate and fluoroborate samples. This spacing must then be a chemical shift; since all possible chemical isomers are observed and accounted for, its origin cannot be due to chemical isomerism. It seems reasonable that the positively charged mercury ions have a preferred conformation close to the oxygen which must be presumed to be the most negative portion of the core of these species. If $\mathrm{Hg_a}$ in Figure 5 of a $-\mathrm{CH}\mathit{Hg}_2$ group is held by electrostatic attraction in a planar or nearly planar Hg–C–C–O system, then $\mathrm{Hg_b}$ must have a rather different environment and therefore a different chemical shift. The spectra of IVA and V in the $-\mathrm{CH}\mathit{Hg}_2$ region appear to have clean doublets with relatively broad peaks; if two types of Hg are present, the shift differences must be below the approximately 20-Hz limit of resolution.

**Table II. Relative Equilibrium Constants**

| initial species | final species | rel equil const[a] |
|---|---|---|
| $\mathrm{CH_3COCH_3}$ | I | $K(10) = 5.5$ |
| I | IIA | $K(11) = 1.1$ |
| I | IIB | $K(20) = 0.91$ |
| IIA | IIIA | $K(21) = 2.0$ |
| IIB | IIIA | $K(12) = 2.3$ |
| IIB | IIIB | $K(30) = 0.33$ |
| IIIA | IVA | $K(22) = 1.2$ |
| IIIA | IVB | $K(31) = 0.33$ |
| IIIB | IVB | $K(13) = 2.3$ |
| IVA | V | $K(32) = 0.42$ |
| IVB | V | $K(23) = 1.6$ |
| V | VI | $K(33) = 0.11$ |

[a] Relative equilibrium constants in units of $1/[\mathrm{Hg}^{2+}]$.

**Relative Stability Constants.** Scheme I shows the successive formation of complexes in a chart arrangement. Each double arrow represents an equilibrium—in the downward direction a mercury replaces a proton from the acetone moiety; the constants are therefore designated $*K$ in the usual convention.[12] Since we are presently unable to measure the concentration of free mercuric ion, the equilibrium constants cannot be calculated directly. However, relative constants are easily found, since area integrals are available for both proton and mercury spectra and the hydrogen ion concentration is easily calculated. Only the $[\mathrm{Hg}^{2+}]$ number is missing. Thus, if the first equilibrium constant expression has $1/[\mathrm{Hg}^{2+}]$ extracted, a relative constant herein called $K(10)$ can be calculated. Hence for the formation of I from acetone

$$*K = [(\mathrm{CH_3COCH_2})\mathrm{Hg}^+][\mathrm{H}^+]/[\mathrm{CH_3COCH_3}][\mathrm{Hg}^{2+}]$$

thus

$$*K = K(10)/[\mathrm{Hg}^{2+}]$$

and

$$K(10) = [(\mathrm{CH_3COCH_2})\mathrm{Hg}^+][\mathrm{H}^+]/[\mathrm{CH_3COCH_3}]$$

The relative equilibrium constant values are given in Table II. It is remarkable that the values differ by so little—a range of only a factor of 50 is observed between the smallest which is $K(33) = 0.11$ for formation of the final hexamercury complex and the largest which is $K(10) = 5.5$ for formation of the initial monosubstituted complex. It might have been expected that the increasing positive charge would have a very much greater retarding effect on further substitution of $\mathrm{H}^+$ by $\mathrm{Hg}^{2+}$ or, in other terms, that coordination of $\mathrm{Hg}^{2+}$ would render the carbon atom a much weaker base toward further coordination. A similar expectation applies to the readiness of further coordination on an already substituted carbon relative to coordination at the distant carbon. A coordinated mercury ion might be expected by virtue of its positive charge strongly to activate the protons on the same carbon relative to protons on the distant carbon, yet the reverse is true since $K(20)$ is smaller than $K(11)$. Electrostatic repulsion of mercury ions on the same carbon apparently overbalances the assumed enhanced proton activation, and the less symmetrically substituted IIB, IIIB, and IVB are all less abundant than their more symmetrical isomers IIA, IIIA, and IVA. It might also be assumed that the accumulation of positive charge attendant upon repeated substitution might at some stage make the residual protons highly acidic, so that ionization of $\mathrm{H}^+$ would occur to reduce the charge. However, even the pentamercury homologue does not exhibit a conjugate base companion. Indeed, the proton resonance of V is not detectably broadened by exchange with solvent protons, apparently indicating retention of the usual considerable activation energy barrier to proton exchange on carbon.

The mercuric ion concentration at equilibrium was below the level of NMR detection even in 10M $\mathrm{HNO_3}$ solution, which should maximize $[\mathrm{Hg}^{2+}]$ by the mass action effect. Experiments in which known concentrations of acetone

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[12] Sillen, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, 1971; publication 17 and a supplement, publication 25.

(1–3 M) in water were used to dissolve or not dissolve small amounts of HgO (equivalent to (2–3) × $10^{-2}$M) permit an estimate of the mercuric ion concentration. In order for HgO to dissolve in aqueous solutions, the mercuric ion concentration in equilibrium with the dominant soluble species $Hg(OH)_2$ must be greater than that in equilibrium with any mercury–acetone complexes formed. At the acetone/mercury concentrations used and at the nearly neutral pH of these experiments, the only species present in significant amount is I. Since the concentration of free mercuric ion in equilibrium with $Hg(OH)_2$ and HgO is calculated from literature data[12] to be 5 × $10^{-13}$ M and since the other concentrations are known, the various equilibrium constants must be at least $10^{+4}$. It is noteworthy that $Cl^-$ ($K_1 = 5.5 \times 10^6$) does not interfere in the titration method of Fernandez,[13] but $Br^-$ ($K_1 = 8.7 \times 10^8$) does; $I^-$ ($K_1 = 7.4 \times 10^{12}$) renders the method useless. The 10–100 ratio of acetone to halide here also suggests a $^*K_1$ of at least $10^{+4}$.

**Other Observations.** The behavior of the nitrate system is somewhat different from the other two noncoordinating anions attempted, fluoroborate and perchlorate. Nitrate ion weakly coordinates to $Hg^{2+}$—successive stability constants are given by Waki and Fritz[10] as 0.83 and 1.88. It is thus possible to prepare mercuric nitrate solutions with a pH of 2 or greater without precipitation of oxy/hydroxy materials. The relatively noncoordinating nature of both perchlorate and fluoroborate is demonstrated by the fact that hydrogen ion concentrations of greater than 1 M are necessary to prevent such precipitation. The difference in behavior of extensively substituted acetone species was also striking in that nitrate solutions remained without precipitation of poly- or permercury acetone species for some days after equilibrium was reached, whereas fluoroborate and perchlorate generally began precipitation as soon as V and VI were detectable in the mercury NMR spectra. An attempt to exploit assumed $K_{sp}$ relationships ended in failure—solutions with 1:1:1 ratios of the three anions actually precipitated sooner than solutions of any one anion at the same total concentration. Presumably solid phases with mixed anions exist and have smaller $K_{sp}$ values than the single anion phases.

A second and more dramatic illustration of nitrate coordination occurred in the course of a crude examination of the kinetics of the formation of species I using NMR peak heights. When the method of initial rates was applied to solutions in the region of 1 M $HNO_3$, 1 M $Hg(NO_3)_2$, and 1 M acetone, the orders with respect to $H^+$ and acetone were approximately 1 but the apparent order with respect to mercuric nitrate was negative. This remarkable result is explained by calculations with the stability constants[10] for nitrate coordination, which show that the concentration of free $Hg^{2+}$ actually decreases with increasing $Hg(NO_3)_2$ concentration near 1 M in 1 M $HNO_3$. The order with respect to free mercuric ion whose concentration was calculated from stability constant data then also appeared to be approximately 1.

Analysis of most solids precipitated in the nitrate system suggest that while the $[Hg_3(CCOC)Hg_3]^{6+}$ moiety may be the predominant solution species, it is not the usual solid phase. Ratios of Hg to $C_3O$ are about 4 in precipitates from solutions of high acidity (4–10 M $HNO_3$). Dissolutions of solids in cold HCl (1–3 M) yield acetone as the sole organic material detectable by proton NMR; attempted drying of the solids at 100 °C or attempted dissolution in HCl at 50 °C or above gave significant amounts of acetate ion and other unidentified products.

Observation of most precipitates under a low power microscope failed to reveal crystals which appeared to be suitable for single-crystal X-ray examination. The solids appeared to be rosettes of many tiny crystals. Some crystals with distinct faces were produced from relatively dilute solutions and will be submitted for X-ray structure determination. Attempts to use halide or cyanide ions after the example of Grdenic[9] et al. are being pursued.

Aldehydes, alcohols, ethers, and esters as well as organic halides all appear to undergo similar sets of reactions. Solubility considerations and the limited NMR detectability of $^{199}Hg$ make work with many of these systems difficult, but others are under active investigation. In several cases, well-crystallized products are obtained and X-ray examination of the products may provide an alternate approach.

## Experimental Section

All $^{199}Hg$ spectra were run on a Bruker AM 400 spectrometer with Aspect 3000 data system. Some $^1H$ spectra were run on the Bruker; others were run on a Varian EM 390.

Aqueous solutions of Hg(II) salts were standardized by the method of Fernandez[13] and added to NMR tubes by pipet. Acids and water were also added by pipet. Acetone was measured by Hamilton syringe. NMR tubes (Ace Glass) were capped by the plastic caps furnished with the tubes—no loss of acetone or decomposition was noted in any samples, some of which were kept for as long as 6 months.

**Registry No.** I, 36484-63-6; IIA, 122470-84-2; IIB, 122470-85-3; IIIA, 122470-86-4; IIIB, 122470-87-5; IVA, 122470-88-6; IVB, 122470-89-7; V, 122470-90-0; VI, 122470-91-1; $CH_3COCH_3$, 67-64-1; $Hg(NO_3)_2$, 10045-94-0.

**Supplementary Material Available:** A listing of the 54 permutations of the nine mercury-containing species (1 page). Ordering information is given in any current masthead page.

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(13) Fernandez, J. B.; Snider, L. T.; Rietz, E. G. *Anal. Chem.* **1951**, *42*, 899.