2663 collected reflections, 2464 independent reflections, 2179 observed reflections, no absorption corrections applied, 165 refined parameters, isotropic refinement, $R = 0.0375$, ($R_w = 0.0574$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-147. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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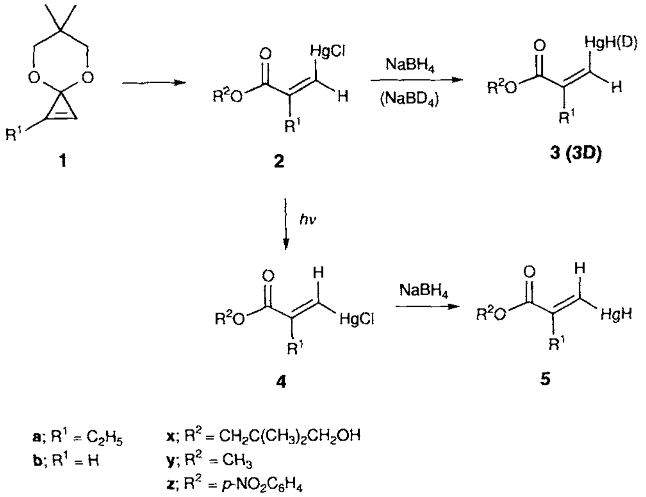
Unusually Stable Organomercury Hydrides and Radicals**

Eiichi Nakamura,* Yong Yu, Seiji Mori, and Shigeru Yamago

There is growing interest in the characterization of organomercury hydrides,[1] which have been elusive species until very recently. Hydride reduction of organomercury chlorides is an important method for generating carbon radicals.[2] The reaction is considered to proceed in three steps: formation of an organomercury hydride, homolysis of the Hg–H bond, and immediate decomposition of the transient organomercury radical.[3] However, experimental evidence for this proposed mechanism has been rather scant. A few alkylmercury hydrides were recently isolated and proved to be very unstable.[1f] The second intermediate, an organomercury radical, has still remained elusive, and no direct proof of its existence has been obtained. Here we report on the synthesis of the unusually stable organomercury hydrides **3** and deuterides **3D**, which are much more stable than the mercury hydrides described so far. Furthermore, these hydrides generate the organomercury radicals **6**, which are stable enough to be trapped intermolecularly.

The reaction of cyclopropenone acetal **1a**[4] with $Hg(OAc)_2$, followed by treatment with a saturated NaCl solution, stereospecifically produced the (*Z*)-olefinic mercury chloride **2ax** in 92% yield. The mercury chlorides **2** with different R^2 groups could also be prepared.[5] Stereospecific conversion of the mercury chlorides to the hydrides **3ay** and **3az** was then achieved



with $NaBH_4$ at 0 °C. The same procedure was applied to the unsubstituted cyclopropene **1b** to produce the acrylate derivatives **3by** and **3bz** in 70–80% yield. Photolysis of the (*Z*) methyl ester **2ay** affords the (*E*) isomer **4ay** (28% yield, 60% recovery of **2ay**), which was reduced to provide the (*E*)-olefinic mercury hydride **5ay** in 78% yield.

The hydridomercury acrylate derivatives **3** and **5** are stable, colorless solids. The stability increases from the methyl ester **3ay** (half-life $t_{1/2}$ = 34 h at 75 °C in C_6D_6) to the *p*-nitrophenyl ester **3az** ($t_{1/2}$ = 74 h at 75 °C in C_6D_6). The *p*-nitrophenyl esters **3az** and **3bz** remain unchanged for many weeks as a solid at 4 °C and in benzene solution at 25 °C. The hydride **3z** decomposes with a first-order rate constant of $k = 2.6 \times 10^{-6}\ s^{-1}$ at 75 °C in degassed C_6D_6. The corresponding deuteride **3D-az** is much longer lived ($k = 9.6 \times 10^{-7}\ s^{-1}$, $t_{1/2}$ = 201 h at 75 °C in degassed C_6D_6).[6] The remarkable stability of **3** is in sharp contrast to the instability of previously known RHgH compounds ($t_{1/2}$ = 100 min at 20 °C for CH_3HgH in benzene).[1f, g] Some spectral properties correlate with the stability of the compounds. The IR stretching frequency (KBr) of the Hg–H bond increases from the methyl ester **3ay** (1969 cm^{-1}) to the *p*-nitrophenyl ester **3az** (1983 cm^{-1}). The Hg–H coupling constant in the NMR experiment increases from 3118.3 Hz for **3ay** to 3218.0 Hz for **3az**. The substituent R^1 (Et, H) does not significantly affect the stability of the hydrides. The *Z* and *E* isomers of the methyl esters **3ay** and **5ay** are of comparable stability ($t_{1/2}$ = 34 h and 23 h, respectively, at 75 °C in degassed C_6D_6). This indicates that coordinative interaction between the ester and the mercury atom is not very important for the stability of the hydrides. In line with this observation is the fact that reduction of 2-(ethoxycarbonyl)ethylmercury(II) chloride[7] with $NaBH_4$ does not give the corresponding isolable mercury hydride, which would be a saturated analog of **3ay**.

Thermolysis of **3ay** and **3az** nearly exclusively produces the divinylmercury compound **8** (90–100% yield) and metallic mercury. Only traces of the normal reductive elimination products **11** (Scheme 1) could be found. Formation of **8** suggests intervention by the dimer **7**, hence implying that **6** is long-lived enough to be chemically trapped. Indeed, when **3ay** was treated with the halogenating agents NCS, Cl_3CBr, CCl_4, and *t*BuBr (listed in order of decreasing halogen donating ability[8]), the halogenated products **9ay** (X = Cl, Br) were formed in 90, 76, 23, and 6% yield, respectively. Addition of hydroquinone (11 mol%) to the reaction mixture resulted in a decrease in the rate of halogenation with Cl_3CBr and formation of the dimer **8ay** (**8ay**: 44%; **9ay**: 51% yield). Use of an inferior radical acceptor, such as

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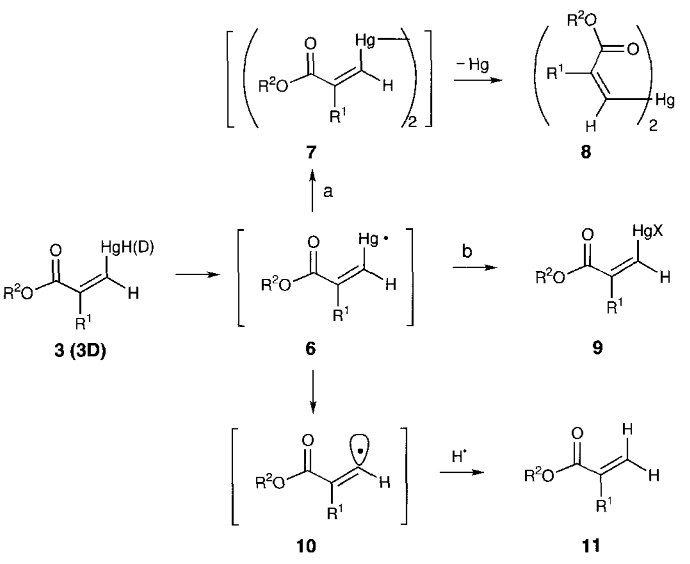
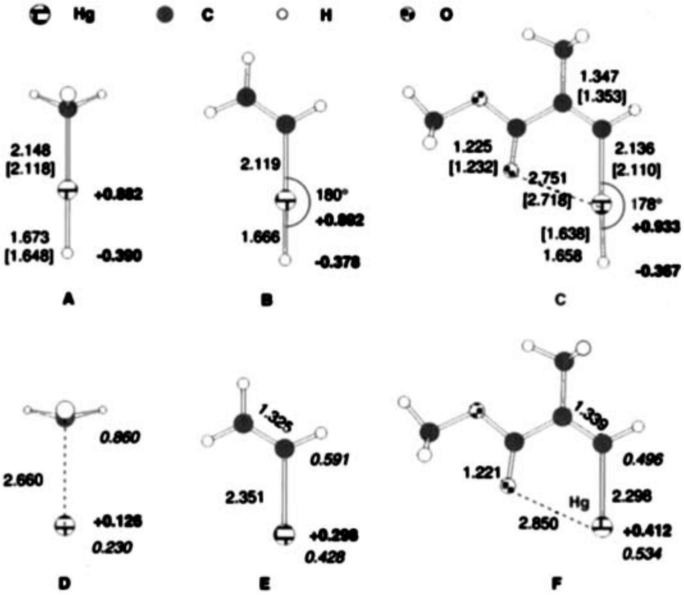


Scheme 1. Thermolysis and trapping of organomercury radicals. All reactions (in C_6D_6) proceeded with complete retention of the olefin geometry: a) 75 °C in C_6D_6. b) NCS (3 equiv, 25 °C, 90 %), Cl_3CBr (13 equiv, 50 °C, 76 % accompanied by 17 % of **8**), CCl_4 (10 equiv, 50 °C, 23 % accompanied by 3 % of **8** and 73 % of **11**), *t*BuBr (13 equiv, 50 °C, 6 % accompanied by 29 % of **8** and 64 % of **11**).

benzylidene malononitrile, resulted in recovery of the trap[1f] and quantitative formation of **8ay**. Notably, we found no evidence that the vinyl radical **10** could be trapped (< 3 %).

What is the origin of the stability of the hydride **3** and the radical **6**? Since little information on the structures and properties of organomercury hydrides and radicals is available in the literature, we carried out quantum mechanical calculations at the electron correlated levels.[9–11] 2-Methoxycarbonyl-(*Z*)-propenylhydridomercury(II) (**C**, C_s symmetry) served as a hydride model. Methylhydridomercury(II) CH_3HgH (**A**, C_{3v} symmetry) and ethenylhydridomercury(II) $CH_2{=}CHHgH$ (**B**, C_s symmetry) served as references. We also examined the corresponding radical models, **D**, **E**, and **F** (Scheme 2).



Scheme 2. Stuctures of CH_3HgH (**A**), ethenylmercury hydride (**B**), 2-methoxycarbonylethenyl-(*Z*)-hydridomercury(II) (**C**), and the corresponding mercury radicals (**D**, **E**, and **F**) optimized at the B3LYP/6-31G(d,p)-SKBJ RECP level. Bond lengths [Å] (B3LYP level; numbers in brackets: MP2 level). Natural charges (B3LYP) are in bold, and atomic spin densities (B3LYP) are in italics.

Table 1. Bond dissociation energies for **A**–**F**. The pertinent bond is indicated by a hyphen. Energies are given in kcal mol⁻¹ at the 6-31G(d,p)-SKBJ RECP level.

Species	B3LYP	CCSD(T)//B3LYP
$CH_3Hg{-}H$ (**A**)	70.3	71.5
$CH_3{-}HgH$ (**A**)	65.2	63.2
$CH_3{-}Hg^{\bullet}$ (**D**)	1.5	0.4
$CH_2CHHg{-}H$ (**B**)	71.8	
$CH_2CH{-}HgH$ (**B**)	72.9	
$CH_2CH{-}Hg^{\bullet}$ (**E**)	5.6	
$CH_3OOCCCH_3CHHg{-}H$ (**C**)	76.2	
$CH_3OOCCCH_3CH{-}HgH$ (**C**)	79.3	
$CH_3OOCCCH_3CH{-}Hg^{\bullet}$ (**F**)	9.8	

C–Hg and O–Hg distances in **C** calculated at the MP2 and B3LYP[12] levels show good agreement with those from the X-ray structure of (*Z*)-$(C_6H_5COCH{=}CH)_2Hg$.[13] Characteristic is the linear arrangement of the C-Hg-H unit, which is bent by 2° due to the influence of the neighboring oxygen atom. The good agreement between calculated (for the monomer model) and experimental values of Hg–H IR frequencies (KBr)[14] suggests that there is very little intermolecular association in **3** in the solid state.

The Hg–H bond lengths and the bond dissociation energies (BDE, Table 1) for **A**–**C** correspond with the much higher stability of the mercury hydrides **3** than alkyl mercury hydrides. Thus, the Hg–H bond progressively shortens upon going from **A** (1.673 Å) to **B** (1.666 Å) to **C** (1.658 Å). The calculated IR frequencies also show the same trend and agree well with the experimental values.[14] The Hg–H BDE (Table 1) increases from **A** to **B** by 1.5 kcal mol⁻¹ and from **A** to **C** by 5.9 kcal mol⁻¹.[15] Furthermore, the electron densities on the hydride and Hg atom (natural charges) progressively decrease from **A** to **B** to **C**. Therefore, the stability of **3** must arise largely from the large electron-accepting ability of the acrylic acid moiety.

Similar substituent effects were also observed for the organomercury radicals **D**, **E**, and **F**. The Hg–C bond in **D** is decidedly longer than that in **A** (24 %), while that in **F** is only 7.5 % longer than that in **C**. The ethenylmercury radical **E** showed an intermediate value of 11 % elongation. The methyl group in **D** is flattened, and the atomic spin density is concentrated on the methyl carbon atom (0.860). The natural charge of Hg in **D** is only +0.126 (+ 0.882 in **A**). All of these properties indicate that **D** possesses the characteristics expected for a complex between $CH_3^{\bullet}$ and Hg^0 rather than $CH_3Hg^{\bullet}$. On the other hand, the C–Hg bond in **F** (2.298 Å) is much shorter than in the other radicals, and the vinyl moiety retains its sp^2 geometry. The mercury atom bears higher spin density (0.534) and is more positively charged (+ 0.412). In agreement with these data, the BDE for the C–Hg bonds in **D** (Table 1) is extremely small (1.5 kcal mol⁻¹ at B3LYP and 0.4 kcal mol⁻¹ at CCSD(T)[16]//B3LYP; 9.8 kcal mol⁻¹ for **F**). Therefore, the commonly accepted instability of **D** must be valid.[2, 3] The radical **F** is expected to be much more stable and have a lifetime long enough to be trapped intermolecularly, as found experimentally.

We have prepared unusually stable mercury hydrides, which in turn give rise to unusually stable organomercury radicals. The experimental and calculated physical data indicate that the stability is due to the electron-withdrawing effects of the acrylic acid moiety. In light of the linear H-Hg-C arrangement, the stabilization of the mercury hydride can be viewed as the "trans effect"[17] of the electron-withdrawing organic group. This will probably prove to be a general feature in mercury hydride chemistry.

Experimental Section

3az: All experiments including chromatography were performed at 0 °C under nitrogen. A stirred 15 mM solution of **2az** in wet ether was treated with 1.8 equiv of $NaBH_4$. After 1 min, the reaction mixture was filtered through a short pad of silica gel (diethyl ether), and the solvent removed in vacuo. Chromatographic purification (silica gel, Et_2O/pentane, 1/9) afforded **3az** ($R_f = 0.61$, EtOAc/hexane, 1/2) in 81% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 1.19$ (t, $J = 6.85$ Hz, 3H, CH_2CH_3), 2.62 (q, $J = 6.85$ Hz, 2H, CH_2CH_3), 7.25 (s, ^2J(Hg,H) = 120.3 Hz, 1H, C=CH Hg), 7.34, 8.30 (d, $J = 8.80$ Hz, Ph), 13.14 (s, ^1J(Hg,H) = 3218.0 Hz, 1H, HgH); ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): $\delta = 13.7$ (CH_2CH_3), 28.9 (CH_2CH_3), 122.6, 125.2, 145.4, 149.2 (Ph), 155.7 (C=CHg), 172.9 (C=O), 181.8 (C=CHg); IR (KBr): $\tilde{\nu} = 1983\ cm^{-1}$(Hg–H).

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[6] Thermolysis reactions were carried out in a vacuum-sealed Pyrex NMR tube previously washed with HNO_3, NH_4OH, and bis(trimethylsilyl)acetamide (14 h). The reaction mixture was thoroughly degassed by several freeze/thaw cycles. The hydrides are rather sensitive to acidic impurity, which generates 2-ethylacrylate by protonolysis of the Hg–H bonds (for example, the deuteride **3D-ay** reacts with CF_3COOH at 50 °C to quantitatively afford the protonolysis product **11** in 20 min). Thus, the rate measurements are always slightly dependent on reaction conditions. This is probably the reason why analytically pure samples have not yet been made.

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[14] The following Hg–H frequencies were calculated for structures at the MP2/6-31G(d,p)-SKBJ RECP] HF level: **A**: 1975 cm^{-1}, **C**: 2004 cm^{-1}. Experimental values [1h]; CH_3HgH, 1940 cm^{-1}; **3az**: 1983 cm^{-1}.

[15] A referee pointed out that the estimated activation energy of CH_3HgH decomposition (ca. 23 kcal mol^{-1}) is much lower than the calculated BDE (70–71 kcal mol^{-1}). We suggest that decomposition of CH_3HgH proceeds by a radical chain reaction involving bimolecular hydrogen abstraction (for instance, by $CH_3^{\bullet}$). Hence, the activation energy of CH_3HgH decomposition is related to but not the same as the BDE, which is a measure of the stability of a single isolated molecule.

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New Ligands for the Titanium(IV)-Induced Asymmetric Reduction of Ketones with Catecholborane[**]

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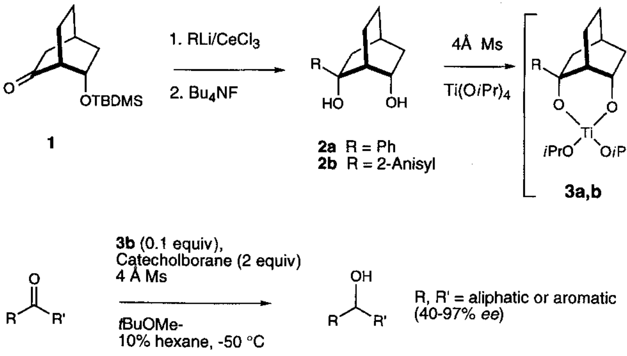
Anette Gudmundsson, and Torbjörn Frejd*

Enantioselective reduction of ketones[1] is an important reaction because the resulting optically active alcohols may be used in many syntheses of complex target molecules. Particularly attractive reduction methods are those that can be performed at ambient conditions and that require only catalytic amounts of the chiral inductor, such as borane reductions either in the presence of oxazaborolidines[2–9] or titanium TADDOLates.[10, 11] During work with optically active bicyclo[2.2.2]octane derivatives, we became interested in the development of these compounds into new, chiral bidentate ligands. Herein, we report on our results with (1*R*, 2*R*, 4*S*, 6*S*)-2-phenylbicyclo[2.2.2]octane-2,6-diol (**2a**) and (1*R*, 2*R*, 4*S*, 6*S*)-2-(2-anisyl)bicyclo-[2.2.2]octane-2,5-diol (**2b**) in the Ti^{IV}-catalyzed reduction of ketones with catecholborane. We also suggest that diols based on the bicyclo[2.2.2]octane framework are named BODOLs (*b*icyclo[2.2.2]*o*ctane*diol*s).

BODOLs **2a** and **2b** (Scheme 1) of high enantiomeric purity (≥98%) were synthesized simply by addition of the corresponding $RLi/CeCl_3$ reagent[12, 13] to the O-TBDMS protected (TBDMS = *tert*-butyldimethylsilyl) optically active hydroxy ketone **1**,[14] followed by deprotection. The catalysts **3a** and **3b** were then prepared by mixing the BODOLs with $Ti(OiPr)_4$ in a 1.2:1 ratio in the presence of molecular sieves (Union Carbide Type A, 4 Å) at 0 °C, and then keeping the mixture at room temperature overnight. A small excess of the BODOLs was used to consume all $Ti(OiPr)_4$, thus avoiding reduction by complexation of the ketones with this achiral Lewis acid. In order to make this ligand exchange effective it was important to activate the powdered molecular sieves at 400 °C for 5–7 h. Very extended times at this temperature resulted in inactive molecular sieves, and heating at lower temperatures (100–300 °C) was not sufficient. We recommend that the amount of the molecular sieves be



Scheme 1. Synthesis of the Ti-BODOL complexes **3a** and **3b** and their application in the reduction of ketones with catecholborane. Ms = molecular sieves.

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