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Vinylmercury Hydrides: Synthesis and Spectroscopic Characterization

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The first vinylmercury hydrides, and among them the parent compound, have been prepared by a chemoselective reduction of the corresponding vinylmercury chlorides with tributylstannane in the presence of a radical inhibitor. These hydrides have been characterized on the basis of their spectral data (^{1}H, ^{13}C, and ^{199}Hg NMR spectroscopy and mass spectrometry). The photoelectron spectra of the ethenylmercury hydride displays bands at 9.79, 10.13, 11.41, and 13.20 eV. On the basis of photoelectron spectra and ab initio quantum chemical calculations some (d−p)π interaction between the vinyl π-system and the mercury d-orbitals could be concluded. Vinylmercury hydrides have been condensed and then revaporized in vacuum at low temperature, but they exhibit a very low stability at room temperature even diluted in toluene ($\tau_{1/2} \approx 1$ min); elemental mercury and the corresponding divinylmercury were formed under these conditions.

Introduction

During the past decade, the synthesis of new compounds containing a heteroatom bonded to hydrogen atoms and to an α-unsaturated system has known an important development. However, only molecules bearing heteroatoms of the 14, 15, and 16 groups of the periodic table have been described.[1] The recent publications dealing with the first spectroscopic characterizations of mercury hydrides prompt us to prepare α-unsaturated mercury hydrides.[2,3] This challenge was particularly exciting owing to the fact that alkyl and aryl derivatives are themselves unstable compounds at room temperature. We report here the synthesis of the first α-unsaturated hydrides of a posttransition metal, the ethenylmercury hydride parent compound ($H_2C{=}CH{-}Hg{-}H$), the (1-methylethenyl)mercury, and the *Z*- and *E*-1-propenylmercury hydrides, and compare them to the corresponding disubstituted compounds. These products were characterized by low-temperature (−40 °C) ^{1}H, ^{13}C, and ^{199}Hg NMR and photoelectron spectroscopy and mass spectrometry. Also some quantum chemical calculations to estimate the molecular geometry and conformation are presented.

Experimental Section

Caution: Mercury compounds are potentially highly toxic materials which must be handled with great care, using vacuum-line manipulation. Divinylmercury derivatives exhibit a powerful, persistent, penetrating stench.

Materials. Mercury(II) chloride (Prolabo or Acros), duroquinone (Acros), and galvinoxyl (Aldrich) were used without further purification. Tributylstannane (Bu_3SnH),[4] methyl- (**1**),[5] ethenyl- (**2a**),[6] 1-methylethenyl- (**2b**), 1-propenylmercury chlorides (**2c**)[7] and divinylmercury (**3a**−**c**)[8] were prepared as previously reported.

Calculations. Calculations have been carried out by the Gaussian 92 suite of programs,[9] using the LANL1DZ pseudopotential.[10] Structural parameters were fully optimized, on the resulting structures second derivative calculations were carried out. Unless otherwise stated, the structures obtained were real minima as shown by the positive harmonic frequencies.

General Procedures. ^{1}H (400.1 and 300.1 MHz), ^{13}C (100.6 and 75.5 MHz), and ^{199}Hg (123.2 MHz) NMR spectra were recorded on ARX400 and AC300 P Bruker spectrometers; ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; ^{199}Hg NMR chemical shifts are relative to Me_2Hg (10% in $C_6D_6{-}C_7H_8$); the NMR spectroscopic data of **2a**−**c**, **3a**−**c**, never fully reported in the literature, are given below.[11] The yields of the unstabilized derivatives **5a**−**c** were

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determined by ^{1}H NMR with an internal reference. High resolution mass spectrometry (HRMS) experiments were performed on a Varian MAT 311 instrument. To record the mass spectrum, vinylmercury hydrides **5a**−**c** were directly introduced from a cell into the ionization chamber of the spectrometer. Photoelectron spectra have been recorded at the He I resonance line with an apparatus described earlier.[12] The instrumental resolution was 45 meV at the ^{2}Ar $P_{3/2}$ line. Calibration was carried out by feeding CH_3I and N_2 simultaneously with the sample.

Synthesis of Vinylmercury Chlorides (2a−c).[6,7] In a 250 mL three-necked flask equipped with a reflux condenser, a dropping funnel, a stirrer, and a nitrogen inlet were introduced the magnesium (2.4 g, 0.1 mole) and 5 mL of dry tetrohydrofuran (THF). A few drops of the vinyl halide were added, and after the reaction was started, the vinyl halide (0.1 mol) in dry THF (100 mL) was added at a rate to maintain a moderate reflux. At the end of the addition, the solution was stirred under reflux during 1 h and then cooled in an ice bath. A solution of $HgCl_2$ (26 g, 96 mmol) in dry THF (40 mL) was added slowly, and the solution was heated under reflux during 30 min. Saturated aqueous ammonium chloride (50 mL) and 50 mL of ethyl ether were added at room temperature; the organic phase was separated, and the aqueous phase was extracted three times with a 2:1 mixture of ethyl ether and THF. After drying on $MgSO_4$, filtration, and then evaporation of the solvent *in vacuo*, the purification was performed by crystallization.

Ethenylmercury Chloride (2a).[6] Yield: 78%. mp: 177 °C. ^{1}H NMR ($(CD_3)_2CO$): δ 5.62 (dd, 1H, $H_2C{=}$, $^{3}J_{HHtrans} = 19.3$ Hz, $^{2}J_{HH} = 2.0$ Hz, $^{3}J_{HgH} = 331.6$ Hz (d)), 5.91 (dd, 1H, $H_2C{=}$, $^{3}J_{HHcis} = 11.7$ Hz, $^{2}J_{HH} = 2.0$ Hz, $^{3}J_{HgH} = 645.9$ Hz (d)), 6.38 (dd, 1H, ${=}CH$Hg, $^{3}J_{HHtrans} = 19.3$ Hz, $^{3}J_{HHcis} = 11.7$ Hz, $^{2}J_{HgH} = 274.7$ Hz (d)). ^{13}C NMR ($(CD_3)_2CO$): δ 132.6 (ddd, $H_2C{=}$, $^{1}J_{CH} = 161.2$ Hz, $^{1}J_{CH} = 154.6$ Hz, $^{2}J_{CH} = 2.0$ Hz, $^{2}J_{HgC} = 27.5$ Hz (d)), 146.8 (ddd, ${=}CH$, $^{1}J_{CH} = 163.8$ Hz, $^{2}J_{CH} = 3.6$ Hz, $^{2}J_{CH} = 1.5$ Hz, $^{1}J_{HgC} = 2302$ Hz (d)). ^{199}Hg NMR ($(CD_3)_2CO$): δ −1171.

(1-Methylethenyl)mercury Chloride (2b).[7] Yield: 48%. mp: 160 °C. ^{1}H NMR ($(CD_3)_2CO$): δ 2.12 (dd, 3H, CH_3, $^{4}J_{HH} = {^{4}J_{HH}} = 1.5$ Hz, $^{3}J_{HgH} = 187.7$ Hz (d)), 5.12 (dq, 1H, $H_2C{=}$, $^{2}J_{HH} = {^{4}J_{HH}} = 1.5$ Hz, $^{3}J_{HgH} = 278.2$ Hz (d)), 5.60 (dq, 1H, $H_2C{=}$, $^{2}J_{HH} = {^{4}J_{HH}} = 1.5$ Hz, $^{3}J_{HgH} = 596.6$ Hz (d)). ^{13}C NMR ($(CD_3)_2CO$): δ 28.6 (qdd, $H_3C{=}$, $^{1}J_{CH} = 127.1$ Hz, $^{3}J_{CH} = 13.7$ Hz, $^{3}J_{CH} = 9.2$ Hz, $^{2}J_{HgC} = 211.6$ Hz (d)), 124.6 (ddq, $H_2C{=}$, $^{1}J_{CH} = 162.7$ Hz, $^{1}J_{CH} = 151.0$ Hz, $^{3}J_{CH} = 7.5$ Hz, $^{2}J_{HgC} = 136.3$ Hz (d)), 160.5 (q, ${=}C$Hg, $^{2}J_{CH} = 7.6$ Hz, $^{1}J_{HgC} = 2418$ Hz (d)).

1-Propenylmercury Chloride (2c).[7] Yield: 55% (*Z*/*E*:1/1). (*Z*) ^{1}H NMR ($CDCl_3$): δ 1.97 (dd, 3H, CH_3, $^{3}J_{HH} = 6.6$ Hz, $^{4}J_{HH} = 0.9$ Hz, $^{4}J_{HgH} = 39.4$ Hz (d)), 4.96 (dq, 1H, CHHg, $^{3}J_{HHcis} = 9.2$ Hz, $^{4}J_{HH} = 0.9$ Hz, $^{2}J_{HgH} = 256$ Hz (d)), 5.99 (dq, 1H, MeCH, $^{3}J_{HHcis} = 9.2$ Hz, $^{3}J_{HH} = 6.6$ Hz, $^{3}J_{HgH} = 578$ Hz (d)). ^{13}C NMR ($(CD_3)_2CO$): δ 21.8 (qdd, CH_3, $^{1}J_{CH} = 126.1$ Hz, $^{2}J_{CH} = 8.14$ Hz, $^{3}J_{CH} = 6.1$ Hz), 141.1 (dq, MeCH, $^{1}J_{CH} = 152.1$ Hz, $^{2}J_{CH} = 6.9$ Hz), 145.0 (ddq, CHHg, $^{1}J_{CH} = 160.2$ Hz, $^{2}J_{CH} = {^{3}J_{CH}} = 6.1$ Hz). (*E*) ^{1}H NMR ($CDCl_3$): δ 1.93 (d, 3H, CH_3, $^{3}J_{HH} = 4.6$ Hz, $^{4}J_{HgH} = 20.4$ Hz), 4.89 (m, 2H, $HC{=}CH$). ^{13}C NMR ($(CD_3)_2CO$): δ 23.7 (qdd, CH_3, $^{1}J_{CH} = 126.2$ Hz, $^{2}J_{CH} = 14.2$ Hz, $^{3}J_{CH} = 6.1$ Hz), 137.8 (dqd, CHHg $^{1}J_{CH} = 164.3$ Hz, $^{2}J_{CH} = 7.6$ Hz, $^{2}J_{CH} = 2.5$ Hz), 138.6 (dqd, MeCH, $^{1}J_{CH} = 165.8$ Hz, $^{2}J_{CH} = 8.1$ Hz, $^{3}J_{CH} = 2.5$ Hz).

Synthesis of Divinylmercury Compounds (3a−c).[8] In a 250 mL three-necked flask, the vinylmagnesium halide (0.1 mol) in THF (100 mL) was prepared as described above. The solution was cooled in an ice bath and a solution of $HgCl_2$ (13 g, 48 mmol) in dry THF (20 mL) was then slowly added. At the end of the addition, the solution was heated under reflux during 30 min. To the cold solution were added saturated aqueous ammonium chloride (30 mL) and ethyl ether (30 mL); the organic phase was separated, and the aqueous phase was extracted three times with ethyl ether. After drying on $MgSO_4$, filtration, and then evaporation of the solvent *in vacuo*, the purification was performed by distillation *in vacuo*. The unpleasant odor is characteristic of the divinylmercury compounds.

Diethenylmercury (3a).[8] Yield: 86%. bp_{20}: 59 °C. ^{1}H NMR ($CDCl_3$): δ 5.40 (dd, 2H, H_2C, $^{3}J_{HHtrans} = 20.7$ Hz, $^{2}J_{HH} = 3.6$ Hz, $^{3}J_{HgH} = 160.8$ Hz (d)), 5.97 (dd, 2H, H_2C, $^{3}J_{HHcis} = 13.8$ Hz, $^{2}J_{HH} = 3.6$ Hz, $^{3}J_{HgH} = 295$ Hz (d)), 6.71 (dd, 2H, HC, $^{3}J_{HHtrans} = 20.7$ Hz, $^{3}J_{HHcis} = 13.8$ Hz, $^{2}J_{HgH} = 132$ Hz (d)). ^{13}C NMR ($CDCl_3$): δ 134.4 (t, H_2C, $^{1}J_{CH} = 153.8$ Hz, $^{2}J_{HgC} = 39$ Hz (d)), 168.2 (d, HC, $^{1}J_{CH} = 148.0$ Hz, $^{1}J_{HgC} = 1127$ Hz (d)). ^{199}Hg NMR ($C_6D_6{-}C_7H_8$): δ −623.

Bis(1-methylethenyl)mercury (3b).[8] Yield: 83%. $bp_{0.2}$: 37 °C. ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 6H, CH_3, $^{3}J_{HHg} = 88.7$ Hz (d)), 4.88 (s, 2H, CH_2, $^{3}J_{HHg} = 129.0$ Hz (d)), 5.63 (s, 2H, CH_2, $^{3}J_{HHg} = 258.4$ Hz (d)). ^{13}C NMR ($CDCl_3$): δ 29.4 (qdd, CH_3, $^{1}J_{CH} = 125.6$ Hz, $^{3}J_{CH} = 10.7$ Hz, $^{3}J_{CH} = 15.3$ Hz, $^{2}J_{CHg} = 128.8$ Hz (d)), 124.5 (tq, CH_2, $^{1}J_{CH} = 149.7$ Hz, $^{1}J_{CH} = 158.0$ Hz, $^{3}J_{CH} = 8.2$ Hz, $^{2}J_{CHg} = 99.9$ Hz), 180.5 (brd s, CH, $^{1}J_{CHg} = 1044$ Hz (d)). ^{199}Hg NMR ($C_6D_6{-}C_7H_8$): −717 ppm.

Di-1-propenylmercury (3c).[8] Yield: 85% (mixture of (*Z,Z*), (*Z,E*), and (*E,E*) compounds in a 6:2:1 ratio). $bp_{0.2}$: 39 °C. **(*Z,Z*)** ^{1}H NMR ($CDCl_3$): δ 1.98 (d, 6H, CH_3, $^{3}J_{HH} = 6.3$ Hz, $^{4}J_{HHg} = 20.8$ Hz (d)), 6.30 (d, 2H, CHHg, $^{3}J_{HHcis} = 11.7$ Hz, $^{2}J_{HHg} = 115.7$ Hz (d)), 7.11 (dq, 2H, MeCH, $^{3}J_{HHcis} = 11.7$ Hz, $^{3}J_{HH} = 6.3$ Hz, $^{3}J_{HHg} = 241.7$ Hz (d)). ^{13}C NMR ($CDCl_3$): δ 23.1 (qdd, CH_3, $^{1}J_{CH} = 125.0$ Hz, $^{2}J_{CH} = 15.8$ Hz, $^{3}J_{CH} = 7.4$ Hz, $^{3}J_{HgC} = 143.7$ Hz (d)), 142.8 (dqd, MeCH, $^{1}J_{CH} = 149.2$ Hz, $^{2}J_{CH} = 6.7$ Hz, $^{2}J_{CH} = 3.3$ Hz, $^{2}J_{HgC} = 27.1$ Hz (d)), 160.6 (ddq, CHHg, $^{1}J_{CH} = 148.7$ Hz, $^{2}J_{CH} \approx {^{3}J_{CH}} \approx 6.7$ Hz, $^{1}J_{HgC} = 1115.7$ Hz (d)). ^{199}Hg NMR ($CDCl_3$): δ −354 (*Z,Z*), −441 (*E,Z*), −522 (*E,E*).

Preparation of Methyl- (4) and Vinylmercury Hydrides (5a−c). General Procedure. The apparatus already described for the reduction of α-unsaturated chloroarsines was used.[13] The flask containing the mercury chloride **1**, **2a**−**c** (1 mmol), small amounts of a radical inhibitor (duroquinone or galvinoxyl (≈10 mg)), and chlorotributylstannane (≈5 mL) as solvent was fitted on a vacuum line, cooled at about 0 °C by immersion in an ice bath, and degassed. The tributylstannane (Bu_3SnH, 440 mg, 1.5 mmol) and small amounts of the same radical inhibitor (duroquinone or galvinoxyl (≈5 mg)) were then slowly added (10 min) with a syringe through the septum. During and after the addition, mercury hydrides **4**, **5a**−**c** were distilled off *in vacuo* from the reaction mixture. A cold trap (−40 °C) removed selectively the less volatile products and compounds **4**, **5a**−**c** were condensed on a cold finger (−196 °C) which was connected at the bottom to a flask or a NMR tube. A solvent can be added at this step. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected in a Schlenk flask or a NMR tube and kept at low temperature (<−80 °C) before analysis.

Photoelectron Spectroscopy. To record the photoelectron spectra (PES), compounds **3a**−**c**, **4**, and **5a**−**c** were synthesized as reported above. In the preparation of mercury hydrides **4**, **5a**−**c**, a cold trap (−40 °C) fitted on the vacuum line (*ca.* 10^{-3} mbar) selectively removed the less volatile products. The analysis of mercury hydrides **4**, **5a**−**c** was completed by recording the photoelectron spectra of the gaseous flow.

Methylmercury Hydride (4).[2b,e] Yield: 84%. ^{1}H NMR ($CDCl_3$, −40 °C): δ 0.06 (d, 3H, $^{3}J_{HH} = 4.3$ Hz, $^{2}J_{HgH} = 107$ Hz (d)), 16.8 (q, 1H, $^{3}J_{HH} = 4.3$ Hz, $^{1}J_{HgH} = 2651$ Hz (d)). ^{13}C NMR ($CDCl_3$, −40 °C): δ 19.9 (qd, $^{1}J_{CH} = 129.1$ Hz, $^{2}J_{CH} = 56.1$ Hz, $^{1}J_{HgC} = 738$ Hz (d)). ^{199}Hg NMR ($C_6D_6{-}C_7H_8$, −30 °C): δ −390. The PE spectrum of **4** displayed two resolved bands at 9.73 and 12.30 eV.

Ethenylmercury Hydride (5a). Yield: 31%. ^{1}H NMR ($CDCl_3$, −40 °C): δ 5.47 (ddd, 1H, CH_2, $^{3}J_{HHtrans} = 20.6$ Hz, $^{2}J_{HH} = {^{4}J_{HH}} = 3.6$ Hz, $^{3}J_{HgH} = 163$ Hz (d)), 6.08 (ddd, 1H, CH_2, $^{3}J_{HHcis} = 13.7$ Hz, $^{4}J_{HH} = 9.6$ Hz, $^{2}J_{HH} = 3.6$ Hz, $^{3}J_{HgH} = 302$ Hz (d)), 6.84 (ddd, 1H, CH, $^{3}J_{HHtrans} = 20.6$ Hz, $^{3}J_{HHcis} = 13.7$ Hz, $^{3}J_{HH} = 2.7$ Hz, $^{2}J_{HgH} = 139$ Hz (d)) 14.4 (ddd, 1H, HgH, $^{4}J_{HH} = 9.6$ Hz, $^{4}J_{HH} = 3.6$ Hz, $^{3}J_{HH} = 2.7$ Hz, $^{1}J_{HgH} = 2800$ Hz (d)). ^{13}C NMR ($CDCl_3$, −40 °C): δ 134.8 (t, CH_2, $^{1}J_{CH} = 155.6$ Hz, $^{2}J_{HgC} \approx 37.3$ Hz (d)), 172.1 (dd, CH, $^{1}J_{CH} = 145.4$ Hz, $^{2}J_{CH} = 69.9$ Hz, $^{1}J_{HgC} = 1120$ Hz (d)). ^{199}Hg NMR ($C_6D_6{-}C_7H_8$, −40 °C): δ −714 ppm. HRMS. Calcd for $(C_2H_4{}^{202}Hg_{\cdot})^{+}$: 230.0019. Found: 230.001. *m*/*z* (%): 230 (9.3), 229 (3.4), 228 (7.3), 227 (5.4), 226 (3.2), 202 (13.4), 201 (7.5), 200 (10.4), 199 (5.8), 198 (3.5), 28 (36.0), 27 (73.3), 26 (18.4). The PE spectrum of **5a** displayed four resolved bands at 9.79, 10.13, 11.41, and 13.20 eV.

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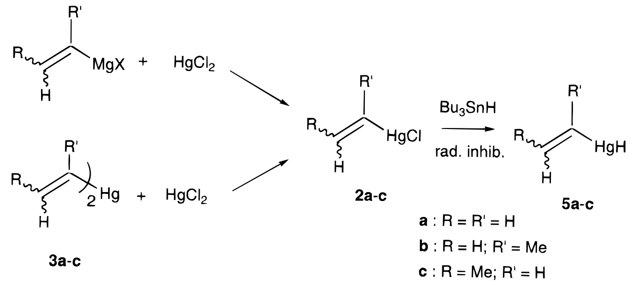
Scheme 1



(1-Methylethenyl)mercury Hydride (5b). Yield: 24%. ^{1}H NMR ($CDCl_3$, −40 °C): δ 2.03 (ddd, 3H, C*H*$_3$, $^4J_{HH} = 2.6$ Hz, $^4J_{HH} = {}^4J_{HH} = 1.6$ Hz, $^3J_{HgH} = 95.0$ Hz (d)), 4.89 (ddq, 1H, C*H*$_2$, $^4J_{HH} = 3.8$ Hz, $^2J_{HH} = 3.0$ Hz, $^4J_{HH} = 1.6$ Hz, $^3J_{HgH} = 134.5$ Hz (d)), 5.70 (ddq, 1H, C*H*$_2$, $^4J_{HH} = 8.3$ Hz, $^2J_{HH} = 3.0$ Hz, $^4J_{HH} = 1.6$ Hz, $^3J_{HgH} = 275.1$ Hz (d)), 14.4 (ddq, 1H, Hg*H*, $^4J_{HH} = 8.3$ Hz, $^4J_{HH} = 3.8$ Hz, $^4J_{HH} = 2.6$ Hz, $^1J_{HgH} = 2687$ Hz (d)). ^{13}C NMR ($CDCl_3$, −40 °C): δ 29.9 (q, *C*H$_3$, $^1J_{CH} = 125.3$ Hz), 124.5 (ddq, *C*H$_2$, $^1J_{CH} = 158.5$ Hz, $^1J_{CH} = 166.6$ Hz, $^3J_{CH} = 8.4$ Hz), 183.4 (dq, *C*Hg, $^2J_{CH} = 66.9$ Hz, $^2J_{CH} = 6.5$ Hz). ^{199}Hg NMR (C_6D_6—C_7H_8, −40 °C): δ −801 ppm. HRMS. Calcd for $(C_3H_6{}^{202}Hg)^+$: 244.0176. Found: 244.017. *m/z* (%): 244 (2.2), 202 (4.1), 200 (3.3), 42 (10.3), 41 (15.8), 40 (5.0), 39 (23.9). The PE spectrum of **5b** displayed three resolved bands at 9.44, 11.0, and 11.8 eV.

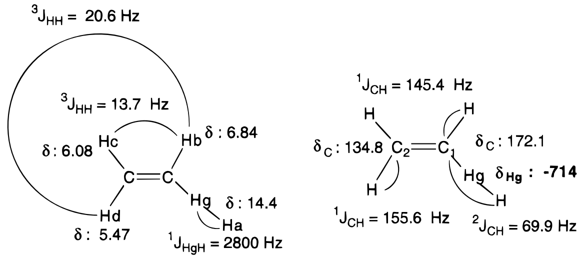
1-Propenylmercury Hydride (5c). Yield: 14% (*Z*/*E*: 2/1). (*Z*) ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.92 (dm, C*H*$_3$, 3H, $^3J_{HH} = 6.3$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} \approx 1.0$ Hz), 6.28 (dm, 1H, C*H*Hg, $^3J_{HHcis} = 12.3$ Hz, $^4J_{HH} = 1.3$ Hz, $^3J_{HH} = 1.3$ Hz, $^2J_{HgH} = 127.4$ Hz (d)), 7.10 (m, 1H, MeC*H*, $^3J_{HHcis} = 12.3$ Hz, $^4J_{HH} = 11.0$ Hz, $^3J_{HH} = 6.3$ Hz, $^3J_{HgH} = 255$ Hz (d)), 15.6 (dm, 1H, Hg*H*, $^3J_{HH} = 11.0$ Hz, $^3J_{HH} = 1.3$ Hz, $^5J_{HH} \approx 1.0$ Hz, $^1J_{HgH} = 2752$ Hz (d)). ^{13}C NMR ($CDCl_3$, −40 °C): δ 23.6 (q, *C*H$_3$, $^1J_{CH} = 126.0$ Hz), 143.3 (d, Me*C*H, $^1J_{CH} = 152.5$ Hz), 160.7 (dd, *C*HHg, $^1J_{CH} = 149.9$ Hz, $^2J_{CH} = 65.9$ Hz, $^2J_{HgC} = 49.9$ Hz (d)). (*E*) ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.87 (dm, 3H, C*H*$_3$, $^3J_{HH} = 6.1$ Hz, $^4J_{HH} = 1.7$ Hz, $^5J_{HH} \approx 0.9$ Hz), 5.82 (dqd, 1H, MeC*H*, $^3J_{HHtrans} = 18.7$ Hz, $^3J_{HH} = 6.1$ Hz, $^4J_{HH} = 4.6$ Hz, $^3J_{HgH} = 139.3$ Hz (d)), 6.35 (ddq, 1H, C*H*Hg, $^3J_{HHtrans} = 18.7$ Hz, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} \approx 1.3$ Hz, $^2J_{HgH} = 151.0$ Hz (d)), 14.8 (dm, 1H, Hg*H*, $^4J_{HH} = 4.6$ Hz, $^3J_{HH} \approx 1.3$ Hz, $^5J_{HH} \approx 0.9$ Hz, $^1J_{HgH} = 2742.0$ Hz (d)). ^{13}C NMR ($CDCl_3$, −40 °C): δ 24.0 (q, *C*H$_3$, $^1J_{CH} = 125.6$ Hz), 146.0 (d, Me*C*H, $^1J_{CH} = 152.3$ Hz), 162.7 (dd, *C*HHg, $^1J_{CH} = 149.9$ Hz, $^2J_{CH} = 53.8$ Hz). Even after several attempts, we never obtained satisfactory ^{199}Hg NMR and photoelectron spectra. By mass spectrometry, the $(M - H)^+$ ion has been measured. HRMS. Calcd for $(C_3H_5{}^{201}Hg)^+$: 242.0095. Found: 242.010.

After a few minutes at room temperature, vinylmercury hydrides **5a**−**c** decomposed, leading to elemental mercury (observed at the bottom of the NMR tube), the corresponding divinylmercury **3a**−**c** (characterized by NMR), and dihydrogen (observed on the PE spectra).

Results and Discussion

Synthesis and Spectroscopic Characterization of Vinylmercury Hydrides. To prepare the precursors of vinylmercury hydrides **5a**−**c**, 1 equiv of the corresponding vinyl Grignard reagent or of divinylmercury[8] was added to 1 equiv of mercury chloride (Scheme 1)[6,7] and the formed vinylmercury chlorides **2a**−**c** were purified by crystallization. The reduction of methylmercury chloride (**1**)[5] into the methylmercury hydride (**4**)[2b−e] was performed by using various reducing agents (LAH, dichloroalane ($AlHCl_2$),[14] sodium borohydride, Bu_3SnH). Ethenylmercury hydride **5a** was only obtained using a mild reducing reagent like $AlHCl_2$ or Bu_3SnH. However, attempts to prepare propenyl derivatives **5b**,**c** by reduction of mercury chlorides **2b**,**c** with these reagents were unsuccessful. Only propene was observed, the cleavage of the C−Hg bond probably proceeding *via* a radical reaction.[3] Propenylmercury hydrides **5b**,**c** were obtained by starting from **2b**,**c** when the reduction was performed with Bu_3SnH in the presence of small amounts of a radical inhibitor (duroquinone or galvinoxyl) (Scheme 1).[15] To limit their decomposition, compounds **4**, **5a**−**c** were distilled off *in vacuo* from the cooled reaction mixture (≈0 °C) during the course of the addition of **1**, **2a**−**c** and separated from the high-boiling compounds by a cold trap (−40 °C) before condensation with a cosolvent at −196 °C. Under these conditions, mercury hydride **5b** was obtained in a moderate yield (24%) and the *Z*- and *E*-isomers of compound **5c** with a low yield (14%) and only on an analytical scale; better yields were observed for hydrides **4** (84%) and **5a** (31%). Vinylmercury hydride **5a** can be condensed under vacuum (10^{-1} mbar) at a temperature lower than −80 °C and then revaporized by heating the trap to −30 °C. Thus, the boiling point of **5a** is somewhat higher than that of the corresponding stannane[16] or stibine[15b] which were not trapped in similar conditions at a temperature higher than −100 °C; this observation is however consistent with the presence for **5a** of monomeric species in the gaseous phase.

Chart 1. Characteristic Spectral Data (^{1}H, ^{13}C, and ^{199}Hg NMR) of **5a**



Characterization of **4**, **5a**−**c** was performed by low-temperature (−40 °C) ^{1}H and ^{13}C NMR spectroscopy and HRMS. The ^{199}Hg NMR and photoelectron spectra of **5a**,**b** were also recorded, but attempts to record the corresponding spectra of compound **5c** were unsuccessful. The ^{1}H and ^{13}C NMR data of compounds **5a**−**c** allow an unambiguous structural assignment, since the chemical shifts and coupling constants are typical of vinylmercury derivatives and are particularly close to those observed for **3a**−**c**. We give as an example the NMR data of the parent compound **5a** (Chart 1 and Figure 1): the signals of the chemical shifts of the vinylic protons were observed between 5.4 and 6.9 ppm ($^3J_{HHtrans} = 20.6$ Hz and $^3J_{HHcis} = 13.7$ Hz). The signal of the chemical shift of the hydrogen linked to the mercury atom of **5a** was observed at 14.4 ppm. This last value is close to the one reported for the phenylmercury hydride[2e] but surprisingly at higher field than those of alkylmercury hydrides (for example **4**: δ_H 16.8 ppm).

There has been considerable discussion of relationships between the proton−proton coupling constant and the nature of the substituent in monosubstituted vinyl compounds.[17] It has been observed that the sum of the coupling constants ($\sum J = {}^3J_{trans} + {}^3J_{cis} + {}^2J_{gem}$) exhibits a good linear dependence on substituent electronegativity, E_X (Pauling value). The $\sum J$ of **5a** (37.9 Hz) and **3a** ($\sum J$: 38.1 Hz) indicate that the HgH or HgR groups are more electropositive than either HgBr ($\sum J$: 33.0

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(14) Ashby, E. C.; Prather, J. *J. Am. Chem. Soc.* **1966**, *88*, 729−733.

(15) Some of us have already reported the use of Bu_3SnH in the presence of a radical inhibitor as reducing agent in the preparation of unstabilized heterocompounds like allenyl-, alkynylarsines,[13] -stannanes or, -stibines: (a) Lassalle, L.; Janati, T.; Guillemin, J.-C. *J. Chem. Soc., Chem. Commun.* **1995**, 699−700. (b) Legoupy, S.; Lassalle, L.; Guillemin, J.-C.; Metail, V.; Senio, A.; Pfister-Guillouzo, G. *Inorg. Chem.* **1995**, *34*, 1466−1471.

(16) Janati, T.; Guillemin, J.-C.; Soufiaoui, M. *J. Organomet. Chem.* **1995**, *486*, 57−62.

(17) (a) Schaefer, T. *Can. J. Chem.* **1962**, *40*, 1−4. (b) Wells, P. R.; Kitching, W.; Henzell, R. F. *Tetrahedron Lett.* **1964**, 1029−1034.

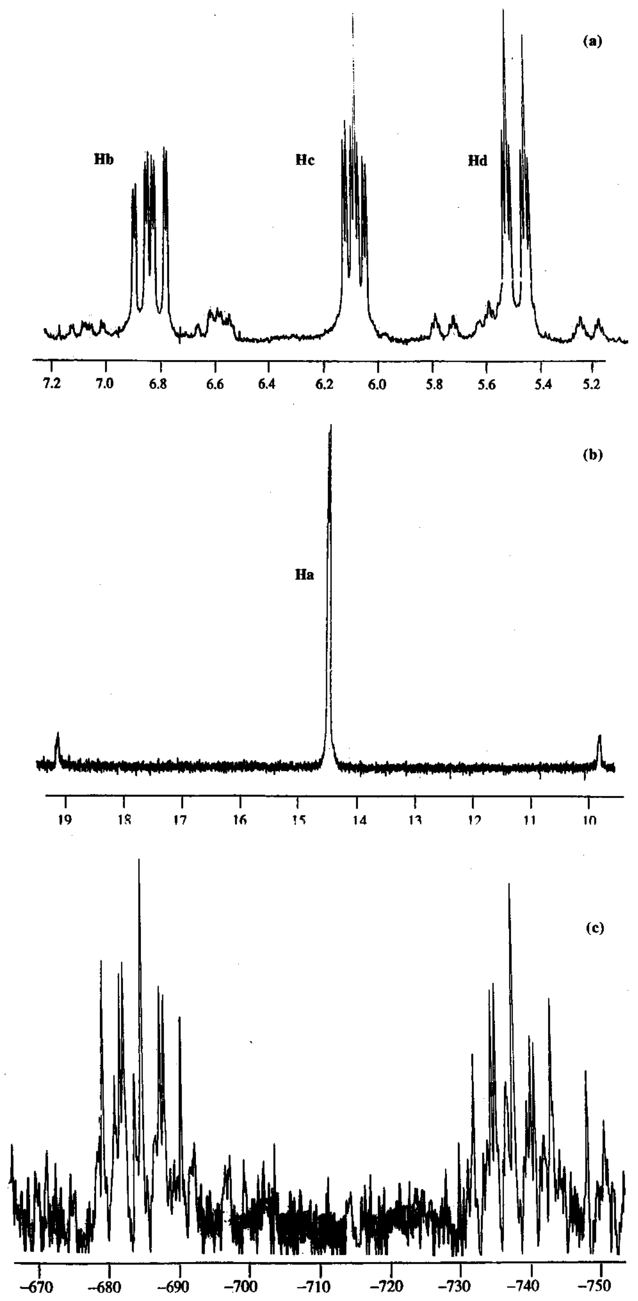

Figure 1. ^{1}H (300 MHz) and ^{199}Hg (123.2 MHz) NMR spectra of **5a**. (a) ^{1}H NMR spectra (Hb, Hc, and Hd); (b) ^{1}H NMR spectra (Ha); (c) ^{199}Hg NMR spectrum (gate decoupling).

Hz),[17a] HgOAc ($\sum J$: 33.0 Hz),[17b] or HgCl group (**2a**, $\sum J$: 33.0 Hz), presumably because $^+$HgR and $^+$HgH groups are more stabilized than those where the mercury atom is connected to a halogen (Cl, Br) or an acetoxy group.

The signals corresponding to the sp^2 carbons of compound **5a** were observed at δ_{C2} 134.8 and δ_{C1} 172.1 ppm. The downfield shift of the signal of the C$_1$ carbon is typical of vinylmercury derivatives like the diethenylmercury **3a**. The ^{199}Hg NMR signal of **5a** (δ_{199Hg}: −714 ppm) can be compared with those of phenylmercury hydride (δ_{199Hg}: −830 ppm)[2e] and diethenylmercury **3a** (δ_{199Hg}: −623 ppm).[18] Otherwise, an upfield chemical shift was observed for the signal of the ethenylmercury chloride **2a** (δ_{199Hg}: −1189 ppm) and a downfield chemical shift for this one of methylmercury hydride **4** (δ_{199Hg}: −390 ppm). It should be noted that the presence of an unsaturated substituent or of a chlorine atom on the heteroatom leads to the observation of a signal corresponding to a downfield chemical shift with respect to those of the alkyl derivatives in the ^{29}Si, ^{119}Sn, or ^{31}P NMR spectra of silanes, stannanes, or phosphines, respectively. So, the NMR data of **5a**−**c** are characteristic of mercury compounds.[18] The structure of **5a** was confirmed by the observation on the mass spectrum of the corresponding molecular ion ((M$^{\bullet+}$) Calcd: 230.0019. Found: 230.001).

Table 1. HF/LANL1DZ Optimized Structural Parameters (Bond Lengths, Å; Bond Angles, deg) of the Monosubstituted Mercury Derivatives **4**, **5a**−**c**, and **6**

	CH_3HgH (**4**)	$H_2C{=}CH$-HgH (**5a**)	$H_2C{=}C(Me)$-HgH (**5b**)	$MeCH{=}CH$-HgH (**5c**)	$HC{\equiv}C$-HgH (**6**)
Hg−C	2.163	2.138	2.153	2.133	2.088
Hg−H	1.696	1.686	1.689	1.687	1.667
C−C		1.344	1.343	1.344	1.214
H−Hg−C	180.0	179.9	179.6	179.9	180.0

Table 2. HF/LANL1DZ Optimized Structural Parameters (Bond Lengths, Å; Bond Angles, deg) of the Disubstituted Mercury Derivatives **3a**−**c**, **7**, and **8**

	CH_3Hg-CH_3 (**8**)	$(H_2C{=}CH)_2$-Hg(**3a**)[a]	$(H_2C{=}C$-$Me)_2Hg$ (**3b**)[b]	$(MeCH{=}$ $CH)_2Hg$ (**3c**)	$(HC{\equiv}C)_2$-Hg (**7**)
Hg−C	2.163	2.128	2.144	2.125	2.055
C−C		1.343	1.343	1.343	1.212
C−Hg−C	180.0	180.0	179.4	179.4	180.0

[a] These structural characteristics refer to all of the structures discussed in the text. [b] Minimum energy conformer.

Geometries. The most important calculated geometrical features of the investigated compounds are shown in Tables 1 and 2. In agreement with earlier observations the bonding angle about mercury is near 180°. The lowest harmonic frequency corresponding to the bending of the HgH bond in CH_3HgH (**4**) is 480 cm^{-1}, showing a rather large propensity of the CHgH structure to remain linear. At the MP2 level of theory, this harmonic frequency shows little change, indicating that the inclusion of the electron correlation has no substantial effect on the geometries of the investigated molecules. Similarly, even for the nonsymmetrical molecules the R−Hg−R bonding angle showed a deviation from linearity of less than 1° (see Tables 1 and 2). The Hg−C bond length was 2.163 Å for the saturated compounds, independently from the number of the methyl groups attached to the mercury atom. The linearity about mercury remained for the disubstituted compound as well. If the mercury was attached to an unsaturated carbon, the Hg−C bond length was getting somewhat shorter, exhibiting bond lengths between 2.133 and 2.153 Å. The shortening of this bond is even more pronounced at the MP2 level of theory, this behavior is usual for conjugative interactions. The ethynylmercury compound **6** exhibits even larger bond shortening, roughly twice as much as that for vinyl compound **5a**. Disubstitution results further decrease in the HgC bond length; thus, the shortest bond length was obtained for diethynylmercury (**7**). All of these observations can be rationalized in terms of some interaction between the rather high-lying filled mercury 5d-orbital and the π*-orbital of the C=C bond.

The diethenyl **3** and diethynyl **7** compounds show even larger Hg−C bond shortening than the monosubstituted compounds (Table 2), resembling a conjugative interaction. This bond shortening, however, which is undoubtedly indicative of an increased double bond character, is not related to a high rotational barrier in the case of the diethenyl compound **3a**. This behavior is in accord with the participation of the d-orbitals in the π-bonding. The d-orbital set has a cylindrical symmetry; thus, its overlap with the p$_z$ orbital of carbon is not restricted to

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(18) Wrackmeyer, B.; Contreras, R. *Annu. Rep. NMR Spectrosc.* **1992**, *34*, 267−329.

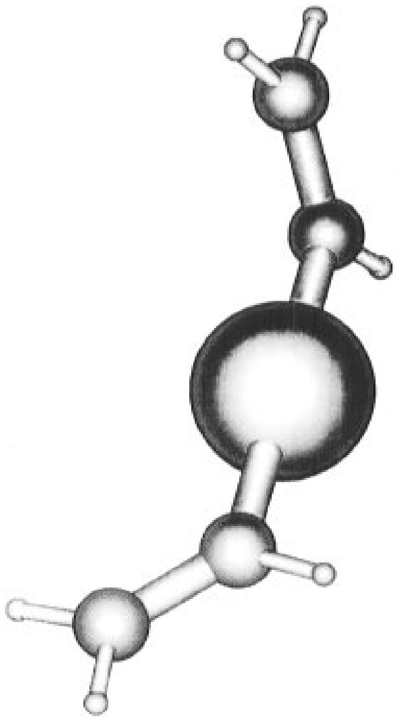

Figure 2. LANL1DZ calculated minimum energy conformer of diethenylmercury **3a**.

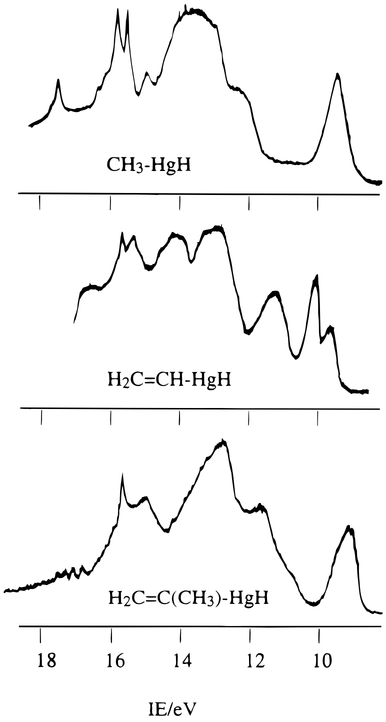

Figure 3. Photoelectron spectra of (top) methylmercury hydride (**4**), (middle) ethenylmercury hydride (**5a**), and (bottom) (1-methylethenyl)-mercury hydride (**5b**).

a single plane as it is usual for a conventional double bond. The minimum energy conformer (according to the calculations) is shown in Figure 2. In this conformer, the two ethenyl moieties are nearly perpendicular to each other. The planar forms (both cis and trans!) have higher energy than the minimum by 0.1 kcal/mol only, at the level of the theory used presently. Both planar structures were characterized by a single imaginary frequency (-26 cm^{-1}), while for the most stable rotated form all of the calculated frequencies were positive (the lowest harmonic frequency, corresponding to the rotation about the C—Hg bond, was 16 cm^{-1}). The "perpendicular form" of di-1-propenyl- and bis(1-methylethenyl)mercury is more stable than the planar form by 0.02 and 0.14 kcal/mol, respectively. Since the calculated energy difference is small, from the present calculated data no reliable conclusion can be drawn for the most preferred conformation of these compounds.

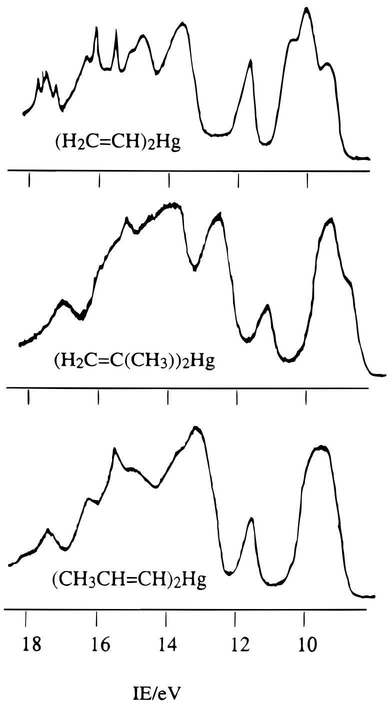

Figure 4. Photoelectron spectra of (top) diethenylmercury (**3a**), (middle) bis(1-methylethenyl)mercury (**3b**), and (bottom) di-1-propenylmercury **3c**.

Table 3. Measured (Expt) and Calculated ($-\epsilon$) Ionization Energies (eV) for the Mercury Hydrides **4** and **5a**,**b**

CH_3HgH (**4**)			$H_2C{=}CH{-}HgH$ (**5a**)			$H_2C{=}C(Me)HgH$ (**5b**)		
expt	$-\epsilon$	assignmt	expt	$-\epsilon$	assignmt	expt	$-\epsilon$	assignmt
9.73	9.87	σ_{CHg}	9.79	9.90	σ_{CHg}	9.44	9.90	σ_{CHg}
			10.13	10.23	π	9.44	9.49	π
			11.41	11.94		11.0 (sh)	11.87	
12.30	11.83		13.20	14.91		11.8	13.80	

The propenyl derivatives have structural characteristics similar to those of the ethenylmercury compounds. The bond shortening (relative to the saturated compound) was smaller in case of the 1-methylethenyl derivative **5b**. This observation is indicative of a decreased interaction with the filled mercury d-orbitals, which is expected, if the π*-orbital is of decreased electron acceptor character. Indeed, as a consequence of hyperconjugation, the methyl group at the α-carbon atom should have such an effect.

Photoelectron Spectra. The photoelectron spectra of the investigated molecules are shown in Figures 3 and 4, the ionization energies with their assignment are listed in Tables 3 and 4. The spectrum of methylmercury hydride **4** is similar to that published before for dimethylmercury **8**.[19] The lowest IE should be assigned to the removal of an electron from the σ_{HgC} orbital. This band is followed by rather diffuse structures, assignable to orbitals localized mainly on the methyl group. The rather sharp features at IE values larger than 15 eV are attributable to ionization of the electrons from the 5d atom-like

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Table 4. Measured (expt) and Calculated (−ϵ) Ionization Energies (eV) for the Dimethylmercury (**8**) and Divinylmercury Compounds (**3a**−**c**)

CH_3HgCH_3 (**8**)			$(H_2C{=}CH)_2Hg$ (**3a**)				$(H_2C{=}CMe)_2Hg$ (**3b**)				$(MeCH{=}CH)_2Hg$ (**3c**)			
expt[a]	−ϵ	assignmt	expt	−ϵ[b]	−ϵ[c]	assignmt	expt	−ϵ[b]	−ϵ[c]	assignmt	expt	−ϵ[b]	−ϵ[c]	assignmt
9.33	9.29	σ_{CHg}	9.31	9.67	9.86	s	8.90	9.28	9.43	p	9.30	9.10	9.35	π
			9.89	9.94	9.88	π	9.36	9.62	9.46	π	9.30	9.55	9.35	π
			10.16	10.08	9.95	π	9.36	9.48	9.48	σ	9.30	9.69	9.70	σ
11.6	11.3		11.32	11.46	11.46		11.09	11.16	11.16		10.96	11.21	11.21	
12.7	14.0		13.40	14.83	14.81		12.50	13.73	13.75		12.20	13.62	13.69	

[a] Values taken from ref 19. [b] The calculated orbital energy of the cis structure. The orbital energy for the trans structure differs by less than 0.02 eV. [c] Orbital energy for the minimum energy structure.

orbitals of mercury. The above assignment has been substantiated by the quantum chemical calculations as well, using Koopmans' ionization energies (Table 3). The multiplet structure of the Hg 5d band system can be explained by spin−orbit interaction in a manner similar in ref 19.

The most characteristic feature of the photoelectron spectra of the double-bonded species is the system of bands at 9.5−10.3 eV. This structure should be attributed to ionizations of the electrons from the σ_{HgC} and the π-orbitals (cf. with the 10.5 eV π-ionization energy of ethylene[20] and the 9.73 eV ionization energy of methylmercury **4**; see above). Similarly, the calculations indicate two ionizations, close in energy. In the spectrum of divinylmercury **3a**, three bands appear at about 10 eV, in agreement with the presence of two π bands and one low-lying σ_{CHg} band. According to the calculations, the HOMO is the σ_{CHg} orbital in the case of the vinylmercury compounds. Since the lowest IE of the methyl compound **4** is at the same ionization energy as that of the vinyl derivative **5a**, the calculated ordering of the orbitals seems to be reasonable. The ethylenic π-ionization energy is somewhat shifted toward lower ionization energies in case the of compound **5a**, while the position of the σ_{HgC} band remains nearly unchanged. This behavior is in agreement with the small π-type interaction with the filled 5d orbitals of mercury. From the calculations some Hg d-orbital contribution in the π-MO could be detected as well. The ionizations from the 5d-orbitals of mercury are at about 15.5 eV in the spectrum. Presumably, due to interaction with the π-system, the corresponding bands might be somewhat broadened too.

Due to the large instability of the 1-propenyl compound, only the spectrum of the 1-methylethenyl derivative could be recorded. This spectrum is characterized by a single band in the 9−10 eV region. From the comparison of the calculated and the measured ionization energies, it becomes apparent that while the σ_{HgC} band remains at an unaltered position, the π-band is shifted toward the lower ionization energies due to the hyperconjugative interaction of the methyl group; thus, the two ionizations appear at the same position.

The spectra of the disubstituted compounds (Figure 4) exhibit three bands in the low ionization energy region, in accordance with the expectations. The three bands of the di-1-propenylmercury **3c** merge into one broad feature. The calculated Koopmans' ionization energies are different for the planar and nonplanar structures, as can be seen in Table 4, while for the cis and trans structures the ionization energies agree numerically. Therefore it seems that the rotation is free at room temperature in case of di-1-propenylmercury **3c**, which has a broad structureless band only. The photoelectron spectrum of diethenylmercury **3a** is characterized by three low-energy ionizations split by 0.85 eV. The lowest energy band appears at the same position as that in the case of dimethylmercury **8**,[19] suggesting an assignment to the σ_{HgC} ionization in agreement with the calculations. The split of the second two bands is 0.27 eV, indicating some interaction between the two π-system of the ethylene moieties. This can be better explained by considering the planar, rather than the perpendicular conformation (cf. the calculated splitting of the π-ionizations for the perpendicular and the planar conformers, Table 4). Ionization of the filled mercury d-orbitals appears at 15.11, 15.60, and 16.98 eV in the spectrum of diethenylmercury **3a**; the position of these bands is clearly shown on the He II spectrum (not shown in Figure 4), with enhanced intensity.

The destabilization of the vinylmercury hydride **5a** π-ionization energy with respect to that of ethene amounts to 0.31 eV. From this fact it can be concluded that the substituent effect of the HgH group is of electron donor type. For comparison, the destabilization of the π-ionization energy in the case of propylene[20] (methyl substituent) is 0.64 eV; for the SiH_3 group, 0.13 eV;[21] and for the PH_2, AsH_2, and SbH_2 groups, −0.35,[22] −0.1,[23] and +0.3[15b] eV, respectively. (Note, that for some group 15 substituents more than one conformer were considered for the description of the spectrum, making a direct comparison somewhat difficult.) Substitution of the OMe group, however, results in a lowering of the ionization energy by as much as 1.45 eV.[24] Thus, the interaction between the filled 5d levels of mercury and the π-system is considerably smaller than with the p_z-orbital of oxygen.

Compounds **5a**−**c** can indefinitely be kept in a solvent at −60 °C. They exhibited a very low stability at room temperature, even when kept under nitrogen in chloroform or toluene (half-life ≈ 1−5 min). Elemental mercury, divinylmercury, and hydrogen were formed under these conditions.[2e]

In conclusion, we have developed a mild synthesis of primary vinylmercury hydrides, unknown so far. Extension of this approach to the preparation of other unstabilized mercury hydrides is currently in progress.

Acknowledgment. The authors thank Dr. P. Guenot for particularly difficult mass spectrometry experiments and Dr. S. Sinbandhit fot NMR experiments. Financial support from the "Programme National de Planétologie" (INSU-CNRS, France) and from OTKA T004097 (Hungary) are gratefully acknowledged.

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