



Facile syntheses of homoleptic diarylmercurials via arylboronic acids

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ARTICLE INFO

Article history:

Received 16 September 2008

Received in revised form 12 October 2008

Accepted 13 October 2008

Available online 22 October 2008

Keywords:

Diarylmercurials

Arylboronic acid

Protodemercuration

Kohn–Sham orbitals

Quaternization

ABSTRACT

A general procedure for the syntheses of diarylmercurials is presented. Reactions proceeded in isopropanol in the presence of a base and arylboronic acid. With one exception, all reactions proceeded in good to excellent yields, and this procedure was applicable to a variety of aromatic and heteroaromatic boronic acids. Products were characterized by multinuclear NMR spectroscopy and microanalysis, and investigated by DFT calculations. The structure of di(4-pyridyl)mercury (**6**) was further authenticated by X-ray crystallography. Combined with previous work on the formation of arylgold(I) complexes via arylboronic acids, this procedure may be generally useful for the arylation of late transition metals.

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1. Introduction

Although it is one of the most toxic non-radioactive elements known, there is much current interest in mercury in various applications. Mercury pollution continues to be a cause of concern for countries around the world, and the European Union has even called for a ban on mercury exports by 2011 [1]. Therefore, it is not surprising that much of this interest is in the selective sensing of mercury ions in solution and the extraction of mercury from the environment [2–6]. However, less attention has currently been given to the syntheses of various mercury-containing species.

Diarylmercurials have traditionally been synthesized by a variety of methods [7]. Seyferth and co-workers treated monoorganomercurials R₂HgX (X = acetate, halide, hydroxide, etc.) with a polyethyleneimine in the presence of water to produce diorganomercurials in a reaction which also produced HgX₂ as a byproduct [7a]. Other investigators have used different methodologies, including the treatment of mercuric chloride with phenylmagnesium bromide (to form diphenylmercury) [7a] and the treatment of mercuric bromide with aryllithium reagents in THF to form a variety of diarylmercurials [7g] in addition to other methods. While all of these procedures are suitable to the syntheses of diarylmercurials in a laboratory, the chief disadvantages include air and water sensitivity of starting materials (aryllithium and Grignard methods in particular), functional group incompatibility (e.g., a ketone or nitro group would be incompatible with Grignard or aryllithium reagents), or lack of atom economy (the reactions

which produce HgX₂ as a byproduct can never yield 100% based on mercury atoms, as elemental mercury or an inorganic mercury salt must be extruded by stoichiometric necessity).

An impressive variety of functionally-substituted arylboronic acids and esters have become commercially available in recent years. Already well-known as successful transmetalating reagents in Suzuki–Miyaura coupling [8], boronic acids and esters have also been successfully applied to the monoarylation of various gold(I) bromides [9], lead acetates [10], and mercuric chloride [11]. In one investigation [12], Challenger and Richards reported that mercuric oxide reacts with arylboronic acids in water to yield diarylmercurials, but the products were only characterized by melting point and in one case, elemental analysis. In this investigation we describe a general procedure for the high-yield syntheses of fully-characterized diarylmercurials in analytical purity starting from readily-available, air and water stable boronic acids and mercury(II) acetate in the presence of base.

2. Results and discussion

2.1. Synthesis

In contrast to previous synthetic approaches, a one-step procedure (done in isopropyl alcohol) starting from mercury(II) acetate and the appropriate boronic acid (>2 equiv.) in the presence of cesium carbonate was found to be a convenient, general procedure for the syntheses of homoleptic diarylmercurials. This is not the first time that mercury(II) acetate has been used as a precursor in the synthesis of organomercurials. Hanke has demonstrated that the reaction of mercury(II) acetate with neat phenyl halides at

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140 °C yields (*para*-halophenyl)mercuric acetate complexes [13], whereas Rausch and co-workers mercurated ferrocene in glacial acetic acid using mercury(II) acetate [14]. Even more relevant is a Hg–C bond formation observed when mercury(II) acetate is treated

with a vinylboronate; the observed product is a bis(vinylated)-mercury(II) complex [15]. Also, as mentioned in the Introduction, Challenger and Richards reported that the reaction of mercuric oxide and arylboronic acids yields diarylmercurials [12], but the

Table 1
Bis(arylmercury(II)) products, yields, and designation of compounds^a

Arylboronic acid	Equivalents of boronic acid	Product	Isolated yield (%)
	2.6		1 77
	2.6		2 62
	2.8		3 83
	2.6		4 78
	2.6		5^b 90
	2.6		6 12
	2.6		7 83
	2.1		8 58
	2.1		9^c 80

^a Hg(OAc)₂ is the mercury precursor for each reaction.

^b Solvent is ethanol (190 proof).

^c Reaction time is 12 h.

products were only characterized by melting point and in one case, elemental analysis.

In this investigation, the base is necessary for the clean formation of products, as a control reaction in the absence of base (using 4-tolylboronic acid, data not included) yielded a mixture of products including the desired product. This methodology is similar to the approach of Gray and co-workers in their protocol for the syntheses of phosphine-ligated arylgold(I) complexes starting from boronic acids [9]. In that system, a control reaction conducted in the absence of base yielded no product. It is possible that the base serves multiple functions including quaternization of boron (as was shown to be necessary in Suzuki–Miyaura coupling [16] and more recently in a system where transmetalation was effected from boron to bismuth [17]) and prevention of protodemercuration [18], although transmetalation by mono- and diarylmercurials does not require a base [19]. Table 1 summarizes the synthetic details.

All products, with the exception of **6**, were synthesized in good to excellent isolated yields. As can be seen, all varieties of functionalities and size were tolerated under these reaction conditions. The acetyl and ethoxycarbonyl functionalities of **2** and **5**, respectively, would not necessarily survive the conditions of Grignard or butyllithium methodology, thus our methodology provides a convenient entrée into diarylmercurials with Grignard and butyllithium sensitive functional groups. Workups (all of which were performed in air) are simple, and all products are nearly insoluble in the reaction milieu, such that precipitation appears to help drive the reaction. However, the successful formation of **5** indicates that precipitation is not necessarily imperative for product formation.

We attempted to extend this specific methodology to the preparation of mixed diarylmercury (II) complexes (i.e., R–Hg–R') using phenylmercury(II) acetate. Even at room temperature over the period of 12 h in the same solvent for several boronic acids (1.3 equiv. boronic acid and base), the majority products observed by NMR were the ligand rearrangement products diphenylmercury and diarylmercury (depending on which boronic acid was used). In the case of mesitylboronic acid, dimesitylmercury was observed along with a small amount of a different mesityl containing species (probably the mixed diarylmercury complex) in an 8:1 ratio of for-

mer to latter (as observed by ^1H NMR). It appears that even milder conditions than those used to synthesize the homoleptic mercury complexes are not conducive to the preparation of heteroleptic diarylmercury complexes.

2.2. NMR spectroscopy

All products were analyzed by ^1H NMR as a confirmation of purity, and new products **6–8** were further analyzed by ^{13}C NMR (and in the case of **7** and **8**, ^{19}F NMR). Product **9** has no appreciable solubility in any common solvents with the exception of DMSO, and even in this solvent, the solubility is high enough only to record a proton NMR spectrum.

The spectra of all products are consistent with C_s symmetry, which indicates that there is fast (relative to the NMR timescale) rotation about the Hg–C bonds in solution. In the case of fluorinated products **7** and **8**, ^1H – ^{19}F and ^{13}C – ^{19}F couplings were observed in the ^9H and ^{13}C NMR spectra, respectively, which accounts for the observed multiplets. Broad ^{199}Hg ($I = 1/2$) satellite peaks were observed in the ^1H NMR of all compounds for only one of the signals (presumably the *ortho* protons). In a recent investigation by Parkin and co-workers, ^{199}Hg satellite peaks of the ethyl resonances of thimerosal were significantly broadened on a 400 MHz NMR spectrometer (relative to a 300 MHz NMR spectrometer), similar to what was observed here [20].

2.3. Computational results and crystal structure of **6**

The electronic structure of the representative complex **6** was examined with nonlocal density-functional theory calculations. A harmonic frequency calculation confirms the calculated structure of **6** to be a potential-energy minimum. The molecular orbital diagram is shown as Fig. 1.

Not unexpectedly, the frontier orbitals are ligand-predominated as gauged by percentage contributions of metal and ligands to the orbitals' electron density. Electron densities are apportioned according to Mulliken's scheme [21]. The geometry was optimized with imposed D_{2d} symmetry, despite that the crystal structure of **6** (Fig. 2) shows only a D_2 structure.

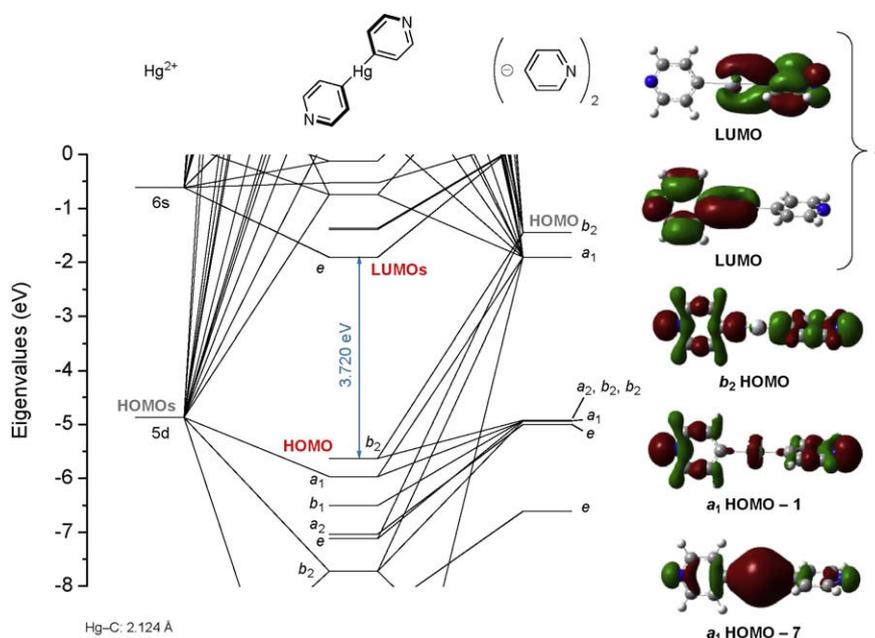


Fig. 1. Kohn–Sham orbital correlation diagram of **6**, optimized in full D_{2d} symmetry. Plots of selected orbitals (0.03 au) appear at right. Methylene chloride solvation is included approximately through a polarized continuum model (PCM).

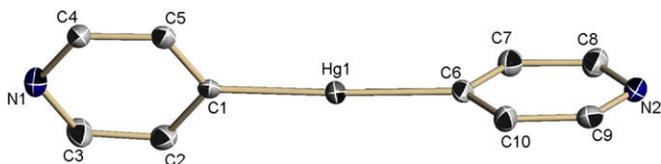


Fig. 2. ORTEP representation of one crystallographically-independent molecule of **6**, showing 50% probability ellipsoids and atom-labeling scheme. Selected bonds distances (Å) and bond angles ($^{\circ}$): Hg1–C1, 2.069(4); Hg1–C6, 2.083(4); C1–Hg1–C6, 177.70(17). The corresponding values for the second crystallographically-independent molecule of **6** are not significantly different.

The calculated Hg–C bond length is 2.124 Å compared to the experimental values of 2.069(4) and 2.083(4) Å (for two crystallographically independent molecules). The highest-occupied Kohn–Sham orbital (HOMO) and the HOMO – 1 are each singly degenerate functions delocalized over the ligands' σ -bonding framework; each bears significant lone-pair character on nitrogen (38.1%, HOMO; 59.3%, HOMO – 1). In a crude simplification, the a_1 HOMO – 1 can be viewed as the in-phase, and the b_2 HOMO as the antiphase combinations of the pyridyl nitrogen lone pairs. These results are not surprising considering the large number of subvan der Waals contacts (involving the pyridyl nitrogen atom) identified in the crystallographic packing of **6** (these data suggest that molecules such as **6**, which feature outwardly-directed nitrogen atoms, would be suitable for applications in supramolecular chemistry). Moreover, this is interesting because crystal engineering more commonly utilizes hydrogen bonding or π – π stacking interactions as rational means to create supramolecular architectures [22].

A toroidal sd-hybrid orbital is evident at mercury in the a_1 HOMO, but this orbital is essentially nonbonding toward the σ -bond 4-pyridyl carbon atoms. The LUMOs of **6** form a doubly degenerate set, each being localized on a different 4-pyridyl ligand; they overlap with the vacant mercury 6s orbital. The a_1 HOMO – 7, which lies some 2.09 eV below the HOMO, accounts for Hg–C bonding. This stabilization concurs with substantial covalency of the Hg–C bond, as expected from their similar Pauling electronegativities: 2.00 for Hg, 2.55 for C.

3. Experimental section

All solvents and reagents were used as received. Arylboronic acids were purchased from Acros Organics and Frontier Scientific. Caution! Organomercury compounds are extremely toxic, and appropriate safety measures should be taken when working with these compounds. All reactions were set up in air but stirred under argon for reasons of safety. Microanalyses (C, H, and N) were performed by Robertson Microlit Laboratories, Inc (Madison, NJ). NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F) were recorded on a Varian AS-400 spectrometer operating at 399.7, 100.5, and 376.1 MHz, respectively. For ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, chemical shifts were determined relative to the solvent residual peaks. For ^{19}F NMR spectra, chemical shifts were determined relative to an internal standard (CFCl_3 in CDCl_3). All ^1H NMR spectra possessed broad ^{199}Hg satellite peaks ($I = 1/2$).

3.1. General procedure

A flask was loaded with mercury(II) acetate (0.09–0.21 mmol), arylboronic acid (2.1–2.8 equiv., see Table 1) and cesium carbonate (equimolar with arylboronic acid). Isopropyl alcohol (3 mL) was added, and the flask sealed with a septum. The contents were heated under argon in a 50–55 $^{\circ}\text{C}$ oil bath for 12–20 h (see Table 1). The mixture was cooled, the solvent removed by rotary evapora-

tion, and the residue extracted with toluene or toluene/THF (except **9**, which was collected by filtration), and filtered. The filtrate was reduced to dryness via rotary evaporation, leaving a pure solid/residue which was triturated with pentane, dried, and collected.

3.1.1. [Hg(4-anisyl) $_2$] (**1**)

The isolated solid was analytically pure. Yield: 45 mg (77%). ^1H NMR (CDCl_3): δ 7.34–7.39 (m, $\text{C}_6\text{H}_4\text{OCH}_3$, 4H), 7.02 (d, $\text{C}_6\text{H}_4\text{OCH}_3$, $J = 8.8$ Hz, 4H), 3.83 (s, $\text{C}_6\text{H}_4\text{OCH}_3$, 6H) ppm. Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{HgO}_2$: C, 40.53; H, 3.40. Found: C, 40.89; H, 3.25%.

3.1.2. [Hg(4-acetylphenyl) $_2$] (**2**)

The isolated solid was analytically pure. Yield: 41 mg (62%). ^1H NMR (CDCl_3): δ 8.03 (d, $\text{C}_6\text{H}_4\text{COCH}_3$, $J = 8.4$ Hz, 4H), 7.56 (d, $\text{C}_6\text{H}_4\text{COCH}_3$, $J = 8.4$ Hz, 4H), 2.62 (s, $\text{C}_6\text{H}_4\text{COCH}_3$, 6H) ppm. Anal. Calc. for $\text{C}_{16}\text{H}_{14}\text{HgO}_2$: C, 43.92; H, 3.68. Found: C, 43.79; H, 3.22%.

3.1.3. [Hg(mesityl) $_2$] (**3**)

The product was spectroscopically pure. Yield: 60 mg (83%). A recrystallized sample (THF/pentane) gave analytically pure material. The ^1H NMR spectral data matched the literature spectral data [23]. Anal. Calc. for $\text{C}_{18}\text{H}_{22}\text{Hg}$: C, 49.25; H, 5.05. Found: C, 49.13; H, 4.96%.

3.1.4. [Hg(ferrocenyl) $_2$] (**4**)

The isolated solid was analytically pure. Yield: 65 mg (78%). ^1H NMR (CDCl_3): δ 4.49 (s br, C_5H_4 , 4H), 4.24 (s, C_5H_5 , 10H), 4.11 (s br, C_5H_4 , 4H) ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{Fe}_2\text{Hg}$: C, 42.10; H, 3.18. Found: C, 41.87; H, 3.11%.

3.1.5. [Hg(3-carboxyethylphenyl) $_2$] (**5**)

The isolated solid was analytically pure. Yield: 71 mg (90%). ^1H NMR (CDCl_3): δ 8.12–8.16 (m, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, 2H), 7.94 (d, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, $J = 7.6$ Hz, 2H), 7.62 (d, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, $J = 7.2$ Hz, 2H), 7.53 (t, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, $J = 7.6$ Hz, 2H), 4.39 (q, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, $J = 7.2$ Hz, 4H), 1.41 (t, $\text{C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_3)$, $J = 7.2$ Hz, 6H) ppm. Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{HgO}_4$: C, 43.32; H, 3.64. Found: C, 43.05; H, 3.51%.

3.1.6. [Hg(4-pyridyl) $_2$] (**6**)

The full procedure is included for this product, as it is slightly different than the general procedure. A flask was loaded with mercury(II) acetate (59 mg, 0.19 mmol), 4-pyridylboronic acid (2.6 equiv., 59 mg, 0.45 mmol) and cesium carbonate (2.6 equiv., 150 mg, 0.46 mmol). Isopropanol (3 mL) was added, and the flask sealed with a septum. The contents were evacuated and backfilled with argon twice, and heated in a 50 $^{\circ}\text{C}$ oil bath for 20 h. The mixture was cooled, the solvent removed by rotary evaporation, and the residue extracted with toluene/THF and filtered. The filtrate solvent was removed by rotary evaporation, the residue triturated with pentane, and the solid collected and dried. As the product mixture could not be washed with methanol (**6** is soluble in methanol), the product was recrystallized by vapor diffusion of pentane into a saturated THF/toluene solution and collected in analytical purity. Yield: 19 mg (12%). ^1H NMR (CDCl_3): δ 8.64 (d, $\text{C}_5\text{H}_4\text{N}$, 4H, $J = 5.6$ Hz), 7.33 (d, $\text{C}_5\text{H}_4\text{N}$, 4H, $J = 5.6$ Hz) ppm. ^{13}C NMR (CDCl_3): δ 177.46 (s), 149.46 (s), 133.20 (s) ppm. Anal. Calc. for $\text{C}_{10}\text{H}_8\text{HgN}_2$: C, 33.67; H, 2.26; N, 7.85. Found: C, 33.81; H, 2.46; N, 7.74%.

3.1.7. [Hg(3,5-difluorophenyl) $_2$] (**7**)

The solid (which was pure by NMR) could be recrystallized in xylene/pentane (vapor diffusion) to give analytically pure material. Yield: 64 mg (83%). ^1H NMR (CDCl_3): δ 6.96–7.01 (m, *ortho*- $\text{C}_6\text{F}_2\text{H}_3$, 4H), 6.72 (tt, *para*- $\text{C}_6\text{F}_2\text{H}_3$, $J = 2.4, 9.2$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3): δ 164.62 (d, $J(^{13}\text{C}-^{19}\text{F}) = 10.2$ Hz), 162.11 (d, $J(^{13}\text{C}-^{19}\text{F}) =$

10.6 Hz), 119.28 (dd, $J(^{13}\text{C}-^{19}\text{F}) = 5.3, 17.9$ Hz), 103.95 (t, $J(^{13}\text{C}-^{19}\text{F}) = 24.9$ Hz) ppm. ^{19}F NMR (CDCl_3): $\delta -110.55$ (d, $J = 5.3$ Hz) ppm. Anal. Calc. for $\text{C}_{12}\text{H}_6\text{F}_4\text{Hg}$: C, 33.77; H, 1.42. Found: C, 34.05; H, 1.54%.

3.1.8. [Hg(2-methyl-5-fluorophenyl)₂] (**8**)

The isolated solid was analytically pure. Yield: 50 mg (58%). ^1H NMR (CDCl_3): δ 7.28 (dd, $\text{C}_6\text{FH}_3(\text{CH}_3)$, $J = 5.2, 8.4$ Hz, 2H), 7.09 (dd, $\text{C}_6\text{FH}_3(\text{CH}_3)$, $J = 2.8, 8.4$ Hz, 2H), 6.85 (td, $\text{C}_6\text{FH}_3(\text{CH}_3)$, $J = 2.8, 8.4$ Hz, 2H), 2.53 (s, $\text{C}_6\text{FH}_3(\text{CH}_3)$, 6H) ppm. ^{13}C NMR (CDCl_3): δ 162.83 (s), 160.37 (s), 139.87 (d, $J(^{13}\text{C}-^{19}\text{F}) = 3.4$ Hz), 131.10 (d, $J(^{13}\text{C}-^{19}\text{F}) = 6.7$ Hz), 123.09 (d, $J(^{13}\text{C}-^{19}\text{F}) = 18.1$ Hz), 114.60 (d, $J(^{13}\text{C}-^{19}\text{F}) = 21.1$ Hz), 24.55 (s, $\text{C}_6\text{H}_3\text{F}(\text{CH}_3)$) ppm. ^{19}F NMR (CDCl_3): $\delta (-119.08)$ – (-119.29) (m) ppm. Anal. Calc. for $\text{C}_{14}\text{H}_{12}\text{F}_2\text{Hg}$: C, 40.15; H, 2.89. Found: C, 39.99; H, 2.66%.

3.1.9. [Hg(2-benzothieryl)₂] (**9**)

The isolated solid was analytically pure. Yield: 34 mg (80%). The product is sparingly soluble only in DMSO, and only ^1H NMR solution data could be obtained. ^1H NMR ($\text{DMSO}-d_6$): δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 6.8$ Hz, 2H), 7.51 (s, 2H), 7.25–7.36 (m, 4H) ppm. Anal. Calc. for $\text{C}_{16}\text{H}_{10}\text{HgS}_2$: C, 41.15; H, 2.16. Found: C, 40.27; H, 1.97%.

3.2. Crystal structure determination of compound **6**

3.2.1. Crystal data

Compound **6**: $\text{C}_{10}\text{H}_8\text{HgN}_2$, $M = 356.77$, orthorhombic, space group *Ibca*, $a = 11.0574(17)$ Å, $b = 21.975(4)$ Å, $c = 30.710(5)$ Å, $U = 7462(2)$ Å³, $Z = 32$, $D_{\text{calc}} = 2.543$ Mg m⁻³, λ (Mo $\text{K}\alpha$) = 0.71069 Å, $\mu = 16.450$ mm⁻¹, $F(000) = 5184$, $T = 100(2)$ K.

3.2.2. Data collection and reduction

A colorless block ca. $0.53 \times 0.31 \times 0.05$ mm³ (grown by slow diffusion of pentane into a saturated 1,2-dichloroethane solution) was mounted in paratone oil on a mitogen tip. A total of 40290 reflections were collected on a Bruker AXS SMART APEXII CCD diffractometer, θ ranging from 1.85–27.23° for data collection. A Lorentz-polarization type absorption correction was applied using AXScale. Merging equivalents gave 4139 independent reflections ($R_{\text{int}} = 0.0678$).

3.2.3. Structure solution and refinement

The unit cell was determined using APEX2 Crystallographic Suite. The structure of **6** was solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL. Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in standard calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (CH_3) or 1.2 (all others) times that of the adjacent carbon or nitrogen atom. The refinement proceeds to $R_1 = 0.0231$, $wR_2 = 0.0823$ with a goodness of fit on F^2 0.820 for 299 refined parameters and 0 restraints, and $R_1 = 0.0367$, $wR_2 = 0.1095$ for all data with electron density ranging from 1.417 to -1.781 e Å⁻³ in the final Fourier synthesis.

3.3. Computational details

Spin-restricted density-functional theory computations were performed within the GAUSSIAN03 program suite. Calculations employed the modified Perdew–Wang exchange functional of Adamo and Barone [24] and the original Perdew–Wang correlation functional [25]. Gas-phase geometry optimization proceeded using the 6–31G(d,p) basis set for non-metal atoms [26,27]. Mercury orbitals were described with the Stuttgart effective core potential

and the associated basis set [28], which was contracted as follows: (8s,7p,6d) → [6s,5p,3d]. Full D_{2d} symmetry was imposed during optimization; a harmonic frequency calculation of the optimized structure confirmed it to be a potential-energy minimum. A single-point calculation was performed on the resulting optimized geometry. In this calculation, nonmetal atoms were described with the TZVP basis set of Godbout and co-workers [29]. The Stuttgart effective core potential and basis set were again used for mercury. Relativistic effects with the Stuttgart ECP and its associated basis set are introduced with a potential term (*i.e.*, a one-electron operator) that replaces the two-electron exchange and Coulomb operators resulting from interaction between core electrons and between core and valence electrons. In this way relativistic effects, especially scalar effects, are included implicitly rather than as four-component, one-electron functions in the Dirac equation. Methylene chloride solvation effects were included implicitly with the polarized continuum model (PCM) of Tomasi and co-workers [30,31]. Percentage compositions of molecular orbitals, overlap populations, and bond orders between fragments were calculated using the AOMIX program [32,33].

Acknowledgements

D.V.P. gratefully acknowledges investors in Creative Chemistry, LLC and Case Western Reserve University for support. T.G.G. gratefully acknowledges the National Science Foundation (Grant CHE-0749086), the donors of the Petroleum Research Fund administered by the American Chemical Society (Grant 42312-G3 to T.G.G.), and Case Western Reserve University for support. Mr. James B. Updegraff III is thanked for assistance with crystallographic work for **6**.

Appendix A. Supplementary material

CCDC 702269 contains the supplementary crystallographic data for compound **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.10.024](https://doi.org/10.1016/j.jorganchem.2008.10.024).

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