

Taking Advantage of Hg–C Bonds: Synthesis of the First Homoleptic Bis- β -diketiminate Complex Bound through the γ -Carbons

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Received March 2, 2010

The most common β -diketiminate ligand, [{N(2,6-^{*i*}Pr₂C₆H₃)C(Me)}₂CH]⁻ (BDI), was used to synthesize a new mercury complex in which two BDI ligands are bound to the metal through the γ -carbons in the solid state. In solution, one of the BDI ligands switches to an N,N'-binding mode; this complex is in equilibrium with the homoleptic species. The thermodynamic parameters, ΔH° (-2.52 kcal mol⁻¹), ΔS° (-9.24 cal mol⁻¹ K⁻¹), and ΔG°_{298} (0.23 kcal mol⁻¹), were measured using variable-temperature ¹H NMR spectroscopy.

The β -diketiminate ligand has seen an explosion in popularity over the past decade.¹ It has been deemed a "Cp" replacement due to its monoanionic nature and the wide range of easily accessible variants along the β -diketiminate backbone (R¹, R², R³, R⁴, and R⁵; Figure 1), thus influencing both the steric and electronic nature of the ligand. Two common nicknames for this ligand class are found: $(R^{1})_{2}$ nacnac, which generally refers to the ligand in which $R^3 = H$, R^2 , $R^4 = Me$, ² and $R^1 = R^5$, and BDI, which generally refers to the most popular β -diketiminate ligand, [{N(2,6-^{*i*}Pr₂C₆H₃)- $C(Me)_{2}CH^{-3,4}$ The β -diketiminate ligand has a remarkable ability to stabilize low-valent complexes in some rather unusual oxidation states. For instance, Jones and co-workers were able to reduce BDI-MgI to a Mg(I) dimer complex that possesses a Mg-Mg bond.⁵ Holland and co-workers utilized this ligand to synthesize a rare three-coordinate transitionmetal dinitrogen complex, as well as 12-electron complexes of iron(II).^{6,7} Hill took advantage of the steric variants along the β -diketiminate backbone and generated a series of In(I) complexes ranging from a mononuclear complex when a bulky N-aryl substituent was used (BDI), a dimer when methyl groups were placed in the 2-, 4-, and 6-positions of the N-aryl substituent (\mathbb{R}^1 and \mathbb{R}^5), to a hexaindium chain when

methyl groups were placed in the least obstrusive 3- and 5-positions of the N-aryl substituent (R^1 and R^5).⁸



Figure 1. Basic skeleton of the β -diketiminate ligand.

By far the most widely used β -diketiminate ligand is [{N- $(2,6-^{i}Pr_{2}C_{6}H_{3})C(Me)$ ²CH⁻ $(BDI \text{ or Dipp}_{2}nacnac)$ ⁹, with over 700 crystal structures reported in the Cambridge Structural Database. With regard to group 12 metals, only the Zn and Cd complexes of this ligand are known.^{10–13} Layh and coworkers have synthesized a β -diketiminate-Hg complex $(L^{1}HgCl)$ in which the N-aryl substituent $(R^{1} \text{ and } R^{5})$ possesses tBu groups in the 2- and 5-positions: R^2 , $R^4 =$ SiMe₃ and $R^3 = H$. In this system, the β -diketiminate ligand is bound through the γ -carbon.¹⁴ Attempts to place more than one β -diketiminate ligand on Hg were not successful. Lappert and co-workers synthesized a sila- β -diketiminate ligand, $[{N(2,6-{}^{i}Pr_{2}C_{6}H_{3})C(Me)}_{2}Si(SiMe_{3})]^{-}(L^{2})$, in which the methine (CH) group is replaced with a Si(SiMe₃).¹⁵ The researchers were able to generate a $(L^2)_2$ Hg complex via a disproportionation reaction with Hg₂Cl₂ and Li-L.² Similar to the case for L¹HgCl, both ligands were bound to the metal center via the Si backbone.

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Figure 2. ORTEP diagram of the dialkylmercury species 1 with ellipsoids at the 30% probability level. H atoms, except for H2, are omitted for clarity. Atoms marked with a prime (') are at equivalent positions (-x, -y, -z).

We have recently synthesized a series of BDI lead aryloxides and alkoxides. The latter complexes show facile reactivity toward heterocumulenes such as carbon dioxide but only sluggish reactivity toward aliphatic electrophiles such as methyl iodide.^{16–18} As this is in sharp contrast to the reactivity of late-transition-metal alkoxides,19 we wanted to explore the other divalent heavy-metal terminal alkoxides in order to ascertain any reactivity trends. Thus, our attention turned to mercury and an attempted synthesis of the BDI-HgCl complex as a precursor to terminal mercury alkoxide and amido complexes. Addition of LiNⁱPr₂ to BDI-H, followed by treatment with a suspension of HgCl₂ (0.5 equiv) results in the formation of colorless crystals in 34% yield (eq 1).²⁰ Crystals suitable for an X-ray diffraction study were grown by slowly cooling a saturated CH₂Cl₂ solution (Figure 2). The molecule lies on an inversion center with the BDI ligand bound through the γ -carbon, or the "backbone" of the BDI ligand. Selected bond lengths and angles are shown in Table 1, and data collection parameters are given in Table 2. Although there are a handful of examples of other C-bound β -diketiminate ligands,^{14,21–23} including BDI complexes,^{9,24–26} this is the first crystallographically characterized compound in which two β -diketiminate ligands are C-bound to a single metal

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 Table 1. Selected Bond Lengths (Å) and Angles (deg) for

 Compound 1

Compound 1			
Hg-C(2)	2.128(3)	C(1) - N(1)	1.277(3)
C(2) - C(1)	1.500(4)	N(1) - C(6)	1.428(3)
C(2) - C(3)	1.501(4)	C(3) - N(2)	1.272(3)
C(1) - C(4)	1.505(4)	N(2) - C(18)	1.430(3)
C(3) - C(5)	1.510(4)		
C(2) - Hg - C(2)'	180.00(10)	C(2) - C(1) - C(4)	115.6(2)
Hg-C(2)-C(1)	107.75(18)	N(1)-C(1)-C(4)	126.1(3)
Hg-C(2)-C(3)	109.81(18)	C(2) - C(3) - N(2)	119.0(2)
C(1) - C(2) - C(3)	114.2(2)	C(3) - N(2) - C(18)	122.2(2)
C(2) - C(1) - N(1)	118.2(2)	C(2) - C(3) - C(5)	115.9(2)
C(1) - N(1) - C(6)	120.2(2)	N(2) - C(3) - C(5)	125.0(3)

Table 2. Crystallographic Data for Compound 1^a

chem formula	$C_{58}H_{82}HgN_4 \cdot 0.33CH_2Cl_2$	
formula wt	1064.03	
temp (K)	173(2)	
wavelength (Å)	0.71073	
cryst size (mm ³)	$0.19 \times 0.16 \times 0.16$	
cryst syst	trigonal	
space group	<i>R</i> 3 (No. 148)	
<i>a</i> (Å)	33.4216(10)	
$b(\mathbf{A})$	33.4216(10)	
c (Å)	12.6432(3)	
α (deg)	90	
β (deg)	90	
γ (deg)	120	
$V(Å^3)$	12230.4(6)	
Z	9	
$\rho_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.37	
abs coeff (mm^{-1})	2.97	
θ range for data collecn (deg)	3.47-26.72	
no. of measd/indep rflns, R(int)	17 578/5739, 0.047	
no. of rflns with $I > 2\sigma(I)$	5104	
no. of data/restraints/params	5739/0/288	
goodness of fit on F^2	1.032	
final R indices $(I > 2\sigma(I))$	R1 = 0.033, wR2 = 0.060	
<i>R</i> indices (all data)	R1 = 0.042, wR2 = 0.062	
largest diff peak and hole (e $Å^{-3}$)	0.60 and -0.50	

^{*a*} This molecule sits on an inversion center. The unit cell contains poorly defined CH_2Cl_2 disordered about a special position which has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

center. Although the geometry of the ligands around Hg is linear, the ligands are in a staggered conformation to each other, which is similar to the case for the sila analogue.¹⁵ The Hg–C bond length of 2.127(3) Å is significantly shorter than that reported for L¹HgCl (2.337(2) Å) but similar to other dialkylmercury complexes.^{27,28} The C–C bond lengths of 1.500(5)–1.501(4) Å are similar to those of other sp²–sp³ C–C single bonds.²⁹ A long-range intramolecular nitrogen–mercury interaction is observed, with a Hg···N2 distance of 2.994 Å, slightly shorter than their combined van der Waals radii of 3.10 Å. This type of interaction is observed with both Layh's mercury complex L¹HgCl as well as Lappert's bis-sila- β -diketiminate mercury complex (L²)₂Hg.^{14,15}



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⁽²⁰⁾ Simple salt metathesis between lithiated β -diketiminate (BDI-Li) and HgCl₂ resulted in the formation of an intractable mixture of products; when LiN(TMS)₂ was used instead of LiNiPr₂, the only isolated BDI-containing product was BDI-Li.



Figure 3. Variable-temperature ¹H NMR spectra of 1 and 2 in CD_2Cl_2 .

The room-temperature ¹H NMR spectrum of **1** reveals the presence of two different compounds in a 3:2 ratio. The major compound can be assigned to the dialkyl species, with a γ -CH resonance at δ 3.98 ppm, similar to that reported for L¹HgCl. The one-bond $^{1}H^{-13}C$ correlation experiment showed correlation between this proton and a carbon found at δ 77.7 ppm. The resonances corresponding to the minor compound are reminiscent of an N,N'bound β -diketiminate ligand, with a backbone γ -CH resonance at δ 4.75 ppm. Integrating in an approximately 1:1 ratio with this resonance is a peak at δ 3.71 ppm. The ¹H⁻¹³C HSQC experiment revealed that the former proton correlates with a carbon at δ 96.2 ppm, which is in the same range as for other N,N'-bound β -diketiminate compounds,^{12,18,30} and the latter proton correlates with a carbon at δ 66.7 ppm, a chemical shift similar to that of the major isomer. No proton-mercury $({}^{1}H-{}^{199}Hg)$ or carbon-mercury (¹³C-¹⁹⁹Hg) coupling was observed. The ¹⁹⁹Hg{¹H} NMR spectrum shows a single resonance at both room temperature (-990 ppm) and -60 °C (-1086 ppm). The corresponding resonance line widths at halfheight are 144 and 236 Hz, respectively (the data were processed with 75 Hz exponential line broadening prior to Fourier transformation). The observed broad line width can be attributed to the close proximity of the (broad) resonances for the two species (1 and 2), leading to the appearance of a single signal, as well as fast relaxation caused by the chemical shift anisotropy of the ¹⁹⁹Hg.³¹ The latter contribution can be confirmed by the observation that the $^{199}\mathrm{Hg}$ line width at half-height is ${\sim}30\%$ larger at 14.1 T than at 9.4 T (190 Hz, with identical processing parameters). As the line width for this system is larger than

the expected magnitude of the coupling constant, no mercury-proton or mercury-carbon coupling could be observed at either temperature. The solid-state IR spectrum (Nujol) revealed three strong bands at 1648, 1624, and 1589 cm⁻¹; although these bands are similar to those for other β -diimine compounds,^{15,32} these data are not conclusive for either isomer, as N,N'-bound β -diketiminate complexes have a wide range of stretching frequencies in the same region.^{16,18,26} The solution-phase IR spectrum was equally inconclusive.

These data are consistent with an equilibrium mixture of two different mercury species in solution: the major isomer in which both β -diketiminate ligands are bound through the γ -carbon (1) and a minor isomer that is still bound to two different β -diketiminate ligands, but one ligand is bound through the N-substituents and the other is bound through the γ -carbon (2; eq 2). Variable-temperature ¹H NMR spectroscopy revealed that 2 is favored at lower temperatures (Figure 3). From these data, we were able to calculate ΔH° (-2.52 ± 0.06 kcal mol⁻¹), ΔS° (-9.24 ± 0.21 cal $\text{mol}^{-1} \text{ K}^{-1}$), and ΔG°_{298} (0.23 ± 0.09 kcal mol⁻¹) for the interconversion between the two isomers. This equilibria is similar to a bis(2,2,6,6-tetramethylheptane-3,5-dione)-Hg complex in which an equilibrium is established between a dialkylmercury species and a mercury complex that is bound to one ligand through the γ -carbon and the other ligand through an oxygen atom.³³ Interestingly, the researchers were only able to observe proton-mercury coupling at -40 °C; however, a lower field NMR spectrometer was used, thus significantly decreasing the line width contributions of relaxation due to chemical shift anisotropy.

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The thermodynamic parameters were not reported for this latter system.



The variable-temperature ¹H NMR spectroscopy experiment also revealed that compound 2 exhibits fluxional behavior on the NMR time scale. At 60 °C, three different resonances corresponding to the isopropyl methine resonances of **2** are observed at δ 3.33, 2.91, and 2.49 ppm integrating to four, two, and two protons each, respectively. The downfield resonance is from the N,N'-bound ligand, and the upfield resonances are from the γ -bound ligand of **2**. At -60 °C, the isopropyl methine resonance on the N,N'-bound ligand of 2 appears as two separate broad resonances, indicating two different environments for the four isopropyl methine protons of this N,N'-bound ligand. This is presumably due to the asymmetry with respect to the γ -bound ligand. At this lower temperature, the bulkiness of the N-aryl groups of both ligands prevent facile rotation around the Hg-C bond. Thus, one aryl group of the N,N'-bound ligand is closer to the methine proton of the γ -carbon of the γ bound ligand than the other aryl group. Using density functional theory (DFT), we calculated an optimized geometry for compound 2 (Figure 4), which supports this hypothesis. From these variable-temperature studies, the ΔG^{\ddagger} value for Hg–C bond rotation was determined to be 11 kcal mol^{-1} . Interestingly, the isopropyl methine protons for the γ -bound ligand of **2** appear as septets above 0 °C and as broad resonances at -30 °C and are not observed at -60 °C. Due to the decreasing solubility of 1 and 2, we were unable to obtain a reliable ¹H NMR spectrum below -60 °C to determine the fate of these disappearing signals at lower temperatures. However, it can be assumed that there is further loss of symmetry of the γ -bound ligand due to restricted rotation around the N-aryl bond; as such, we would expect four individual signals for each of the isopropyl methine protons for the γ -bound ligand at temperatures below -60 °C. Interestingly, only two resonances corresponding to the back-bone methyl groups (N-C(Me)-C-C(Me)-N are observed for compound 2, even at -60 °C. Although the aliphatic and aromatic regions of the ¹H NMR spectrum varied with temperature, due to the overlapping signals, we were unable to gain any further information from this data.



DFT was also used to calculate the ground-state energies for compounds 1 and 2. From these data, we were able to calculate ΔH° (-2.52 ± 0.06 kcal mol⁻¹), ΔS° (-9.24 ± 0.21 cal mol⁻¹ K⁻¹), and $\Delta G^{\circ}_{298} (0.23 \pm 0.09 \text{ kcal mol}^{-1})$ for the interconversion between the two isomers. Because of the low level of theory applied, the calculated ΔH° value (0.60 kcal mol^{-1}) was higher than our measured value and the magnitude of the calculated ΔS° value (-14 cal mol⁻¹ K⁻¹) was greater (although still negative). Due to these discrepancies, the ΔG°_{298} value (4.9 kcal mol⁻¹) was significantly higher than our experimental results. However, we were able to utilize these calculations in order to predict ¹H NMR chemical shifts, and reassuringly, γ -CH for isomer 1 was calculated to resonate at δ 4.21 ppm, whereas the Hg-bound γ -CH of isomer **2** was calculated to resonate at δ 3.72 ppm and γ -CH of the N,N'-bound β -diketiminate ligand of isomer **2** was calculated to resonate at δ 4.48 ppm.

Isolated crystals of compound 1 are relatively air stable, but this compound undergoes thermal decomposition after 48 h at room temperature in solution. Attempts at selectively protonating one of the BDI ligands to form mercury alkoxide or sulfide complexes were not successful. Addition of isopropyl alcohol to 1 led to an intractable mixture of products. Treatment of 1 with 4-methylbenzenethiol gave BDI-H as the only BDI-containing compound.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried from the appropriate drying agent, distilled, degassed, and stored over 4 Å sieves. The ¹H, ¹³C, and ¹⁹⁹Hg NMR spectra were recorded on a Varian 400 MHz spectrometer or a Varian 600 MHz spectrometer. Both spectrometers were equipped with X{¹H} broad-band-observe probes. The ¹H and ¹³C NMR chemical shifts are given relative to residual solvent peaks, and the ¹⁹⁹Hg chemical shifts were determined from the deuterium lock signal and quoted relative to HgMe₂ at 0 ppm.³⁴ The ¹H–¹³C HSQC and ¹H–¹³C HMBC spectra were recorded using the Varian Chem-Pack 4.1 sequences gHSQCAD and gHMBCAD. The data for the X-ray structure were collected at 173 K on a Nonius Kappa CCD diffractometer (λ (Mo K α) = 0.71073 Å) and refined using the SHELXL-97 software package.³⁵

[CH{(CH₃)₂CN-2,6-iPr₂C₆H₃}]Hg (1). Lithium diisopropylamide (1.20 mmol, 2 M in THF) was added dropwise to a toluene solution of BDI-H (500 mg, 1.20 mmol). The red solution was stirred for 30 min, cooled to -78 °C, and added dropwise to a stirred suspension of HgCl₂ (163 mg, 0.60 mmol) in toluene at -78 °C. This mixture was stirred overnight and slowly warmed to room temperature. The resulting gray suspension was filtered through Celite, and the volatiles were evacuated, producing a pale green precipitate that was washed several times with pentane to afford a white powder in 34% yield (0.24 mol, 213 mg). Colorless crystals suitable for X-ray diffraction were grown from a concentrated DCM solution stored in an ethylene glycol bath at 8 °C for 3 days and -12 °C for 1 week. ¹H NMR (399 MHz, CDCl₃, 303 K): δ 6.93–7.17 (m, 6H, ^{Ar}CH), 4.75 (s, 1H, γ-CH), 3.98 (s, 1H, γ-CH), 3.71 (s, 1H, γ-CH), 3.33 (sept, J = 6.4 Hz, 4H, CHMe₂), 2.97 (sept, J = 6.8 Hz, 2H, $CHMe_2$), 2.91 (m, 2H, $CHMe_2$), 2.81 (sept, J = 6.9 Hz, 2H,

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 $CHMe_2$), 2.49 (sept, J = 6.7 Hz, 2H, $CHMe_2$), 1.85 (s, 6H, NCMe),1.72 (s, 6H, NCMe), 1.51 (s, 6H, NCMe), 1.18 (d, J = 6.8 Hz, 12H, CHMe), 1.14 (d, J = 6.9 Hz, 12H, CHMe), 1.11 (d, J = 6.8 Hz, 6H, CHMe), 1.10 (d, J = 6.8 Hz, 12H, CHMe), 1.06 $(d, J = 6.8 \text{ Hz}, 6\text{H}, CHMe), \delta 0.98 (d, J = 6.8 \text{ Hz}, 12\text{H}, CHMe),$ 0.89 (d, J = 6.7 Hz, 6H, CHMe), 0.85 (d, J = 6.9 Hz, 6H, CHMe). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 171.38 (NCMe), 169.97 (NCMe), 164.34 (NCMe), 146.46 (o-C), 141.48 (o-C), 137.03 (*ipso-C*), 136.46 (*ipso-C*), 123.50 (^{Ar}C), 123.21 (^{Ar}C), 122.99 (^{Ar}C), 122.89 (^{Ar}C), 122.76 (^{Ar}C), 122.63 (^{Ar}C), 121.92 (^{Ar}C) , 96.23 (γ -C), 77.72 (γ -C), 66.69 (γ -C), 28.51 (CHMe), 28.51 (CHMe), 28.21 (CHMe), 27.78 (CHMe), 27.69 (CHMe), 25.32 (NCMe), 24.48 (CHMe), 23.75 (CHMe), 23.20 (CHMe), 22.97 (CHMe), 22.49 (CHMe), 21.91 (NCMe), 21.40 (NCMe). ¹⁹⁹Hg NMR (71.5 MHz, CDCl₃, 303 K): δ –989.7. IR (Nujol, cm⁻¹): 3050, 1921, 1866, 1806, 1720, 1648 (s), 1624 (s), 1589 (s), 1439 (s), 1358 (s), 1328 (s), 1245, 1207 (s), 1188 (s), 1163 (s), 1107, 1068, 1059, 1042, 972, 936, 916, 789 (s), 760 (s), 690, 523. IR (CCl₄, cm⁻¹): 3061 (w), 2963, 2869, 2990 (br), 2004 (br), 1856 (br), 1635, 1549 (br, s), 1461, 1436, 1409, 1382, 1363, 1322, 1253 (s), 1216 (s), 1165 (w). Anal. Calcd: C, 67.25; H, 7.98; N, 5.41. Found: C, 67.16; H, 8.07; N, 5.39.

Key Chemical Shifts for 1. ¹H NMR (399 MHz, CDCl₃, 303 K): δ 3.98 (s, 1H, γ -CH), 2.97 (sept, J = 6.8 Hz, 2H, CHMe₂), 2.81 (sept, J = 6.9 Hz, 2H, CHMe₂), 1.85 (s, 6H, NCMe), 1.11 (d, J = 6.8 Hz, 6H, CHMe), 1.10 (d, J = 6.8 Hz, 12H, CHMe), 0.8 (d, J = 6.8 Hz, 6H, CHMe), 1¹C{1H} NMR (100 MHz, CDCl₃): δ 171.38 (NCMe), 146.46 (*o*-C), 136.46 (*ipso*-C), 77.72 (γ -C), 28.51 (CHMe), 23.20 (CHMe), 22.97 (CHMe), 21.91 (NCMe).

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Key Chemical Shifts for 2. N,N'-bound ligand: ¹H NMR (399 MHz, CDCl₃, 303 K) δ 4.75 (s, 1H, γ -CH), 3.33 (sept, J = 6.4 Hz, 4H, CHMe₂), 1.72 (s, 6H, NCMe), 1.18 (d, J = 6.8 Hz, 12H, CHMe), 1.14 (d, J = 6.9 Hz, 12H, CHMe); $^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) 164.34 (NCMe), (*ipso*-C), 141.48 (*o*-C), 141.26 (*o*-C), 96.23 (γ -C), 27.78 (CHMe), 27.69 (CHMe), 25.32 (NCMe), 24.48 (CHMe). γ -bound ligand: ¹H NMR (399 MHz, CDCl₃, 303 K) δ 3.71 (s, 1H, γ -CH), 2.91 (m, 2H, CHMe₂), 2.49 (sept, J = 6.7 Hz, 2H, CHMe₂), 1.51 (s, 6H, NCMe), 0.98 (d, J = 6.8 Hz, 12H, CHMe), 0.89 (d, J = 6.7 Hz, 6H, CHMe), 0.85 (d, J = 6.9 Hz, 6H, CHMe); $^{13}C{}^{1}H{}$ NMR (399 MHz, CDCl₃) δ 169.97 (NCMe), 137.03 (*ipso*-C), 66.69 (γ -C), 28.21 (CHMe), 28.51 (CHMe), 23.75 (CHMe), 23.20 (CHMe), 22.49 (CHMe), 21.40 (NCMe).

Computational Details. All calculations were performed using the density function theory in the Gaussian 03 program. The geometry optimization was performed at the B3LYP level by using a double- ζ basis set (LanL2DZ) along with the effective core potential (LanL2ECP) for the Hg atom and the 3-21G basis set for all other atoms. Zero-point vibrational energy corrections were also included.^{36,37} ¹H NMR spectra were estimated with the gauge invariant atomic orbital DFT (GIAO-DFT) calculations at the B3LYP/LanL2DZ/3-21G level.

Acknowledgment. We are grateful for financial support from the EPSRC (LF, Grant No. EP/E032575/1).

Supporting Information Available: Figures giving a van't Hoff plot of the equilibria between 1 and 2, variable-temperature ¹H NMR spectra showing resonances between δ 8 and 0 ppm, and ¹H-¹³C gHSQCAD and ¹H-¹³C gHMBCAD spectra, a table giving Cartesian coordinates of the optimized structures of 1 and 2, text giving the complete ref 31, and a CIF file giving crystallographic data for complex 1. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽³⁷⁾ Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284.