collidinium chloride was formed. DIEA (190 μL, 8 equiv) was added to the resin, immediately followed by addition of the suspension. The mixture was shaken for the reaction times given in Figure 1, filtered, and washed.

DIC/HOAt coupling: Fmoc amino acid (414 μmol; 3 equiv) and HOAt (57 mg; 3 equiv) were dissolved in a small volume of $CH_2Cl_2$/DMF (1:1). DIC (65 μL; 3 equiv) was added and the mixture was shaken. After 15 min, this solution was added to the Fmoc-deprotected peptidyl resin (swollen in DMF) and shaken for the reaction times given in Figure 1.

HATU coupling: Fmoc amino acid (552 μmol; 4 equiv) and HATU (210 mg; 4 equiv) were dissolved in a small volume of $CH_2Cl_2$/DMF (1:1). DIEA (190 μL; 8 equiv) was added and the mixture was shaken. After 15 min, this solution was added to the Fmoc-deprotected peptidyl resin (swollen in DMF) and shaken for the reaction times given in Figure 1.

Cleavage and deprotection: Following Fmoc deprotection, the dodecapeptidyl–TCP resin was washed and HFIP/$CH_2Cl_2$ 1:5 (5 mL) was added. The suspension was shaken for 15 min, after which the filtrate was collected and evaporated to dryness under reduced pressure. The cleavage procedure was repeated twice. Yield: 155 mg linear dodecapeptide OmA(7-6) (116 μmol; 84 %), HPLC purity ($\lambda = 214$ nm): 90 %.

This peptide (155 mg; 116 μmol; 1 equiv) was dissolved in $CH_2Cl_2$ (400 mL). HOAt (32 mg; 2 equiv), 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide (EDCI; 45 mg; 2 equiv) and DIEA (160 μL; 8 equiv) were added successively. After stirring for 16 h at RT, 2/3 of the solvent was evaporated under reduced pressure. The organic phase was washed with saturated $NaHCO_3$, 8 % citric acid, and brine, dried over $Na_2SO_4$, and evaporated to dryness. The cyclopeptide **1** was purified by flash chromatography (silica gel, ethyl acetate/methanol 95:5). Yield: 57 mg **1** (43 μmol; 31 %).

Analytical data for **1**: $^1$H and $^{13}$C NMR data of the synthetic omphalotin A correspond to the literature data for the natural compound.[1b] HR-MS (ESFTICR-MS): calcd: $m/z$ 659.94668, found: $m/z$ 659.94805 ($[M+2H]^{2+}$) (Figure 2). For further analytical data and experimental details, see Supporting Information.

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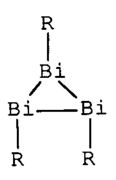
# Synthesis of the Dibismuthene Complex $[\{\mu\text{-}\eta^2\text{-}(cis\text{-}Me_3SiCH_2Bi)_2\}\{W(CO)_5\}_2]$ from a Cyclobismuthane and $[W(CO)_5(thf)]$

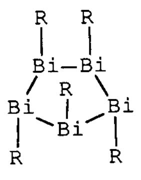
Lucia Balázs, Hans Joachim Breunig,* and Enno Lork

Owing to relativistic effects it is expected that two valence electron pairs of bismuth should be inert.[1, 2] Consequently, Bi$^{\text{I}}$ compounds should be relatively stable and their reactivity should differ considerably from that of corresponding compounds the lighter homologues. To date there is little evidence for these effects because true Bi$^{\text{I}}$ compounds are rare.[2] The first organometallic examples are *trans*-dibismuthenes, RBi=BiR[3] and two cyclobismuthanes, $(RBi)_n$ ($n = 3,4$),[4a] which are protected by very bulky aryl groups or by the $(Me_3Si)_2CH$ group, respectively. Recently, the ring compounds $(RBi)_4$ ($R = (Me_3Si)_3Si$) and $R_6Bi_8$ ($R = (Me_3Si)_3Sn$) were described.[4b]

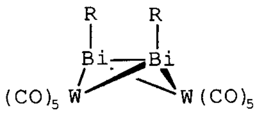
Searching for less hindered Bi$^{\text{I}}$ compounds, for which the specific properties might emerge more clearly, we have studied the bismuth ring system trimethylsilylmethylbismuth(I) (**1**), whose main components are the new cyclobismuthane **1a**, a three-membered ring, and **1b**, the first bismuth five-membered ring. Three- and five-membered rings are well known in the chemistry of P, As, and Sb.[5]



**1a**



**1b**



**2**

R = $Me_3SiCH_2$

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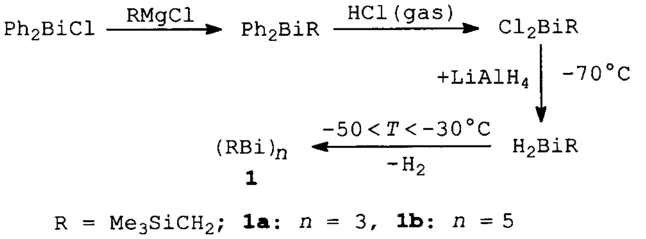
The reaction of **1** with $[W(CO)_5(thf)]$ gives $[\{\mu\text{-}\eta^2\text{-}(\textit{cis}\text{-}Me_3SiCH_2Bi)_2\}\{W(CO)_5\}_2]$ (**2**), the first complex with a dibismuthene ligand. Particular features of **2** are the *cis* arrangement of the alkyl groups and the bridging "side-on" coordination of the dibismuthene. The combination of these motifs is novel not only for bismuth, but also for the rich coordination chemistry of the lighter homologues $(RE)_2$ (E = N, P, As, Sb).[6] The bismuth compounds closest related to **2** are complexes with bridging RBi ligands[6a] or dibismuth complexes.[6a, 7] Attempts to synthesize a dibismuthene complex using synthetic procedures which are well established in the chemistry of other pnicogens,[6b] that is by reaction of $(Me_3Si)_2CHBiCl_2$ with $Na_2[W_2(CO)_{10}]$, led to other products.[7b]

For the synthesis of the cyclobismuthanes **1** (Scheme 1) first diphenylbismuth chloride is transformed to $Me_3SiCH_2BiPh_2$ by a Grignard reaction. Substitution with HCl gives $Me_3SiCH_2BiCl_2$.[8] Hydrogenation with $LiAlH_4$ in diethyl ether at −70°C leads to the colorless hydride $Me_3SiCH_2BiH_2$, which decomposes with a red coloration of the solution above −50°C with formation of hydrogen and **1**. Removal of the solvent gives **1** in 90% yield as a dark red, air-sensitive, pyrophoric solid, which is very soluble in organic solvents. Solutions of **1** are stable for a long time below −28°C, but decompose completely at room temperature within 24 h with formation of $R_3Bi$, $R_4Bi_2$, and Bi. The ring system in solution was analyzed by $^1$H NMR spectroscopy at different temperatures and concentrations; the spectrum of **1** at +5°C in $C_6D_6$ is shown in Figure 1.



Scheme 1. Synthesis of the cyclobismuthanes **1a** and **1b**.

The characteristic signals of the main components of **1**, namely the three-membered ring **1a** and the five-membered ring **1b**, are easily recognized. The three-membered ring **1a** adopts the usual configuration with one *trans*- and two *cis*-oriented substituents. The latter are bound to stereogenic bismuth atoms; their methylene protons are not equivalent. In the $^1$H NMR spectra there are two singlet signals in a 2:1 ratio of intensities for the methyl groups, and four signals of an AB spin system, as well as a singlet signal for the methylene protons. In the five-membered ring **1b** the substituents adopt a maximum number of *trans* positions. Two pairs of the substituents correspond to each other, and consequently the spectrum displays three singlet signals in a 2:2:1 ratio of intensities for the methyl groups and nine lines in the methylene region (two AB spin systems for the diastereotopic $CH_2$ groups at the stereogenic bismuth atoms and one singlet for the $CH_2$ protons at the nonstereogenic bismuth atom). In addition to the signals of **1a** and **1b** there are two signals with low intensities of a component with equivalent alkyl groups.[9] These signals are most probably for the four-membered ring, *cyclo*-$(Me_3SiCH_2Bi)_4$ in the *all-trans* configuration, which is present in mixture up to a maximum of 1%. Changes in the external conditions lead to interconversions of the ring systems **1a** and **1b**. There are ring–ring equilibria [Eq. (1)], for which according to Le Chatelier's principle the concentrations of the more strained three-membered ring increase

$$\underset{\textbf{1a}}{5\,(RBi)_3} \rightleftharpoons \underset{\textbf{1b}}{3\,(RBi)_5} \qquad (1)$$

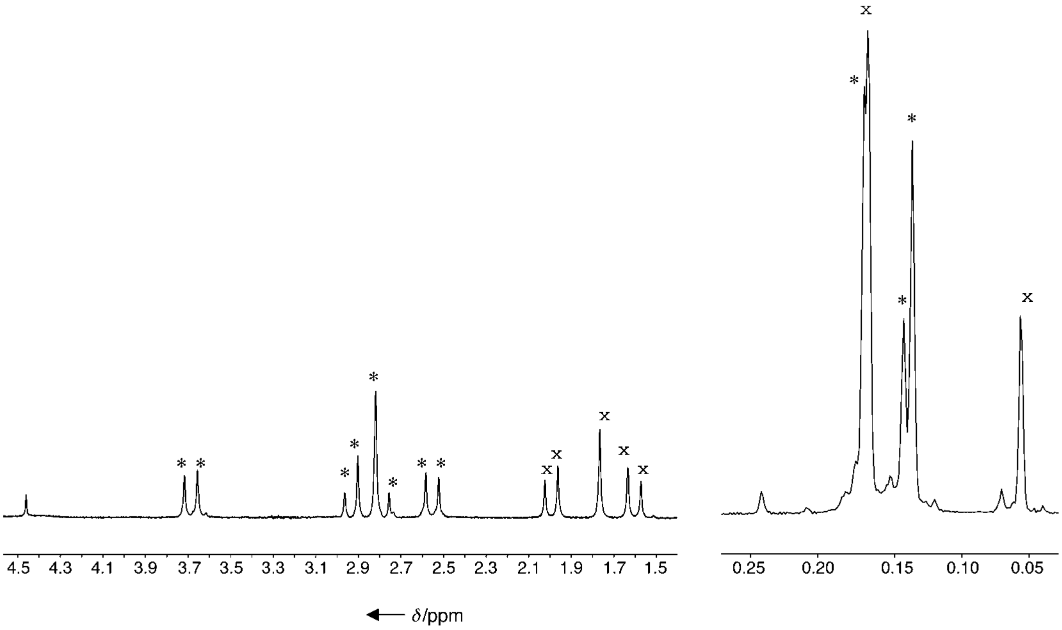


Figure 1. $^1$H NMR spectrum of a solution of **1** in $C_6D_6$ at 5°C. Labels: × for **1a** and * for **1b**.

on dilution and heating. As shown in Figure 1 the three- and five-membered rings exist in an approximately 1:1 molar ratio at 5 °C. It is likely that at low temperatures and in the solid state the five-membered ring is the main component.[10]

The equilibrium between **1a** and **1b** is unusual, since solutions of bis(trimethylsilyl)methylbismuth contain three- and four-membered rings, and trimethylsilylmethylantimony as well as other alkylpnicogen ring systems with "slim" substituents exist in the crystal or in solution almost exclusively as five-membered rings.[5c] Bulky substituents are usually required for the stabilization of pnicogen three-membered rings; they form in ring–ring equilibria only at much higher temperatures.[5a]

The unique character of the Bi ring system **1** is exemplified also in the reaction with $[W(CO)_5(thf)]$, which leads to the dibismuthene complex **2**, a red crystalline compound, which is well soluble in hydrocarbons and melts at 95 °C. The structure of **2** was determined by single-crystal X-ray diffraction.[11] It is a complex of a *cis*-dibismuthene coordinated "side-on" bridging to two $W(CO)_5$ units in a bicyclic butterfly structure (Figure 2). The Bi–Bi bond in **2** (3.003(1) Å) is longer than in free dibismuthenes $RBi{=}BiR$ with aryl substituents in *trans* positions ($R = [(Me_3Si)_2CH]_3C_6H_2$ 2.8206(8),[3a] $R = (Me_3C_6H_2)_2C_6H_3$ 2.832(1) Å[3c]), or in the dibismuth complexes $[Bi_2\{W(CO)_5\}_3]$ (2.818(3) Å)[7a] and $[Bi_2\{Sm(C_5Me_5)_2\}_2]$ (2.851(1) Å).[7d] It lies in the range of the Bi–Bi single bonds of $(Ph_2Bi)_2$ (2.990(2) Å),[12a] $[Et_4Bi_2][Al\mathit{t}Bu_3]$ (2.9831(1) Å),[12b] or $[\{(Me_3Si)_2CHBi\}_4]$ (2.972(5)–3.042(3) Å[6]). Also in diphosphene complexes with "side-on" coordination the P–P bond lengths are considerably longer than in free diphosphenes.[6b] The Bi–W distances in **2** (3.118(1), 3.124(1) Å) are similar to those in $[Bi_2\{W(CO)_5\}_3]$ (3.083(3)–3.134(3) Å).[7a] They are longer than the Bi–W bond lengths in $[Ph_3BiW(CO)_5]$ (2.829 Å),[13a] $[(Ph_3P)_2N][Ph_2Bi\{W(CO)_5\}_2]$ (2.882–2.885 Å),[13b] and $[(Bi_2)W_2(CO)_8\{MeBiW(CO)_5\}]$(2.851–3.001 Å).[7b] The Bi-Bi-C bond angles and the $Bi_2W$ dihedral angles in **2** are 96.4(4) and 155.5°, respectively. Thus, the wings of the butterfly structure are widely extended.

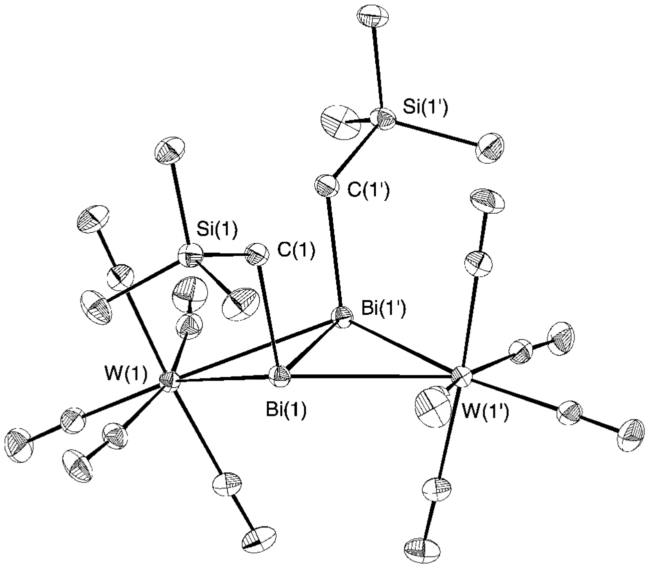


Figure 2. Structure of **2** in the crystal (the ellipsoids represent 30% probability). Selected distances [Å] and angles [°]: Bi(1)-Bi(1') 3.0024(7), Bi(1)-C(1) 2.303(6), Bi(1)-W(1') 3.118(1), Bi(1)-W(1) 3.124(1); C(1)-Bi(1)-Bi(1') 96.2(2), C(1)-Bi(1)-W(1') 103.2(1), Bi(1')-Bi(1)-W(1') 61.34(2), C(1)-Bi(1)-W(1) 104.3(2), Bi(1')-Bi(1)-W(1) 61.15(2), W(1')-Bi(1)-W(1) 117.88(3).

Our recent study of the reaction of $(RSb)_n$ ($n = 4$, 5; $R = Me_3SiCH_2$) with $[W(CO)_5(thf)]$ under very similar conditions allows a very direct comparison of the reactivity of analogous antimony(I) and bismuth(I) compounds. In the case of the reaction of the cyclostibanes no distibene analogue of **2** is formed, instead two Sb atoms of the five-membered ring are coordinated in a terminal fashion and *cyclo*-$[1,3\text{-}\{W(CO)_5\}_2(RSb)_5]$ is formed.[14]

With **1** and $[(Me_3Si)_2CH_2Bi]_n$ ($n = 3,4$) there are now two cyclic alkylbismuth(I) systems known, and the differences to the lighter homologues are emerging. The unusual preference for three-membered rings in ring–ring equilibria is remarkable. Monomeric alkylbismuth(I) species were not identified. They are, however, possible intermediates in ring–ring transformations or in the formation of **2**.

## *Experimental Section*

All operations were carried out in an argon atmosphere in dry solvents.

**1**: A Grignard solution prepared from $Me_3SiCH_2Cl$ (10.0 g, 81.6 mmol) and magnesium (2.4 g, 100.9 mmol) in THF (110 mL) was added dropwise to a suspension of $Ph_2BiCl$ (32.2 g, 80.8 mmol) in THF (100 mL). The reaction mixture was stirred for 2 h at 0 °C and for 18 h at room temperature. The THF was removed in vacuum and the residues were extracted with petroleum ether. After the removal of the solvent, $Me_3SiCH_2BiPh_2$ remained as a yellowish oil (30.8 g; 84.7%), which crystallized at room temperature to give colorless needles. HCl gas was introduced for 2 h at 0 °C into a solution of $Me_3SiCH_2BiPh_2$ (28.0 g, 62.2 mmol) in $CHCl_3$ (130 mL), the mixture was stirred for 30 min, and subsequently the solvent was removed to give $Me_3SiCH_2BiCl_2$ as a yellowish solid (17.5 g; 76.7%). MS (70 eV): $m/z$ (%): 351 (78) $[M^+ - Me]$, 336 (38) $[M^+ - 2Me]$, 279 (25) $[M^+ - R]$, 244 (17) $[BiCl^+]$, 209 (100) $[Bi^+]$. $LiAlH_4$ (2.8 g, 73.0 mmol) was added portionwise to a precooled (−70 °C) solution of $Me_3SiCH_2BiCl_2$ (12.8 g, 34.9 mmol) in $Et_2O$ (200 mL) and the mixture was stirred. Filtration at −30 °C through a precooled frit covered with kieselgur gave a dark red solution from which **1** (9.3 g; 90%) remained as a red solid after the removal of the solvent in vacuum. M.p. 38–40 °C; elemental analyses calcd (%) for $C_{20}H_{55}Bi_5Si_5$: C 16.22, H 3.74; found: 15.87, H 3.89; $^1H$ NMR of **1a** (200 MHz, $C_6D_6$, 5 °C, TMS):$\delta = 0.059$ (s, 9H; $CH_3$), 0.17 (s, 18H; $CH_3$), AB spin systems with A: 1.602, B: 1.991 ($^2J(H,H) = 12.1$ Hz, 4H; $CH_2$), 1.765 ppm (s, 2H; $CH_2$); $^1H$ NMR of **1b** (200 MHz, $C_6D_6$, 5 °C, TMS): $\delta =$ 0.138 (s, 18H; $CH_3$), 0.144 (s, 9H; $CH_3$), 0.173 (s, 18H; $CH_3$), AB spin systems with A: 2.5515, B: 3.684 ($^2J(H,H) = 12.2$ Hz, 4H; $CH_2$), and A: 2.786, B: 2.933 ($^2J(H,H) = 12.3$ Hz, 4H; $CH_2$), 2.818 ppm (s, 2H; $CH_2$); MS (CI, $NH_3$): $m/z$ (%): 975 (3) $[R_4Bi_3^+]$, 888 (2) $[R_3Bi_3^+]$, 854 (82) $[R_3Bi_3^+ - 2Me]$, 766 (6) $[R_4Bi_2^+]$, 400 (100) $[R_2Bi^+ + NH_3]$, 383 (35) $[R_2Bi^+]$.

**2**: A solution of $[W(CO)_5(thf)]$ (0.44 g, 1.11 mmol) in THF (100 mL) was added to a solution of **1** (1.0 g, 1.1 mmol) at 0 °C in THF (30 mL) and stirred for 3 h at 0 °C. After removal of the solvent the residues were extracted with petroleum ether (60 mL) and the extracts were filtered through a frit covered with kieselgur. Concentration of the solution, followed by cooling to −28 °C gave red crystals of **2**. M.p. 95–96 °C; elemental analysis (%) calcd for $C_{18}H_{22}O_{10}Si_2W_2Bi_2$: C 17.43, H 1.79; found: C 18.01, H 1.86; $^1H$ NMR (200 MHz, $C_6D_6$, 25 °C): $\delta = 0.17$ (s, 9H; $CH_3$), 1.94 ppm (s, 2H; $CH_2$); $^{13}C$ NMR (50 MHz, $C_6D_6$, 25 °C, TMS): $\delta = 1.26$ (s; $CH_3$), 191.10, 192.02, 200.04 ppm (s, CO); IR (petroleum ether): $\tilde{\nu} = 2054$, 1956 $cm^{-1}$,

1433-7851/02/4113-2311 $ 20.00+.50/0

$(C{=}O)$; MS (CI, $NH_3$): $m/z$ (%): 1239 (8) $[M^+]$, 1152 (25) $[M^+ - R]$, 943 (18) $[RBiW_2(CO)_{10}^+]$, 707 (100) $[R_2BiW(CO)_5^+]$, 324 (29) $[W(CO)_5^+]$.

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[1] As a consequence of the spin–orbit coupling the 6p orbitals split into one p(1/2) and two p(3/2) orbitals. The former is spherically symmetric and like the 6s orbital stabilized by relativistic effects. In addition to the inert s electron pair there should be an inert p electron pair and $Bi^I$ should be stable in the configuration $6s^2$, $6p(1/2)^2$, $6p(3/2)^0$: P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563–594.

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[9] a) $\delta = 4.45$ ppm ($CH_2$); for the $CH_3$ groups several signals in the region $\delta = 0.07–0.24$ ppm are possible.

[10] $c(\mathbf{1a}):c(\mathbf{1b}) = 0.3$ in the range from $-15$ to $-80\,^{\circ}C$, 0.95 at $5\,^{\circ}C$, 2 at $25\,^{\circ}C$. The value 0.3 is also observed for a solution of the solid prepared and analyzed at $-60\,^{\circ}C$. Equilibration occurs only above $-15\,^{\circ}C$.

[11] X-ray structure analysis of **2** ($C_{18}H_{10}Bi_2O_{10}Si_2W_2$): $M_r = 1240.20$; crystal dimensions $0.5 \times 0.4 \times 0.35$ mm$^3$; monoclinic, space group $C2/c$, $a = 22.809(5)$, $b = 8.622(2)$, $c = 18.381(4)$ Å, $\beta = 124.20(3)^{\circ}$, $V = 2.9897(12)$ nm$^3$, $Z = 4$, $\rho_{calcd} = 2.755$ Mg m$^{-3}$, $\mu = 19.529$ mm$^{-1}$. A crystal was fixed on a glass fiber with Kel-F oil and measured on a STOE-IPDS at $-100\,^{\circ}C$. With graphite-monochromated $Mo_{K\alpha}$ radiation (0.71073 Å) 20417 reflections were measured ($2.16 < \theta < 26.06^{\circ}$). A total of 2863 reflections remained after averaging ($R_{int.} = 0.0732$), and the structure was solved by direct methods. The refinements converged after an empirical (DIFABS) absorption correction at $wR_2 = 0.0550$ (refinement against $F^2$) for all 20417 reflections and 160 variables ($R1 = 0.0218$ for 2863 reflections with $I > 2\sigma(I)$). Heavy atoms were refined anisotropically and the H atoms were refined with a riding model and a common isotropic temperature factor. Max./min. residual electron densities: $1.317/-0.842$ e Å$^{-3}$. The structure solution and refinement was carried out using SHELX-97,[15] and the Diamond program was used for the graphical representation.[16] CCDC-175881 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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# Remarkably Large Geometry Dependence of $^{57}Fe$ NMR Chemical Shifts**

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With the continuous improvement of NMR hardware and acquisition techniques, transition-metal NMR spectroscopy is losing much of its formerly exotic character. NMR spectra of nuclei with low NMR receptivity or large quadrupole moments, in compounds hitherto believed to pose insurmountable problems, can now be measured within reasonable time.[1] One recent example is aqueous $[Fe(CN)_5(NO)]^{2-}$ (**1**), the $^{57}Fe$ chemical shift $\delta(^{57}Fe)$ of which was determined as $\delta = 2004$ ppm.[1b] What is particularly noteworthy about this result is that this Fe nucleus is significantly shielded with respect to that of $[Fe(CN)_6]^{4-}$ (**2**; $\delta = 2455$ ppm). Both anions are prominent textbook examples in coordination chemistry.[2] Since an interpretation of this difference in $^{57}Fe$ nuclear magnetic shielding is not straightforward, we resorted to quantum-chemical calculations of these $\delta(^{57}Fe)$ chemical shifts, which have been shown to be accessible with reasonable accuracy at suitable levels of density functional theory (DFT).[3] Such computations are normally performed for isolated static molecules in their equilibrium geometry at 0 K. For **1** and **2**, such an approach initially afforded computed values, $\delta = 2254$ and 4120 ppm, respectively, which are in rather poor accord with the experimental data obtained in aqueous solution. For the highly charged tetraanion **2** in particular, the error of the DFT value with respect to experiment amounts to more than $\Delta\delta = 1600$ ppm. Evidently, interactions between the complex and the solvent must be taken into account.

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