(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(**1a**):c(**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 CB2 1EZ, 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**

Michael Bühl,* Frank T. Mauschick, Frank Terstegen, and Bernd Wrackmeyer

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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We have recently suggested a computational protocol to model solvent and thermal effects on transition-metal chemical shifts.[4] The procedure involves DFT-based Car–Parrinello molecular dynamics (CPMD) simulations of the metal complex in a periodic water box, and averaging of the δ values computed for a number of snapshots along the trajectory. For $\delta(^{51}V)$ of vanadate species, relatively small differences between the equilibrium and the averaged values, δ_e and $\delta^{300\,K}$, respectively, have been obtained, on the order of a few dozen ppm. To test if such a dynamical approach would be able to describe larger effects, we now report a similar study of $\delta(^{57}Fe)$ values of **1** and **2**, modeled in aqueous solution. Indeed, substantial thermal and solvent effects are obtained, which can be traced back to relatively modest variations in geometrical parameters.

As will be documented elsewhere,[5] CPMD results for highly charged **2** were plagued by artifacts due to limited box sizes under the periodic boundary conditions. We therefore decided to adopt a dynamical approach without such periodicity, where the metal complex, described by a well-established DFT method, is placed into a large water cluster which is described by a suitable force field.[6] Similar molecular dynamics simulations, usually with purely force-field based methods, are frequently used to study solvent effects.[7] Initial simulations were performed for **2** and for $[Fe(CO)_5]$ (**3**), the standard used in ^{57}Fe NMR spectroscopy, in the gas phase (that is without solvent and at pure DFT level). Figure 1 illustrates the evolution of the averaged magnetic

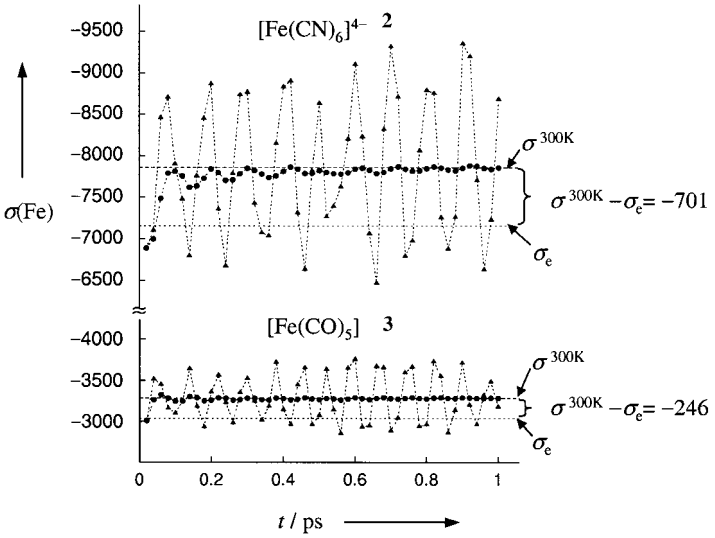

Figure 1. Absolute ^{57}Fe magnetic shielding constants $\sigma(^{57}Fe)$ for $[Fe(CO)_5]$ (**3**, bottom) and $[Fe(CN)_6]^{4-}$ (**2**, top), computed for snapshots from a 1 ps MD simulation. Triangles: raw data; circles: running average values (average value up to this point); dashed lines: final average values $\sigma^{300\,K}$, dotted lines: equilibrium values σ_e.

shieldings[8] over 1 ps. On going from the equilibrium value to the average at 300 K, a substantial deshielding is obtained for the ^{57}Fe nucleus in **3**, $\sigma^{300\,K} - \sigma_e = -246$, and an even larger one, $\sigma^{300\,K} - \sigma_e = -701$, for that in **2**. Thus, the chemical shift of **2** relative to that of **3** increases by 455 ppm upon thermal averaging in the gas phase.[9] When **2** is placed in an aqueous environment, in contrast, a similar averaging affords a substantial shielding of the metal nucleus, $\sigma^{300\,K} - \sigma_e = +1281$. The resulting δ values are collected in Table 1.

Table 1. ^{57}Fe chemical shifts δ (GIAO-B3LYP) and mean Fe–C distances r [Å] based on molecular dynamics (MD) simulations in vacuo and in aqueous solution.

Level of approximation	$[Fe(CN)_6]^{4-}$ **2**	$[Fe(CN)_5(NO)]^{2-}$ **1**
δ_e (//QM-opt)[a]	4120	2254
$\delta^{300\,K}$ (//MD)[b]	4575	2466
$\delta^{300\,K}$ (//MD/H_2O[c])	2593	2076
δ Experiment/H_2O[d]	*2455*	*2004*
r_e (QM-opt)[a]	1.973	1.955[e]
$r^{300\,K}$ (MD)[b]	1.987	1.969[e]
$r^{300\,K}$ (MD/H_2O[c])	1.924	1.943[e]

[a] Isolated molecule, optimized at the BP86/AE1 level. [b] Average values from 1 ps simulations of the isolated molecule at about 300 K. [c] Average values from 1 ps simulations at about 300 K in water. [d] Guadinium counterions, from reference [1b]. [e] Only minute differences are found in the mean distances to the cyano groups *trans* and *cis* to the NO ligand.

Inspection of the molecular structures reveals that the deshielding and shielding effects of thermal averaging and solvation, respectively, are paralleled by noticeable elongation and shortening, respectively, of the average Fe–C bond length r (Table 1). As these changes amount to a few pm only, the ^{57}Fe magnetic shielding appeared to be very sensitive to this geometrical parameter. In fact, an explicit computation of the Fe–C bond-length/shielding derivative[10] in isolated **2** afforded a value of $\partial\sigma(Fe)/\partial r_{FeC} = -35\,100$ ppm Å^{-1}.[11] In absolute terms, this value is much larger than an experimental estimate for a related complex, $[Co(CN)_6]^{3-}$, for which $\partial\sigma(Co)/\partial r_{CoC} = -8000$ ppm Å^{-1} has been deduced[12] from isotope effects on the metal chemical shift. Most of the gas-to-liquid shift simulated for **2**, $\Delta\delta = -1982$ ppm, can thus be attributed to the concomitant shortening of the Fe–C bonds (compare MD and MD/H_2O entries in Table 1) by $\Delta r = -0.063$ Å, which, together with the bond-length/shielding derivative, would correspond to a value of $\Delta\delta = -2211$ (see below for a discussion of the direct solvent effect). The final, simulated $\delta(^{57}Fe)$ value of 2593 ppm in aqueous solution is in reasonable, qualitative accord with that obtained from the experiment ($\delta = 2455$ ppm).

Corresponding simulations were performed for the nitrosyl complex **1**, both in the gas phase and in water. The resulting trends in the computed $\delta(^{57}Fe)$ values are qualitatively the same as those just described for **2**, but are much more attenuated (Table 1). For instance, the gas-to-liquid-shift is computed as $\Delta\delta = -390$ ppm, about a fifth of that in **2**. The final, simulated $\delta(^{57}Fe)$ value in aqueous solution ($\delta = 2076$ ppm) is in good accord with that obtained from the experiment ($\delta = 2004$ ppm). Likewise, the observed shielding on going from **2** to **1**, $\Delta\delta = -451$ ppm,[1b] is qualitatively reproduced, at $\Delta\delta = -545$ ppm, in the simulations. The latter, apparently, afford a reasonable description of **1** and **2** in aqueous solution.

What is the structure of the solvation shells? Based on purely geometric criteria for the existence of an

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O(water)–H···X(ligand) hydrogen bond,[13] the average numbers of such hydrogen bonds in aqueous **1** and **2** is computed to be 7.4 and 15.3, respectively. The N atoms of the cyano ligands are the sole H-bond acceptors, and no such bonds are formed involving the nitrosyl group in **1**. As expected, the highly charged complex **2** attracts more water molecules than complex **1**.[14] In both cases, these first solvation shells are not static on the ps time scale of the MD simulations, but show exchange between H-bonded and free water molecules. Interestingly, the direct effect of the coordinated water molecules on the values of $\delta(^{57}\mathrm{Fe})$ is much lower than the aforementioned gas-to-liquid shifts. If, in the snapshots from the aqueous solutions, the water molecules are deleted from the NMR inputs (affording the isolated complexes, but in the geometries of the solvated ones), $\delta^{300\,\mathrm{K}}$ values of 2448 and 2140 are obtained for **2** and **1**, respectively. These values are much closer to the corresponding MD/H_2O data than to the MD results of the isolated complexes (Table 1). The main effect of hydration on the value of $\delta(^{57}\mathrm{Fe})$ is thus indirect, as it is the concomitant change of the geometrical parameters that governs the solvent effect. The same has been surmised in other cases, for instance for the value of $\delta(^{11}\mathrm{B})$ in aqueous BH_3NH_3.[15, 16]

What is, finally, the origin of the stronger shielding of the ^{57}Fe nucleus in **1** relative to that in **2**? In both cases, the magnetic shielding is governed by huge paramagnetic contributions, σ^{p}. Analysis of the MOs of **2** (in an idealized O_h symmetric structure employing the averaged parameters from the simulation in water) reveals that strong contributions to σ^{p} can arise from the coupling of each of the triply degenerate HOMOs, through the action of the magnetic operator, with a suitable low-lying virtual MO.[17] One such combination is depicted in the upper part of Figure 2. The situation is more complicated in **1**, since many of the orbital degeneracies are lifted due to the lower symmetry. For instance, the t_{2g} HOMO in **2** splits into b_1 and e MOs in **1**, with similar energy gaps for the respective, magnetically allowed transitions (Figure 2 bottom). In the nitrosyl complex, however, the metal d contribution to the MOs is significantly reduced with respect to that in **2**. This is consistent with reduced paramagnetic contributions and, thus, an apparent shielding of the ^{57}Fe nucleus in **1**. The lower geometry-sensitivity of the value of $\delta(^{57}\mathrm{Fe})$ in **2** relative to that in **1** is probably also rooted in these reduced paramagnetic contributions.

In summary, we have modeled the ^{57}Fe chemical shifts of iron cyanide complexes in aqueous solution using a dynamical, combined QM/MM approach. To our knowledge, this is the first application of this methodology to transition metal NMR parameters, and complements related schemes based on CPMD simulations. Large thermal and solvation effects on $\delta(^{57}\mathrm{Fe})$ are computed, on the order of 1000 ppm and more, which can be attributed to a remarkable sensitivity of the ^{57}Fe magnetic shielding constant to the Fe–C bond length. It is to be expected that this sensitivity should manifest itself in unusual temperature dependencies or isotope effects on the $\delta(^{57}\mathrm{Fe})$ values of these complexes. Recently,[1c] the isotope-induced chemical shift $^{1}\Delta^{12/13}\mathrm{C}(^{57}\mathrm{Fe})$ has been determined for the first time for ferrocene, and work in this direction is in progress for $[Fe(CN)_6]^{4-}$ (**2**). Insights are obtained into the structure and dynamics of the first solvation shell around the complexes and into the mechanism governing the trend of the values of $\delta(^{57}\mathrm{Fe})$ upon ligand variation. The possibility to model thermal and solvent effects on NMR chemical shifts will certainly broaden the scope of applications beyond those already possible with computations for hypothetical, static molecules.

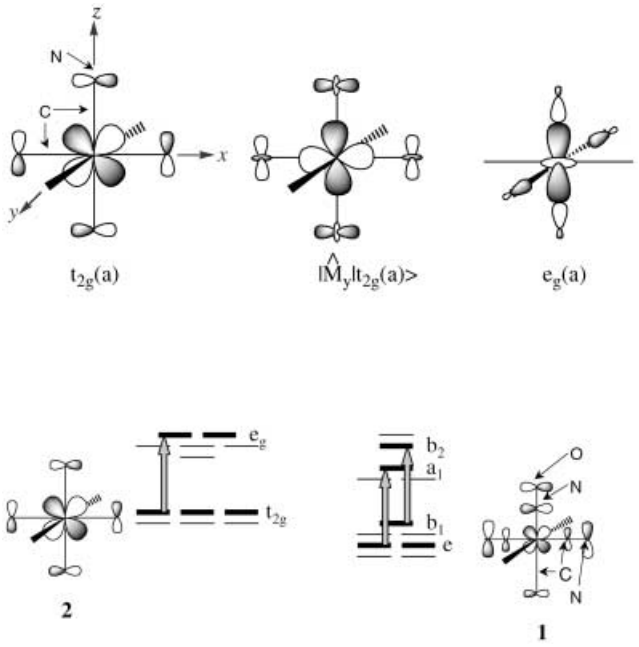

Figure 2. Top: Schematic representation of important MOs of **2**. Left: HOMO; middle: transformed HOMO after action of the angular momentum operator in *y* direction, $\hat{M}y$, on it; right: low-lying virtual orbital suitable for overlap with the transformed HOMO. Bottom: Qualitative scheme of near-frontier MOs in **1** and **2**, including important magnetic transitions (gray arrows, only one for degenerate transitions shown); one of each t_{2g} and e orbitals is also sketched to illustrate the reduced metal d character in the latter.

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[2] For instance: N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, **1997**.

[3] a) M. Bühl, *Chem. Phys. Lett.* **1997**, *267*, 251–257; review: b) M. Bühl, M. Kaupp, V. G. Malkin, O. L. Malkina, *J. Comput. Chem.* **1999**, *20*, 91–105.

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[5] M. Bühl, F. T. Mauschick, unpublished results.

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Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124). Water was described by the CHARMm force field of the MSI-CHARMm 25b2 program (QUANTA98, Molecular Simulations, Inc., 9685 Scranton Rd. San Diego, CA 92121. The published results were generated by using the program CHARMm. This program is distributed by Molecular Simulations Inc.). For the coupling between QM and MM parts, a polarized embedding scheme was used (corresponding to model B in: D. Bakowies, W. Thiel, *J. Phys. Chem.* **1996**, *100*, 10580–10594). MD simulations were performed by using the ChemShell program (P. Sherwood, A. H. deVries, *ChemShell - A Shell for Computational Chemistry*, CCLRC Daresbury Laboratory, **1999**, see http://www.dl.ac.uk) for NVT ensembles at approximately 300 K. For the aqueous species, the complexes were placed at the center of a spherical water cluster with a diameter of 30 Å, containing a total of 449 water molecules. After a short minimization (100 steps), the outmost layer to a depth of 5 Å from the surface was completely frozen to avoid evaporation of the minidroplet in the subsequent MD run. The aqueous species were simulated for 4 ps with a time step of 1 fs. Data sampling was started after the first 3 ps, which were taken for equilibration. In addition, the O–H distances in the water monomers were frozen with the SHAKE algorithm. Isolated complexes were simulated (after 0.5 ps of equilibration) for 1 ps with a time step of 0.5 fs.

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[8] Magnetic shieldings were computed for equilibrium geometries and for snapshots taken from the MD simulations at the GIAO-B3LYP level (see ref. [3a] for details), by employing a medium-sized grid and DZ basis, that is, the augmented Wachters basis on Fe and DZ basis (W. Kutzelnigg, U. Fleischer, M. Schindler in *NMR Basic Principles and Progress*, *Vol. 23*, Springer, Berlin, **1990**, pp. 165–262) on all other atoms. The use of the smaller DZ basis, rather than the larger basis II (that has been employed, for instance, in ref. [3a]) resulted in relatively small changes of the computed δ values, for instance by $\Delta\delta = 40$ ppm for **2**, but makes the large number of NMR computations for the snapshots more tractable. In the chemical-shift calculations, the 20 nearest solvent water molecules were included explicitly. Representative snapshots were taken every 20 fs. Chemical shifts are reported relative to $[Fe(CO)_5]$ (**3**), optimized or simulated at the same respective level (σ_e and σ^{300K} values -3036.6 and -3282.3, respectively, see Figure 1). Neat **3** is the accepted standard in ^{57}Fe NMR spectroscopy. We have only performed a simulation for the gas phase, not for the liquid, which would be a formidable task in itself, but have used the averaged σ^{300K} value from the gas-phase simulation as a reference value also for the solution studies. It should be kept in mind that this procedure could introduce a systematic error for the computed gas-to-liquid shifts, and that more attention should be paid to the trends in the δ values between **1** and **2**, rather than to their actual values.

[9] It should be noted that this value only represents the "classical" thermal effect and is not averaged over the zero-point motion. More than qualitative agreement with experiment is not to be expected anyway, due to the rather limited basis sets employed in the computations.

[10] Obtained by performing NMR computations for a total of four static structures with elongated or compressed Fe–C distances (in steps of 0.02 Å) and a linear fit of the resulting σ values.

[11] A similar value, 35200 ppm Å^{-1}, is obtained when the larger basis II is used for the ligands.

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[13] In typical hydrogen-bonded systems containing O–H···O moieties, the O···O distance is smaller than 3.5 Å and the O–H bond is directed towards the second oxygen atom such that the O–H···O angle is larger than 140° (see for instance: E. Schwegler, G. Galli, F. Gygi, *Phys. Rev. Lett.* **2000**, *84*, 2429–2432); the same criteria have been applied to the O–H···X moieties in **1** and **2**.

[14] Counterions, which have not been considered explicitly, are likely to affect the fine structure of the solvation shell, but would probably not change the qualitative picture.

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[16] Simple optimization of **2** in a polarizable continuum, as has been done for BH_3NH_3 in ref. [15], also leads to Fe–C bond contraction, but gives much too short Fe–C bond lengths, below 1.90 Å.

[17] For similar pictorial rationalizations of paramagnetic contributions see, for instance: Y. Ruiz-Morales, T. Ziegler, *J. Phys. Chem. A* **1998**, *102*, 3970–3976.

A Triple-Decker Sandwich Complex of Barium

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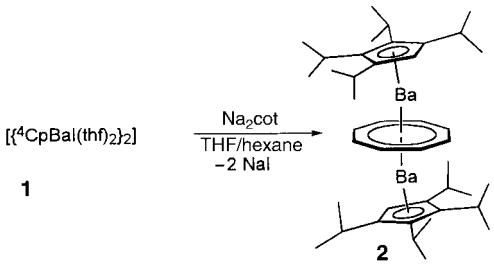
While triple-decker sandwich complexes are common in transition-metal chemistry,[1–8] very few comparable complexes of main-group metals are known that are ionic and show strong bending with centroid-M-centroid angles of 134° ($[Cp_3Tl_2]^-$ ($Cp = C_5H_5$)[9]), 116° ($[Cp_3Cs_2]^-$[10]), 155/152° ($[(C_5Me_5)_3Sn_2]^+$[11]), or 124/130° ($[(\eta^6\text{-}C_7H_8)_2(\mu,\eta^5{:}\eta^5\text{-}C_5Me_5)In_2]^+$[11]). We showed several years ago that bending in sandwich complexes of the heavy alkaline-earth metals can be eliminated with extremely bulky alkylcyclopentadienyl ligands.[12]

Herein we report on the first triple-decker complex of barium. At ambient temperature the half-sandwich complex $[\{^4CpBaI(thf)_2\}_2]$ (**1**; $^4Cp = C_5H(CHMe_2)_4$)[13] reacts slowly with Na_2cot (cot = cyclooctatetraene) in THF/hexane (5:1) [Eq. (1)]. The colorless product is readily soluble in THF, soluble in toluene, and moderately soluble in pentane. ^{1}H and



(1)

^{13}C NMR spectra show one set of signals for two magnetically equivalent ^{4}Cp rings (see Experimental Section) and one signal for one cot ligand at $\delta = 6.02$ ppm (^{1}H) and $\delta =$ 95.3 ppm (^{13}C). On exposure to air the microcrystalline compound turns intense yellow immediately, then orange-red within seconds, and finally pale yellow with a strong cot smell.

EI mass spectra show a signal corresponding to a dinuclear $[^4CpBa(cot)Ba^4Cp]^+$ ion with the correct isotope pattern as well as signals for the fragments $[^4CpBa(cot)Ba]^+$ and

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