Chromium Complexes

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A Tale of Two Isomers (Continued): Is the Phenyl Hydride Complex of Chromium More Stable than Its Benzene-Bridged Isomer?**

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The interest in chromium complexes is heightened by the catalytic activity of many such compounds in the selective oligomerization of olefins.[1] The metallacyclic mechanism, which is generally proposed to account for the observed selectivity of the process, involves a reductive elimination step which is expected to be facile if 1) the product is stable, and 2) the hydride and the alkyl group are close together.[2] Both conditions are fulfilled in one of the two dichromium complexes recently characterized by Theopold and co-workers,[3] which were perceived as the initial and final states of a reductive C–H elimination process proceeding from a phenyl hydride complex of Cr^{II} ($[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-Ph})(\mu\text{-H})]$, **1**, $\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac}$ = 2,4-pentane-*N*,*N*′-bis(2,6-diisopropylphenyl)ketiminate) to its "inverse-sandwich" isomer, in which a central benzene molecule bridges two presumably reduced chromium moieties ($[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)]$, **2**, Figure 1). An inverse-sandwich complex very similar to **2** had been independently reported by Tsai et al.[4] Questions arise, however, about the unexpectedly high stability of **1**, which contradicts the assumed tendency to form a strong aromatic C–H bond. A tentative explanation invoked the lack of compatibility between the spin states of chromium in **1**, which exhibits antiferromagnetic coupling between the Cr^{II} ions, and in **2**, the high-spin ($S = 3$) ground state of which was interpreted as resulting from very strong ferromagnetic coupling between the supposed Cr^{I} metal centers, mediated by the benzene ligand.[3]

Herein we report DFT calculations and geometry optimizations[5,6] carried out on simplified models of **1** and **2**, in which the aryl and methyl substituents of the nacnac ligands have been replaced by hydrogen atoms. These calculations cast new light on the electronic structure of both isomers and on the remarkable stability of **1** by showing that 1) the reductive elimination forming complex **2** does not affect the metal moieties, which formally remain Cr^{II}, but rather the benzene molecule, which becomes $(\text{C}_6\text{H}_6)^{2-}$; and 2) the energy gained in forming the C–H bond is not sufficient to offset the destabilization resulting from the two-electron reduction of benzene, so that the phenyl hydride isomer **1** is actually more stable than **2** by 26.5 kcal mol^{-1}, in spite of an important deformation presumably induced by the bulky substituents.

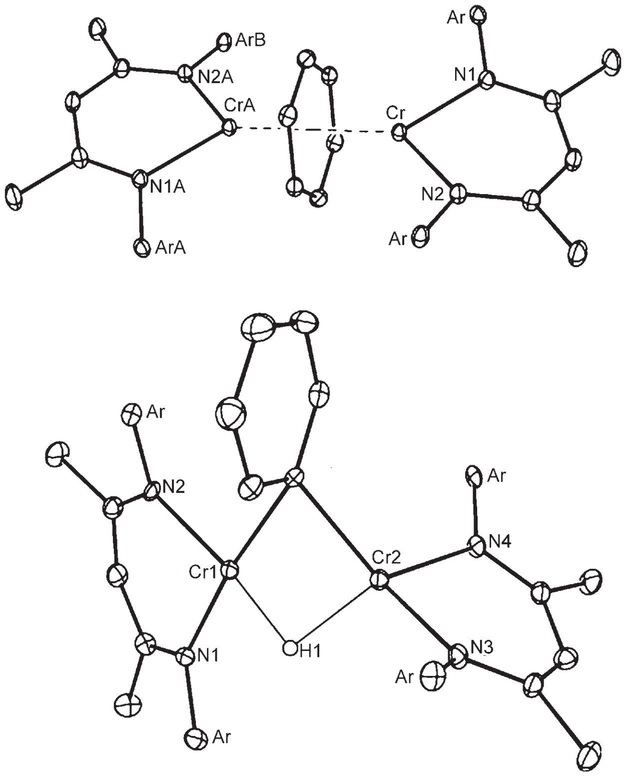

Figure 1. The molecular structure observed for isomers **2** (top) and **1** (bottom).

Among the various spin states that could be considered a priori for the model of the inverse-sandwich isomer **2**, only a septet state provides a reasonable HOMO–LUMO gap (2.5 eV) and a substantial bonding energy (1.66 eV) with respect to separate, neutral molecular fragments, namely, benzene plus two Cr^{I}(nacnac) complexes. The energy of the fragments was obtained in the optimal geometries calculated for their ground states, the closed-shell state of benzene and

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an open-shell sextet state for the d^5 Cr^I complex (see the Supporting Information). Starting with C_{2h} symmetry for **2**, which approached D_{2h} at convergence, the ground state was found to be ^7B_g, in accordance with the spin state of $S=3$ deduced from magnetic-susceptibility measurements.[3] The optimized geometry of the model complex convincingly reproduces the symmetry and the observed structural parameters of **2**: the Cr–N bond lengths (2.01 Å) are slightly shorter, and the average Cr–C distances (2.34 Å) somewhat longer than the observed values. The C–C bond lengths calculated for the central C_6H_6 ring (average 1.45 Å) are significantly longer than those of benzene, which is also in agreement with the observed structure of **2** (1.44 Å). However, an unexpected result was the distribution of the spin density: the total spin assigned to each chromium atom amounts to 3.60 *e*, which is much higher than the expected spin density of around 3 *e*. This excess of spin density is compensated by a strongly negative density of −1.19 *e* that is almost equally distributed over the six carbon atoms of the benzene ligand. An analysis of the frontier orbitals indeed confirms that the metal atoms are formally Cr^{II} with Mulliken charges of +0.60 *e* each, whereas the benzene ring has been doubly reduced, and two singly occupied π* orbitals engage in bonding interactions with chromium in the β (negative) spin orbital manifold (Figure 2). Although the Mulliken charge of benzene remains far from the formal value of −2 *e* because of the covalency of the interactions and also because of π donation, it is nevertheless significantly negative (−0.54 *e*). This charge and the high energy of the semi-occupied π* orbitals make the reduced C_6H_6 fragment an ideal site for an electrophilic attack.

The unsubstituted model of the hydride-bridged complex **1** was first optimized without any constraint, but, at variance with isomer **2**, the calculated structure significantly departs from the experimental structure, most probably because of the strain induced in the real molecule by the bulky *i*Pr_2-(C_6H_3) groups. The environment of both metal atoms becomes nearly square planar, and H1 and C64 (phenyl) lie in the same plane as the {Cr(nacnac)} moieties, so that the optimized geometry of the complex is very close to C_{2v} symmetry (Figure 3 a).

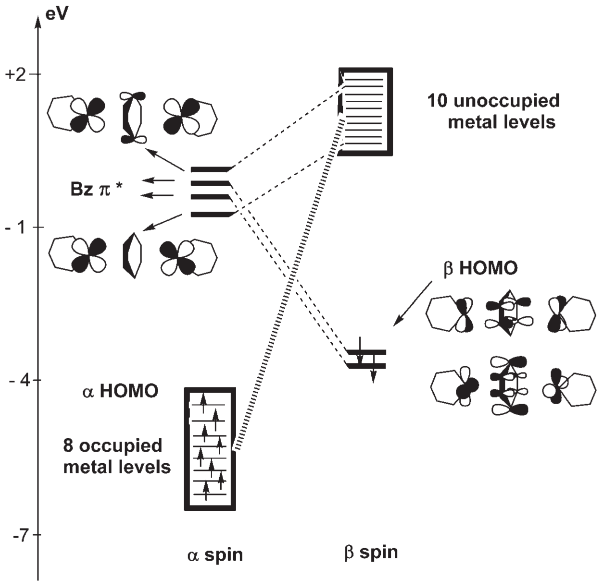

Figure 2. Frontier orbitals obtained for the high-spin (^7B_g) state of lowest energy obtained for the model of isomer **2** from UB3LYP calculations.

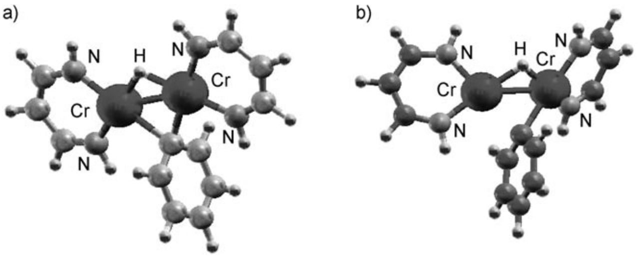

Figure 3. Geometries optimized for the model of isomer **1** from UB3LYP calculations: a) without constraint; b) by constraining one N-Cr-Cr-N torsional angle to its observed value.

The spin eigenfunction of lowest energy is a nonet state, corresponding to the spin alignment of the eight electrons of the Cr^{II} dimer. Other spin states, corresponding to a total (singlet) or partial (quintet) covalent coupling of the metal electrons, were found much higher. The Cr⋯Cr distance is computed to be longer than observed (2.86 Å vs. 2.63 Å) but the Cr–hydride (1.81 Å) and the Cr–C (2.26 Å) distances are consistent with the experimental values. A most surprising result, however, is the stability of this isomer with respect to the inverse-sandwich form: an energy difference of 1.28 eV (29.6 kcal mol^{-1}) was calculated in favor of the model of **1**, which is supported by an increase of the HOMO–LUMO gap to 3.5 eV. As noted above, this unexpected order of the relative stabilities is a consequence of the energetically demanding reduction of benzene in **2**, which is itself due to the reluctance of chromium in this complex to adopt a d^5 configuration. The unexpectedly low energy of the phenyl hydride provides a straightforward explanation for its puzzling stability and for the need for an indirect pathway to obtain isomer **2**.

The antiferromagnetic coupling observed in **1** was looked for by obtaining a single determinant, broken-symmetry (BS) singlet state according to the procedure advocated by Noodleman.[7] The BS state was indeed found to be most stable and had an adiabatic energy difference of 1014 cm^{-1} (2.9 kcal mol^{-1}) with respect to the high-spin (HS) state, which confirms the existence of an antiferromagnetic, singlet ground state, coupling the eight metallic electrons. The calculated energy difference between the ground states of the models of **1** and **2** therefore reaches 32.5 kcal mol^{-1}. At variance with the case most frequently encountered, the metal–metal distance optimized for the BS state appreciably differs from that of the high-spin state. It decreases from 2.86 to 2.78 Å; the Cr–H and the Cr–C distances also decrease by 0.03 and 0.01 pm, respectively, showing that the mediation of the antiferromagnetic interaction by the bridging ligands induces a significant bonding character.

To reproduce the observed distortion of the molecular structure without explicitly introducing the bulky substituents in the calculation, one N-Cr-Cr-N dihedral angle was constrained to retain its experimental value while re-optimizing the whole geometry. Indeed this sole constraint resulted in reproducing the dihedral angle of approximately 130° observed between the Cr-Cr-H1 and the Cr-Cr-C64 planes (Figure 1, Figure 3 b). The energy loss due to the distortion is equal to 6.0 $\mathrm{kcal\,mol^{-1}}$, which means that the observed structure of **1** remains more stable than **2** by 26.5 $\mathrm{kcal\,mol^{-1}}$, assuming that the strength of the antiferromagnetic coupling was not modified.

To summarize, DFT calculations carried out on unsubstituted models of isomers **1** and **2** confirm that the inverse-sandwich complex **2** has a spin ground state of $S=3$. However, this compound cannot be considered the product of a typical reductive C–H elimination process, since the Cr atoms retain the formal oxidation state of II, and the two-electron reduction affects the bridging benzene molecule and lengthens the C–C bonds substantially. The model of the phenyl hydride complex **1** deprived of its bulky substituents displays a highly symmetric structure at variance with the experimentally observed geometry. Constraining one N-Cr-Cr-N dihedral angle restores the observed structure at a cost of 6.0 $\mathrm{kcal\,mol^{-1}}$. The lowest spin eigenstate is ^{9}A, but broken-symmetry calculations confirm the existence of an antiferromagnetic coupling of the metal electrons. Quite unexpectedly, even in its distorted geometry the model of **1** is calculated to be significantly more stable than its inverse-sandwich isomer. This result provides a simple, though unforeseen interpretation of the high thermal stability of **1**.

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[1] a) D. S. Wass, *Dalton Trans.* **2007**, 816 – 819; b) J. T. Dixon, M. J. Green, F. M. Hess, D. H. Morgan, *J. Organomet. Chem.* **2004**, *689*, 3641 – 3668.

[2] a) R. D. Köhn, *Angew. Chem.* **2008**, *120*, 251 – 253; *Angew. Chem. Int. Ed.* **2008**, *47*, 245 – 247.

[3] W. H. Monillas, G. P. A. Yap, K. H. Theopold, *Angew. Chem.* **2007**, *119*, 6812 – 6814; *Angew. Chem. Int. Ed.* **2007**, *46*, 6692 – 6694.

[4] Y.-C. Tsai, P.-Y. Wang, S.-A. Chen, J.-M. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 8066 – 8067.

[5] Gaussian 03 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.

[6] All calculations were carried out by using the B3LYP functional and valence double-ζ (D95V) atomic basis sets for H, C, and N, supplemented with one polarization function. Chromium was described with a Hay–Wadt small-core potential and a valence double-ζ (LANL2DZ) basis set supplemented with one f-type polarization function. As noticed by a reviewer, the reliability of DFT is controversial for the calculation of energy differences between states of different spin multiplicities in transition-metal compounds, when the difference in spin pairing occurs mostly or exclusively on the metal. Cases have been documented for which GGA functionals and, to a lesser extent, the standard B3LYP functional advantage the state of lower spin multiplicity (see, for example, "Principles and Applications of Density Functional Theory in Inorganic Chemistry I": J. N. Harvey, *Struct. Bonding (Berlin)* **2004**, *112*, 151 – 183; A. Ghosh, P. Taylor, *Curr. Opin. Chem. Biol.* **2003**, *7*, 113 – 124). Even though the molecular spin states of the two isomers considered in the present work are strikingly different, both arise from the same high-spin quintet configuration assigned to the $\mathrm{Cr^{II}}$ atoms in the two compounds. The spin state of the metal atoms is therefore basically the same in both complexes.

[7] L. Noodleman, C. Y. Peng, D. A. Case, J. M. Mouesca, *Coord. Chem. Rev.* **1995**, *144*, 199 – 244, and references therein.