

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**, $\{i\text{Pr}_2(\text{C}_6\text{H}_3)_2\text{nacnac} = 2,4\text{-pentane-}N,N'\text{-bis}(2,6\text{-diisopropylphenyl})\text{ketiminate}$) 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

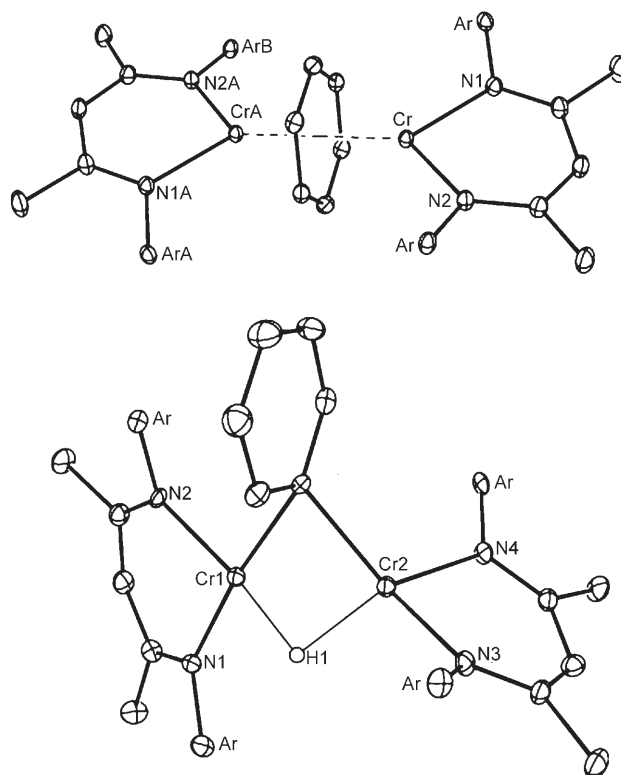


Figure 1. The molecular structure observed for isomers **2** (top) and **1** (bottom).

have been replaced by hydrogen atoms.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 $26.5 \text{ kcal mol}^{-1}$, in spite of an important deformation presumably induced by the bulky substituents.

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 $3.60e$, which is much higher than the expected spin density of around $3e$. This excess of spin density is compensated by a strongly negative density of $-1.19e$ 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 $+0.60e$ 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 $-2e$ because of the covalency of the interactions and also because of π donation, it is nevertheless significantly negative ($-0.54e$). 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 $i\text{Pr}_2(\text{C}_6\text{H}_3)$ groups. The environment of both metal atoms becomes nearly square planar, and H1 and C64 (phenyl) lie in the same plane as the $\{\text{Cr}(\text{nacnac})\}$ moieties, so that the optimized geometry of the complex is very close to C_{2v} symmetry (Figure 3a).

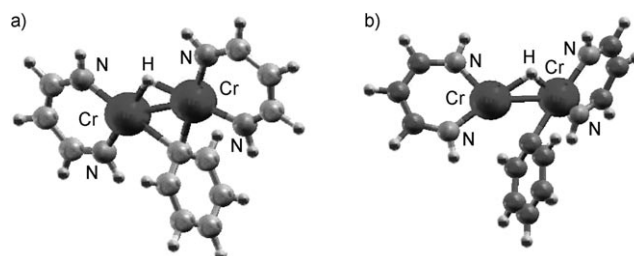


Figure 3. Geometries optimized for the model of isomer **1** from UB3LYP calculations: a) without constraint; b) by constraining one N–Cr–Cr–N torsional angle to its observed value.

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.

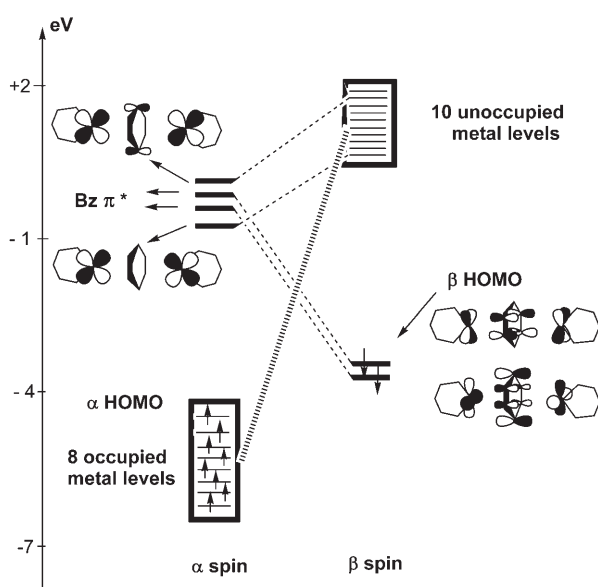


Figure 2. Frontier orbitals obtained for the high-spin (7B_g) state of lowest energy obtained for the model of isomer **2** from UB3LYP calculations.

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 3b). The energy loss due to the distortion is equal to 6.0 kcal mol⁻¹, which means that the observed structure of **1** remains more stable than **2** by 26.5 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 kcal mol⁻¹. The lowest spin eigenstate is ⁹A, 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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