

Binding and activation of small molecules by a quintuply bonded chromium dimer†

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Cite this: *Chem. Commun.*, 2014, 50, 2579Received 15th November 2013,
Accepted 8th January 2014

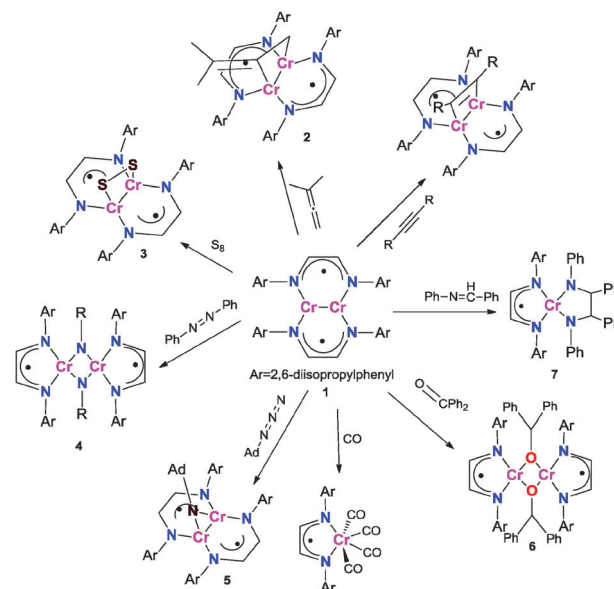
DOI: 10.1039/c3cc48746f

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The quintuply bonded $[\text{H}^{\text{iPr}}\text{Cr}]_2$ reacts with various small molecules, revealing a pattern of two kinds of transformations. Unsaturated molecules that are neither polar nor oxidizing form binuclear $[2+n]$ cycloaddition products retaining Cr–Cr quadruple bonds. In contrast, polar or oxidizing molecules effect the complete cleavage of the Cr–Cr bond.

Occasioned by the discovery of a dinuclear chromium complex featuring a sterically accessible quintuple metal–metal bond, we have begun to explore the reactivity of this novel functional group unique to transition metal chemistry. Recent studies indicate that M–M quintuple bonds have a remarkable reaction chemistry.^{1–16} Herein we describe the products of reactions between quintuply bonded $[\text{H}^{\text{iPr}}\text{Cr}]_2$ (**1**, where $\text{H}^{\text{iPr}} = \text{Ar}-\text{N}=\text{C}(\text{H})-(\text{H})\text{C}=\text{N}-\text{Ar}$, with $\text{Ar} = 2,6\text{-diisopropylphenyl}$)¹⁷ and various small molecules (Scheme 1). These reactions are of interest in their own right and make for fascinating comparisons with the reactivities of other binuclear metal complexes.

1 reacts rapidly with molecules containing multiple bonds. For example, we have previously described $[2+2]$ cycloaddition reactions between **1** and alkynes.¹⁸ While the analogous reaction with ethylene is apparently reversible, **1** adds to the destabilized C=C double bond of 1,1-dimethylallene, yielding another isolable $[2+2]$ cycloaddition product, namely $[\text{H}^{\text{iPr}}\text{Cr}]_2(\mu-\eta^1:\eta^1\text{-H}_2\text{CCMe}_2)$ (**2**, see Fig. 1). The terminal C=C bond of the allene ligand has added across the two metal centers, forming a four-membered dimetallacycle. The C53–C54 distance of 1.466(5) Å and the Cr–Cr distance of 1.9462(8) Å are consistent with a two-electron reduction of allene and concomitant oxidation of the Cr–Cr center, which, however, retains the short Cr–Cr distance characteristic of a quadruple bond (see Table 1). The other C=C bond of the allene remains essentially unperturbed (1.346(5) Å).



Scheme 1 Reactions of **1** with alkyne, allene, sulfur, $\text{PhN}=\text{NPh}$, AdN_3 , CO, benzophenone and benzylideneaniline.

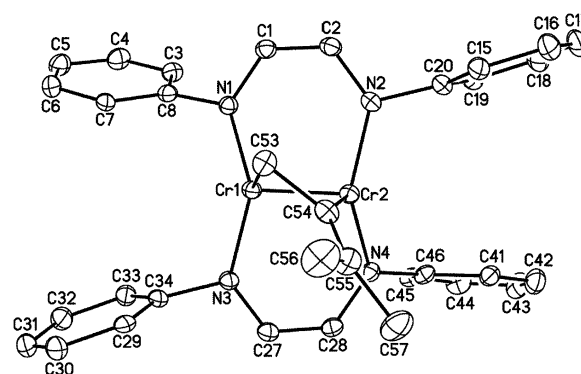


Fig. 1 The molecular structure of **2** (30% probability level). Ligand *i*-Pr groups and H-atoms have been omitted for clarity.

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† Electronic supplementary information (ESI) available: Preparative and crystallographic data. CCDC 971178–971183. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48746f

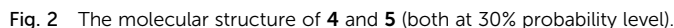
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^a Twist angle (X-X)-(Cr-Cr) (X = C or S). ^b Dihedral angle between two ligand planes (see the ESI for details). ^c Average bond lengths in the α -diimine backbones. ^d Average.

Oxygen atom sources, such as O₂, N₂O, and NO led to decomposition of **1** accompanied by loss of the diimine ligand. This motivated us to extend the exploration to less oxidizing chalcogens. Thus, treatment of an Et₂O–toluene solution of **1** with elemental sulphur, at room temperature, caused the initially green solution to turn deep blue. A standard work-up of the reaction and recrystallization from diethyl ether yielded the simple binuclear adduct, [H⁺L^{ipr}Cr]₂(S₂) (**3**) in modest yield (20%). The molecular structure of **3** is depicted in Fig. S1 (ESI[†]); it features a four-membered Cr₂S₂ ring. The “supershort” (Cr–Cr < 2.0 Å) Cr–Cr bond of **3** (1.9305(8) Å) is appreciably longer than that in **1** (1.8028(9) Å), indicating an oxidation from Cr(I) to Cr(II) and hence a bond order reduced to 4. The S–S bond length of 2.0513(10) Å approximates that of Kempe’s disulfide analog (2.058(4) Å),² which, however, features perpendicular coordination of the S₂^{2−} unit and that of Cp₂Cr₂(μ-S)₂(μ-η¹-η¹-S₂) (2.028(2) Å).¹⁹ As is typical of the [2+2] cycloaddition products of **1**, the Cr₂S₂ core is not perfectly planar. The (S–S)–(Cr–Cr) twist angle for the core is 15.6°, somewhat smaller than the analogous angles in the alkyne adducts and **2**.

An isoelectronic - but less oxidizing - analog of O_2 is azobenzene ($\text{PhN}=\text{NPh}$). When one equivalent of the latter



The average bond lengths of C–C, C–N bonds in the backbone of the α -diimine ligand are 1.395(11) and 1.380(9) Å, characteristic of a diimine radical anion; accordingly, chromium is in the formal oxidation state +III ($S = 3/2$). The effective magnetic moment of **4** at room temperature was 2.4(1) μ_B , consistent with antiferromagnetic coupling, both between the metal and its radical ligand as well as between the chromium atoms.

The reaction between $(\mu\text{-}\eta^1\text{:}\eta^1\text{-H}^i\text{L}^i\text{Pr})_2\text{Cr}_2$ (**1**) and sterically demanding Ad-N_3 afforded another imido complex, namely

$[\text{H}^{\text{iPr}}\text{Cr}]_2(\text{NAd})$ (**5**), as shown in Fig. 2 (bottom). Only one imido group has been added across the Cr–Cr bond. Once again, we suggest that a five-membered [2+3] cycloaddition product may be formed first, which rapidly extrudes N_2 . The bond distances and angles of **5** are comparable to those of other known bridging imido complexes of chromium.^{22–26} Similar to the geometries of the [2+2] cycloaddition products, the elongated Cr–Cr distance of 1.9575(11) Å is consistent with the two-electron oxidation of the Cr_2 unit (to $\text{Cr}(\text{II})$). **5** is also diamagnetic, presumably due to metal–metal quadruple bonding.

Finally, we were interested in studying the reactivity of **1** toward unsaturated molecules featuring X–Y bonds (X, Y = C, N, O). Exposure of a benzene solution of **1** to CO (1 atm) produced the dark blue carbonyl $[\text{H}^{\text{iPr}}\text{Cr}(\text{CO})_4]$, as confirmed by ^1H NMR spectroscopy.²¹ The reaction of **1** with benzophenone resulted in dinuclear $[\text{H}^{\text{iPr}}\text{Cr}(\mu\text{-OPh})_2]$ (**6**). The structure of **6** (shown in Fig. S2, ESI†) reveals a benzophenone-bridged dimer with square planar Cr centers. The average carbon–oxygen bond length of the benzophenone is 1.355(5) Å, which is much longer than the 1.230(3) Å in benzophenone,²⁷ suggesting some degree of reduction of the C=O bonds. The average bond lengths of C–C, C–N bonds of the backbone of the α -diimine ligand are 1.360(6) and 1.336(6) Å, consistent with those of a monoanionic diimine ligand.²¹ These structural features suggest that **6** is a $\text{Cr}(\text{II})$ complex. Like $[\text{H}^{\text{iPr}}\text{Cr}(\mu\text{-Cl})_2]$,¹⁷ **6** exhibited a simple isotropically shifted and broadened ^1H NMR spectrum in C_6D_6 , with chemical shifts at 96, 14.6, 3.2, 1.56, and -13.0 ppm. $\mu_{\text{eff}}(\text{RT})$ of this complex was found to be 5.1(2) μ_{B} (3.6(1) μ_{B} per chromium), which is consistent with two antiferromagnetically coupled $\text{Cr}(\text{II})$ metal centers ($S = 2$) coordinated by ligand radicals ($S = 1/2$).

In contrast to **6**, reductive coupling of C=N double bonds was observed upon exposure of **1** to four equivalents of trans-benzylideneaniline. The reaction was found to form the coupling product, $[\text{H}^{\text{iPr}}\text{Cr}(\kappa^2\text{-N}_2\text{C}_{26}\text{H}_{22})]$ (**7**). The crystal structure is shown in Fig. 3. **7** adopts tetrahedral coordination about chromium

with the α -diimine apparently being in the singly reduced state (see Table 1). The room temperature effective magnetic moment of **7** was found to be 2.9(1) μ_{B} , consistent with a $\text{Cr}(\text{III})$ metal center ($S = 3/2$) strongly coupled to a ligand radical ($S = 1/2$).

In summary, reactivity studies on a quintuply bonded dichromium complex supported by α -diimine ligands have been extended to a variety of molecules. The products are varied and their structures differ from those established for quintuply bonded complexes supported by other ligands. A pervasive feature of **1** seems to be the formation of [2+ n] cycloaddition products with nonpolar substrates. Polar, heteroatomic multiple bonds on the other hand effect complete cleavage of the metal–metal bond.

This work was supported by the NSF (CHE-0911081).

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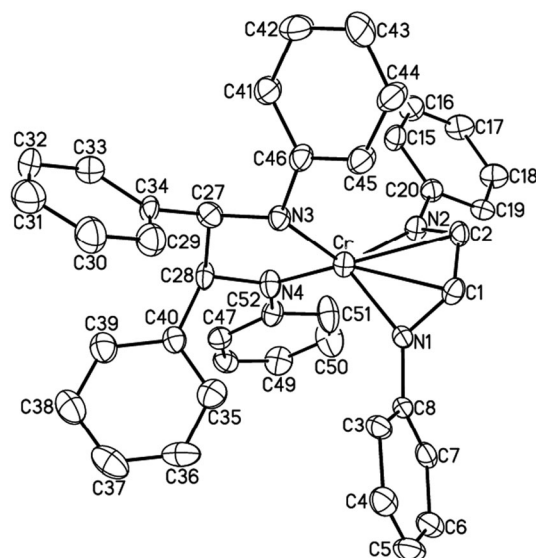


Fig. 3 The molecular structure of **7** (30% probability level).

