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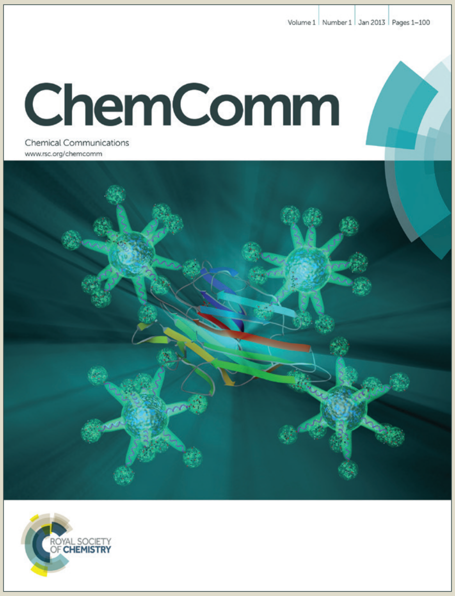

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# Binding and Activation of Small Molecules by a Quintuply Bonded Chromium Dimer

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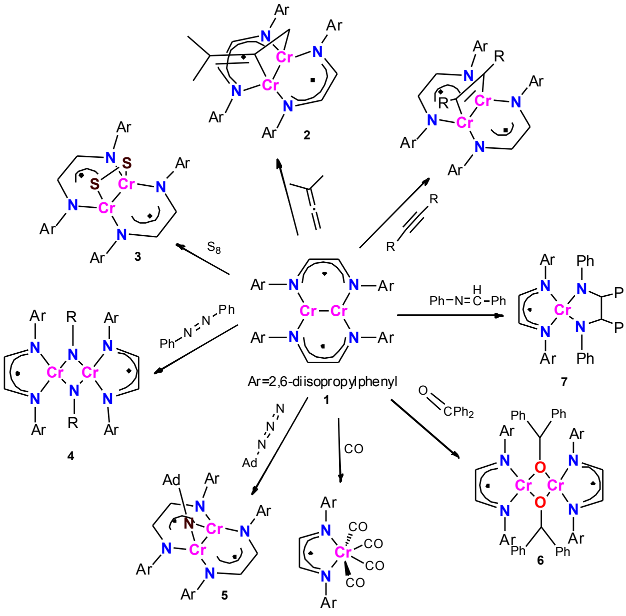
**The quintuply bonded [$^{H}L^{iPr}Cr]_2$ reacts with various small molecules, revealing a pattern of two kinds of transformations. Unsaturated molecules that are neither polar nor oxidizing form binuclear [2+n} cycloaddition products retaining Cr-Cr quadruple bonds. In contrast, polar or oxidizing 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 remarkable reaction chemistry.[1-8,9-15,16] Herein we describe the products of reactions between quintuply bonded [$^{H}L^{iPr}Cr]_2$ (**1**, where $^{H}L^{iPr}$ = Ar-N=C(H)-(H)C=N-Ar, with Ar = 2, 6-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.



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

**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 [$^{H}L^{iPr}Cr]_2(\mu-\eta^1:\eta^1-H_2CCCMe_2)$ (**2**, see Figure 1). The terminal C=C bond of the allene ligand has added across the two metal centers, forming a four-membered dimetallcycle. 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). The core of **2** adopts an almost planar geometry with a (C-C)-(Cr-Cr) twist angle of 24.3°, similar to the aforementioned alkyne adducts.[18] The $^{1}H$ NMR spectrum of **2** exhibited sharp resonances consistent with a diamagnetic ground state of the molecule.

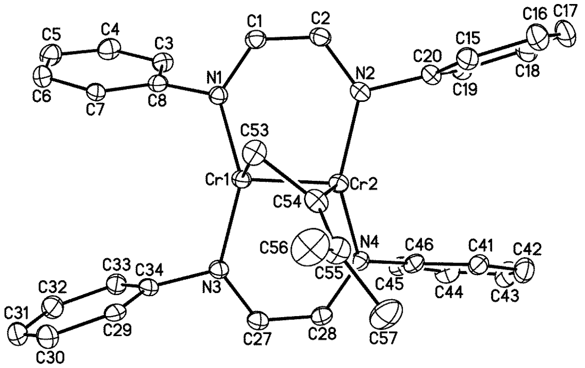


**Figure 1.** The molecular structure of **2** (30% probability level). Ligand i-Pr groups and H-atoms have been omitted for clarity.

Oxygen atom sources, such as $O_2$, $N_2O$, 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 $Et_2O$/toluene solution of **1** with elemental sulphur, at room temperature, caused the initially green solution to turn deep blue. Standard work-up of the reaction and recrystallization from diethyl ether yielded the simple binuclear adduct, [$^{H}L^{iPr}Cr]_2(S_2)$ (**3**) in modest yield (20%). The molecular structure of **3** is depicted in Figure S1; it features a four-membered $Cr_2S_2$ ring. The "supershort" (Cr-Cr < 2.0Å) 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 $S_2^{2-}$ unit, and that of $Cp_2Cr_2(\mu\text{-}S)_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-}S_2)$ (2.028(2)Å)[19]. As is typical of the [2+2] cycloaddition products of **1**, the $Cr_2S_2$ core is not perfectly planar. The (S-S)-(Cr-Cr) twist angle for the core is 15.6º, somewhat smaller than the analogous angles in the alkyne adducts and **2**.

**Table 1** Selected interatomic distances (Å) and angles (º).

| | Cr-Cr | C-C* | C-N* | θ[a] | δ[b] |
|---|---|---|---|---|---|
| **1** | 1.8028(9) | 1.350(5) | 1.368(3) | N/A | N/A |
| **2** | 1.9462(8) | 1.337(5) | 1.380(4) | 24.3º | 151º |
| **3** | 1.9305(8) | 1.367(3) | 1.360(3) | 15.6º | 143º |
| **4** | 2.498(4) | 1.395(11) | 1.380(9) | N/A | N/A |
| **5** | 1.9575(11)† | 1.346(6) | 1.385(6) | N/A | 142º† |
| **6** | 3.1667(15) | 1.360(6) | 1.336(6) | N/A | N/A |
| **7** | N/A | 1.383(6) | 1.355(5) | N/A | N/A |
| **1**-butyne[18] | 1.9248(7) | 1.352(4) | 1.370(4) | 23.7º | 146º |

[a] twist angle (X-X)-(Cr-Cr) (X = C or S). [b] dihedral angle between two ligand planes (see SI for detail). *Average bond lengths in the α-diimine backbones. †Average

Table **1** contains selected bond lengths and angles for compounds **2-7**. All the 'cycloaddition' products of **1** that maintain Cr-Cr bonds, i.e. **2**, **3**, and **1**-2-butyne, exhibit the twisted $\mu\text{-}\eta^1\text{:}\eta^1$ bonding mode for the $X_2$ ligands (X = C, S); this differs from the perpendicular (i.e. $\mu_2\text{-}\eta^2\text{:}\eta^2$) bonding motif more typically observed for complexes with metal-metal bonds, e.g. in Kempe's aminopyridinato dichromium complexes.[2-4, 20] At the same time, the dihedral angles (δ) between the α-diimine ligand planes are significantly larger than those of the aminopyridinato complexes (e.g. 107º for both the disulfide and the tolylacetylene adduct). In other words, the $[L_2Cr_2]$ fragments of the α-diimine complexes are considerably flatter than those with aminopyridinato ligands. The near preservation of the planar geometry of **1** and the formation of unsaturated four-membered $Cr_2X_2$ rings as opposed to tetrahedrane-like structures is unlikely to be steric in origin. An electronic explanation may be rooted in the electronic flexibility afforded by the redox-active α-diimine ligands; this remains to be explored.

An isoelectronic – but less oxidizing - analog of $O_2$ is azobenzene (PhN=NPh). When one equivalent of the latter was added to a solution of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}{}^{H}L^{iPr})_2Cr_2$ (**1**) in diethyl ether, subsequent work-up and recrystallization produced red-brown crystals of dinuclear complex $[{}^{H}L^{iPr}Cr(\mu\text{-}NPh)]_2$ **(4)** in 40% isolated yield. **4** is a dinuclear complex with bridging imido ligands (Figure 2, top). This reaction may well go through an unstable [2+2] cycloaddition intermediate, which suffers oxidative addition, due to the high electronegativity of nitrogen. The molecular structure of **4** features four-coordinate chromium (ignoring the rather long Cr-C interactions) adopting pseudo-tetrahedral geometry, which is the preferred geometry of 4-coordinate Cr(III). The N=N double bond has been severed completely ($N\cdots N_{avg}$ = 2.695Å). Similarly, the distance between the two chromium atoms in **4** is 2.498(4)Å, indicating the absence of any significant bonding interactions.

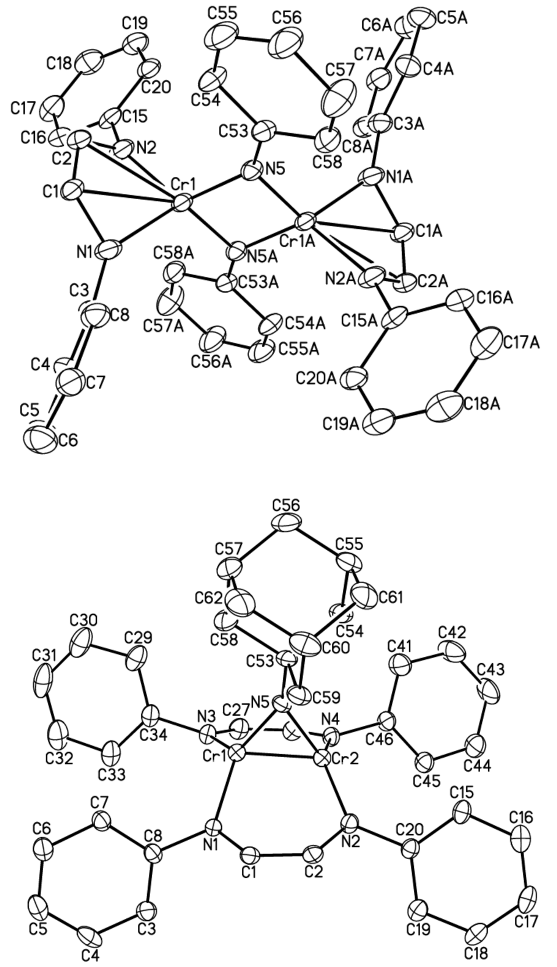


**Figure 2** The molecular structure of **4** and **5** (both at 30% probability level).

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), consistent with antiferromagnetic coupling, both between the metal and its radical ligand as well as between the chromium atoms.

The reaction between $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}{}^{H}L^{iPr})_2Cr_2$ (**1**) and sterically demanding Ad-$N_3$ afforded another imido complex, namely $[{}^{H}L^{iPr}Cr]_2(NAd)$ (**5**), as shown in Figure 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 Cr(II)). **5** is also diamagnetic presumably due to metal-metal quadruple bonding.

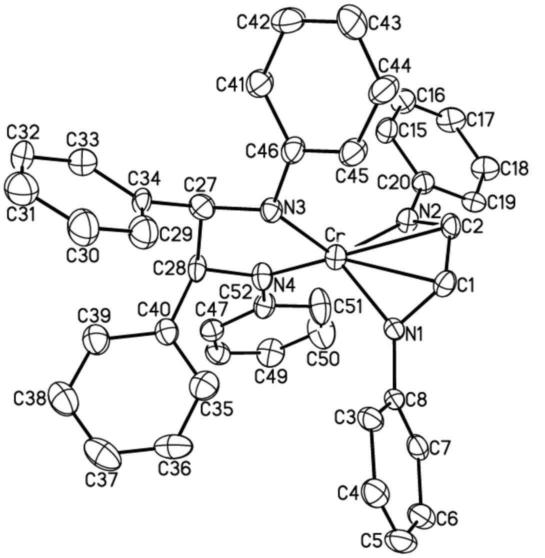


**Figure 3** The molecular structure of **7** (30% probability level).

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 ${}^{H}L^{iPr}Cr(CO)_4$, as confirmed by ${}^{1}H$ NMR spectroscopy.[21] The reaction of **1** with benzophenone resulted in dinuclear $[{}^{H}L^{iPr}Cr(\mu\text{-}OPh_2)]_2$ (**6**). The structure of **6** (shown in Figure S2) 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 Cr(II) complex. Like $[{}^{H}L^{iPr}Cr(\mu\text{-}Cl)]_2$,[17] **6** exhibited a simple isotropically shifted and broadened ${}^{1}H$ NMR spectrum in $C_6D_6$, with chemical shifts at 96, 14.6, 3.2, 1.56, and -13.0 ppm. $\mu_{eff}$(RT) of this complex was found to be 5.1(2) $\mu_B$ (3.6(1) $\mu_B$ per chromium), which is consistent with two antiferromagnetically coupled Cr(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, ${}^{H}L^{iPr}Cr(\kappa^2\text{-}N_2C_{26}H_{22})$ (**7**). The crystal structure is shown in Figure 4. **7** adopts tetrahedral coordination about chromium with the a-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) $\mu_B$, consistent with a Cr (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.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: preparative and crystallographic data; See DOI: 10.1039/b000000x/

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