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

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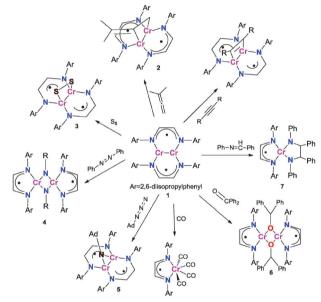
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The quintuply bonded [HLiPrCr]2 reacts with various small molecules, revealing a pattern of two kinds of transformations. Unsaturated molecules that are neither polar nor oxidizing form binuclear [2+n] cycloaddition products retaining Cr-Cr quadruple 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 $[^{H}L^{iPr}Cr]_{2}$ (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.

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 [HLiPrCr]₂(μ-η¹:η¹-H₂CCCMe₂) (2, see Fig. 1). The terminal C=C bond of the allene ligand has added across the two metal centers, forming a fourmembered dimetallacycle. The C53-C54 distance of 1.466(5) Å and the Cr-Cr distance of 1.9462(8) Å are consistent with a twoelectron 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).

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Scheme 1 Reactions of 1 with alkyne, allene, sulfur, PhN=NPh, AdN₃, CO, benzophenone and benzylideneaniline.

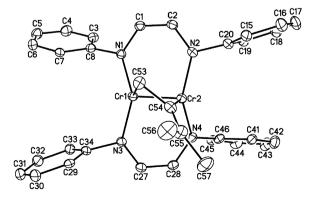


Fig. 1 The molecular structure of 2 (30% probability level). Ligand i-Pr groups and H-atoms have been omitted for clarity

[†] 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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Table 1 Selected interatomic distances (Å) and angles (°)

	Cr-Cr	$C-C^c$	$C-N^c$	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)	24.3°	151°
3	1.9305(8)	1.367(3)	1.360(3)	15.6°	143°
4	2.498(4)	1.395(11)	1.380(9)	N/A	N/A
5	$1.9575(11)^d$	1.346(6)	1.385(6)	N/A	$142^{\circ d}$
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)	23.7°	146°
	3.1667(15) N/A	1.360(6) 1.383(6)	1.336(6) 1.355(5)	N/A N/A	

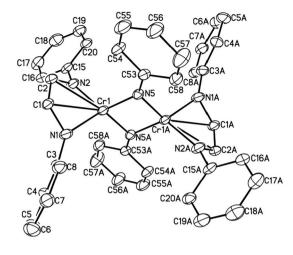
 $[^]a$ Twist angle (X–X)–(Cr–Cr) (X = C or S). b Dihedral angle between two ligand planes (see the ESI for details). c Average bond lengths in the α-diimine backbones. ^d Average.

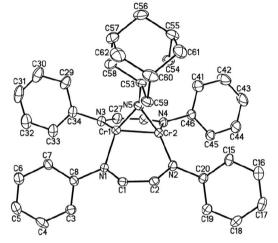
The core of 2 adopts an almost planar geometry with a (C-C)-(Cr-Cr) twist angle of 24.3°, similar to the aforementioned alkyne adducts. 18 The ¹H NMR spectrum of 2 exhibited sharp resonances consistent with a diamagnetic ground state of the molecule.

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, [HLiPrCr]₂(S₂) (3) in modest yield (20%). The molecular structure of 3 is depicted in Fig. S1 (ESI†); it features a four-membered Cr_2S_2 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), which, however, features perpendicular coordination of the S₂²⁻ unit and that of $Cp_2Cr_2(\mu-S)_2(\mu-\eta^1-\eta^1-S_2)$ (2.028(2) Å). 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.

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 μ - η^1 : η^1 bonding mode for the X_2 ligands (X = C, S); this differs from the perpendicular (i.e. μ_2 - η^2 : η^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. 107° for both the disulfide and the tolylacetylene adduct). In other words, the [L2Cr2] 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 fourmembered Cr₂X₂ 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 O2 is azobenzene (PhN=NPh). When one equivalent of the latter





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

was added to a solution of $(\mu-\eta^1:\eta^1-HL^{iPr})_2Cr_2$ (1) in diethyl ether, subsequent work-up and recrystallization produced redbrown crystals of dinuclear complex [HLiPrCr(μ-NPh)]₂ (4) in 40% isolated yield. 4 is a dinuclear complex with bridging imido ligands (Fig. 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 pseudotetrahedral geometry, which is the preferred geometry of 4-coordinate Cr(III). The N=N double bond has been severed completely $(N \cdot \cdot \cdot N_{\text{avg}} = 2.695 \text{ Å})$. Similarly, the distance between the two chromium atoms in 4 is 2.498(4) Å, indicating the absence of any significant bonding interactions.

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) $\mu_{\rm B}$, consistent with antiferromagnetic coupling, both between the metal and its radical ligand as well as between the chromium atoms.

The reaction between (μ-η¹:η¹-HLiPr)2Cr2 (1) and sterically demanding Ad-N₃ afforded another imido complex, namely ChemComm Communication

 $[^{H}L^{iPr}Cr]_{2}(NAd)$ (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 Cr(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 HLiPrCr(CO)4, as confirmed by H NMR spectroscopy.²¹ The reaction of 1 with benzophenone resulted in dinuclear [HL^{iPr}Cr(μ-OPh₂)]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 Cr(II) complex. Like [HL^{iPr}Cr(μ-Cl)]₂, ¹⁷ 6 exhibited a simple isotropically shifted and broadened ¹H NMR spectrum in C₆D₆, with chemical shifts at 96, 14.6, 3.2, 1.56, and -13.0 ppm. $\mu_{\text{eff}}(RT)$ of this complex was found to be 5.1(2) $\mu_{\rm B}$ (3.6(1) $\mu_{\rm B}$ per chromium), which is consistent with two antiferromagnetically coupled $Cr(\pi)$ 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 transbenzylideneaniline. The reaction was found to form the coupling product, ${}^HL^{iPr}Cr(\kappa^2-N_2C_{26}H_{22})$ (7). The crystal structure is shown in Fig. 3. 7 adopts tetrahedral coordination about chromium

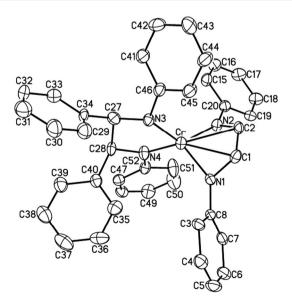


Fig. 3 The molecular structure of 7 (30% probability level).

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) $\mu_{\rm B}$, 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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