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

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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 [HLiPrCr]_2 (1, where HLiPr = Ar–N=CH–(H)C=CH–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 [LiPrCr]_2(μ-η:η^1)-H_2CCCMe_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, PhN=NPPh, 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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Table 1  Selected interatomic distances (Å) and angles (°)

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<th>Cr-Cr</th>
<th>C-C'</th>
<th>C-N'</th>
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<th>(\phi^b)</th>
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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 \(\alpha\)-diimine backbones. \(^d\) Average.

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

The core of 4 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.

Oxygen atom sources, such as \(\text{O}_2\), \(\text{N}_2\text{O}\), and \(\text{NO}\) 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 \(\text{Et}_2\text{O}-\text{toluene}\) solution of 1 with elemental sulphur, at room temperature, caused the initially green solution to turn deep blue. A standard work-up and recrystallization from diethyl ether yielded the simple binuclear adduct, \([\text{HLiPrCr}]_2(\text{S}_2)\) (3) in modest yield (20%). The molecular structure of 3 is depicted in Fig. S1 (ESI†); it features a four-membered \(\text{Cr}_2\text{S}_2\) 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),\(^2\) which, however, features perpendicular coordination of the \(\text{S}_2^2\) unit and that of \(\text{Cr}_2\text{S}_2(\mu-\eta^2-\eta^1-\text{S}^2)\) (2.028(2) Å).\(^3\) As is typical of the [2+2] cycloaddition products of 1, the \(\text{Cr}_2\text{S}_2\) 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-butene, exhibit the twisted \(\mu-\eta^1-\eta^1\) bonding mode for the \(\text{X}_2\) ligands (X = C, S); this differs from the perpendicular (i.e. \(\mu-\eta^2-\eta^2\)) 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 (\(\phi\)) between the \(\alpha\)-diimine ligand planes are significantly larger than those of the amino-pyridinato complexes (e.g. 107° for both the disulfide and the tolylacetylene adduct). In other words, the \([\text{L}_2\text{Cr}_2]\) fragments of the \(\alpha\)-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 \(\text{Cr}_2\text{X}_2\) rings as opposed to tetrahedra-like structures is unlikely to be steric in origin. An electronic explanation may be rooted in the electronic flexibility afforded by the redox-active \(\alpha\)-diimine ligands; this remains to be explored.

An isoelectronic – but less oxidizing – analog of \(\text{O}_2\) is azobenzene (Ph-N=NPh). When one equivalent of the latter was added to a solution of \((\mu-\eta^1-\eta^1,\mu^1-\text{HLiPr})\)\(_2\text{Cr}_2\) (1) in diethyl ether, subsequent work-up and recrystallization produced reddish crystals of dinuclear complex \([\text{HLiPrCr}(\mu-\text{NPh})]\)\(_2\) (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 pseudo-tetrahedral geometry, which is the preferred geometry of 4-coordinate Cr(m). The N–N double bond has been severed completely (\(\text{N}^- \cdot \text{N}^-\text{avg} = 2.695\) 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 \(\alpha\)-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 +II (S = 3/2). The effective magnetic moment of 4 at room temperature was 2.4(1) \(\mu_B\), consistent with antiferromagnetic coupling, both between the metal and its radical ligand as well as between the chromium atoms.

The reaction between \((\mu-\eta^1-\eta^1,\mu^1-\text{HLiPr})\)\(_2\text{Cr}_2\) (1) and sterically demanding Ad–N\(_3\) afforded another imido complex, namely...
toward unsaturated molecules featuring X–Y bonds (X, Y = C, N, O). Similar to the bridging imido complexes of chromium. 22–26

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 $^{1}L^{19}Cr(CO)_{6}$, as confirmed by $^{1}H$ NMR spectroscopy. 21 The reaction of 1 with benzophenone resulted in dinuclear $^{1}L^{19}Cr(OPh)_{2}$ (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 centers. The average carbon–oxygen bond length of the benzophenone–diimine complex is 1.360(6) Å, which is much longer than the 1.230(3) Å in benzophenone, 27 suggesting some degree of reduction of the center (X = CR–Cr=). Once again, we found to be 5.1(2) μB per chromium, which is consistent with a Cr(III) metal center. The molecular structure of 7 (30% probability level). The bond distances and angles of 7 are 5.19, 3.2, 1.56, and 3.15 (SI).

Notes and references