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

Jingmei Shen,‡ Glenn P. A. Yap and Klaus H. Theopold*

The quintuply bonded [\(\text{HLiPrCr} \)]\(_2\) 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 [\(\text{HLiPrCr} \)]\(_2\) (1, where \(\text{HLiPr} = \text{Ar–N}Q\text{C(H)–(H)C}Q\text{N–Ar}\), with \(\text{Ar} = 2,6\)-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 [\(\text{HLiPrCr} \)]\(_2\)(\(\mu-\eta^1:1\eta^1\text{C}_{5}C\text{C}C\text{Me}_{3}\)) (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==NPh, AdN\(_3\), CO, benzophenone and benzylideneaniline.

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA. E-mail: theopold@udel.edu

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‡ Current address: Department of Chemical and Biological Engineering, Northwestern University, USA.

Fig. 1  The molecular structure of 2 (30% probability level). Ligand i-Pr groups and H-atoms have been omitted for clarity.
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. 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, $[^1\text{H},^3\text{LiPr}]_2\text{Cr}_2(S_2)$ (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), which, however, features perpendicular coordination of the S2 ring and that of $\text{Cr}_2\text{S}_2(\mu-\eta^1:\eta^2-\text{N}^\text{Ph})_2$ (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 $\mu-\eta^1:\eta^1$ bonding mode for the $X_2$ ligands (X = C, S); this differs from the perpendicular (i.e. $\mu-\eta^1:\eta^1$) bonding motif more typically observed for complexes with metal–metal bonds, e.g. in Kempe’s aminopyridinato dichromium complexes. At the same time, the dihedral angles (δ) between the π-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 $[\text{L}_2\text{Cr}_2]$ fragments of the π-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 Cr2X2 rings as opposed to tetrahedrane-like structures is unlikely to be sterically hindered. An electronic explanation may be rooted in the electronic flexibility afforded by the redox-active π-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 was added to a solution of ($\mu-\eta^1:\eta^1\text{H},^3\text{LiPr}$)$_2\text{Cr}_2$ (1) in diethyl ether, subsequent work-up and recrystallization produced red-brown crystals of dinuclear complex $[^1\text{H},^3\text{LiPr}]_2\text{Cr}([\text{NPh}])_2$ (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 pseudotetrahedral geometry, which is the preferred geometry of 4-coordinate Cr(m). The N–N double bond has been severed completely (N–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 π-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 2.41(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 ($\mu-\eta^1:\eta^1\text{H},^3\text{LiPr}$)$_2\text{Cr}_2$ (1) and sterically demanding Ad–N$_3$ afforded another imido complex, namely...
[1\textsuperscript{149}I\textsuperscript{69}Cr\textsubscript{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\textsubscript{2}. The bond distances and angles of 5 are comparable to those of other known bridging imido complexes of chromium.\textsuperscript{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\textsubscript{2} unit (to Cr\textsuperscript{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 [1\textsuperscript{149}I\textsuperscript{69}Cr(CO)]\textsubscript{2}, as confirmed by \textsuperscript{1}H NMR spectroscopy.\textsuperscript{21} The reaction of 1 with benzophenone resulted in dinuclear [1\textsuperscript{149}I\textsuperscript{69}Cr(\mu-OPh\textsubscript{2})]\textsubscript{2} (6). The structure of 6 (shown in Fig. S2, ESI\textsuperscript{†}) 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,\textsuperscript{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 \textsuperscript{149}I–diimine ligand are 1.360(6) and 1.336(6) Å, consistent with those of a monoanionic diimine ligand.\textsuperscript{21} These structural features suggest that 6 is a Cr\textsuperscript{II} complex. Like [1\textsuperscript{149}I\textsuperscript{69}Cr(\mu-Cl)]\textsubscript{2},\textsuperscript{17} 6 exhibited a simple isotropically shifted and broadened \textsuperscript{1}H NMR spectrum in C\textsubscript{6}D\textsubscript{6} with chemical shifts at 96, 14.6, 3.2, 1.56, and \textendash 13.0 ppm. \(\mu_{\text{eff}}(\text{RT})\) of this complex was found to be 5.1(2) \(\mu_{\text{B}}\) (3.61(1) \(\mu_{\text{B}}\) 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=\textendash N double bonds was observed upon exposure of 1 to four equivalents of trans-benzylideneaniline. The reaction was found to form the coupling product, [1\textsuperscript{149}I\textsuperscript{69}Cr(\kappa^2-N\textsubscript{2}C\textsubscript{8}H\textsubscript{7})] (7). The crystal structure is shown in Fig. 7. 7 adopts tetrahedral coordination about chromium with the \(\pi\)-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) \(\mu_{\text{B}}\), consistent with a Cr\textsuperscript{II} 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 \(\pi\)-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