ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

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

Cite this: *Chem. Commun.*, 2014, **50**, 2579

Received 15th November 2013, Accepted 8th January 2014

DOI: 10.1039/c3cc48746f

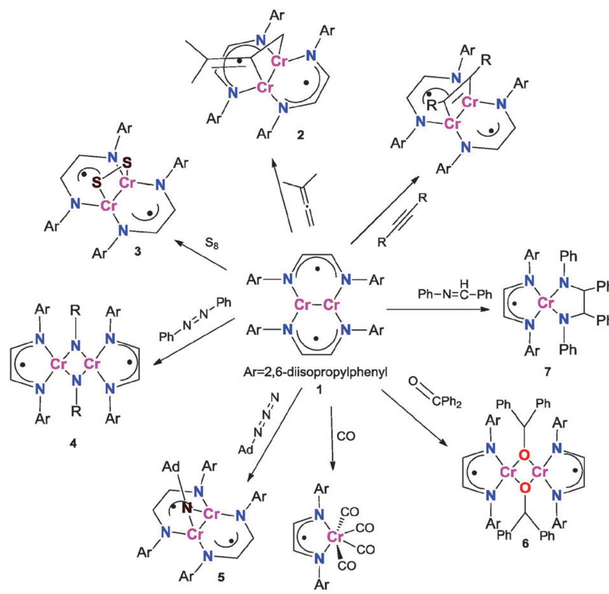
www.rsc.org/chemcomm

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

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 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 [$^{H}L^{iPr}$Cr]$_2$(μ-η^1: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═NPh, AdN$_3$, CO, benzophenone and benzylideneaniline.

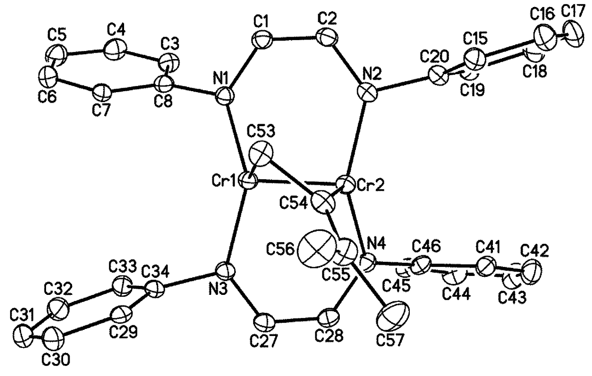


Fig. 1 The molecular structure of **2** (30% probability level). Ligand i-Pr groups and H-atoms have been omitted for clarity.

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

† 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

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

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°[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°

[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 ^{1}H NMR spectrum of **2** exhibited sharp resonances consistent with a diamagnetic ground state of the molecule.

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. A 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 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),[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 15.6°, 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 $\mu\text{-}\eta^1\text{:}\eta^1$ 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.* 107° 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 (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(III). The N═N double bond has been severed completely ($N\cdots N_{avg}$ = 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.

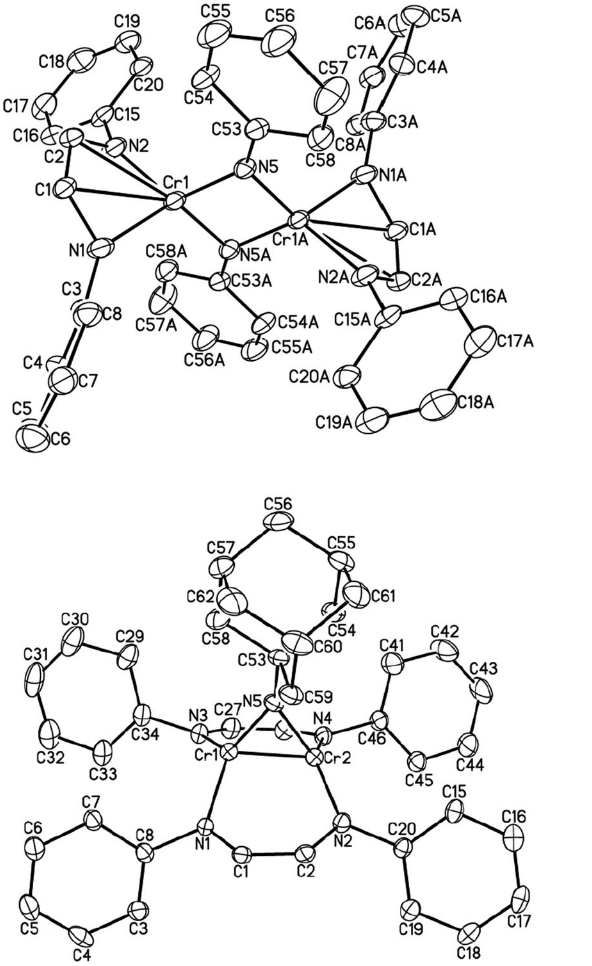


Fig. 2 The molecular structure of **4** and **5** (both at 30% probability level).

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

The reaction between $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}^{H}L^{iPr})_2Cr_2$ (**1**) and sterically demanding Ad–N_3 afforded another imido complex, namely

$[^{H}L^{iPr}Cr]_2(NAd)$ (**5**), as shown in 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 $^{H}L^{iPr}Cr(CO)_4$, 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 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 $[^{H}L^{iPr}Cr(\mu\text{-}Cl)]_2$,[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. μ_{eff}(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 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 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 Cr(III) metal center (S = 3/2) strongly coupled to a ligand radical (S = 1/2).

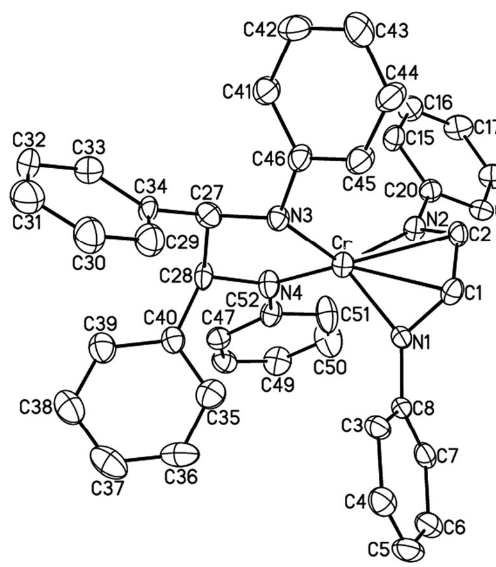


Fig. 3 The molecular structure of **7** (30% probability level).

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).

Notes and references

1 A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi and R. Kempe, *Chem.–Eur. J.*, 2013, **19**, 9825–9832.
2 E. S. Tamne, A. Noor, S. Qayyum, T. Bauer and R. Kempe, *Inorg. Chem.*, 2012, **52**, 329–336.
3 C. Schwarzmaier, A. Noor, G. Glatz, M. Zabel, A. Y. Timoshkin, B. M. Cossairt, C. C. Cummins, R. Kempe and M. Scheer, *Angew. Chem., Int. Ed.*, 2011, **50**, 7283–7286.
4 A. Noor, E. S. Tamne, S. Qayyum, T. Bauer and R. Kempe, *Chem.–Eur. J.*, 2011, **17**, 6900–6903.
5 A. Noor and R. Kempe, *Chem. Rec.*, 2010, **10**, 413–416.
6 F. R. Wagner, A. Noor and R. Kempe, *Nat. Chem.*, 2009, **1**, 529–536.
7 A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Nat. Chem.*, 2009, **1**, 322–325.
8 A. Noor, F. R. Wagner and R. Kempe, *Angew. Chem., Int. Ed.*, 2008, **47**, 7246–7249.
9 P.-F. Wu, S.-C. Liu, Y.-J. Shieh, T.-S. Kuo, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Chem. Commun.*, 2013, **49**, 4391–4393.
10 H.-G. Chen, H.-W. Hsueh, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem., Int. Ed.*, 2013, **52**, 10256–10260.
11 S.-C. Liu, W.-L. Ke, J.-S. K. Yu, T.-S. Kuo and Y.-C. Tsai, *Angew. Chem., Int. Ed.*, 2012, **51**, 6394–6397.
12 Y. L. Huang, D. Y. Lu, H. C. Yu, J. S. Yu, C. W. Hsu, T. S. Kuo, G. H. Lee, Y. Wang and Y. C. Tsai, *Angew. Chem., Int. Ed.*, 2012, **51**, 7781–7785.
13 Y.-C. Tsai, H.-Z. Chen, C.-C. Chang, J.-S. K. Yu, G.-H. Lee, Y. Wang and T.-S. Kuo, *J. Am. Chem. Soc.*, 2009, **131**, 12534–12535.
14 Y. C. Tsai, C. W. Hsu, J. S. Yu, G. H. Lee, Y. Wang and T. S. Kuo, *Angew. Chem., Int. Ed.*, 2008, **47**, 7250–7253.
15 Y.-C. Tsai, Y.-M. Lin, J.-S. K. Yu and J.-K. Hwang, *J. Am. Chem. Soc.*, 2006, **128**, 13980–13981.
16 C. Ni, B. D. Ellis, G. J. Long and P. P. Power, *Chem. Commun.*, 2009, 2332–2334.
17 K. A. Kreisel, G. P. Yap, O. Dmitrenko, C. R. Landis and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 14162–14163.
18 J. Shen, G. P. Yap, J. P. Werner and K. H. Theopold, *Chem. Commun.*, 2011, **47**, 12191–12193.
19 L. Y. Goh and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1986, 1474–1475.
20 M. J. Calhorda and R. Hoffmann, *Organometallics*, 1986, **5**, 2181–2187.
21 K. A. Kreisel, G. P. Yap and K. H. Theopold, *Inorg. Chem.*, 2008, **47**, 5293–5303.
22 W. H. Monillas, G. P. A. Yap and K. H. Theopold, *Inorg. Chim. Acta*, 2011, **369**, 103–119.
23 W. H. Monillas, G. P. Yap, L. A. MacAdams and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 8090–8091.
24 A. A. Danopoulos, D. M. Hankin, G. Wilkinson, S. M. Cafferkey, T. K. N. Sweet and M. B. Hursthouse, *Polyhedron*, 1997, **16**, 3879–3892.
25 A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1995, 2111–2123.
26 B. Moubaraki, K. S. Murray, P. J. Nichols, S. Thomson and B. O. West, *Polyhedron*, 1994, **13**, 485–495.
27 E. B. Fleischer, N. Sung and S. Hawkinson, *J. Phys. Chem.*, 1968, **72**, 4311–4312.