

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

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

Cite this: *Chem. Commun.*, 2014, 50, 2579Received 15th November 2013,
Accepted 8th January 2014

DOI: 10.1039/c3cc48746f

www.rsc.org/chemcomm

The quintuply bonded $[\text{H}^i\text{PrCr}]_2$ 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.

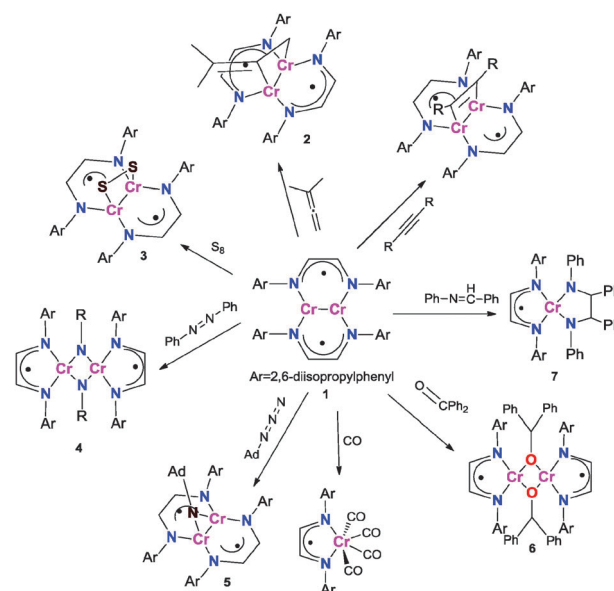
Occasioned by the discovery of a dinuclear chromium complex featuring a sterically accessible quintuple metal–metal bond, we have begun to explore the reactivity of this novel functional group unique to transition metal chemistry. Recent studies indicate that M–M quintuple bonds have a remarkable reaction chemistry.^{1–16} Herein we describe the products of reactions between quintuply bonded $[\text{H}^i\text{PrCr}]_2$ (**1**, where $\text{H}^i\text{Pr} = \text{Ar}-\text{N}=\text{C}(\text{H})-(\text{H})\text{C}=\text{N}-\text{Ar}$, with $\text{Ar} = 2,6\text{-diisopropylphenyl}$)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 $[\text{H}^i\text{PrCr}]_2(\mu-\eta^1:\eta^1\text{-H}_2\text{CCMe}_2)$ (**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).

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.



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

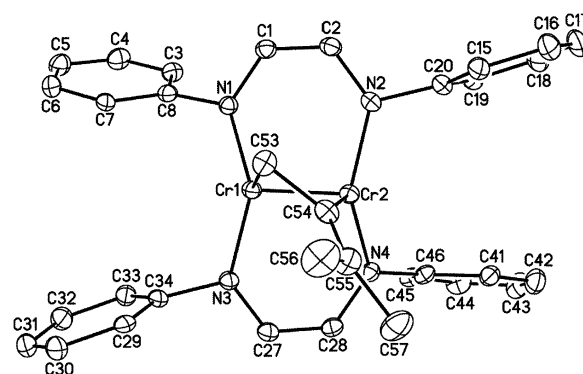


Fig. 1 The molecular structure of **2** (30% probability level). Ligand *i*-Pr groups and H-atoms have been omitted for clarity.



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°

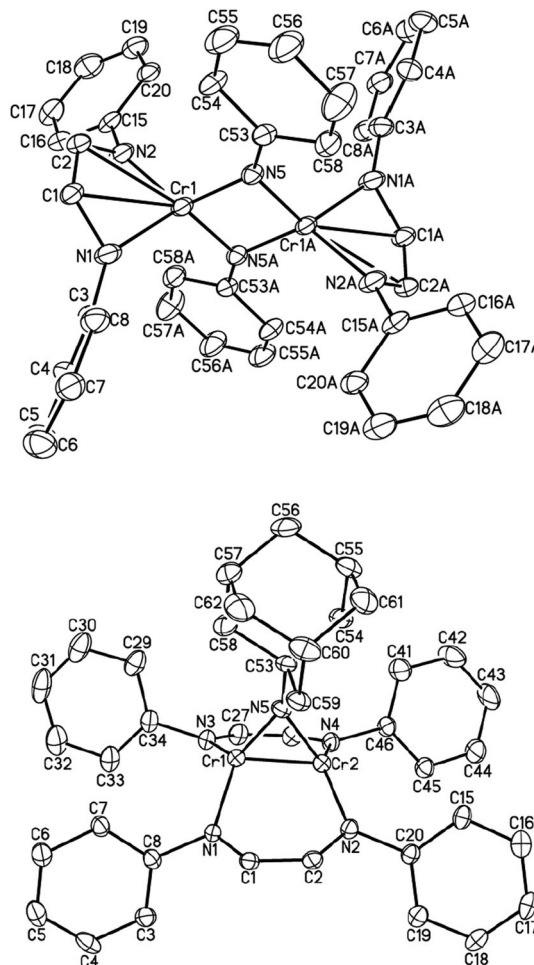
^a Twist angle (X–X)–(Cr–Cr) (X = C or S). ^b Dihedral angle between two ligand planes (see the ESI for details). ^c Average bond lengths in the α -diimine backbones. ^d Average.

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 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, [¹HⁱPrCr]₂(S₂) (**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),² which, however, features perpendicular coordination of the S₂²⁻ unit and that of Cp₂Cr₂(μ -S)₂(μ - η^1 - η^1 -S₂) (2.028(2) Å).¹⁹ 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-butynyl, exhibit the twisted μ - η^1 : η^1 bonding mode for the X₂ ligands (X = C, S); this differs from the perpendicular (*i.e.* μ - 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 four-membered 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

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

was added to a solution of (μ - η^1 : η^1 -HⁱPr)₂Cr₂ (**1**) in diethyl ether, subsequent work-up and recrystallization produced red-brown crystals of dinuclear complex [¹HⁱPrCr(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 pseudo-tetrahedral geometry, which is the preferred geometry of 4-coordinate Cr(III). The N=N double bond has been severed completely ($N \cdots N_{\text{avg}} = 2.695$ 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 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 (μ - η^1 : η^1 -HⁱPr)₂Cr₂ (**1**) and sterically demanding Ad–N₃ afforded another imido complex, namely



$[\text{H}^{\text{iPr}}\text{Cr}]_2(\text{NAd})$ (**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 $\text{Cr}(\text{II})$). **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 $[\text{H}^{\text{iPr}}\text{Cr}(\text{CO})_4]$, as confirmed by ^1H NMR spectroscopy.²¹ The reaction of **1** with benzophenone resulted in dinuclear $[\text{H}^{\text{iPr}}\text{Cr}(\mu\text{-OPh}_2)]_2$ (**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 $\text{Cr}(\text{II})$ complex. Like $[\text{H}^{\text{iPr}}\text{Cr}(\mu\text{-Cl})]_2$,¹⁷ **6** exhibited a simple isotropically shifted and broadened ^1H NMR spectrum in C_6D_6 , with chemical shifts at 96, 14.6, 3.2, 1.56, and -13.0 ppm. $\mu_{\text{eff}}(\text{RT})$ 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 $\text{Cr}(\text{II})$ 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, $[\text{H}^{\text{iPr}}\text{Cr}(\kappa^2\text{-N}_2\text{C}_{26}\text{H}_{22})]$ (**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 $\text{Cr}(\text{III})$ 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.

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.

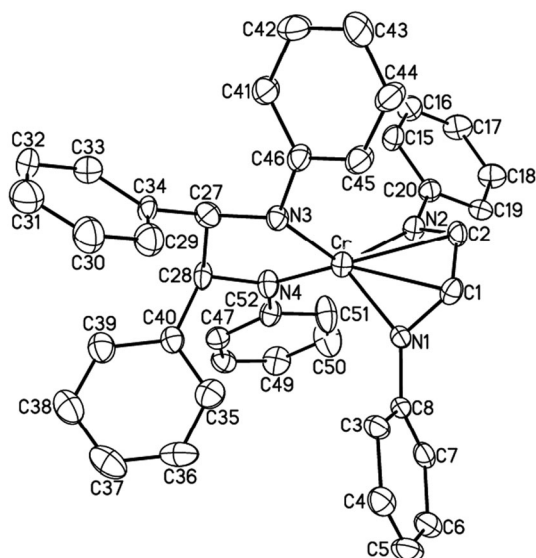


Fig. 3 The molecular structure of **7** (30% probability level).

