

# Carboalumination of a chromium–chromium quintuple bond

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**Bonds are at the very heart of chemistry. Although the order of carbon–carbon bonds only extends to triple bonds, metal–metal bond orders of up to five are known for stable compounds, particularly between chromium atoms. Carbometallation and especially carboalumination reactions of carbon–carbon double and triple bonds are a well established synthetic protocol in organometallic chemistry and organic synthesis. We now extend these reactions to compounds containing chromium–chromium quintuple bonds. Analogous reactivity patterns indicate that such quintuple bonds are not as exotic as previously assumed. Yet the particularities of these reactions reflect the specific nature of the high metal–metal bond orders.**

The nature of the chemical bond remains of fundamental interest, having fascinated scientists, and in particular chemists, for a long time<sup>1–4</sup>. The spectrum of bond orders that are well accessible in stable compounds has recently been extended towards five<sup>5</sup>. Quintuple bonding has since been observed in a number of homo-bimetallic chromium complexes<sup>6–10</sup>. As well as provoking theoretical discussions<sup>11–23</sup> that focus on a better understanding of such unusual bonds, chromium–chromium multiple bonds are of particular interest as they provide the shortest metal–metal distances<sup>7–10,24–30</sup>. In addition to the synthesis and (electronic) structure of such compounds and bonds, their reactivity is also of interest to chemists. However, there was little known about the reactivity of quintuple bonds until recently<sup>5–10</sup>. We report here on the reactivity of a chromium–chromium quintuple bond, and in particular about its carboalumination. Carbometallation and especially carboalumination reactions of carbon–carbon double and triple bonds are a well established synthetic protocol in organometallic chemistry and organic synthesis. These reactions proceed via *syn*-addition for double bonds and via *cis*-addition for triple bonds<sup>31,32</sup>. Analogous reactivity patterns of chromium–chromium quintuple bonds would indicate that such bonds are not as exotic as was previously assumed. Yet the particularities of these reactions might also reflect specific consequences of the extremely high metal–metal bond orders.

The deprotonation of (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine (**1**) with *n*-BuLi followed by reaction with CrCl<sub>2</sub> leads to the dimeric (in the solid state) chloro-bridged and THF-coordinated Cr(II) aminopyridinate (**2**) (Fig. 1). The strained N,N-coordination of the anionic nitrogen ligand (N–Cr–N angle of 64.99(9)°) gives rise to distorted trigonal bipyramidal coordination of the chromium atoms. Compound **2** is a rare example of a Cr(II) complex in which deprotonated **1** does not act as a bridging ligand<sup>9</sup>.

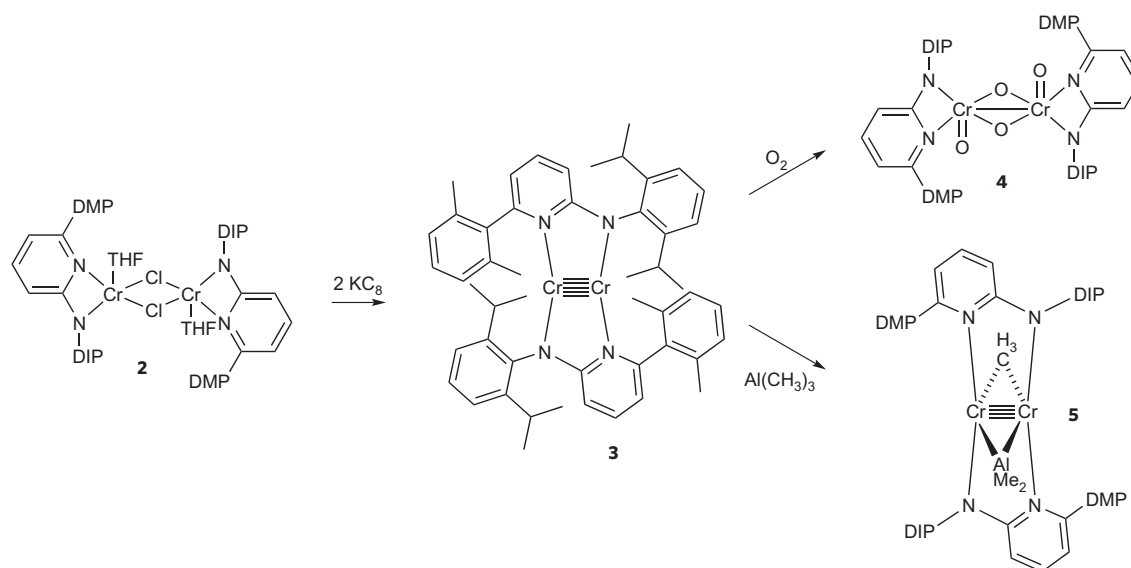
Reduction of **2** with KC<sub>8</sub> gives the homo-bimetallic complex **3**, which has an ultrashort quintuple bond of 1.750(1) Å (refs 8–10) between the two metal atoms. The molecular structure of **3** determined by X-ray crystal structural analysis is shown in Fig. 2. For a model system, in which the sterically demanding aryl substituents were replaced by hydrogen atoms, a ( $\sigma_g$ )<sup>2</sup>( $\pi_u$ )<sup>4</sup>( $\delta_g$ )<sup>4</sup> configuration

of the chromium-based molecular orbitals (MOs) has been obtained. These five MOs can be found among the seven highest occupied orbitals. The two  $\delta_g$  MOs are always the highest occupied molecular orbital (HOMO) and the HOMO–1, and the two  $\pi_u$  MOs are the HOMO–5 and HOMO–6. The energies of  $\sigma_g$  MO and two ligand-centred MOs with a strong amido nitrogen contribution lie between these two groups of orbitals<sup>9</sup>. The magnetic susceptibility of **3** was measured between 2 and 300 K; between 80 and 300 K it is very small, positive and nearly temperature independent. The temperature-independent paramagnetism (TIP), provided through Zeeman perturbation, is  $280 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . This behaviour indicates an *S* = 0 ground state, which is indicative of strongly coupled *d*<sup>5</sup>–*d*<sup>5</sup> bonding electrons. The diamagnetic ground state and the TIP contribution are consistent with previously published quintuply bonded species (where TIP =  $620 \times 10^{-6}$  to  $1,500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ )<sup>5,6</sup>.

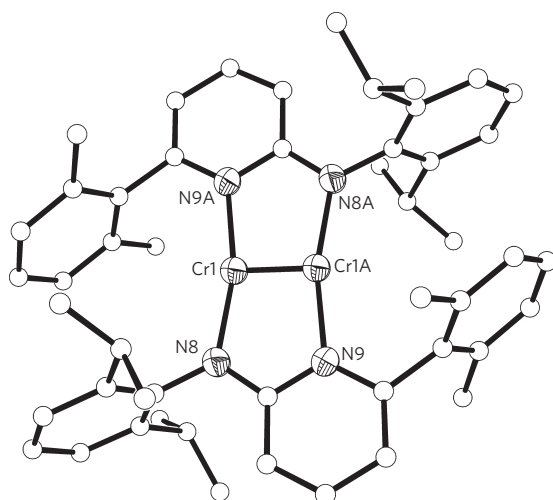
In comparison with the derivative described by us recently<sup>9</sup>, we consider **3** to be an ideal compound for investigating quintuple bond reactivity as it can be made in significantly better yields and on a larger scale. Compound **3** is sterically optimized: it has reduced steric bulk at the pyridine rings to provide less shielding and consequently better access for small molecules; however, the steric bulk is still large enough for the compound to be synthesized efficiently. Reaction of **3** with oxygen forms a diamagnetic dimeric Cr(V) oxo complex, **4**, in which two oxo ligands bridge and two oxo ligands coordinate terminally (Fig. 1). The molecular structure of **4** determined by X-ray crystal structure analysis is shown in Fig. 3. Chromium oxo complexes of this type are rare<sup>33,34</sup> and were first reported by Herberhold and co-workers<sup>35</sup>. The work of Tsai and co-workers<sup>36</sup> (the toluene sandwich) and Theopold and co-workers<sup>37</sup> (the dinitrogen sandwich), published simultaneously, indicates that the oxidation of Cr(I) complexes without quintuple bonding leads to mononuclear Cr(V) complexes with two terminal oxo ligands. In contrast, the oxidation of bimetallic **3** with oxygen gives rise to bimetallic oxo-bridged **4**.

Owing to the importance of carboalumination reactions for the functionalization of carbon–carbon double and triple bonds, we were interested in studying such reactions for metal–metal quintuple bonds. The reaction of **3** with AlMe<sub>3</sub> results in a colour change

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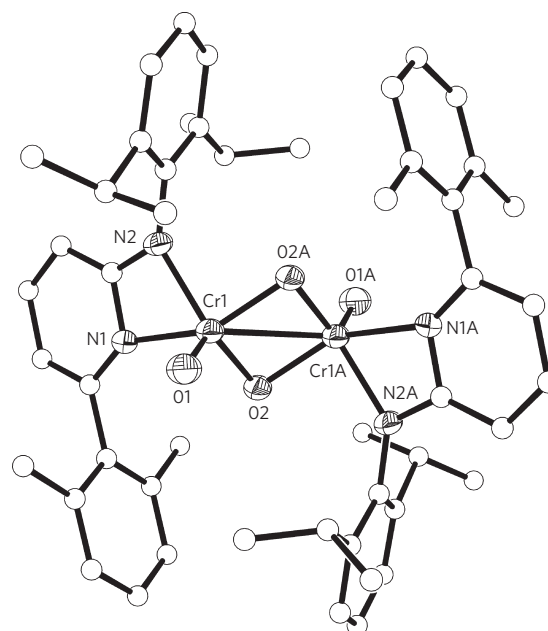
**Figure 1** | Synthesis of **3**, **4** and **5**. (DIP = 2,6-diisopropylphenyl, DMP = 2,6-dimethylphenyl, THF = tetrahydrofuran.).



**Figure 2** | Molecular structure of **3**. Ellipsoid drawing (50% probability level) for all non-carbon atoms without hydrogen atoms and solvent molecule(s). The non-labelled atoms are carbon. Selected bond lengths and angles: Cr1–Cr1A = 1.750(1) Å, Cr1–N8 = 2.000(3) Å, Cr1–N9 = 2.027(3) Å; Cr1–Cr1A–N8A = 98.65(8)°, Cr1–Cr1A–N9 = 96.34(9)°, N2–Cr1–N1 = 165.01(11)°.

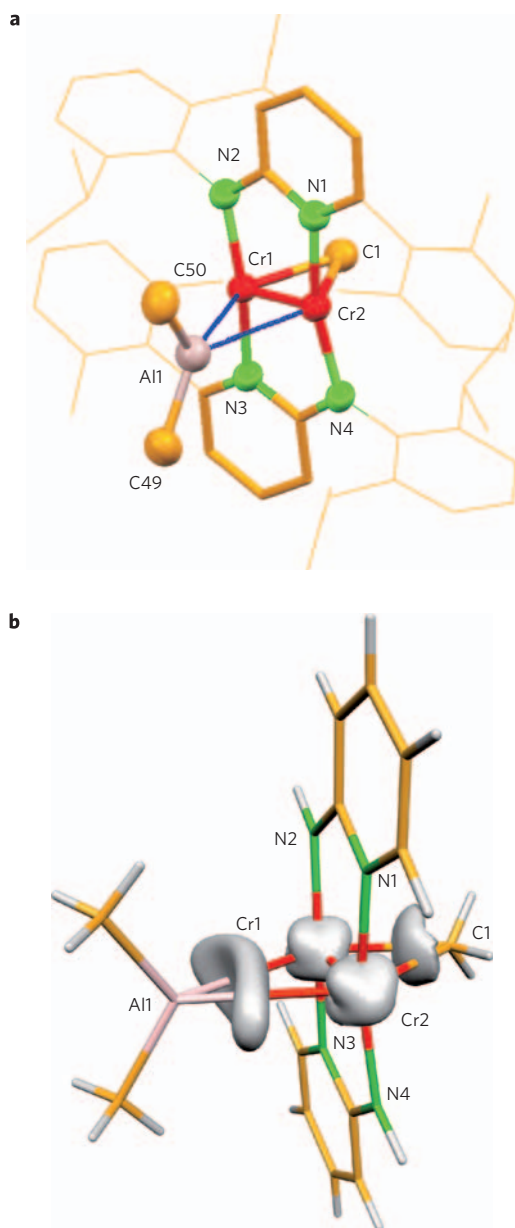
from purple to brown. The resulting diamagnetic carboalumination product **5** is obtained in very good yield. The molecular structure of **5** is shown in Fig. 4a.

The formation of the central structural unit in **5** can be viewed as the insertion of the chromium–chromium quintuple bond into one of the aluminium–carbon bonds. A side-on coordination of the multiple bond to the dimethyl aluminium fragment is observed. To the best of our knowledge, no comparable structures are known. The observed chromium–aluminium distances (2.90 Å on average) are unusually long: coordination compounds containing direct aluminium–chromium bonding exhibit bond lengths between 2.38 and 2.48 Å (refs 38,39). However, the chromium–carbon distances of the bridging methyl group in **5** are consistent with the values observed previously in Cr(II) complexes (2.18–2.52 Å)<sup>30,40–42</sup> (this unusually broad range of distances is a result of the attempt to form unsymmetric bridges in selected



**Figure 3** | Molecular structure of **4**. Ellipsoid drawing (50% probability level) for all non-carbon atoms without hydrogen atoms and solvent molecule(s). The non-labelled atoms are carbon. Selected bond lengths and angles: Cr1–N1 = 2.053(2) Å, Cr1–N2 = 1.946(2) Å, O1–Cr1 = 1.563(2) Å, O2–Cr1 = 1.791(2) Å, Cr1–Cr1A = 2.5314(10) Å; Cr1–Cr1A–O1A = 121.69(9)°, Cr1–Cr1A–O2 = 45.02(7)°, N2–Cr1–N1 = 65.20(10)°.

systems<sup>30</sup>). A TIP of  $97 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  was observed for **5**. The electronic structure of **5** was examined by means of density functional theory calculations. All structure optimizations were carried out at the BP86/TZVP level (that is, using the BP86 exchange–correlation functional of density functional theory and a TZVP one-electron basis set of Gaussian-type atomic orbitals). Bonding analyses were based on single-point calculations at the B3LYP/TZVPP level<sup>43–46</sup> followed by analysis of the electron localization function (ELF)<sup>47</sup>, and by natural bond orbital analysis and natural population analysis<sup>48</sup>. The calculations were carried out with reduced model ligands in which the substituents drawn as a wire frame in Fig. 4a were replaced by



**Figure 4 | Molecular structure and electron localization function (ELF) isosurface of 5.** **a**, Ellipsoid drawing (50% probability level) for all non-carbon atoms without hydrogen atoms and solvent molecule(s). Colour code: Al = light pink, Cr = red, C = orange and N = green. Selected bond lengths and angles: Cr1–Cr2 = 1.8365(8) Å, Cr1–N2 = 2.014(3) Å, Cr2–N1 = 2.040(3) Å, C1–Cr1 = 2.227(4) Å, C1–Cr2 = 2.252(4) Å, Al1–Cr1 = 2.8945(14) Å, Al1–Cr2 = 2.9076(14) Å; Cr2–Cr1–N2 = 98.13(8)°, Cr2–Cr1–N3 = 94.81(8)°, Cr1–Cr2–N1 = 94.60(8)°, Cr1–Cr2–C1 = 65.08(12)°, Cr1–Cr2–Al1 = 71.16(4)°, N2–Cr1–N1 = 166.16(12)°. **b**, ELF = 0.70 isosurface for the simplified model of 5. The coordination of free electron pairs of formal  $\text{Al}(\text{CH}_3)_2$  and  $\text{CH}_3$  fragments to the Cr–Cr bond are apparent. The ELF areas around the nitrogen ligands, the aluminium methyl groups and the hydrogen atoms at C1 were removed for improved clarity.

hydrogen atoms (Fig. 4b). The Wiberg bond index estimate<sup>49</sup> for the formal chromium–chromium bond order in 5 is 3.5, compared with a value of 4.4 for the starting compound 3. This is consistent with a formal oxidative addition of an aluminium–carbon bond to a chromium–chromium quintuple bond, resulting in the formation of a formal quadruple bond and formally anionic  $\text{Al}(\text{I})(\text{CH}_3)_2$  and  $\text{CH}_3$  ligands. The ELF isosurface diagram (Fig. 4b) shows clearly

the formally monoanionic  $\text{Al}(\text{CH}_3)_2$  and  $\text{CH}_3$  ligands coordinating to the chromium–chromium bond. The addition increases the natural population analysis partial charge on chromium from +0.49 to +0.67, whereas the  $\text{Al}(\text{CH}_3)_2$  and  $\text{CH}_3$  fragments exhibit negative charges of –0.12 and –0.47, respectively. This indicates appreciable charge transfer towards the chromium–chromium bond, in particular from the anionic dimethyl  $\text{Al}(\text{I})$  fragment. Relatively low bond indices of approximately 0.30 between chromium and  $\text{Al}(\text{CH}_3)_2$  and approximately 0.27 between chromium and  $\text{CH}_3$  indicate a dominance of dative bonding (confirmed also by the ELF, Fig. 4b).

The investigations described here indicate the potential of the reactivity of metal–metal quintuple bonds in providing access to new structure and bonding situations. However, an analogy of such multiple bonding systems to the simplest carbon–carbon double and triple bonds has become apparent. It is expected that further investigations of the reactivity of quintuple bonds will be stimulated by the present results.

## Methods

**Synthesis of 5.** All steps were carried out under rigorous exclusion of air and moisture.  $\text{Al}(\text{CH}_3)_3$  (0.1 ml) was added to 3 (0.042 g) in hexane (5 ml) at room temperature. The reaction mixture was heated overnight at 70 °C, during which time a colour change from purple to brown was observed. The mixture was then filtered and the filtrate was kept at room temperature to produce brown–red crystals at a yield of 0.042 g (92%). The structure of 5 was confirmed by NMR spectroscopy, and elemental analysis was consistent with the observed structure.

## Crystallographic data.

**Compound 3** Space group:  $P\bar{1}$ ;  $a = 11.9930(9)$ ,  $b = 12.5339(10)$ ,  $c = 12.5675(10)$  Å;  $\alpha = 62.264(6)^\circ$ ,  $\beta = 77.005(6)^\circ$ ,  $\gamma = 63.040(6)^\circ$ ,  $R_1 = 0.064$  [ $I > 2\sigma(I)$ ],  $wR_2$  (all data) = 0.195.

**Compound 4** Space group:  $P2_1/c$ ;  $a = 12.6130(10)$ ,  $b = 14.6670(12)$ ,  $c = 13.6720(12)$  Å;  $\beta = 116.302(6)^\circ$ ,  $R_1 = 0.053$  [ $I > 2\sigma(I)$ ],  $wR_2$  (all data) = 0.133.

**Compound 5** Space group:  $P\bar{1}$ ;  $a = 12.3650(6)$ ,  $b = 15.7570(8)$ ,  $c = 20.6880(9)$  Å;  $\alpha = 79.256(4)^\circ$ ,  $\beta = 72.858(4)^\circ$ ,  $\gamma = 85.939(4)^\circ$ ,  $R_1 = 0.064$  [ $I > 2\sigma(I)$ ],  $wR^2$  (all data) = 0.186.

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## Author contributions

A.N. carried out the synthesis experiments and analysed the spectroscopic data. G.G. performed the X-ray single crystal structure analyses. R.M. and M.K. carried out the computational studies. S.D. performed the magnetic susceptibility experiments. R.K. originated the central idea and wrote the manuscript with contributions from all the co-authors.

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