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## COMMUNICATION

## Reactions of a quintuply bonded chromium dimer with alkynes†

Jingmei Shen,<sup>a</sup> Glenn P. A. Yap,<sup>a</sup> Jan-Philipp Werner<sup>b</sup> and Klaus H. Theopold<sup>\*a</sup>

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Quintuply bonded  $[{}^{H}L^{iPr}Cr]_2$  reacts with alkynes  $RC \equiv CR$ (R = Me, Et, Ph, CF<sub>3</sub>) to form exclusively 1:1 adducts  $[{}^{H}L^{iPr}Cr]_2(RCCR)$ . All products feature relatively short Cr–Cr distances (1.919–1.962 Å) and elongated C–C bonds (1.315–1.436 Å), consistent with [2+2] cycloaddition reactions. The hydrocarbon adducts are 4-membered metallacycles, the bridging alkynes of which are progressively skewed with respect to the Cr–Cr axis. In contrast, perfluoroalkyne adds across the metal ligand moiety.

Element-element multiple bonds are functional groups of heightened reactivity, and multiple bonds between metals are no exception.<sup>1</sup> Until fairly recently, the latter were for all intents and purposes restricted to bond orders ranging from 2-4,<sup>2</sup> but the discovery by Power *et al.* of the first isolable molecule featuring a formal quintuple bond between two chromium atoms, *i.e.*, Ar'CrCrAr',<sup>3</sup> was followed by several reports of dinuclear chromium compounds sporting ever shorter metal-metal distances and laying claim to quintuple bonds between two d<sup>5</sup> ions.<sup>4</sup> Whereas the race toward 'fusing' two metal atoms has seemingly abated for now (the current record appears to be 1.73 Å), 5,6 there remains the elucidation of the reactivity of this new kind of bond, which is only now beginning.7-9 Herein we describe a series of compounds resulting from pericyclic reactions between quintuply bonded [HLiPrCr]2 (1, where  ${}^{H}L^{iPr} = Ar - N = C(H) - (H)C = N - Ar$ , with Ar =2,6-diisopropylphenyl)<sup>10</sup> and internal alkynes.

Treatment of Et<sub>2</sub>O solutions of **1** with excess of 2-butyne, 3-hexyne, or diphenylacetylene at room temperature caused instant color changes from green to deep purple. Standard work-up of the reactions yielded the simple adducts  $[^{H}L^{iP}Cr]_{2}(RCCR)$  (R = Me (**2a**), Et (**2b**), Ph (**2c**), see Scheme 1). No further reaction of **2a–c** with excess alkyne was observed. The air-sensitive complexes **2a–c** have been



Scheme 1 Synthesis of  $[{}^{H}L^{iPr}Cr]_{2}(RCCR)$  (R = Me (2a), Et (2b), Ph (2c).

characterized by the X-ray diffraction; the molecular structure of representative **2a** is depicted in Fig. 1, along with selected interatomic distances and angles.

Inspection of the structure reveals that **2a** (and similarly **2b** and **2c**, see ESI†) does not adopt the typical perpendicular (*i.e.*  $\mu_2$ - $\eta^2$ : $\eta^2$ ) bonding mode of the alkyne, which is generally thought to maximize alkyne–metal interaction and is favored by Kempe's analogues.<sup>11</sup> Rather, the structure more closely approximates a binuclear metallacycle—*i.e.*, a coplanar  $\mu_2$ - $\eta^1$ : $\eta^1$ -C<sub>2</sub>R<sub>2</sub> geometry such as would result from a formal [2+2] cycloaddition between a quintuple and a triple bond, generating a polyunsaturated four-membered ring. The relevant bond lengths are in accord with that view; thus the C–C bond length of 1.326(5) Å is exactly what might be



Fig. 1 The molecular structure of **2a** with thermal ellipsoids at the 30% probability level; H-atoms and ligand isopropyl groups have been omitted for clarity. Selected distances [Å] and angles [°]: Cr1–Cr2 1.9248(7), Cr1–N1 1.927(2), Cr1–N3 1.933(2), Cr2–N2 1.901(2), Cr2–N4 1.903(2), Cr1–C55 1.965(3), Cr2–C54 2.039(3), C55–C54 1.326(5), N1–C1 1.366(4), C1–C2 1.351(4), N2–C2 1.372(4), N3–C27 1.372(4), C27–C28 1.356(4), N4–C28 1.368(4), N1–Cr1–Cr2 104.15(7), N1–Cr1–N3 128.395(10), Cr2–Cr1–N3 103.67(7), N1–Cr1–C55 118.453(12), Cr2–Cr1–C55 83.94(10), N3–Cr1–C55 106.98(12), N2–Cr2–N4 139.21(10), N2–Cr2–Cr1 105.57(8), N4–Cr2–Cr1 103.24(7), N2–Cr2–C54 109.52(12), N4–Cr2–C54 106.75(12), Cr1–Cr2–C54 71.16(9).

<sup>&</sup>lt;sup>a</sup> Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19711, USA. E-mail: theopold@udel.edu;

*Fax:* +1 302 831-6335; *Tel:* +1 302 831-1546

<sup>&</sup>lt;sup>b</sup> Institut für Anorganische und Angewandte Chemie,

Universität Hamburg, Hamburg, Germany.

*E-mail: jan-philipp.werner@chemie.uni-hamburg.de; Tel: +49 (0)40 42838 3112* 

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Synthesis and characterization of **2a–c** and **3**; crystal structures of **2b** and **2c**; details of the calculations. CCDC 839343–839347. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15218a

expected of a carbon-carbon double bond (cf. 1.339(1) Å in ethylene)<sup>12</sup> and the Cr-Cr distance of 1.9248(7) falls into the range of 'supershort' chromium-chromium quadruple bonds (Cr-Cr < 2.0 Å)<sup>2</sup> Indeed, this elongation of the two multiple bonds in return for the formation of two new Cr-C single bonds (at 1.965(3) and 2.039(3) Å) provides independent chemical evidence for the presence of a quintuple metalmetal bond in 1 (Cr–Cr = 1.8028(9) Å).<sup>10</sup> We note that the backbone bond lengths of the diimine ligands in 1 and 2a do not appreciably differ; thus the two electrons used to reduce the alkyne to an alkenediyl ligand must have come from the chromium atoms rather than from the redox non-innocent ligands; the latter maintain radical anion character throughout the reaction.<sup>13,14</sup> If the formal oxidation state of chromium in **2a** is Cr(II), as seems reasonable, it must have been Cr(I) in **1**, consistent with our original assignment of a quintuple bond between two d<sup>5</sup>-ions.

On closer inspection, the structures of 2a-c reveal some additional detail. The alkyne centroids are slightly closer to one chromium, being displaced some way toward a putative  $\mu_2$ - $\eta^1$ : $\eta^2$ -C<sub>2</sub>R<sub>2</sub> geometry. To wit, the intraannular distances in 2a are: Cr1-C54, 2.308(3) Å; Cr2-C55, 2.603(4) Å, placing the alkyne somewhat closer to Cr1. Furthermore, the Cr<sub>2</sub>C<sub>2</sub> cores of the molecules are not perfectly planar. For example, the C=C bond of 2a is twisted from coplanarity with the Cr-Cr bond by 23.7°. This twist angle increases with the steric bulk of the alkyne substituents (2b:  $35.8^{\circ}$  and 2c:  $41.7^{\circ}$ ); thus steric interactions with the ligand isopropyl groups are at least partially responsible for this torsion. There may, however, also be an electronic contribution; a second order Jahn-Teller distortion, resulting in mixing of metal-metal bonding MOs with an alkyne  $\pi^*$ -orbital, has been proposed to account for this type of skew.<sup>15,16</sup> In the solid state, molecules of **2a** possess no symmetry whatsoever; however, the deviation from  $C_{2y}$ symmetry is slight and may be anticipated to give rise to fluxional behavior.

The <sup>1</sup>H NMR spectra of **2b** and **2c** in  $C_6D_6$  are those expected of diamagnetic complexes, featuring a multitude of sharp resonances between 0 and 8 ppm. However, the room temperature spectrum of 2a exhibited broad resonances, which is presumably caused by a low barrier, fluxional process. Due to the asymmetric structure of its  $N_4Cr_2C_2$  core, 2a is expected to exhibit resonances of eight unique <sup>i</sup>Pr-CH<sub>3</sub> and four unique <sup>i</sup>Pr–CH (while still allowing for fast rotation about the N–C<sub>Ar</sub> bonds). Accordingly, variable temperature <sup>1</sup>H NMR spectra in toluene-d<sub>8</sub> between -40 °C and 30 °C showed a coalescence phenomenon resulting in six isopropyl methyl resonances (in a 1:1:1:1:2:2 intensity ratio) and three methine signals (in a 1:1:1 ratio) at low temperature. Presumably, two pairs of the closely spaced <sup>i</sup>Pr-Me resonances are accidentally degenerate and the missing fourth methine resonance may be obscured by the residual toluene resonance (at 2.09 ppm). In other words, the low temperature spectrum is consistent with the solid-state structure of 2a. However, the activation barrier for the fluxional process-via a twist of the propeller shaped molecule about the Cr-Cr bond, combined with a subtle slide of the alkyne-is rather low. The coalescence temperature of *ca.* 20 °C is commensurate with  $\Delta G^{\ddagger} \approx 15$  kcal mol<sup>-1</sup>. Curiously, we note that the 2-butyne methyl resonance

remains one singlet down to -90 °C. This too may simply be an accidental degeneracy; alternatively, it would suggest that rotation of the 2-butyne ligand is a separate, very fast process with a much lower barrier, which cannot be frozen out even at -90 °C. Control experiments established that neither alkyne dissociation, nor alkyne exchange occurs in solution on a chemical time scale.

The electronic structures of model complexes 2a'-c' were examined by DFT calculations.<sup>†</sup> All structure optimizations were performed at the BLYP/def2-SVP (LANL08(f) for the metal atoms) level using molecules in which the 2,6-diisopropylphenyl substituents had been replaced by hydrogen atoms. Geometry optimizations on 1 gave bond distances that were in good agreement with the X-ray structures. All reported structural parameters refer to singlet ground state structures. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA).<sup>17,18</sup>

The calculated bond orders for the chromium-chromium bonds of the alkyne adducts are 3.43 (2a'), 3.22 (2b') and 3.56(2c'), to be compared with the value of 4.59 for precursor 1'. Concomitantly, the erstwhile  $C \equiv C$  triple bonds now have bond orders of 1.98, 1.90 and 1.90, respectively. These reduced values are consistent with a formal oxidative addition of the  $C \equiv C$  triple bonds to the Cr–Cr quintuple bond, resulting in the formation of Cr-Cr quadruple bonds and C=C double bonds. The natural population analysis for 2a' indicates that the sum of partial charges on the chromium atoms increases from +1.022 to +1.231, whereas the bound MeC=CMe fragment picks up a negative charge of -0.412. This indicates the charge transfer from the Cr-Cr multiple bonds to C=C bonds. We also note diminution of the total negative charge on the ligand N atoms from -3.241 to -2.965. There is thus some charge transfer from the  $\alpha$ -dimine ligands to the alkyne.

It was of some interest to explore whether a significant increase in the driving force of the reaction might change its course. Given the net electron transfer from the chromium complex to the alkynes, a more electron deficient alkyne would probe this question. Accordingly, **1** was exposed to an excess of hexafluoro-2-butyne; upon addition of  $CF_3C \equiv CCF_3$  at room temperature, the color of the solution immediately changed from green to deep purple again, but turned to red after about one hour. <sup>1</sup>H NMR spectroscopy of the purple intermediate **3** showed it to be diamagnetic. To isolate **3**, the reaction was allowed to proceed for only 20 minutes, where-upon single crystals were grown from toluene at -30 °C.

To our surprise, the structure determination of **3** (see Fig. 2) revealed a connectivity much different from **2a–c**. The fluorinated alkyne has been added across a metal–ligand moiety, resulting in the formation of both carbon–carbon and carbon–chromium bonds. The functionalized ligand has been transformed into a localized iminoamide. While the Cr–Cr distance of **3** (1.9615(6) Å) is only marginally longer than those of **2a–c**, the C–C bond of the alkyne has been elongated to 1.436(3) Å, indicating much more extensive reduction. In transition metal chemistry, the compounds most closely related to **3** are Frühauf's products of 1,3 dipolar additions across M–X=C bonds (X = O, S, N).<sup>19–25</sup> In main group chemistry, the reversible addition of alkynes to dinuclear



Fig. 2 The molecular structure of 3 with thermal ellipsoids at the 30% probability level; H-atoms, solvent molecules and ligand isopropyl groups have been omitted for clarity. Selected distances [Å] and angles [°]: Cr1-Cr2 1.9615(6), Cr1-N1 1.9157(19), Cr1-N4 2.0883(18), Cr2-N2 1.901(2), Cr2-N3 1.898(2), Cr1-C54 2.008(2), Cr1-C55 2.112(2), 1.987(2), C55-C54 1.436(3), C27-C55 Cr2-C54 1.553(3). N1-C1 1.372(3), C1-C2 1.353(3), N2-C2 1.371(3), N3-C27 1.476(3), 1.501(3), N4-C28 1.282(3), N1-Cr1-Cr2 106.99(6), C27–C28 N1-Cr1-C54 114.75(9), Cr2-Cr1-C54 60.07(6), N1-Cr1-N4 128.55(7), Cr2-Cr1-N4 103.36(5), C54-Cr1-N4 116.28(8), N1-Cr1-C55 146.10(8), Cr2-Cr1-C55 81.44(6), C54-Cr1-C55 40.69(9), N4-Cr1-C55 78.37(8), N3-Cr2-N2 156.62(8), N3-Cr2-Cr1 99.44(6), N2-Cr2-Cr1 102.88(6), N3-Cr2-C54 84.70(9), N2-Cr2-C54 112.21(9), Cr1-Cr2-C54 61.14(6).

gallium complexes of a chelating diamide provides a recent analogue.<sup>26</sup> However, what makes **3** unique is the apparent retention of its metal–metal multiple bond.

DFT calculation on 3' confirmed that its Cr–Cr bond order is 3.17, similar to those in compounds **2a–c'**. However, the bond order of the alkyne derived C–C bond is 1.12, much reduced from the earlier examples and close to a C–C single bond, in accord with the longer bond distance. In the same vein, the CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub> fragment accumulates a negative partial charge of –0.604 at the central carbons, which significantly exceeds that of MeC $\equiv$ CMe in 2a'. Interestingly, the sum of NPA charge of Cr (1.036) hardly differs from that of 1; instead the negative partial charge of the ligand N atoms decreases from –3.241 (in 1') to –2.883 (in 3). These numbers support the view that 3 features a disproportionate transfer of charge from the ligands to the alkyne, leaving the chromium little changed.

Calculations were also used to address the change in product. Full optimizations of **2a** and **3** and their reaction products were performed at the BLYP/def2-SVP/LAN2L08(f) level using the actual, non-curtailed molecules. In both cases, the [2+2] cycloaddition product is more stable than the product of the ligand functionalization. However, for 2-butyne the energy difference is 13.4 kcal mol<sup>-1</sup>, whereas it decreases to a scant 4.8 kcal mol<sup>-1</sup> for hexafluoro-2-butyne. We suggest that the greater exothermicity of the latter reaction leads to an earlier transition state, and that frontier orbital control of the reaction path (the HOMO of **1** is entirely ligand based) asserts itself. In summary, we have explored the alkyne chemistry of a quintuply bonded Cr dimer,  $[{}^{H}L^{iPr}Cr]_2$  (1). With electron rich internal alkynes 1 forms [2+2] cycloaddition products  $[{}^{H}L^{iPr}Cr]_2(\mu_2-\eta^1:\eta^1-C_2R_2)$ , *i.e.*, 4-membered dimetallacycles retaining a Cr–Cr quadruple bond. In contrast, electron poor CF<sub>3</sub>C  $\equiv$  CCF<sub>3</sub> adds across the metal ligand bond of 1. This dichotomy reflects the unique nature of HOMO of the starting material, which is ligand based. We are currently investigating the reactivity of 1 with other unsaturated organic molecules.

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