Chromium Mediated Reductive Coupling of Isonitrile Forms Unusual Heterocycles

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S *Supporting Information*

ABSTRACT: The quintuply bonded α-diimine chromium dimer $[^{H}L^{iPr}Cr]_2$ reductively couples cyclohexyl isocyanide to produce various novel nitrogen heterocycles. Tetramerization yielded, inter alia, the aromatic squaramidinate, i.e. $[C_4(NCy)_4]^{2-}$, whereas hexamerization produces a substituted 1,4-diaza-bicyclo[3.3.0]octadiene dianion. These unprecedented transformations complement the coupling reactions of isoelectronic CO, and they may prove synthetically useful.

The coupling of simple unsaturated molecules to yield more elaborate organic structures is one of the hallmarks of organometallic chemistry in the pursuit of synthesis.[1] A particular challenge in this regard has been the transformation of carbon monoxide (CO) into precursors for the manufacture of chemicals and liquid fuels.[2] While the formation of C–C bonds between cis-ligated CO ligands as well as their isoelectronic analogs, isonitriles (RNC), has long been known to produce heterosubstituted alkynes,[3] the formation of small carbocycles such as deltate ($C_3O_3^{2-}$) and squarate ($C_4O_4^{2-}$) have only recently been accomplished in mild inner transition-metal-mediated reactions.[4] Comparable 'reductive couplings' of isonitriles to cyclic molecules appear to be unknown, even though the existence of isonitrile polymers as opposed to unstable CO oligomers heralds potential.[5] A notable recent development in isonitrile coupling has been the formation of 1,4-diazadiene-2,3-diyl fragments by dinuclear Mg(I) β-diketiminates.[6] In this vein, we now report formation of several new heterocycles generated by the reductive coupling of an isonitrile with low-valent chromium.

As part of an exploration of the reactivity of the quintuply bonded Cr(I) dimer $[^{H}L^{iPr}Cr]_2$ ($^{H}L^{iPr} = N,N'$-bis(2,6-diisopropylphenyl-1,4-diazadiene) with various organic substrates,[7] we have also investigated its reaction with isonitriles. Thus, slow addition of an excess of cyclohexyl isocyanide (CyNC) to a toluene solution of $[^{H}L^{iPr}Cr]_2$ yielded a mixture of products (see Scheme 1). Least surprising is the formation of the diamagnetic octahedral adduct $^{H}L^{iPr}Cr(CNCy)_4$ (**1**), in approximately 40% yield (its molecular structure is shown in Figure S1). Pink **1** is isostructal and isoelectronic to the previously reported $^{H}L^{iPr}Cr(CO)_4$, which has been analogously prepared by carbonylation of $[^{H}L^{iPr}Cr]_2$.[8] The remaining products were less soluble, enabling separation by fractional crystallization. Two paramagnetic compounds, green **2** and purple **3**, were thus isolated in modest yields of 27% and 10%, respectively.

Scheme 1. Reductive Coupling Products of CyNC
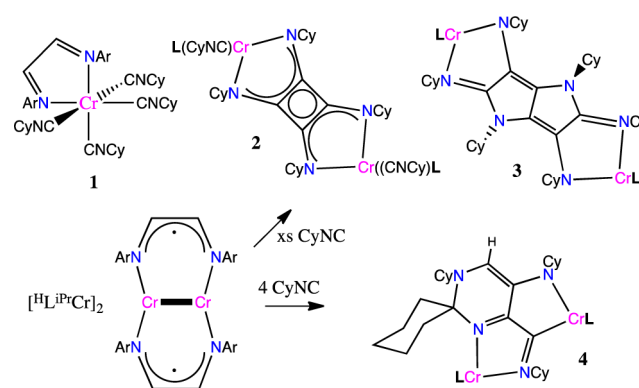
The molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively. Both are binuclear Cr complexes,
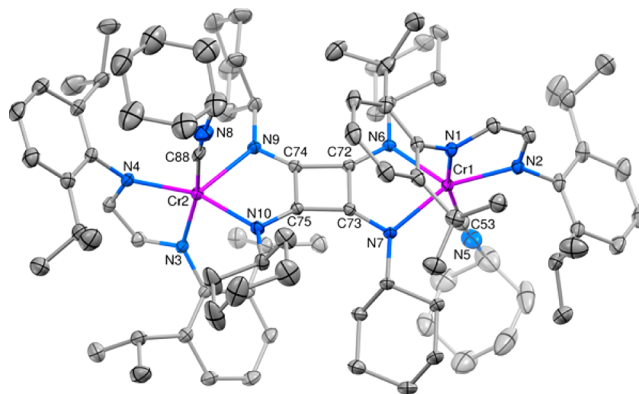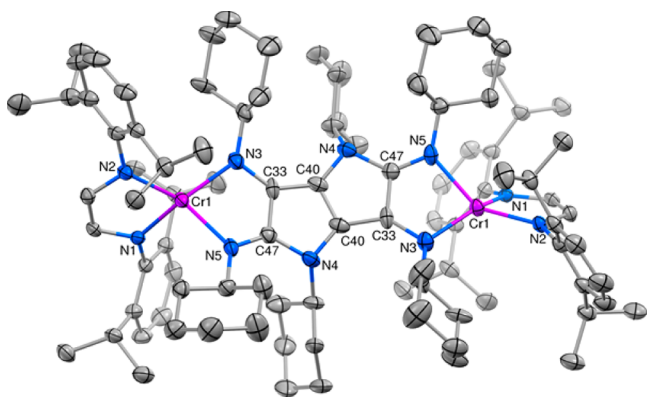

Figure 1. Molecular structure of **2** (30% probability level); selected interatomic distances (Å) and angles (deg): Cr1–N6, 2.155(2); Cr1–N7, 2.139(2); Cr2–N9, 2.202(2); Cr2–N10, 2.112(2); C72–C73, 1.435(4); C72–C74, 1.489(4); C73–C75, 1.470(4); C74–C75, 1.441(4); C72–N6, 1.311(3); C73–N7, 1.320(3); C74–N9, 1.315(3); C75–N10, 1.314(3); N6–Cr1–N7, 81.94(9); N9–Cr2–N10, 82.17(9).

containing six isocyanide moieties each. Albeit formally isomers, their structures are very different, and we did not observe them to interconvert under any conditions. The core of **2** features a planar four-membered carbocycle carrying a CyN-substituent at each carbon; the latter pairwise coordinate to the two spatially
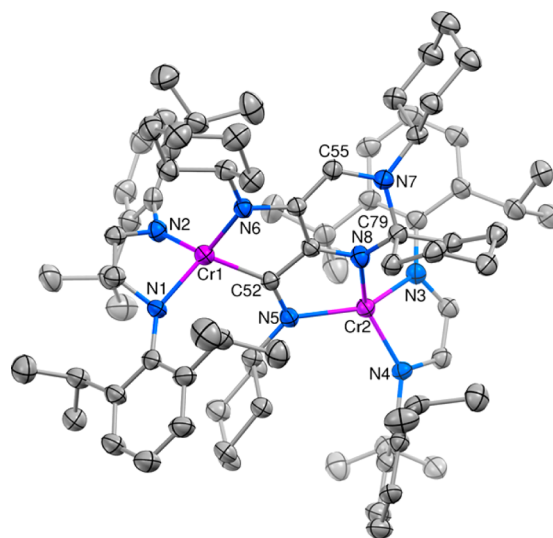
Figure 2. Molecular structure of **3** (30% probability level); selected interatomic distances (Å) and angles (deg): Cr1−N3, 1.974(3); Cr1−N5, 2.079(3); N3−C33, 1.376(5); N5−C47, 1.286(4); C33−C47, 1.440(5); C33−C40, 1.418(5); C40−C40a, 1.390(7); C40−N4, 1.393(4); N4−C47, 1.455(5); N1−Cr1−N2, 81.31(12); N3−Cr1−N5, 81.85(13).

separated (Cr...Cr, 6.935 Å) $^{H}L^{iPr}$Cr fragments. The coordination spheres of the approximately trigonal bipyramidal chromium atoms are completed by one normal isocyanide ligand each. The bridging 'C$_4$(NCy)$_4$' fragment is clearly reminiscent of squarate, suggesting its formation by a reductive coupling of four isocyanide molecules. Indeed, its metric parameters (C−C$_{avg}$, 1.459 Å; C−N$_{avg}$, 1.315 Å) are clearly consistent with it being a dianionic 'squaramidinate' (C−C$_{avg}$, 1.480 Å; C−N$_{avg}$, 1.316 Å) rather than a neutral tetrakis-(imino)cyclobutane (C−C$_{avg}$, 1.518 Å; C−N$_{avg}$, 1.263 Å), as ascertained by DFT calculations.[9] The associated resonance structures delocalize two π-electrons over the four ring-carbons, signifying aromatic stabilization. While tetrakis(phenylimino) cyclobutane (C$_4$(NPh)$_4$) has been prepared by organic synthesis and reduced to tetraphenylsquaramidine (C$_4$(NPh)$_2$(NHPh)$_2$),[10] the isolation of **2** marks the first reductive tetramerization of an isocyanide mediated by a metal complex.

Complex **3** crystallized in the monoclinic space group C2/c, with a crystallographically imposed inversion center located at the midpoint of the Cr1−Cr1a vector (Cr...Cr, 8.867 Å). Now the two Cr atoms are linked by an unusual heterobicyclic structure obtained by fusing six cyclohexyl isocyanide molecules into a hexamer. If neutral, the latter would be a 1,4-diaza-bicyclo[3.3.0]octene with four exocyclic imine functionalities. However, its bond distances are once again indicative of a dianionic structure, best represented by the resonance structure depicted in Scheme 1.[9] Either way, this structure is not an analog of rhodizonate (C$_6$O$_6^{2-}$), the product of the reductive coupling of six CO molecules forged by molten potassium.[11] However, the oxygen analog of the core structure of **3** is certainly feasible and might conceivably result from a transition metal mediated CO coupling. For utilitarian purposes it was of interest to liberate the newly created heterocycle from the metal; consistent with its presumed anionic nature this was easily accomplished by treatment of **3** with an excess of degassed water. The diprotonated molecule (CyNC)$_6$H$_2$ (**5**) was isolated from the hydrolysis products in modest yield; its molecular structure has been determined and is shown in Figure 5S. Notably, an analogous (xylyl-susbtituted) organic molecule had been isolated from a reaction of a Pd(II) hydride with XylNC.[12] Its formation had been proposed to involve

successive migratory insertions; however, this seems unlikely in our case, and we favor a reductive coupling pathway instead.

The formation of a mixture of products might be considered disadvantageous from a preparative viewpoint. We wondered whether restricting the stoichiometry might favor the formation of a tetramer over a hexamer, and accordingly, we have reacted [$^{H}L^{iPr}$Cr]$_2$ with just 4 equiv of cyclohexyl isocyanide. To our surprise, this reaction produced neither **2** nor **3**; instead, yet another chromium-bound tetramer (**4**, see Scheme 1) was formed in ca. 40% yield. Its molecular structure, as determined by X-ray diffraction, is depicted in Figure 3. Once again, the

Figure 3. Molecular structure of **4** (30% probability level); selected interatomic distances (Å) and angles (deg): Cr1−N6, 1.887(2); Cr1−C52, 1.954(3); Cr2−N5, 2.046(2)); Cr2−N8, 2.034(3); N6−Cr1−C52, 88.34(12); N5−Cr2−N8, 79.51(10).

coupling product bridges the two chromium fragments. However, **4** is less pleasingly symmetric then either **2** or **3**; the two chromium atoms are differently ligated, and a consideration of the relevant interatomic distances and coordination geometries (that of Cr1 can be described as distorted square planar, whereas Cr2 is clearly tetrahedral, befitting a Cr(III) ion) suggests a possible description of **4** as a mixed-valent (Cr^{I}Cr^{III}) complex. Furthermore, one of the cyclohexyl substituents has suffered a C−H activation, with the hydrogen atom (of C79) presumably ending up on C55 of the sole six-membered heterocycle of the tetramer. Other coupling products may be envisioned, in terms of both structure and number of coupled substrate molecules; besides, surely the choice of isonitrile would affect the outcome. These observations suggest that the metal mediated reductive coupling of isonitriles may constitute a promising one-step process for the preparation of structurally complex nitrogen heterocycles.

At this stage, we have little information about the mechanism(s) of the transformations described above. We know that [$^{H}L^{iPr}$Cr]$_2$ has a tendency to form [2 + 2] cycloaddition products as well as bis(ligand) adducts, suggesting the formation of intermediates such as [$^{H}L^{iPr}$Cr]$_2$(μ-η^1:η^1-CNCy) and/or [$^{H}L^{iPr}$Cr(CNCy)]$_2$ retaining metal−metal bonds. ^{1}H NMR monitoring of the reaction of [$^{H}L^{iPr}$Cr]$_2$ with CyNC revealed the formation of at least one transitory paramagnetic intermediate, but we have not yet been

able to determine its structure. Reactions with other isonitriles will be necessary to address these mechanistic questions.

To summarize, we have shown that the quintuply bonded chromium dimer $[^HL^{iPr}Cr]_2$ effects the reductive coupling of isonitriles to produce a range of unusual nitrogen containing heterocycles. These reactions are reminiscent of, but go beyond, the metal-mediated coupling reactions of isoelectronic carbon monoxide. It is interesting to speculate whether the extremely short chromium–chromium bond (1.803(1)Å) and/or the redox ambiguity of the α-diimine ligands of $[^HL^{iPr}Cr]_2$ are critical to the success of this chemistry.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental, computational, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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