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# Mechanism-based design of labile precursors for chromium(i) chemistry†

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**Dinitrogen complexes of the type  $\text{Tp}^{\text{R,R}}\text{Cr}-\text{N}_2-\text{CrTp}^{\text{R,R}}$  are not the most labile precursors for Cr(i) chemistry, as they are sterically protected from obligatory associative ligand substitution. A mono-nuclear alkyne complex –  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\eta^2-\text{C}_2(\text{SiMe}_3)_2)$  – proved to be much more reactive.**

Half a century after the discovery of the first dinitrogen complex, by Allen and Senoff,<sup>1</sup> coordination compounds of the rather inert  $\text{N}_2$  molecule are still much sought after, due in large part to their substitutional lability and concomitant role as precursors for a wide variety of transition metal complexes.<sup>2</sup> For example, our interest in the activation of  $\text{O}_2$  and other small molecules has benefited greatly from the availability of  $\text{Tp}^{\text{tBu,Me}}\text{Co}(\text{N}_2)$  and  $[(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}]_2(\mu-\eta^2:\eta^2-\text{N}_2)$ , respectively.<sup>3,4</sup> While these two molecules differ in the mode of coordination of the designated leaving group, both undergo facile ligand substitution to yield a plethora of compounds incorporating the  $\text{Tp}^{\text{tBu,Me}}\text{Co}$  and  $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}$  fragments.<sup>5,6</sup> We were interested in the intersection of these two chemistries, and accordingly we now report the preparation of dinitrogen complexes of various  $\text{TpCr}$  fragments, which exhibited some notable differences in reactivity.

$\text{KC}_8$  reduction under nitrogen of blue  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{THF})\text{Cl}$  in  $\text{Et}_2\text{O}/\text{THF}$  (4 : 1) at room temperature yielded green needles of  $[\text{Tp}^{\text{tBu,Me}}\text{Cr}]_2(\mu-\eta^1:\eta^1-\text{N}_2)$  (**1**) in 42% yield (see ESI† for experimental detail and characterization of all compounds). The molecular structure of **1**, as determined by X-ray diffraction, is shown in Fig. 1. The dinuclear complex contains a single  $\text{N}_2$  ligand bridging the two staggered  $\text{TpCr}^{\text{I}}$  fragments, featuring end-on coordination of the dinitrogen to chromium. The N–N bond distance of 1.211(4) Å is substantially elongated over that of the free ligand (1.098 Å),<sup>7</sup> and the Cr–N7 bond – at 1.838(3) Å – is very short, certainly by comparison to the average Cr– $\text{N}_{\text{Tp}}$

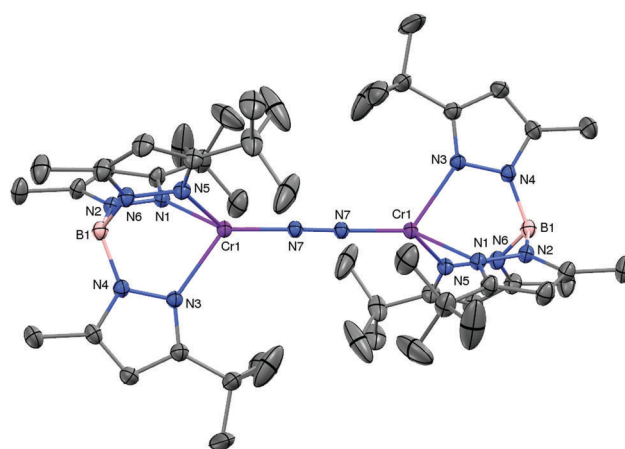


Fig. 1 The molecular structure of  $[\text{Tp}^{\text{tBu,Me}}\text{Cr}]_2(\mu-\eta^1:\eta^1-\text{N}_2)$  (**1**, 30% probability level). Selected interatomic distances (Å) and angles (°): N7–N7A, 1.213(5); Cr–N7, 1.838(3); Cr–N1, 2.205(3); Cr–N3, 2.200(3); Cr–N5, 2.190(3);  $\text{N}_{\text{Tp}}-\text{Cr}-\text{N}_{\text{Tp,avg}}$ , 87.3;  $\text{N}_{\text{Tp}}-\text{Cr}-\text{N7}_{\text{avg}}$ , 127.2.

distance (2.198 Å). Both measures are consistent with strong  $\pi$ -backbonding from the low-valent chromium to the dinitrogen ligand. In accord with the crystallographically imposed inversion symmetry of **1**, its IR spectrum (KBr) did not show a discernable N–N stretching vibration. **1** is a paramagnetic substance with isotropically shifted and broadened  $^1\text{H}$  NMR resonances. At room temperature, it has an effective magnetic moment of  $\mu_{\text{eff}} = 3.9(1) \mu_{\text{B}}$ , a possible interpretation of which is that the bridging  $\text{N}_2$  ligand mediates antiferromagnetic coupling between the two  $\text{Cr}^{\text{I}}$  (high-spin  $d^5$ ,  $S = 5/2$ ) ions.

With **1** in hand, we embarked on an exploration of its reactivity with a variety of small molecules. As expected, the low-valent dinitrogen complex reacted rapidly with molecules that yielded products in which the chromium was oxidized. Examples include  $\text{O}_2$ ,  $\text{S}_8$ ,  $\text{N}_2\text{O}$ , and  $\text{RN}_3$ . While the chalcogenide chemistry will be detailed elsewhere, we offer the product of the reaction of **1** with adamantyl azide, *i.e.* purple  $\text{Tp}^{\text{tBu,Me}}\text{Cr}=\text{NAD}$  (**2**) as a representative example. **2** is the sole terminal imido complex of trivalent chromium.<sup>8</sup> Its molecular structure is depicted in Fig. 2. The pseudo-tetrahedral

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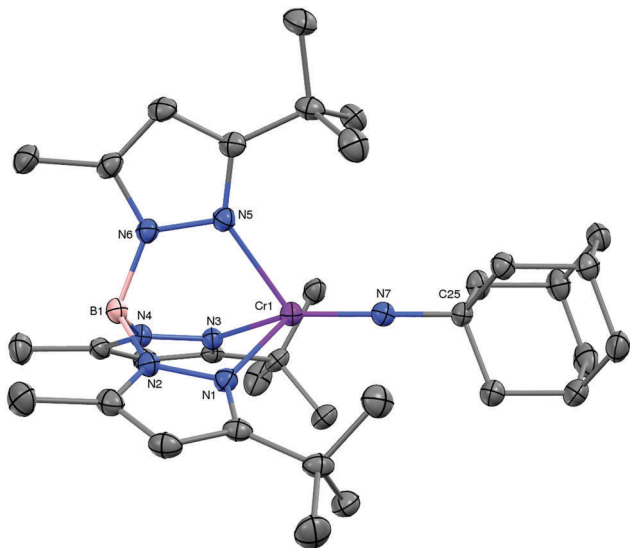


Fig. 2 The molecular structure of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}=\text{NAd}$  (**2**, 30% probability level). Selected interatomic distances (Å) and angles ( $^\circ$ ): Cr–N7, 1.687(2); N7–C25, 1.455(3); Cr–N1, 2.132(2); Cr–N3, 2.151(2); Cr–N5, 2.160(2); Cr1–N7–C25, 178.8(2) $^\circ$ ;  $\text{N}_{\text{Tp}}\text{–Cr–N}_{\text{Tp,avg}}$ , 88.0;  $\text{N}_{\text{Tp}}\text{–Cr–N7}_{\text{avg}}$ , 126.7.

complex features a linear imido ligand with a Cr–N distance of 1.687(2) Å; the latter is close the computationally predicted 1.708 Å for  $\text{Tp}^{\text{tBu,Me}}\text{Cr}=\text{N}^{\text{tBu}}$ .<sup>9</sup> Consistent with the intermediate formal oxidation state of chromium it is also on the very long side of such distances.<sup>10</sup> The effective magnetic moment of **2** measured  $\mu_{\text{eff}} = 3.7(1) \mu_{\text{B}}$ , which is consistent with a quartet spin ground state ( $d^3$ ,  $S = 3/2$ ).

To our surprise, reactions of **1** with good  $\pi$ -acceptors did either not proceed at all, or yielded decomposition products only after prolonged exposure. Thus, **1** did not react with alkenes (e.g., ethylene) or alkynes (e.g., 2-butyne), and lengthy exposure to an excess of CO (1 atm, 18 h) yielded only the ligand fragmentation product  $(\text{tBu,Me}^{\text{pzh}})_2\text{Cr}(\text{CO})_4$ , possibly due to traces of adventitious impurities ( $\text{H}_2\text{O}$ ?). We have reason to believe (*vide infra*) that all of these attempted reactions are thermodynamically favorable and would yield stable  $\pi$ -complexes. However, they apparently face insurmountable kinetic barriers, distinguishing **1** as a peculiarly substitution inert dinitrogen complex. To rationalize this disparity in reactivities, which has some precedent in titanium chemistry,<sup>11</sup> we hypothesized that the reactions with oxidants may proceed *via* initial outer sphere electron transfer, thereby activating the Cr– $\text{N}_2$  bond with respect to dissociation. Non-oxidizing ligands, on the other hand, may be forced to undergo an associative ligand substitution, because the Cr– $\text{N}_2$  bond of **1** is too strong to permit a dissociative reaction path. The 13-electron configuration of the individual Cr atoms may make a ligand dissociation – yielding a bare, trigonal pyramidal 11-electron  $\text{Tp}^{\text{tBu,Me}}\text{Cr}$  fragment – energetically unfeasible. In this scenario, the effective steric shielding of the metal atoms by interleaving *tert*-butyl substituents of the opposing  $\text{Tp}^{\text{tBu,Me}}$  ligands may prove impossible to penetrate, rendering the Cr– $\text{N}_2$ –Cr core of **1** impervious to ligand attack.

We then resolved to test the two essential pillars of this mechanistic hypothesis, namely (i) the lack of dissociation of **1**,

Table 1 Selected structural parameters of dinitrogen complexes  $[\text{Tp}^{\text{R,R'}}\text{Cr}]_2(\mu\text{-N}_2)$

Compound	<b>1</b> ( $\text{Tp}^{\text{tBu,Me}}$ )	<b>3</b> ( $\text{Tp}^{\text{tBu,iPr}}$ )	<b>4</b> ( $\text{Tp}^{\text{iPr,iPr}}$ )
N–N [Å]	1.213(5)	1.209(3)	1.214(4)
Cr–N [Å]	1.838(3)	1.8395(16)	1.773(2)
Cr–N <sub>Tp</sub> [Å]	2.198	2.191	2.094

and (ii) the steric blocking of associative ligand substitution pathways. A dissociation of **1** in the absence of  $\text{N}_2$  must yield either one or two equivalents of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}$  or a solvate thereof ( $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{S})$ ,  $\text{S} = \text{Et}_2\text{O}$ , THF). Alternatively, in the presence of gaseous  $\text{N}_2$ , an associative reaction with the latter may produce two equivalents of mononuclear intermediate  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{N}_2)$ . Either way, the reversible dissociation into mononuclear fragments should lead to scrambling of mixtures of suitably labeled dinuclear  $\text{N}_2$  complexes. In order to test this prediction we have prepared  $[\text{Tp}^{\text{tBu,iPr}}\text{Cr}]_2(\mu\text{-N}_2)$  (**3**), a close analog of **1**. **3** has been fully characterized, and selected structural parameters are listed in Table 1. In a control experiment, the reduction of an equimolar mixture of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{THF})\text{Cl}$  and  $\text{Tp}^{\text{tBu,iPr}}\text{Cr}(\text{tBu,iPr}^{\text{pzh}})\text{Cl}$  yielded a 1:2:1 mixture of **1**,  $[\text{Tp}^{\text{tBu,Me}}\text{Cr}](\mu\text{-N}_2)[\text{CrTp}^{\text{tBu,iPr}}]$ , and **3**; the proportions of the products were measured by LIFDI-MS,<sup>12</sup> which exhibited strong molecular ion ( $\text{M}^+$ ) peaks for these compounds. The ratio of the products did not change upon heating the mixture to reflux in THF. However, when a mixture of **1** and **3** in THF under vacuum was heated to 70  $^\circ\text{C}$  for two days, subsequent analysis of the mixture by LIFDI-MS showed no evidence for the formation of the mixed ligand complex  $([\text{Tp}^{\text{tBu,Me}}\text{Cr}](\mu\text{-N}_2)[\text{CrTp}^{\text{tBu,iPr}}])$ . Similarly, when the same experiment was repeated under a  $\text{N}_2$  atmosphere, no signal for the mixed compound was detected in the mass spectrum. These results prove that **1** (and **3**) do not detectably dissociate in THF solution, even when heated for prolonged periods. A dissociative mechanism ( $\text{I}_\text{d}$  or  $\text{D}$ ) for the ligand substitution of **1** is thereby ruled out.<sup>13</sup>

An alternative associative mechanism should be facilitated by lesser steric hindrance of the Tp ligands. To explore this possibility, we have prepared  $[\text{Tp}^{\text{iPr,iPr}}\text{Cr}]_2(\mu\text{-N}_2)$  (**4**). It is interesting to note that the N–N bond distance of **4** (see Table 1) does not significantly differ from those of **1** or **3**; the extent of  $\pi$ -backbonding is apparently similar in all three compounds. However, the Cr–N distances in **4** are appreciably shorter (by 0.066(2) Å), suggesting that lesser steric interactions between the opposing ligands allow for a closer approach of the two TpCr fragments. Space filling models of **1** and **4** (see Fig. S3, ESI<sup>†</sup>) also suggest greater accessibility of the chromium centers in **4**. In stark contrast to **1**, exposure of **4** to 1 atm of  $\text{CO}(\text{g})$  resulted in an immediate color change from violet to yellow and precipitation of octahedral  $\text{Tp}^{\text{iPr,iPr}}\text{Cr}(\text{CO})_3$  (**5**, see Fig. S4, ESI<sup>†</sup>). It appears that the diminished steric protection of Cr by the  $\text{Tp}^{\text{iPr,iPr}}$ -ligand causes a dramatic increase in the rate of ligand substitution; this observation argues strongly in favor of an associative substitution mechanism ( $\text{I}_\text{a}$  or  $\text{A}$ ).

The results described above suggest that the preparation of coordination compounds of the  $\text{Tp}^{\text{tBu,Me}}\text{Cr}^\text{I}$  fragment will require a precursor that is subject to facile associative ligand



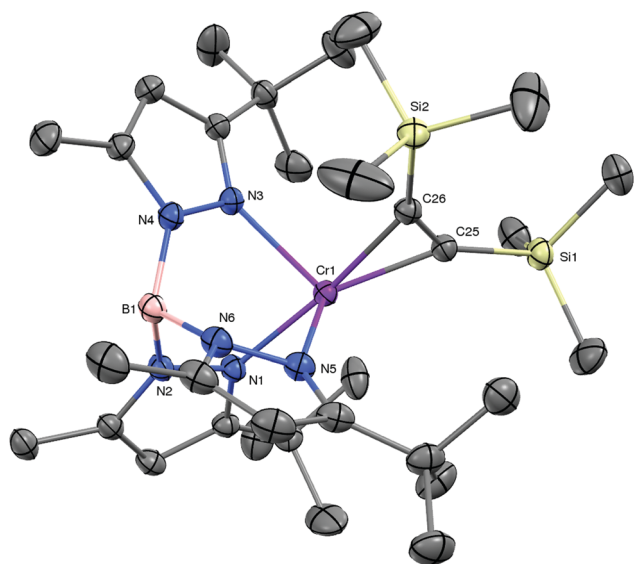
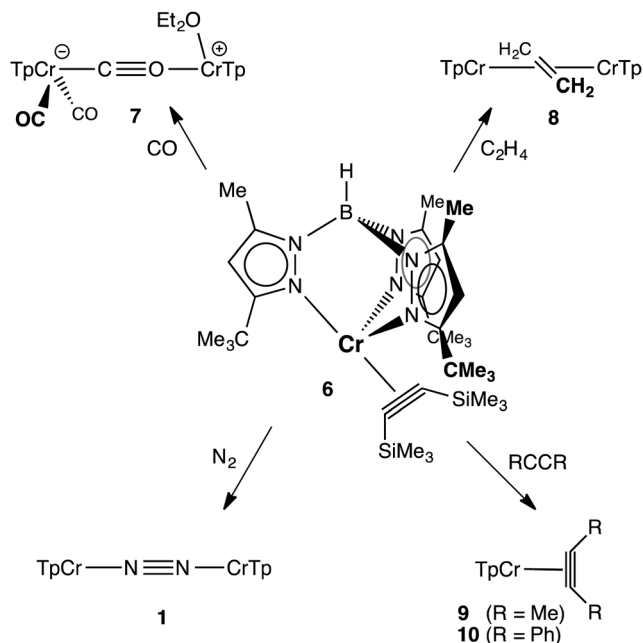


Fig. 3 The molecular structure of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$  (**6**, 30% probability level). Selected interatomic distances (Å) and angles ( $^\circ$ ): Cr–C25, 2.0480(19); Cr–C26, 2.0835(18); C25–C26, 1.288(3); Cr–N1, 2.1015(15); Cr–N3, 2.1614(16); Cr–N5, 2.1504(16);  $\text{N}_{\text{Tp}}\text{--Cr--N}_{\text{Tp,avg}}$ , 87.7;  $\text{N1--Cr--C25/C26}_{\text{centroid}}$ , 172.5;  $\alpha$  (angle of deviation of alkyne centroid from B–Cr axis) = 49.3 $^\circ$ .

substitution; in all likelihood this will require a mononuclear structure to disrupt the molecular sheath protecting the Cr–N<sub>2</sub>–Cr core of **1**. Based on related *nacnac*Cr chemistry, and inspired by Rosenthal *et al.*,<sup>14</sup> we selected  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$  (**6**) as a likely candidate.<sup>15</sup>  $\text{KC}_8$  reduction of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{THF})\text{Cl}$  in  $\text{Et}_2\text{O}/\text{THF}$  under vacuum in the presence of bis(trimethylsilyl)acetylene yielded brown crystals of **6** in 75% yield. The molecular structure of **6** (depicted in Fig. 3) features a severely distorted coordination environment, in which the centroid of the alkyne's triple bond is displaced from the B–Cr axis of the threefold symmetric TpCr fragment by 49 $^\circ$ . This *cis*-divacant octahedral structure creates two symmetry equivalent openings for attack by external ligands. The relatively long Cr–C<sub>alkyne</sub> distances (2.048(2) and 2.084(2) Å) and the comparatively modest structural reorganization of the coordinated alkyne – by comparison with other complexes of the type  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\eta^2\text{-C}_2\text{R}_2)$  (R = Me, Ph; see ESI†) – herald a rather tenuous hold of Cr upon this sterically encumbered alkyne. In accord with this notion, ‘spring-loaded’ **6** proved much more reactive toward ligand substitution than **1**!

The reactions of **6** with various  $\pi$ -acceptors are summarized in Scheme 1; the molecular structures of the products – as determined by X-ray diffraction – are included in the ESI.† When carried out in ethereal solvents (THF,  $\text{Et}_2\text{O}$ ), these reactions were facile and proceeded in good yield. The carbonylation of **6** is notable in that it stopped short of the formation of  $\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{CO})_3$  (*i.e.*, the analog of **5**). The actual product,  $\kappa^2\text{-Tp}^{\text{tBu,Me}}\text{Cr}(\text{CO})_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-CO})(\text{Et}_2\text{O})\text{CrTp}^{\text{tBu,Me}}$  (**7**) is best rationalized as the product of a disproportionation, resulting in a mixed-valent ( $\text{Cr}^0\text{Cr}^{\text{II}}$ ) isocarbonyl complex. The divalent chromium – formally a cation – has apparently lost its affinity for additional  $\pi$ -acids. The dinuclear ethylene complex,  $[\kappa^2\text{-Tp}^{\text{tBu,Me}}\text{Cr}]_2\text{-}(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2\text{H}_4)$  (**8**), while a rare case of ethylene  $\pi$ -bonded to two



Scheme 1 Ligand substitution reactions of **6**.

metals,<sup>16</sup> finds precedent in the analogous  $[(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}]_2\text{-}(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2\text{H}_4)$ .<sup>4</sup> Like the latter, it did not react further with ethylene, exhibiting no activity for catalytic oligomerization or polymerization of ethylene.<sup>6a</sup> The irreversible reactions of **6** with less hindered alkynes were expected, being of interest mostly for the formation of pseudotetrahedral alkyne complexes **9** and **10**, as evidenced by  $^1\text{H}$  NMR. More surprising was the observation that **6** reacted with  $\text{N}_2$  (1 atm), forming **1** and free alkyne quantitatively! The spontaneous substitution of an alkyne ligand by  $\text{N}_2$  is rather unusual. It is a measure of the instability and lability of **6** and – if additional proof was needed – suggests that it is an excellent precursor for  $\text{Tp}^{\text{tBu,Me}}\text{Cr}^{\text{I}}$  chemistry.

We are now exploring the small molecule activation chemistry of  $\text{TpCr}(\text{I})$  fragments, judiciously using the synthons described above. The results of these studies will be reported in due course.

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