ORGANOMETALLICS

Catalytic Formation of Asymmetric Carbodiimides at Mononuclear Chromium(II/IV) Bis(alkoxide) Complexes

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Supporting Information

ABSTRACT: Herein we report the synthesis of Cr imido complexes in bis(alkoxide) ligand environments and their nitrene transfer reactivity with isocyanides. The reaction of $Cr_2(OR)_4$ (OR = OC^tBu₂Ph) with bulky aryl or alkyl azide results in the formation of the trigonal-planar Cr(IV) mono(imido) complexes $Cr(OR)_2(NR^1)$, whereas less bulky aryl azides form the Cr(VI) bis(imido) complexes $Cr(OR)_2(NR^1)_2$. Cr(IV) mono(imido) complexes undergo facile reaction with 1 equiv of 2,6-dimethylphenyl isocyanide (CNR²) to form the corresponding carbodiimides R^1NCNR^2 . In contrast, no reaction of $Cr(OR)_2(NR^1)_2$ complexes with CNR^2 is observed. The reaction of $Cr(OR)_2(NR^1)$ with excess



isocyanide leads to the isolation of the Cr(II) complex $Cr(OR)_2(CNR^2)_4$, along with the observation of the anticipated carbodimide product. $Cr(OR)_2(CNR^2)_4$, which can also be obtained by treating $Cr_2(OR)_4$ with 4 equiv of isocyanide, reacts with azides N_3R^1 (R^1 = adamantyl, mesityl) to produce the respective carbodiimides. Catalytic formation of carbodiimides R^1NCNR^2 is observed from the mixtures of azides R^1N_3 (R^1 = mesityl, 2,6-diethylphenyl, 2-isopropylphenyl, adamantyl) and several different aryl isocyanides CNR^2 using 2.5 mol % of $Cr_2(OR)_4$.

INTRODUCTION

Carbodiimides are widely used organic compounds that hydrolyze readily and thus serve as excellent dehydration agents. Large-scale applications of carbodiimides include as stabilizers and antihydrolysis agents in polymers production, as coupling agents in peptide synthesis, and in various organic transformations. $^{1-6}$ Carbodiimides are synthesized by a plethora of transition-metal-catalyzed routes,⁷ including oxidative coupling of amines with isocyanides⁸ and coupling of two isocyanates R'NCO with loss of 1 equiv of $CO_{2^{\prime}}^{9}$ as well as by transition-metal-free stoichiometric routes such as the reaction of isocyanates with phosphinimines $(aza-Wittig)^{10}$ and by tin-mediated addition of silylamines to isocyanates.¹¹ Coupling of an [NR] (nitrene) group (originating in organoazides) with isocyanide is among the most attractive methods to synthesize carbodiimides, as (1) a large variety of azides are easily accessible using simple synthetic procedures, (2) both symmetrical and asymmetrical carbodiimides can be synthesized, and (3) the only side product in this reaction is the environmentally friendly dinitrogen. Therefore, numerous efforts have been made to make carbodiimides via coupling of isocyanides and organoazides. Most of these coupling reactions take place at low-coordinate late-transition-metal catalysts stabilized by nitrogen, carbon, or phosphorus ligands, where the M=NR functionality is suggested to serve as the reactive intermediate.¹²⁻²¹ The combination of the soft, electron-rich late transition metals and the hard π -donating imido functionality make the imido functionality reactive and thus susceptible to transfer. In contrast, imido compounds of earlier transition metals are significantly more stable, because the higher oxidation state of the early transition metals and the availability of empty d orbitals allow them to form strong multiple M–N bonds with a powerful σ and π donor, the imido group (NR). Thus, whereas the stoichiometric and catalytic reactivity of the oxophilic early-transition-metal imido complexes with isocyanates to form symmetric carbodiimides is well-established (Figure 1A),²² their reactivity in the imido-

Catalyzed by late transition metal complexes

Figure 1. Two common catalytic methods to synthesize carbodiimides: (A) synthesis of symmetric carbodiimides via early-transitionmetal catalysis; (B) synthesis of asymmetric carbodiimides via latetransition-metal catalysis.

group transfer to isocyanides to form asymmetric carbodiimidies is not very common (Figure 1B).²³⁻²⁶ Furthermore, these imido—isocyanide couplings tend to be stoichiometric at the early-transition-metal centers, whereas catalysis is common with later metals. Heyduk and co-workers have recently

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reported an early-transition-metal-based (Zr(IV)) catalyst for catalytic nitrene–isocyanide coupling where catalysis is facilitated by the use of a redox-active ligand at Zr.²⁷ Herein we report that a low-coordinate early-transition-metal (Cr(IV)) imido complex in the bis(alkoxide) ligand environment serves as an active catalyst in the formation of a variety of asymmetric aryl isocyanides.

We have recently reported the synthesis of a series of 3d complexes in bis(alkoxide) ligand environments (M- $(OR)_2(THF)_2$, M = Mn-Co, OR = OC'Bu_2Ph).²⁸ The mononuclear iron complex Fe $(OR)_2(THF)_2$ was found to undergo strikingly different reactivity with alkyl versus aryl azides.²⁹ In the case of an alkyl (adamantyl, Ad) azide, reductive coupling was observed to yield the Fe(III)-bound hexazene complex (RO)_2Fe(μ - κ_2 : κ_2 -AdNNNNNAd)Fe(OR)_2.^{29a} In the case of aryl azides, nitrene formation occurs followed by dimerization to form the respective diazene or complex rearrangement to form bridging imido species (Scheme 1).^{29b}

Scheme 1. Consecutive Treatment of Fe(OR)₂-Type Complexes with Azides/Isocyanides Does Not Lead to the Formation of Carbodiimides



We have attempted to intercept the transient nitrene complex by the addition of isocyanide (2,6-dimethylphenyl isocyanide, CNR^2), in order to form a new C–N bond in the carbodiimide. However, the addition of a mixture of isocyanide and azide to the Fe(II) precursor has led instead to the formation of the stable bis(isocyanide) complex $Fe(OR)_2(CNR^2)_2$, which proved unreactive with excess azide.^{29b} Thus, since the isocyanide coordination at the Fe^{II}(OR)₂ center precludes formation of the metal nitrene functionality, we decided to investigate the interaction of preformed stable metal nitrene (imido) species in bis(alkoxide) ligand environments with various isocyanides. To obtain a stable metal imido complex, we turned toward chromium. While Cr-imido complexes are generally stable, we hoped that in the case of the coordinatively unsaturated Cr(IV) imido complex we would be able to observe ligation of an isocyanide next to the imido functionality and perhaps to force C-N bond formation and carbodiimide liberation via heating or photolysis. In this paper, we demonstrate that trigonal planar $Cr^{IV}(OR)_2(NR^1)$ species undergo surprisingly facile reaction with several different isocyanides to give Cr(II) isocyanide complexes and the respective carbodiimides. Furthermore, we also report catalytic conversion of mixtures of bulky aryl azides and isocyanides to asymmetric carbodiimides.

RESULTS AND DISCUSSION

Synthesis of the Cr(II) Precursor Cr₂(OR)₄ (1). The synthesis and reactivity of chromium complexes reported in this paper are summarized in Scheme 2. Unlike the previously synthesized $M(OR)_2(THF)_2$ (M = Mn-Co),^{28b} we were not able to obtain " $Cr(OR)_2(THF)_2$ " by treating the seesaw cluster $[Cr_2Li_2X_2(OR)_4]^{28a}$ with TlPF₆. Seeking an alternative route to $Cr(OR)_2(THF)_2$, we synthesized the previously reported $Cr((N(SiMe_3)_2)_2(THF)_2^{.30}$ Purple $Cr(N(SiMe_3)_2)_2(THF)_2$ undergoes protonolysis with HOR³¹ to form green homodinuclear $Cr_2(OR)_4$ (1; 60% yield). It is worth noting that the protonolysis reaction was conducted in THF, and no $Cr(OR)_2(THF)_2$ formation was observed. The structure of 1, featuring two trigonal-planar Cr(II) centers each bridged by two alkoxides, is given in Figure 2. Compound 1 is related to the previously synthesized $Cr_2(OSi^tBu_3)_4^{32}$ and $Cr_2(OCH^tBu_2)_2(OC^tBu_3)_2$.³³ The Cr-Cr separation is 2.651(1) Å in complex 1, in comparison with 2.637(2)/ 2.6800(2) Å in $Cr_2(OSi^tBu_3)_4$ and 3.075(1) Å in $Cr_2(OCH^tBu_2)_2(OC^tBu_3)_2$ (Table 1). The solution magnetic moment of compound 1 was found to be $\mu_{obs} = 2.5 \pm 0.3 \mu_B$ (2.8 $\mu_{\rm B}$ in Cr₂(OSi^tBu₃)₄), indicative of some antiferromagnetic

Scheme 2. Synthetic Transformations at Chromium Bis(alkoxide) Platforms Described in This Paper





Figure 2. Molecular structure of $Cr_2(OC^tBu_2Ph)_4$ (1).

 Table 1. Selected Structural Data for the Compounds

 Reported in This Paper

complex	Cr–OR _{terminal} (Å)	Cr–NR′ (Å)	RO-Cr-OR (deg)
1	1.833(2)/1.835(2)		
2	1.766(2)/1.777(2)	1.651(2)	114.41(8)
3	1.780(1)/1.783(1)	1.632(1)	117.57(5)
4	1.760(1)/1.789(1)	1.656(2)	116.38(7)
5	1.776(4)/1.795(4)	1.641(5)/1.664(5)	111.41(18)
6	$1.770(5)/1.780(5)^{a}$	1.648(7)/1.667(7)	113.4(3)
7	1.945(4)/1.944(4)		173.17(16)

^{*a*}Of the two independent molecules present in the asymmetric unit, data for only one are presented. The second molecule features similar structural data.

interaction between the Cr(II) centers. As the electronic structure of the related compound $Cr_2(OSi^tBu_3)_4$ has been studied in great detail,³² it was not pursued in this work.

Synthesis and Characterization of Cr(IV) Imido Complexes. To study the group-transfer chemistry of $Cr_2(OR)_4$ (1), we treated complex 1 with 2 equiv of mesityl azide (N₃Mes), adamantyl azide (N₃Ad), or 2,6-diethylphenyl azide (N₃DEP) (Scheme 2). This reaction, followed by recrystallization, affords the deep red Cr mono(imido) complexes Cr(OR)₂(NMes) (2, 81%), Cr(OR)₂(NAd) (3, 64%), and Cr(OR)₂(NDEP) (4, 23%). Treatment of 1 with excess azide N₃R¹ (R¹ = Mes, Ad) does not form the corresponding bis(imido) complexes. We also note that the treatment of 1 with bulkier azides (2,6-diisopropylphenyl azide and 2,4,6-triphenylphenyl azide) failed to form the corresponding imido complexes. All Cr mono(imido) compounds were

found to be extremely air sensitive. Complexes 2 and 3 were characterized by X-ray crystallography, IR spectroscopy, UVvis spectroscopy, solution magnetic moment measurements, and elemental analysis. Compound 4 was isolated in low yield, due to its high solubility in pentane, and therefore was characterized only by X-ray diffraction and IR spectroscopy. Xray-quality crystals of the imido complexes 2-4 were obtained from pentane (2 and 4) and hexane (3) at -35 °C. The structures (Figure 3) display trigonal-planar Cr centers (sums of angles around Cr are 359.9° (2), 360.0° (3), and 359.6° (4)) with relatively short Cr-imido distances of 1.651(2) Å (2), 1.632(1) Å (3), and 1.656(2) (4). We note that Wolczanski and co-workers reported several related trigonal Cr imido species bearing a silox ligand, $Cr(OSi^tBu_3)_2(NR)$. The structure of Cr(OSi^tBu₃)₂(N-2,6-diphenylphenyl) similarly demonstrated trigonal geometry at the Cr center and a short Cr-N bond distance of 1.649(2) Å.³² Solution magnetic moments of compounds 2 and 3, obtained using the Evans method,³⁴ were found to be $\mu_{obs} = 2.5 \pm 0.3 \ \mu_B$ and $\mu_{obs} = 3.3 \pm 0.4 \ \mu_B$, respectively, in comparison with 2.7–2.8 μ_B values observed for Cr(OSi^tBu₃)₂(NR).³² These values are indicative of triplet ground states, which are consistent with DFT calculations (see below).

The bis(alkoxide) monoimido species 2 and 3 were optimized as a singlet, triplet, and quintet at the B3LYP/6-31G(d) level of theory. No simplifications were made to the bulky alkoxide ligands. For 2, the triplet was calculated to be lowest in free energy, followed by the singlet (+11.42 kcal/mol) and then the quintet (+20.74 kcal/mol). A similar pattern was observed for 3 with triplet < singlet (+13.31 kcal/mol) < quintet (+33.97 kcal/mol). This finding is consistent with the experimental and calculated spin states in the related Cr=NR' species supported by siloxide ligands.³² On the basis of the large thermodynamic preference for the triplet state that matches the experimental magnetic data, we focused on the triplet for the structural and electronic analysis. A trigonalplanar arrangement about Cr was observed in the optimized structures of 2 and 3 (Figure 4). Excellent agreement with the X-ray data is observed for the Cr–N bond lengths in 2 (1.655 vs 1.651 Å) and 3 (1.635 vs 1.632 Å). It is worth noting that one of the alkoxide arms is oriented with the phenyl group anti to the imido group in 2, in contrast to the crystallographic orientation, where one of the 'Bu groups is anti to the imido group in both alkoxide arms.

The electronic structure of 2 was investigated by calculating the corresponding orbitals³⁵ that are shown in Figure 5. A similar analysis for 3 may be found in the Supporting Information. There are two singly occupied molecular orbitals



Figure 3. Molecular structures of compounds 2 (left), 3 (middle), and 4 (right).



Figure 4. Optimized structures of triplet **2** (left) and **3** (right). Important bond lengths are given in Å. Note that parts of the alkoxide ligands are excluded from the image for clarity.



Figure 5. Corresponding orbitals for triplet 2. Orbital isosurfaces are plotted at an isodensity value of 0.05 au.

based on the Cr ion and two doubly occupied π orbitals between the imido fragment and Cr that are mainly based on NR'. On the basis of this orbital occupation pattern, **2** and **3** are best characterized as having a Cr(IV) ion that is triply bonded to the NR' fragment.³⁶

Synthesis of Cr(VI) Bis(imido) Complexes. Azides featuring relatively bulky R groups (R = adamantyl, mesityl, 2,6-diethylphenyl) led selectively to the formation of mono-(imido) complexes. We have also investigated the reactivity of the Cr(II) precursor with selected aryl azides featuring less

bulky Ar groups (Ar = 4-methoxyphenyl, 4-trifluorophenyl). The reaction of compound 1 with 2 equiv of 4-methoxyphenyl azide or 4-trifluorophenyl azide results in the formation of deep red-brown Cr(VI) diimido complexes $Cr(OR)_2(NAr)_2$ that are isolated as brown crystals in 46% and 30% yields, respectively. The reaction of 1 with 1 equiv of 4-methoxyphenyl azide also leads to the formation of Cr(VI) bis(imido) species, as demonstrated by ¹H NMR and IR spectroscopy. We were not able to isolate or observe mono(imido) species from these reactions. For [Cr(OSi⁶Bu₃)₂], it was also reported that bulky azides form mono(imido) species while nonbulky azides form bis(imido) complexes at room temperature.³²

Cr(VI) bis(imido) complexes **5** and **6** are diamagnetic species that were characterized by ¹H and ¹³C NMR (and ¹⁹F for **6**) spectroscopy, IR spectroscopy, X-ray crystallography, and elemental analysis. NMR spectroscopy is consistent with an effective $C_{2\nu}$ symmetry in solution, displaying a single type of ¹Bu group and a phenyl group for both [OR] ligands. X-ray crystallography (Figure **6**) demonstrates pseudotetrahedral complexes featuring RO–Cr–OR angles of 111.4(2)° (**5**) and 113.4(3)° (**6**) and ArN–Cr–NAr angles of 104.9(3)° (**5**) and 106.6(4)° (**6**). Cr–imido bond distances are 1.641(5)/ 1.664(5) Å for **5** and 1.648(7)/1.667(7) Å for **6**.

Reactions of Cr Imido Complexes with Isocyanides. The focus of the current work is on the investigation of the reactivity of Cr imido species with isocyanides. To test the stoichiometric reactivity of the Cr mono(imido) complexes, complexes **2** and **3** were treated with 1 equiv of 2,6-dimethylphenyl isocyanide (2,6-Me₂PhNC) in C₆D₆ in the presence of an internal standard. Monitoring of the reaction by ¹H NMR spectroscopy (see Figure 7) revealed the disappearance of the isocyanide peaks and the appearance of new peaks that were attributed to formation of the respective carbodiimides N-(2,6-dimethylphenyl)-N-mesitylmethanediimine¹⁹ and N-adamantyl-N-(2,6-dimethylphenyl) methanediimine (eq 1). The observed NMR yields of the carbodiimides was also confirmed by mass spectrometry.

$$Cr(OR)_{2}(NR^{l}) + 2,6-Me_{2}PhNC$$

$$\rightarrow (2,6-Me_{2}Ph)N=C=NR^{l} + [Cr]$$
(1)

To gain insight into this reaction, we calculated the binding of 2,6-dimethylphenyl isocyanide to the triplet Cr(IV) imido intermediates. We denote these isocyanide-bound intermediates as 2-CNR'' and 3-CNR'' for mesityl and adamantyl,

Figure 6. Molecular structures of compounds 5 (left) and 6 (right).



Figure 7. (**A**) C_6D_6 spectrum of isocyanide 2,6-Me₂NC (δ 6.71, 6.57, and 2.05 ppm) in the presence of an internal standard (trimethoxybenzene, δ 6.25 and 3.30 ppm) in the 1–8 ppm region. (**B**) Spectrum of the mixture from (**A**) with complex **2**, demonstrating the formation of (2,6-Me₂Ph)N=C=NMes (δ 6.85, 6.65, 2.30, 2.28, and 2.07 ppm).

respectively. Formation of **2–CNR**" and **3–CNR**" is slightly uphill by 11.7 and 5.3 kcal/mol. Isocyanide binding disrupts π bonding to the imido group (see Figure 8, left), as evidenced by elongation of the Cr–N bond from 1.655 to 1.672 Å for **2–CNR**" and from 1.635 to 1.653 Å for **3–CNR**". Concurrently, the Cr–N–R' angle decreases from 177.1 to 168.5° in **2–CNR**" and from 178.6 to 160.9° in **3–CNR**". Next, we attempted to find a transition state for nucleophilic attack by this coordinated isocyanide on the imido group. Attempts with mesityl have been unsuccessful thus far, but the optimized transition state for adamantyl is shown in Figure 8 (right).

This transition state is calculated to be uphill in free energy by 23.3 kcal/mol relative to free isocyanide and 3, which should be accessible under the experimental conditions. Elongation of the Cr–N and shortening of the Cr–C bond lengths to 1.721 and 1.924 Å is observed. The new C-N bond is still relatively long at 1.899 Å; however, visualization of the normal mode corresponding to the imaginary frequency shows significant motion along the C-N bond. The triple-bond character of isocyanide is slightly reduced, with elongation from 1.172 Å in 3-CNR" to 1.197 Å in this transition state. An intrinsic reaction coordinate³⁷ calculation demonstrated that this transition state connects 3-CNR" to a species with carbodiimide bound to $Cr(OR)_2$. Optimization of the carbodiimide adducts for both mesityl and adamantyl (see the Supporting Information for structural details) resulted in structures that are uphill relative to free isocvanide and 2/3 by 9.2 and 0.6 kcal/mol, respectively. The endergonic reaction energy for 2 may indicate why we have been unable to identify the transition state for carbodiimide formation with this species. Alternative pathways involving multiple isocyanides bound to Cr (vide infra) and the possible role of the quintet surface in this mechanism are currently being explored.

Using 1 equiv of isocyanide, we were able to observe the formation of carbodiimide; however, we were not able to isolate the Cr-containing product. Thus, we decided to treat Cr mono(imido) species with excess isocyanide. The reaction of complex 2 with 5 equiv of 2,6-methylphenyl isocyanide resulted in complete conversion to the respective carbodiimide, as indicated by ¹H NMR spectroscopy (eq 2). Solvent removal and crystallization at -35 °C from hexanes produced deep brown crystals of $Cr^{II}(OR)_2(CNR^2)_4$ (7; 56%). Chromium-ligated isocyanides can be further converted to carbodiimides: the reaction of complex 7 with 5 equiv of MesN₃ produced the corresponding carbodiimide in 96% yield (based on isocyanide), as indicated by ¹H NMR spectroscopy (eq 3). We were not able to isolate a chromium-containing product from this reaction.

$$Cr(OR)_{2}(NMes) + 5ArNC$$

$$\rightarrow MesN = C = NAr (100\%)$$

$$+ Cr(OR)_{2}(CNAr)_{4} (56\%)$$
(2)

$$Cr(OR)_{2}(CNAr)_{4} + 5MesN_{3}$$

$$\rightarrow MesN=C=NAr (96\%) + [Cr]$$
(3)

Compound 7 was characterized by X-ray crystallography, IR spectroscopy, and solution magnetic moment measurements. The X-ray structure of compound 7 (Figure 9) reveals a pseudooctahedral Cr(II) complex containing two alkoxide ligands and four isocyanides. This compound is a rare example



Figure 8. Optimized structure of 3-CNR'' (left) and the transition state for carbodiimide formation for 3 (right). Important bond lengths are labeled in Å and bond angles in deg. Note that parts of the alkoxide ligands and isocyanide/imido substituents are excluded from the image for clarity.

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Figure 9. Molecular structure of complex 7.

of a Cr complex combining isocyanide and alkoxide ligands.³⁸ Wolczanski and co-workers synthesized [Cr- $(OSi^{t}Bu_{3})_{2}(CN^{t}Bu)_{2}$]. On the basis of the two CN absorptions (major peak at 2192 cm⁻¹, minor peak at 2099 cm⁻¹), the compound was proposed to exist as a mixture of cis and trans (major) isomers.³² In 7, the bulky alkoxides occupy mutually trans (axial) positions, whereas isocyanides form an equatorial plane. The IR spectrum of 7 reveals the CN group absorption at 2063 cm⁻¹ (singlet), versus 2116 cm⁻¹ in free 2,6-dimethylphenyl isocyanide.^{39,40} Other Cr(II) isocyanide complexes generally demonstrate lower CN stretching frequencies,⁴¹ thus indicating relatively electron-deficient isocyanides in the bis(alkoxide) complex 7 or in [Cr-(OSi^tBu₃)₂(CN^tBu)₂].

Reactions of Cr(VI) Bis(imido) Complexes with Isocyanides. We have also investigated the reactivity of Cr(VI) bis(imido) complexes 5 and 6 with 2,6-methylphenyl isocyanide. The experiments were conducted in a manner similar to the experiments involving [NR] transfer from Cr(IV) mono(imido) complexes: C₆D₆ solutions of the relevant Cr(VI) complex were treated with C_6D_6 solutions containing 6 equiv of 2,6-methylphenyl isocyanide and the internal standard trimethoxybenzene. In both cases, no reaction was observed (eq 4). Figure 10 demonstrates the ¹H NMR spectrum of complex 6 in the range 1-9 ppm (A), the spectrum of the isocyanide in the presence of the internal standard in the same range (B), and the ¹H NMR spectrum resulting upon mixing a solution of the isocyanide/standard from A with the solution of the complex from B (C). Spectrum C clearly demonstrates that no change takes place. We therefore conclude that the formation of Cr(VI) bis(imido) complexes encumbers the imido group transfer to isocyanides. It is possible that, due to the steric hindrance, Cr(VI) bis(imido) cannot bind an additional ligand (isocyanide), thus preventing formation of carbodiimide. We note that Wilkinson, Hursthouse, and co-workers reported imido group transfer to an isocyanide at the Cr(VI) bis(imido) complex $Cr(N^tBu)_2(Mes)_2$ at room temperature to form an isolable metal-bound carbodiimide.⁴² We have also investigated the possibility of carbodiimide formation by treating complex 7 with the nonbulky azides N_3R^1 ($R^1 = 4$ -methoxyphenyl, 4trifluorophenyl). Monitoring the reaction by ¹H NMR spectroscopy indicated no formation of the respective carbodiimides (see the Supporting Information).



Figure 10. (A) ¹H NMR spectrum of complex 6 in the 1–9 ppm range. (B) Spectrum of 2,6-dimethylphenyl isocyanide in the presence of an internal standard (TMB). (C) Spectrum of the mixture of the isocyanide and complex 6, demonstrating the lack of formation of the corresponding carbodiimide.

 $Cr(OR)_2(N(4-CE_3Ph))_2 + ArNC \rightarrow no reaction$ (4)

Catalytic Formation of Carbodiimides. Having established the stoichiometric reactivity modes of bis(alkoxide) Cr imido complexes with 2,6-dimethylphenyl isocyanide, we turned to investigate the catalytic reactivity of the Cr(II) precursor with various mixtures of aryl/alkyl azides and isocyanides. The experiments were conducted by treating 2.5 mol % of complex 1 with R^2NC ($R^2 = 2,6-Me_2Ph$, 4-OMePh, Ad, 2-Cl-6-MePh) and various organoazides at room temperature for 24 h in C_6D_6 . In selected cases (Table 2, entries 4, 8, and 9), the mixture was heated to 60 °C. The results of the catalytic experiments are given in Table 2. The combination of organoazides R^1N_3 (entries 1–3 and 5–7) featuring relatively bulky aryl substituents (R^1 = Mes, 2,6-Et₂Ph, 2-^{*i*}PrPh) with aryl isocyanides R^2NC ($R^2 = 2,6$ -Me₂Ph, 4-OMePh, 2-Cl-6-MePh) successfully forms carbodiimides in high yields. In contrast, combination of an adamantyl group at either the azide or isocyanide with a mesityl/2,6-dimethylphenyl counterpart produced only low yields of the resulting carbodiimide product (see entries 4 and 8) at room temperature. The yield can be somewhat increased for R^1 = Mes and R^2 = Ad by heating to 60 °C for several hours; further heating leads to the decomposition of starting materials. As expected from the stoichiometric experiments (see above), no carbodiimides form for aryl azides with any groups lacking ortho substituents ($R^1 = 4$ -CF₃Ph, 4-OMePh; entries 10 and 11). Similarly, no carbodiimides form for the very bulky aryl azides 2,6-diisopropylphenyl azide and 2,4,6-triphenylphenyl azide (for an example of 2,6-diisopropylphenyl azide, see entry 12), for which no Cr(IV) imido formation was observed.

The carbodiimides N-(2,6-dimethylphenyl)-N'-mesitylmethanediimine (entry 1), N-(2,6-diethylphenyl)-N'-(2,6-

Table 2. Catalytic Forn	nation of Asymmetric	Carbodiimides fro	om the Correspondi	ing Azides	and Isocyanides
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Entry	Azide	Isocyanide	Carbodiimide	NMR Yield (%)	Isolated Yield (%)
1				100	63
2	Et Et			93	56
3	/Pr N ₃			94	63
4	N ₃		N=C=N-	24 23ª	
5		MeO	N=C=N-OMe	100	40
6	Et Et	MeO-		71	e
7				62	32
8		-NC		0 ^b 50 ^c	
9	N ₃	-NC		0 0 ^d	0
10	F ₃ C			0	
11	MeO-			0	
12				0	

^{*a*}Heated to 60 °C for 15 h. ^{*b*}The reaction at room temperature produced only a small amount of the product; we were not able to quantify the amount of carbodiimide formed due to its small amount, and peaks overlap with those of the starting materials. ^{*c*}Heated to 60 °C for 8 h. ^{*d*}Heated to 60 °C for 14 h. ^{*c*}We were not able to obtain his carbodiimide in pure form due to the presence of a small unknown impurity. ^{*f*}All of the experiments were conducted at room temperature for 24 h unless otherwise indicated.

dimethylphenyl)methanediimine (entry 2), N-(2,6-dimethylphenyl)-N-(2-isopropylphenyl)methanediimine (entry 3), N-mesityl-N-(4-methoxyphenyl)methanediimine (entry 5), and N-mesityl-N-(2-chloro-6-methylphenyl)methanediimine (entry 7) were isolated in moderate yields and characterized by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information for details). We also obtained catalytic formation of N-(2,6-diethylphenyl)-N-(4-methoxyphenyl)methanediimine (entry 6) in good yield; however, we were not able to obtain this carbodiimide in pure form due to a persistent unknown impurity. The product was detected by ESI-MS. Whereas catalytic formation and isolation of N-(2,6-dimethylphenyl)-N'-mesitylmethanediimine was previously reported by Warren and

co-workers,^{19c} other carbodiimides are new compounds that have not been reported before. All newly synthesized carbodiimides appear to be mildly air sensitive. Their NMR spectra are unremarkable and are given in the Supporting Information. All carbodiimides give rise to a molecular ion in ESI-MS (see the Experimental Section). The most notable IR feature of carbodiimides involves strong signals around 2140 cm⁻¹ (see the Supporting Information for details) attributed to the N=C=N stretch.⁴³

SUMMARY AND CONCLUSIONS

We have demonstrated that bulky aryl and alkyl azides form selectively Cr(IV) imido complexes supported by two bulky

alkoxides, whereas nonbulky aryl azides lead to the formation of Cr(VI) bis(imido) complexes. Trigonal-planar Cr(IV) imido bis(alkoxide) complexes are capable of nitrene transfer to isocyanides to form carbodiimides, whereas Cr(VI) bis(imido) complexes are inert to this transformation. DFT calculations indicate a possible mechanism for carbodiimide formation; however, the calculated product with carbodiimide coordinated to $Cr(OR)_2$ was unable to be isolated experimentally. The reaction is catalytic for selected azides and aryl isocyanides, with two major limitations: (1) relatively small azides do not form carbodiimide product due to the formation of unreactive Cr(VI) bis(imido) complexes and (2) excessively bulky azides do not form any carbodiimide product, as they are incapable of imido formation. Our future endeavors in this project will focus on bulkier alkoxide ligands which may restrict even small azides to the formation of mono(imido) complexes, thus increasing the scope of possible substrates for carbodiimide formation.

EXPERIMENTAL SECTION

General Methods and Procedures. All reactions involving airsensitive materials were executed in a nitrogen-filled glovebox. LiOR,²⁸ mesityl azide,^{19c} 2-isopropylphenyl azide,^{44a} 2,6-diisopropylphenyl azide,^{44b} 2,6-diethylphenyl azide,^{44c} and $Cr[N(SiMe_3)_2]_2(THF)_2^3$ were synthesized according to previously reported procedures. Chromium(II) chloride was purchased from Strem. Lithium bis-(trimethylsilyl)amide, adamantyl azide, 4-(trifluoromethyl)phenyl azide solution, 4-azidoanisole solution, 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, 1-adamantyl isocyanide, and 2-chloro-6methylphenyl isocyanide were purchased from Aldrich and used as received. All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBraun solvent purification system and stored over 3 Å molecular sieves. Compounds 1-7 were characterized by ¹H and ¹³C NMR, IR, and mass spectroscopy, solution state magnetic susceptibility, X-ray crystallography, and elemental analysis. Isolated carbodiimides were characterized by ¹H and ¹³C NMR, IR, and mass spectrometry and elemental analysis. NMR spectra were recorded at the Lumigen Instrument Center (Wayne State University) on a Varian Mercury 400 MHz NMR spectrometer in C₆D₆ at room temperature. Chemical shifts and coupling constants (*J*) are reported in parts per million (δ) and hertz, respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. Solution state effective magnetic moments were determined using the Evans method. Lowresolution mass spectra were obtained at the Lumigen Instrument Center utilizing a Waters Micromass ZQ mass spectrometer (direct injection, with capillary at 3.573 kV and cone voltage of 20.000 V). Only selected peaks in the mass spectra and in the IR spectra are reported below. Analyses were performed by Midwest Microlab LLC and Galbraith Laboratories, Inc.

Synthesis and Characterization of Chromium Complexes. [$Cr_2(OR)_4$] (1). A solution of 5 mL of HOR³¹ (57.6 mg, 0.261 mmol) in THF was added at once to Cr[N(SiMe_3)_2]_2(THF)_2 (67.5 mg, 0.131 mmol) in THF. The solution gradually turned from light violet to green. The reaction mixture was stirred for 6 h, upon which the solvent was removed, and crystallization from hexanes at -35 °C overnight produced green crystals of Cr₂(OR)₄ (38.2 mg, 60% yield). IR (cm⁻¹): 2996 (m), 2916 (m), 2349 (m), 1059 (m), 949 (s), 745 (s), 706 (s). Anal. Calcd for C₆₀H₉₂Cr₂O₄: C, 73.4; H, 9.5. Found: C, 72.8; H, 9.2. $\mu_{\text{eff}} = 2.5 \pm 0.3 \mu_{\text{B}}$ (calcd 2.8 μ_{B}).

 $Cr(OR)_2(NMes)$ (2). A solution of 74 μ L of MesN₃ in ether (0.764 M) was added to a solution of complex 1 (28.1 mg, 0.0286 mmol) in toluene in one portion. The solution immediately changed color from green to deep red. The reaction mixture was stirred for 4 h, upon which the solvent was removed. Crystallization from pentane at -35 °C gave crystals of deep red Cr(OR)₂(NMes) (29.1, 81% yield). IR (cm⁻¹): 2943 (m), 2877 (w), 2122 (m), 1601 (m), 1479 (m), 1389

(m), 1202 (s), 1094 (s), 1053 (m), 1012 (m), 893 (w), 851 (m), 777 (s), 702 (s), 762 (s). $\mu_{eff} = 2.5 \pm 0.3 \mu_B$ (calcd 2.8 μ_B). Anal. Calcd for $C_{39}H_{57}CrNO_2$: C, 75.1; H, 9.2. Found: C, 74.9; H, 9.4.

Cr(*OR*)₂(*NAd*) (3). A solution of 5 mL of AdN₃ (4.7 mg, 0.0265 mmol) in toluene was added to a solution of compound 1 (12.3 mg, 0.0125 mmol) in toluene in one portion. The solution immediately changed color from green to deep red. The reaction mixture was stirred for 4 h, upon which the solvent was removed. Crystallization from hexanes at -35 °C overnight gave crystals of deep red Cr(OR)₂(NAd) (10.1 mg, 64% yield). IR (cm⁻¹): 2900 (m), 2891 (m), 1487 (m), 1440 (m), 1387 (m), 1360 (m), 1206 (m), 1053 (s), 1009 (s), 901 (m), 771 (s), 704 (s). $\mu_{eff} = 3.3 \pm 0.4 \,\mu_{B}$ (calcd 2.8 μ_{B}). Anal. Calcd for C₄₀H₆₁CrNO₂: C, 75.1; H, 9.6, N, 2.2. Found: C, 75.2; H, 9.8, N, 2.2.

*Cr(OR)*₂(*NDEP*) (4). A solution of 5 mL of N₃DEP (2.4 mg, 0.014 mmol) in toluene was added to a solution of compound 1 (28.0 mg, 0.029 mmol) in toluene in one portion. The solution immediately changed color from green to deep red. The reaction mixture was stirred for 4 h, upon which the solvent was removed. Crystallization from pentane at -35 °C over 2 weeks gave crystals of deep red Cr(OR)₂(NDEP) (8.5 mg, 23% yield). The low isolated yield of compound 4 is likely due to its high solubility. The crystallized compound was characterized by X-ray crystallography and IR spectroscopy; the low isolated yield of the compound and prolonged crystallization times prevented us from further characterization of this compound. IR (cm⁻¹): 2967 (w), 2878 (w), 2832 (w), 1597 (w), 1474 (w), 1432 (w), 1204 (m), 1092 (w), 1067 (s), 744 (s), 706 (s).

Cr(*OR*)₂(*N*(4-*CH*₃*OPh*))₂ (**5**). A solution of 4-azidoanisole (0.5 M in *tert*-butyl methyl ether, 0.110 mL) was added to a 5 mL solution of complex **1** (26.0 mg, 0.0265 mmol) in toluene. The solution color changed immediately from green to deep brown. The reaction mixture was stirred for 4 h, upon which the volatiles were removed. Crystallization from hexanes at −35 °C overnight gave deep brown crystals of Cr(OR)₂(N(4-CH₃OPh))₂ (18.2 mg, 46%). IR (cm⁻¹): 2963 (w), 1585 (s), 1485 (m), 1250 (s), 1157 (s), 991 (m), 829 (s). ¹H NMR (C₆D₆): δ 8.66 (d, ³J_{HH} = 7.6 Hz, 2H), 7.75 (d, ³J_{HH} = 8.8 Hz, 2H), 7.39 (m, 2H), 7.17 (m, 8H), 6.37 (d, ³J_{HH} = 8.8 Hz, 4H), 3.05 (s, 6H), 1.49 (s, 36H). ¹³C NMR (C₆D₆): δ 147.76, 130.17, 129.00, 127.11, 127.05, 125.88, 125.69, 113.61, 54.81, 44.59, 31.05 ppm. Anal. Calcd for complex **5**: C, 72.1; H, 8.3, N, 3.8. Found: C, 72.3; H, 8.4; N, 3.7.

Cr(*OR*)₂(*N*(4-*CF*₃*Ph*))₂ (*b*). To a solution of 5.0 mL of complex 1 (37.2 mg, 3.79 mmol) in toluene was added 4-(trifluoromethyl)phenyl azide solution (0.5 M in *tert*-butyl methyl ether, 0.30 mL) dropwise. Immediately gas evolution was observed, along with a change in solution color to deep brown. The reaction mixture was stirred for 4 h, upon which the solvents were removed in vacuo to yield a brown residue. Crystallization from hexanes at -35 °C overnight gave deep brown crystals of Cr(OR)₂(N(4-CF₃Ph))₂ (15.6 mg, 30%). IR (cm⁻¹): 2966 (w), 1597 (w), 1319 (s), 1165(m), 1103 (m), 975 (s), 833 (m). ¹H NMR (C₆D₆): δ 8.38 (d, ³J_{HH} = 9.2 Hz, 2H), 7.68 (d, ³J_{HH} = 6.8 Hz, 2H), 7.01 (m, 4H), 7.22 (m, 2H), 6.93 (d, ³J_{HH} = 8.0 Hz, 4H), 6.76 (d, ³J_{HH} = 8.4 Hz, 4H), 1.38 (s, 36H) . ¹³C NMR (C₆D₆): δ 163.76, 146.44, 129.73, 129.00, 127.03, 126.40, 126.18, 126.00, 124.21, 100.70, 44.86, 30.91 ppm. Anal. Calcd for complex **6**: C, 65.3; H, 6.7, N, 3.5. Found: C, 65.4; H, 6.6; N, 3.4.

Reaction of Cr(OR)₂(NMes) (2) with 1 Equiv of 2,6-Dimethyl Isocyanide. To a solution of 5.0 mL of complex 2 (35.2 mg, 0.056 mmol) in C_6D_6 were added 1 equiv of 2,6-dimethylphenyl isocyanide (7.3 mg, 0.056 mmol) and 1 equiv of 1,3,5-trimethoxybenzene (TMB, 9.3 mg, 0.055 mmol) in C_6D_6 . The solution changed color from green to deep brown and was stirred for 2 h, upon which a ¹H NMR spectrum was taken to show complete conversion to the corresponding carbodiimide.

Reaction of $Cr(OR)_2(NMes)$ (2) with 5 Equiv of 2,6-Dimethylphenyl Isocyanide: Observation of Carbodiimides and Isolation of Compound 7. To a solution of 5.0 mL of complex 2 (19.8 mg, 0.032 mmol) in C_6D_6 were added 5 equiv of 2,6dimethylphenyl isocyanide (19.5 mg, 0.149 mmol) and 1 equiv of TMB (5.6 mg, 0.0333 mmol) in C_6D_6 . The solution changed color

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from green to deep brown and was stirred for 2 h, upon which a ¹H NMR spectrum was taken to show complete conversion to the corresponding carbodiimide. Once the complete conversion was established, the volatiles were removed in vacuo to yield a brown residue. The residue was dissolved in hexanes and placed in the freezer at -35 °C to produce deep orange crystals of complex 7 (16.9 mg, 56%).

Independent Synthesis of Cr(OR)₂(CN(2,6-Me₂Ph))₄ (7) from the Cr(II) Precursor Cr₂(OR)₄ (1). A solution of 5 mL of CN(2,6-Me₂Ph) (34.0 mg, 0.259 mmol) in toluene was added to a solution of compound 1 (30.9 mg, 0.0315 mmol) in toluene in one portion. The solution immediately changed color from green to deep brown. The reaction mixture was stirred for 4 h, upon which the solvent was removed. Crystallization from hexanes at -35 °C overnight produced crystals of deep orange Cr(OR)₂(CN(2,6-Me₂Ph))₄ (40.1 mg, 65% yield). $\mu_{eff} = 2.3 \pm 0.2 \mu_B$ (calcd 2.8 μ_B). Anal. Calcd for complex 7: C, 78.1; H, 8.1, N, 5.5. Found: C, 77.2; H, 8.6; N, 5.4.

Reaction of $Cr(OR)_2(N(4-CH_3OPh))_2$ (5) with 2,6-Dimethylphenyl Isocyanide. To a solution of 5.0 mL of complex 5 (12.7 mg, 0.0173 mmol) in C_6D_6 were added 6 equiv of 2,6-dimethylphenyl isocyanide (14.4 mg, 0.110 mmol) and 1 equiv of TMB (5.30 mg, 0.0315 mmol) in C_6D_6 . The solution was stirred for 2 days, upon which an ¹H NMR spectrum was taken to show no formation of the corresponding carbodiimide and no consumption of the starting isocyanide and complex 5.

Reaction of $Cr(OR)_2(N(4-CF_3Ph))_2$ (6) with 2,6-Dimethylphenyl lsocyanide. To a solution of 5.0 mL of complex 6 (26.6 mg, 0.033 mmol) in C₆D₆ were added 6 equiv of 2,6-dimethylphenyl isocyanide (2.5 mg, 0.192 mmol) and 1 equiv of TMB (6.0 mg, 0.036 mmol) in C₆D₆. The solution was stirred for 2 days, upon which a ¹H NMR spectrum was taken to show no formation of the corresponding carbodiimide and no consumption of the starting isocyanide and complex 6.

General Procedure for Catalytic Formation of Carbodiimides. *NMR-Scale Reactions*. All of the reactions were performed in an N₂-filled glovebox by the addition of 24 equiv of isocyanide, 20 equiv of organoazide, and TMB standard solution in C_6D_6 to a solution of 2.5 mol % of complex 1 (approximately 15–30 mg) in C_6D_6 . The reaction mixture was stirred for 24 h and a ¹H NMR spectrum was taken to calculate the percent yield of the carbodiimide produced.

Synthesis of the Isolated Carbodiimides. The isolated carbodiimides were synthesized according to the following procedure: all of the reactions were performed in an N₂-filled glovebox by the addition of 20 equiv of isocyanide and 20 equiv of organoazide in THF to a solution of 2.5 mol % of complex 1 (approximately 15–30 mg) in THF. The reaction mixture was stirred for 24 h, upon which volatiles were removed in vacuo. The brown residue was purified on silica under an inert atmosphere using hexanes. Carbodiimides were isolated by collecting the light orange or pale yellow layer and subsequent evaporation (oils) or recrystallization at -35 °C (solids). Full characterization data for the isolated carbodiimides are found in the Supporting Information.

Computational Details. Electronic structure calculations were carried out using density functional theory as implemented in Gaussian09.⁴⁵ Geometry optimizations were initially performed at the B3LYP^{46–49} level of theory using the 6-31G(d) basis set. No symmetry constraints were imposed during geometry optimizations, and optimized structures were confirmed to have stable wave functions^{50,51} and to be local minima by analyzing the harmonic frequencies.^{52,53} Thermodynamic quantities assumed standard approximations⁵⁴ and a temperature of 298.15 K to estimate the free energy of each species. Cartesian coordinates, frequencies, and thermodynamics for all species may be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00703.

Crystallographic data (CIF)

Cartesian coordinates for the calculated structures (XYZ) Characterization data for carbodiimides, NMR, IR, UV– vis, and mass spectra, Evans data, X-ray crystallographic details, and DFT calculation details (PDF)

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Notes

The authors declare no competing financial interest.

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