

Article

Synthesis of Chromium(II) Complexes with Chelating Bis(alkoxide) Ligand and Their Reactions with Organoazides and Diazoalkanes

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Abstract: Synthesis of new chromium(II) complexes with chelating bis(alkoxide) ligand [OO]^{Ph} (H₂[OO]^{Ph} = [1,1':4',1''-terphenyl]-2,2''-diylbis(diphenylmethanol)) and their subsequent reactivity in the context of catalytic production of carbodiimides from azides and isocyanides are described. Two different Cr(II) complexes are obtained, as a function of the crystallization solvent: mononuclear Cr[OO]^{Ph}(THF)₂ (in toluene/THF) and dinuclear Cr₂([OO]^{Ph})₂ (in CH₂Cl₂/THF). The electronic structure and bonding in Cr[OO]^{Ph}(THF)₂ were probed by DFT calculations. Isolated Cr₂([OO]^{Ph})₂ undergoes facile reaction with 4-MeC₆H₄N₃, 4-MeOC₆H₄N₃, or 3,5-Me₂C₆H₃N₃ to yield diamagnetic Cr(VI) bis(imido) complexes; a structure of Cr[OO]^{Ph}(N(4-MeC₆H₄))₂ was confirmed by X-ray crystallography. The reaction of Cr₂([OO]^{Ph})₂ with bulkier azides N₃R (MesN₃, AdN₃) forms paramagnetic products, formulated as Cr[OO]^{Ph}(NR). The attempted formation of a Cr-alkylidene complex (using N₂CPh₂) forms instead chromium(VI) bis(diphenylmethylenediazido) complex Cr[OO]^{Ph}(=NNCPh₂)₂. Catalytic formation of carbodiimides was investigated for the azide/isocyanide mixtures containing various aryl azides and isocyanides. The formation of carbodiimides was found to depend on the nature of organoazide: whereas bulky mesityl led to the formation of carbodiimides with all isocyanides; no carbodiimide formation was observed for 3,5-dimethylphenylazide or 4-methylphenylazide. Treatment of Cr₂([OO]^{Ph})₂ or H₂[OO]^{Ph} with NO⁺ leads to the formation of [1,2-b]-dihydroindenofluorene, likely obtained via carbocation-mediated cyclization of the ligand.

Keywords: alkoxides; azides; carbodiimides

1. Introduction

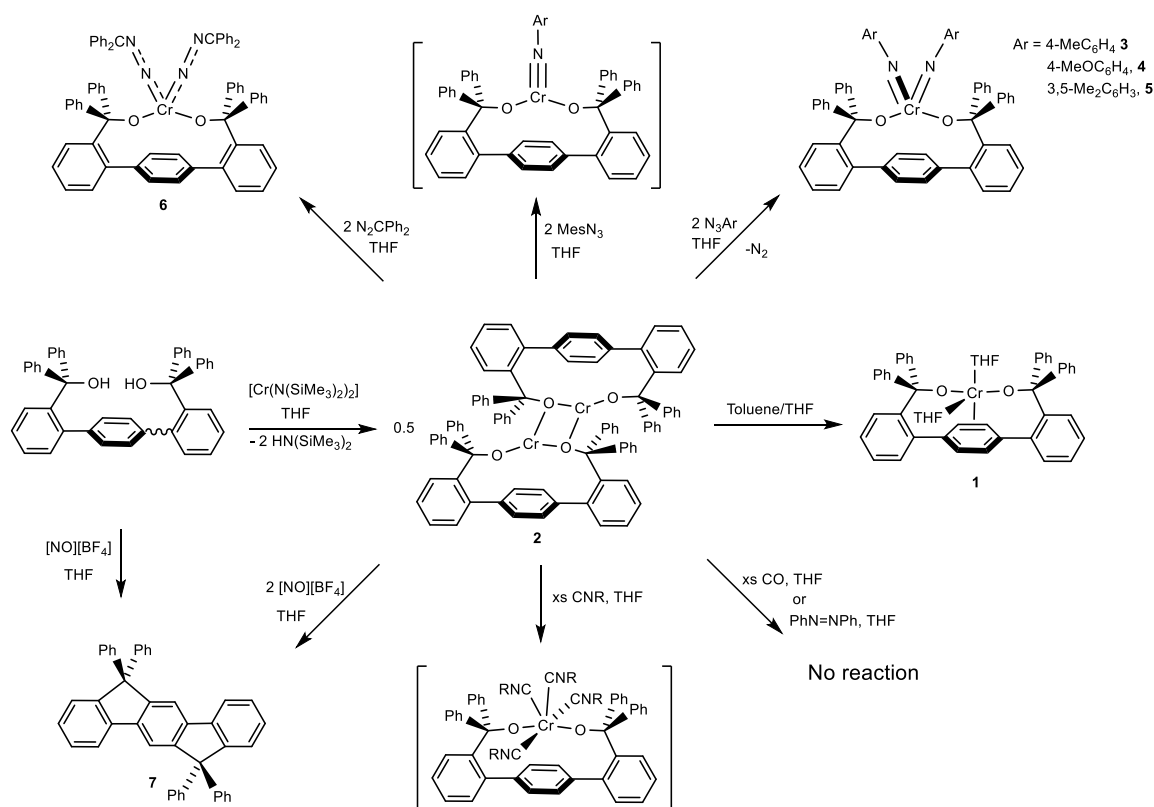
Organoazides constitute efficient and sustainable precursors for the formation of reactive nitrene functionality, which engenders many useful transformations, including C-H bond amination, aziridination, formation of azoarenes and carbodiimides, and others [1–7]. Transition metals generally enable milder conditions for the formation of nitrenes and higher selectivity in their subsequent transfer. The majority of nitrene-transfer studies are focused on middle and late transition metals, which generally feature weaker metal-imido bonds and therefore exhibit more reactive nitrene functionalities [8–21]. In contrast, early transition metals (particularly chromium) typically exhibit less reactive nitrene functionalities due to the stability of multiple metal-nitrogen bonds [22–28]. However, recent studies demonstrated the ability of coordinatively unsaturated

chromium(IV)-imido to transfer nitrene to olefins or isocyanides to form aziridines and carbodiimides, respectively [29–31]. C-C and C-H bond activation reactions featuring reactive chromium(IV) imido were also reported [32]. As part of our ongoing investigation of nitrene- and carbene-transfer chemistry mediated by 3d complexes in bulky alkoxide ligand environments [33,34], we have reported synthesis and reactions of chromium-imido complexes featuring two bulky monodentate alkoxides [OC^tBu₂Ph] [31]. We have demonstrated that Cr^{IV}(OC^tBu₂Ph)₂(NR') complexes, which were formed for bulky R' groups (R' = Mes, 2,6-Et₂C₆H₃, Ad) enabled catalytic transfer of nitrene group [NR'] to isocyanides to form carbodiimides. In contrast, the reaction of less bulky *para*-substituted aryl azides N₃R' (R' = 4-MeC₆H₄, 4-MeOC₆H₄, 4-CF₃C₆H₄) formed Cr(VI) complexes Cr^{VI}(OR)₂(NR')₂ which were catalytically inactive. Recently, we have reported a new chelating bis(alkoxide) ligand [OO]^{Ph} [35], that created similar bis(alkoxide) ligand environment but warranted higher degree of stability of the resulting iron complex Fe[OO]^{Ph}, and consequently led to a broader range of catalytic nitrene transfer compared with related Fe(OR)₂ systems [36,37]. Herein we report our synthetic, structural, and catalytic studies on the chemistry of Cr^{III}[OO]^{Ph} with organoazides and diazoalkanes, and compare this reactivity with the previously reported Cr^{II}(OC^tBu₂Ph)₂ system.

2. Results and Discussion

2.1. Synthesis and Structures of Cr(II) Precursors

Treatment of the chromium(II) amide precursor with one equivalent of H₂[OO]^{Ph} in THF produces a green solid. Recrystallization of the product from toluene/THF mixture yields mononuclear pale green Cr[OO]^{Ph}(THF)₂ (**1**) related to the mononuclear Cr(OC^tBu₂(3,5-Ph₂Ph))₂(THF)₂ [38]. In contrast, recrystallization of the product from a mixture of two polar solvents (CH₂Cl₂ and THF) forms pale green-blue homodinuclear complex Cr₂[OO]^{Ph}₂ (**2**, Scheme 1) isolated in 79% yield. Homodinuclear complex **2** is structurally related to the previously reported alkoxide-bridged Cr₂(OC^tBu₂Ph)₄ [31], Cr₂(OC^tBu₃)₂(μ²-OC^tBu₂H)₂ [39], and siloxide-bridged Cr₂(OSi^tBu₃)₄ [40]. We note that monodentate alkoxides [OC^tBu₂Ph] and [OC^tBu₂(3,5-Ph₂Ph)] formed dinuclear or mononuclear complexes selectively [31,38], whereas the chelating ligand appears to support both types of geometries in the solid state, depending on the nature of the crystallization medium.



Scheme 1. Synthesis and reactivity of Cr(II) complex in the chelating bis(alkoxide) ligand environment.

The structures of complexes **1** and **2** are given in Figure 1. The structure of **1** is similar to the previously reported structure of Fe[OO]^{Ph}(THF)₂ [35]. However, the structure of Fe[OO]^{Ph}(THF)₂ exhibited very long distance between the metal and the central phenyl (>3 Å) indicating no interaction [35]. In contrast, the distance between the chromium center and the central phenyl in **1** is 2.49(1) Å, which suggests bonding between the metal and the phenyl ring. The inter-alkoxide RO–Cr–OR and THF–Cr–THF angles are 173.6(2) ° and 88.1(2) °, respectively. Two independent molecules of homodinuclear complex **2** were found in the asymmetric unit exhibiting similar structural parameters; only one is shown. Each [OO]^{Ph} ligand provides one terminal and one bridging alkoxide donor; no coordination to the central phenyl is observed in this case (Cr–Ph ≥ 3.0 Å). While the overall geometry and metrics in **2** are similar to those of Cr₂(OC^tBu₂Ph)₄ and related complexes [32,39,40], the metal centers in **2** exhibit significant distortion of trigonal planar geometry as indicated by the considerable difference in O–Cr–O angles (Figure 2) and displacement of Cr from the trigonal plane (varies between 0.105–0.348 Å).

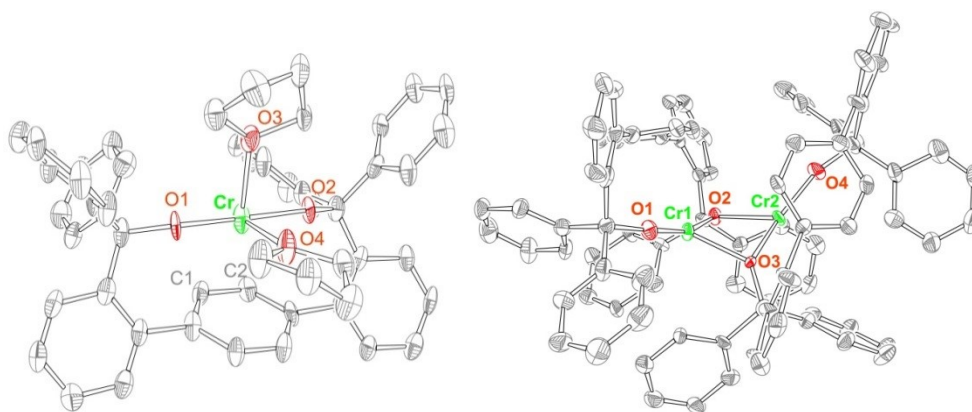


Figure 1. X-ray structures of **1** (left) and **2** (right), 50% probability ellipsoids. H atoms and co-crystallized solvent molecules were omitted for clarity. Selected bond distances (Å) and angles (°)

for 1: Cr O1, 1.924(6), Cr O2, 1.935(6), Cr O3, 2.156(7), Cr O4, 2.277(6), Cr --- Ph 2.49(1), O1 Cr1 O2, 173.6(2), O1 Cr1 O3, 86.7(2), O2 Cr1 O3, 90.0(3), O1 Cr1 O4, 85.9(2), O2 Cr1 O4, 88.5(2), O3 Cr1 O4, 88.1(2). Selected bond distances (Å) and angles (°) for 2: Cr1 O1, 1.788(5), Cr2 O4, 1.799(5), Cr1 O2, 1.976(5), Cr1 O3, 2.013(6), Cr2 O3, 1.981(5), Cr2 O2, 2.049(5), Cr1 --- Cr2, 2.896(2), O2 Cr1 O3, 81.2(2), O1 Cr1 O2, 150.2(3), O1 Cr1 O3, 120.1(2).

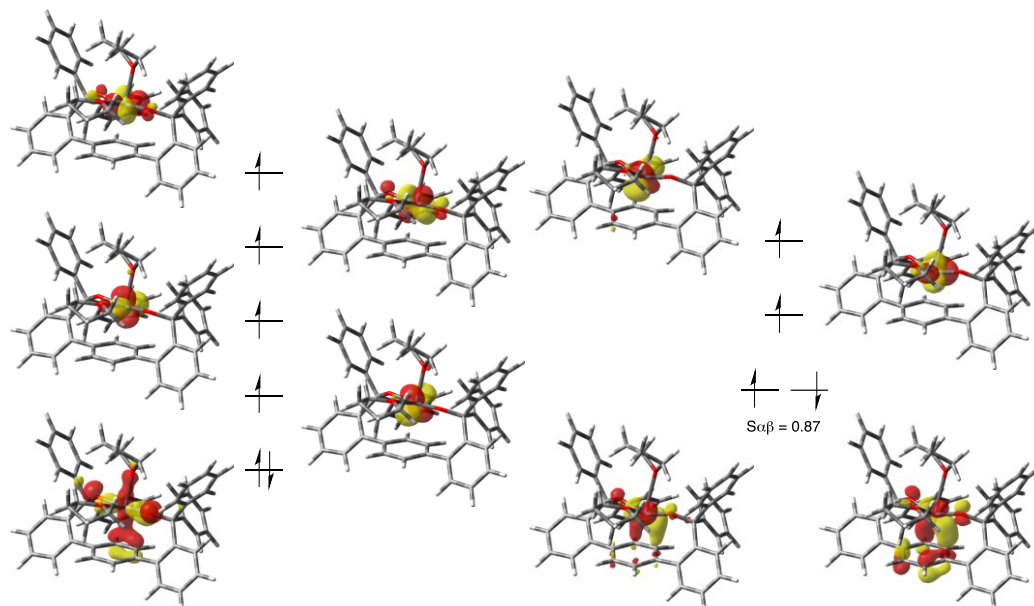


Figure 2. Corresponding orbital diagrams for **1q** (left) and **1r** (right) at the BP86-D3/def2-SVP level of theory. Orbitals are plotted with an isosurface value of 0.05 au.

To better understand the electronic structure and bonding in **1**, DFT calculations were performed. Singlet (**1s**), triplet (**1t**), and quintet (**1q**) states were optimized. **1q** is lowest in free energy, followed by **1t** at 19.7 kcal/mol, and **1s** at 28.6 kcal/mol. The optimized structure of **1q** agrees well with the crystallographically determined structure and has bond lengths of Cr–O1 = 1.915 Å, Cr–O2 = 1.928 Å, Cr–O3 = 2.203 Å, Cr–O4 = 2.281 Å, Cr–C1 = 2.475 Å, and Cr–C2 = 2.525 Å; both **1t** and **1s** are inconsistent with the x-ray data (Table S1, SI). Based on the spin density localized at Cr, **1q** is best described as a high-spin Cr(II) species. Similar to what was observed in the optimization of different spin states of Fe[OO]^{Ph}(THF)₂ [35], the higher-energy, lower spin states **1t**/**1s** exhibit much shorter Cr–phenyl contacts of 2.1–2.2 Å. Mayer bond orders for Cr–C1/C2 are calculated to be 0.25 and 0.23 in **1q**. In comparison, quintet Fe[OO]^{Ph}(THF)₂ (with Fe–C distances of 2.8–2.9 Å) has smaller bond orders of 0.06 and 0.09, whereas **1t** has larger bond orders of 0.64 and 0.65. For perspective, M–O_{THF} bond orders are 0.2–0.3 and the M–O_{alkoxide} bond orders are 0.6–0.9. Frontier orbital diagrams of **1q** and **1t** (Figure 2) illustrate the Cr–phenyl bonding in both spin states. The much stronger bonding in **1t** is due to the *d*→*π* backbonding that is possible with intermediate-spin Cr(II) ion. This back-bonding is not significant in **1q** due to half-occupation of that *d*-orbital in the high-spin Cr(II) ion. Collectively, these computational data suggest a weak covalent interaction between Cr and the bridging phenyl moiety in **1**.

We have also investigated the structures of **1** and **2** in solution. Both compounds give rise to paramagnetic NMR spectra, as anticipated. The UV-vis spectra of **1** and **2** (collected in THF) are very similar, exhibiting a peak around 710 nm, and a shoulder around 510 nm (Figures S39 and S40, SI). The solution magnetic moment of **1** (3.0(3) μB, C₆D₆) was found to be significantly lower than the expected spin-only value of 4.9 μB. Recalculated for the structure of Cr₂[(OO)^{Ph}]₂, the observed magnetic moment is 2.6(2) μB (per Cr), that is close to the observed value of 2.5(3) μB reported for Cr₂(OC^tBu₂Ph)₂ [31]. These data suggest that **1** undergoes dimerization in solution to form **2**.

2.2. Reactions of Chromium(II) Complexes with Organoazides, Azoarenes, and Diazoalkanes

Following the synthesis of the chromium(II) precursor, its reactivity with organoazides was investigated. Complex **2** was utilized as a precursor in group-transfer reactions. Similar to $\text{Cr}_2(\text{OC}^t\text{Bu}_2\text{Ph})_4$ [31], **2** was found to exhibit profoundly distinct reactivity with non-bulky (4-tolyl, 4-methoxyphenyl, and 3,5-dimethylphenyl) vs. bulky (mesityl, adamantyl) organoazides. Treating a green solution of **2** with two equivalents of *para*-tolylazide in THF leads to a dark-brown solution, from which diamagnetic **3** is isolated in 69% yield by recrystallization from THF/ether. Similarly, treating **2** with two equivalents of 4-MeOC₆H₄N₃ or 3,5-Me₂C₆H₃N₃ forms brown solutions containing diamagnetic products **4** and **5** in 54% and 59%, respectively. We were not able to obtain X-ray quality crystals of **4** and **5**, however, their NMR and UV-Vis data (see SI) suggests close similarity to **3**. The overall connectivity of **3** was confirmed by X-ray structure determination (Figure 3). The structure reveals distorted tetrahedral geometry, consistent with Cr(VI) bis(imido) formulation. No chromium-phenyl interaction is observed in this case, with the chromium-phenyl distance exceeding 3.5 Å. As the structure was of relatively low quality, its metric parameters will not be further discussed.

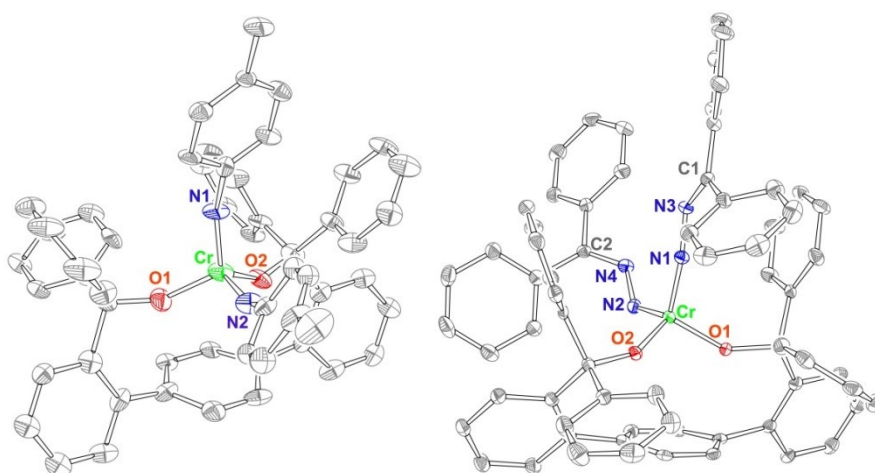


Figure 3. X-ray structure of **3** (left) and **6** (right), 50% probability ellipsoids. H atoms and co-crystallized solvent molecules were omitted for clarity. Selected bond distances (Å) for **6**: Cr O1 1.807(2), Cr O2 1.777(2), Cr N1 1.645(3), Cr N2 1.716(3), N1 N3 1.305(4), N2 N4 1.301(4). Selected bond angles (°): O2 Cr O1 110.0(1), N1 Cr N3 99.7(2), N1 Cr O2 110.5(1), N2 Cr O2 109.2(1), N1 Cr O1 113.1(1), Cr N1 N3 159.8(2), Cr N2 N4 131.2(2).

In contrast, the reaction of the chromium(II) precursor with two equivalents of bulkier mesityl azide (per Cr) produces a paramagnetic brown solution, containing approximately one equivalent of unreacted azide. Similarly, treating chromium(II) precursor with two equivalents of adamantyl azide also produces paramagnetic product, along with unreacted azide. We were not able to obtain X-ray quality crystals of the products. The formation of trigonal Cr(IV) mono(imido) complexes is proposed, based on similar formation of brown paramagnetic $\text{Cr}^{\text{IV}}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{NMes})$ and $\text{Cr}^{\text{IV}}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{NAd})$ upon reaction of $[\text{Cr}(\text{OC}^t\text{Bu}_2\text{Ph})_2]$ with excess azide. We note that selective formation of Cr(IV) mono(imido) complexes upon reaction with bulkier organoazides was also observed for the chromium(II) system ligated by two monodentate siloxides, $[\text{Cr}(\text{OSi}^t\text{Bu}_3)_2]$ [40].

In addition to the reactions of Cr(II) precursor with organoazides, we have also studied its reactivity with azobenzene, with the goal to produce Cr(VI) bis(imido) via azobenzene cleavage. Cleavage of the N=N double bond in azoarenes at a single metal center is rare [41–44]. Heating the mixture of complex **2** with azobenzene to 60 °C in C₆D₆ for 24 h did not lead to the formation of $\text{Cr}^{\text{VI}}[\text{OO}]^{\text{Ph}}(\text{NPh})_2$ as indicated by ¹H NMR spectroscopy.

Next, the reactivity of the Cr(II) bis(alkoxide) precursor with diazoalkanes was investigated, targeting formation of Cr(IV)/Cr(VI)-alkylidene complexes. Cr-alkylidene complexes are rare [26,45,46], and their reactivity is relatively unexplored. The related cobalt(II) bis(alkoxide) complex $\text{Co}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{THF})_2$ formed high-valent cobalt-alkylidene upon reaction with N₂CPh₂ and

N₂C(Ph)(CO₂Me) [47], whereas the corresponding iron complex Fe(OC^tBu₂Ph)₂(THF)₂ reductively coupled diazoalkanes/diazoesters via terminal nitrogens to form bridging tetrazene species [48]. Different reactivity mode was observed for the chromium bis(alkoxide). Treatment of **2** with diphenyldiazomethane results in the formation of brown Cr[OO]^{Ph}(NNCPh₂)₂ species (**6**), which was characterized by X-ray crystallography. The complex appears unstable in both solid state and solution. Our repeated attempts to collect NMR spectrum on the X-ray quality crystals produced spectra with varying but significant number of decomposition products (benzophenone azine, free ligand); peaks attributable to the complex were broad and not informative. Wolczanski and coworkers have reported similar reactivity of Cr₂(OSi^tBu₃)₄ with N₂CPh₂ to yield Cr(OSi^tBu₃)₂(N₂CPh₂)₂ complex [40]; their complex also demonstrated limited stability.

The structure of **6** and selected metrics are given in Figure 3. The chromium center exhibits distorted tetrahedral geometry. Interestingly, the Cr-N bonds are different, one being significantly shorter (1.645(3) Å) than the other (1.716(3) Å). The shorter bond could be indicative of the higher metal-nitrogen bond order (triple), while the longer one indicates metal-nitrogen double bond. The Cr-N-N bond angles of the [NNCPh₂] functionality are consistent with the above formulations: for the triply bonded [Cr=N1-N3] hydrazido, the angle is closer to linear (159.8(2) °), whereas for the doubly bonded [Cr=N2-N4] the angle is smaller (131.2(2) °). It is noted that the N1-N3 and N2-N4 bonds are similar (1.304(4) vs. 1.301(4) Å), being intermediate between single and double. Similar dependence of the Cr-N-N angle within diphenylmethylenhydrazido functionalities on the chromium-nitrogen bond order was reported by Wolczanski, Cundari and coworkers for the related Cr(OSi^tBu₃)₂(=N₂CPh₂)₂ [40]. The major difference between the present structure and the structure reported by Wolczanski is that in Cr(OSi^tBu₃)₂(=N₂CPh₂)₂ the Cr-N bonds were similar (1.664(2) and 1.666(2) Å), leading to similar Cr-N-N bond angles (150.2(2) and 150.4(3) °).

DFT calculations on **6** were performed to analyze the electronic structure of this species. Singlet (**6s**), triplet (**6t**), and quintet (**6q**) states were optimized and the singlet was found to be lowest in free energy followed by the triplet (+15.1 kcal/mol) then the quintet (+33.9 kcal/mol). Only the optimized structure of **6s** is consistent with the experimental x-ray structure (Table S3, SI) and has no unpaired electrons. As the localized frontier orbitals in Figure 4 demonstrate, there are two σ-bonding interactions with the more linear diazoalkane ligand (HOMO-1/LUMO+3, HOMO-3/LUMO) compared to one with the less linear diazoalkane ligand (HOMO/LUMO+4), though the HOMO-1/LUMO+3 pair shows interaction with both diazoalkane ligands. The modest difference in Mayer bond orders of 1.61 vs. 1.52 for Cr-N1 vs. Cr-N2 suggests that both Cr-N bonds are between doubly and triply bonded, but that bonding to N1 is stronger.

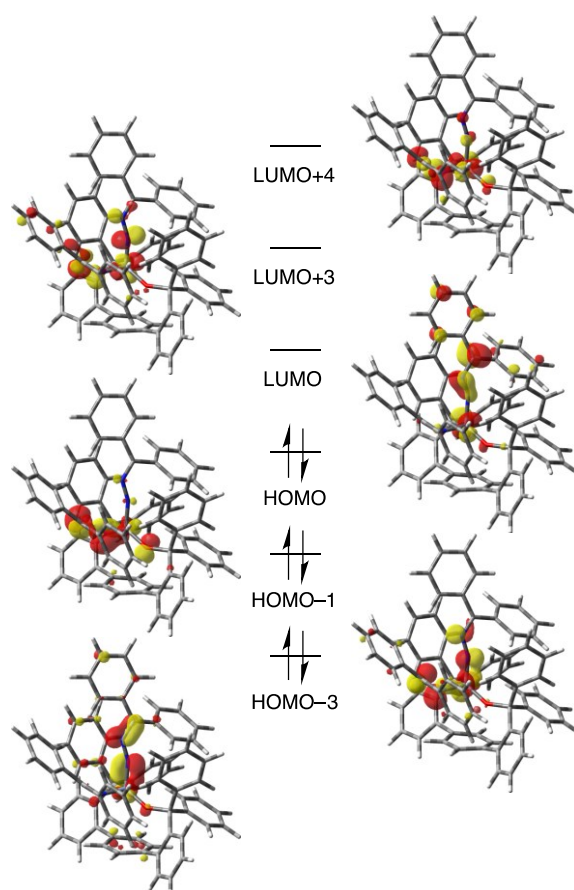


Figure 4. Frontier orbital diagram for **6s** at the BP86-D3/def2-SVP level of theory. Orbitals are plotted with an isosurface value of 0.05 au.

2.3. Reactivity of Cr(II) with CO, CNR, and NO⁺

Following the investigation of the reactivity of Cr(II) bis(alkoxide) precursor with organoazides and diazoalkanes, its reactivity with isocyanides, carbon monoxide, and nitrosonium was explored next. It was previously shown that $\text{Cr}_2(\text{OC}^t\text{Bu}_2\text{Ph})_4$ reacted with isocyanides to form $\text{Cr}^{\text{II}}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{CNR})_4$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$); formation of $\text{Cr}^{\text{II}}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{CNR})_4$ enabled subsequent development of the catalytic cycle for the production of carbodiimides. Hoping that the more stable and sterically demanding chelating bis(alkoxide) system will enable better catalytic reactivity in CNR and perhaps CO transfer, reactions of $\text{Cr}[\text{OO}]^{\text{Ph}}$ with xylyl isocyanide and carbon monoxide were investigated. The reactivity of nitrosonium $(\text{NO})(\text{BF}_4)$ were also studied, in light of the isoelectronic nature between NO^+ and CO/CNR .

Addition of excess xylyl isocyanide to the light-green solution of **2** (dissolved in THF) forms brown solution immediately. ¹H NMR spectrum of the product indicates its paramagnetic nature. Although our multiple attempts to obtain X-ray quality crystals of the isocyanide product did not lead to fruition, UV-vis spectrum of the crude product is similar to the UV-vis spectrum of isolated $\text{Cr}^{\text{II}}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))_4$ (peaks around 400 and 460 nm, Figure S44) suggesting the similarity of the products. In contrast, no color change was observed after treating the solution of **2** in THF with CO. Subsequent recrystallization from toluene/THF mixture formed instead the crystals of compound **1**, further confirming the lack of reactivity with CO.

The reaction of **2** with NO^+ took an unexpected turn. Addition of $(\text{NO})(\text{BF}_4)$ to the green solution of **2** (THF) led to the development of cloudy yellow solution over the course of several hours. Subsequent recrystallization from THF yields colorless crystals of 6,6,12,12-tetraphenyl-6,12-dihydroindeno[1,2-b]fluorene **7** (Figure 5) isolated in 92% yield. The reaction course does not depend on the presence of Cr: treatment of the ligands precursor $\text{H}_2[\text{OO}]^{\text{Ph}}$ with $(\text{NO})(\text{BF}_4)$ yields the same product **7**. Cyclization of terphenyl bis(carbinol)s via carbocation

intermediates to give various substituted dihydroindeno[1,2-b]fluorenes had been previously reported [49,50]. We surmise that the reaction proceeds via nitrosonium abstraction of hydroxyl (to yield nitrous acid) followed by cyclization as described in Scheme 2.

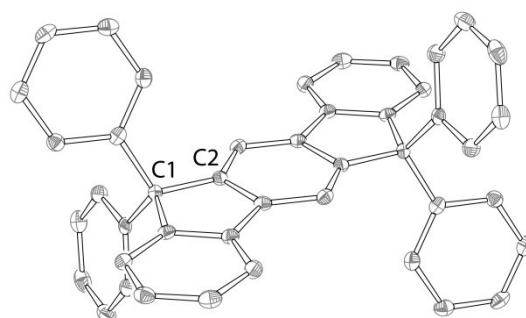
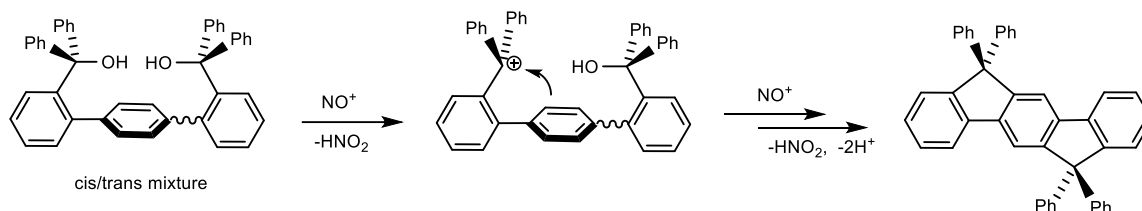


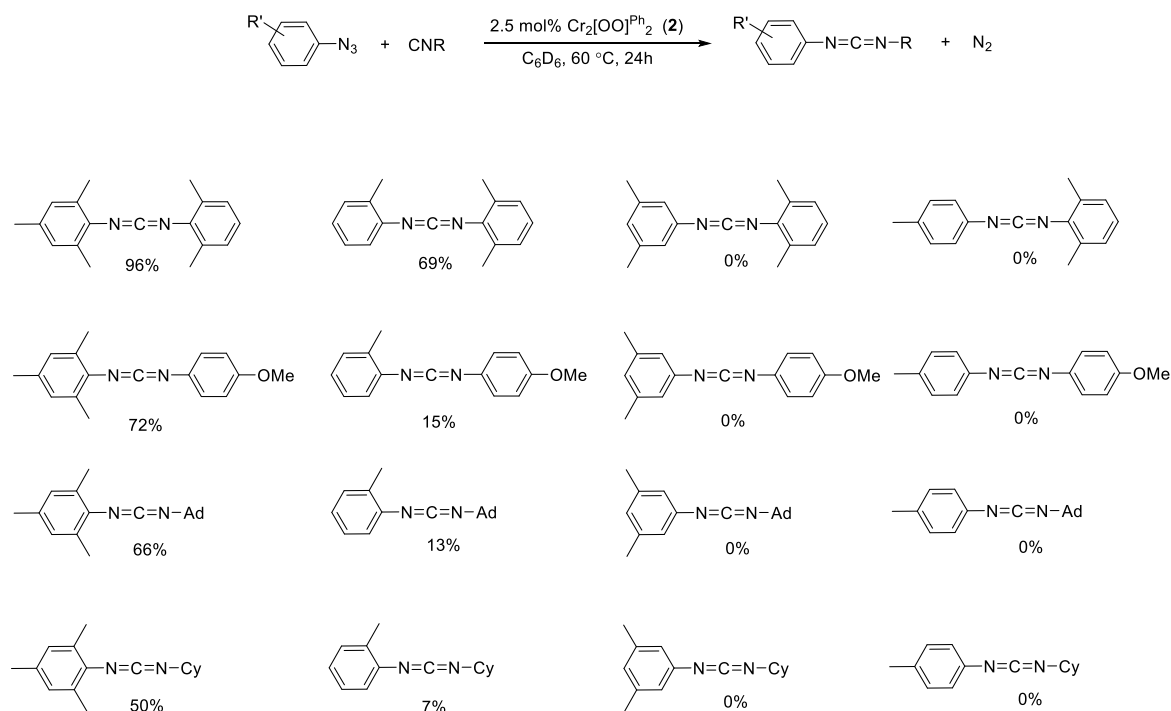
Figure 5. X-ray structure of 7, 50% probability ellipsoids. H atoms and co-crystallized solvent molecules were omitted for clarity.



Scheme 2. Cyclization mechanism of $\text{H}_2[\text{OO}]^{\text{Ph}}$.

2.4. Catalytic Reactivity in the Formation of Carbodiimides

Given the ability of the $\text{Cr}^{\text{II}}[\text{OO}]^{\text{Ph}}$ precursor to undergo stoichiometric reactions with organoazides and isocyanides, we turned next to investigate its catalytic reactivity in formation of carbodiimides. A matrix of 4 representative aryl azides of varying steric bulk (mesityl, 2-methylphenyl, 3,5-dimethylphenyl, and 4-methylphenyl) and 4 representative isocyanides (xylyl, 4-methoxyphenyl, adamantyl, and cyclohexyl) was investigated (Scheme 3). All reactions were carried out in C_6D_6 at 60 °C for 24 h; the nature of the reaction products and their yields were determined by ^1H NMR spectroscopy. The outcome of the catalytic reaction appears to be a primary function of the organoazide nature. Catalytic formation of carbodiimides is observed for the bulkier mesityl azide. The reaction of mesityl azide with xylyl isocyanide gives nearly quantitative yield; good to moderate yields (72–50%) are observed for other isocyanides. For the *ortho*-monosubstituted 2-methylphenyl azide, the reaction with xylyl isocyanide produces carbodiimide in a good yield, whereas other isocyanides give low yields of the corresponding products. No carbodiimide formation is observed for 3,5-dimethylphenyl azide and 4-methylphenyl azide. These results are rationalized by the nature of the chromium-imido intermediate, as was described in our previous study [31]. Whereas bulkier azide forms a chromium(IV)-imido, which is capable of isocyanide coordination and subsequent N-C bond formation, tetrahedral chromium(VI) bis(imido) (formed with non-bulky aryl azides) does not coordinate an isocyanide and therefore does not catalyze N-C bond formation.

Scheme 3. Catalytic formation of carbodiimides mediated by **2**.

3. Materials and Methods

3.1. General

CrCl₂ and LiN(Si(CH₃)₃)₂ were purchased from Strem chemicals and Sigma-Aldrich, respectively, and used as received. Previously reported methods were used to synthesize Cr(N(SiMe₃)₂)(THF)₂ and the ligand precursor H₂[OO]^{Ph} [35,51]. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. Non-deuterated solvents were purchased from Sigma-Aldrich chemicals and purified using MBraun solvent purification system. Characterization of compounds was carried out using ¹H and ¹³C NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. Selected chemicals were characterized by X-ray crystallography. NMR spectra of carbodiimides and complexes were recorded using Agilent 400 MHz spectrometer and Agilent DD2 600 MHz spectrometer, respectively, in C₆D₆ at room temperature at Lumigen Instrument center. Chemical shifts and coupling constants (J) are reported in parts per million and Hertz, respectively. Elemental analysis analyses were carried out by Midwest Microlab LLC under air-free conditions. Thermo Fisher Scientific LTQ Orbitrap XL mass spectrometer at the Lumigen Instrument Centre was used for high resolution mass spectra. IR spectra of powdered samples were recorded on Shimadzu IR Affinity-1 FT-IR spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. Shimadzu UV-1800 spectrometer was used to collect UV-visible spectra. All air-sensitive reactions were carried out in a nitrogen-filled glovebox.

3.2. Synthesis of Cr Complexes 1-6 and Compound 7

Cr₂[(OO)^{Ph}]₂ and Cr[(OO)^{Ph}](THF)₂ (1** and **2**).** A solution of ligand precursor H₂[OO]^{Ph} (0.034 g, 0.057 mmol) in THF (5 mL) was added to a solution of Cr(N(SiMe₃)₂)(THF)₂ (0.030 g, 0.057 mmol) in THF (5 mL). The color of the reaction changed from purple to light green over a course of 4 h. The solvent was removed under vacuum and the resulting residue recrystallized in DCM-THF mixture at -35 °C to obtain light green crystals of **2** in 79% yield (0.029 g, 0.023 mmol). Anal. Calcd for C₈₈H₆₄Cr₂O₄: C, 81.97, H, 5.00. Found: C, 80.82, H, 6.23. λ_{max} (ε_M (L⁻¹ cm⁻¹ mol⁻¹)) 706 nm (28000). IR (cm⁻¹): 2947 (m), 2337 (m), 1334 (w), 1151 (w), 987 (m), 840 (m), 756 (s), 702 (s). A similar procedure was used to synthesize Cr[(OO)^{Ph}](THF)₂ (**1**) but recrystallization was done in toluene with small

amount of THF. Calcd for $C_{52}H_{46}CrO_4$: C, 79.17, H, 6.13. Found C, 78.37, H, 5.39. IR (cm^{-1}) 2916 (m), 2353 (m), 1458 (m), 1365 (w), 1319 (w), 1149 (w), 1026 (m), 995 (w), 833 (m), 779 (s), 740 (m), 709 (m), 686 (m).

Synthesis of $Cr[OO]^{Ph}(N(4-CH_3C_6H_4))_2$ (3). A solution of 4-azidotoluene (0.020 g, 0.15 mmol) in THF was added to a 5 mL solution of $Cr_2([OO]^{Ph})_2$ (0.050 g, 0.038 mmol). Upon addition, the solution color changed from light green to brown; the release of N_2 was also observed. The reaction was stirred for 24 h. The solvent was removed under vacuum and the solid residue was recrystallized from ether-THF mixture at $-35\text{ }^{\circ}C$ to afford dark brown crystals in 69% yield (0.046 g, 0.054 mmol). 1H NMR (600 MHz, C_6D_6 , 298 K): δ 7.58 (d, 2H, $J_{HH} = 7.6$ Hz, H_a), 7.6 (d, 8H, $J_{HH} = 6.1$ Hz, H_i), 7.41 (s, 4H, H_e), 7.10–7.12 (m, 2H, H_b), 7.03–7.07 (m, 12H, H_g & H_h), 6.93–6.96 (m, 4H, H_c & H_d), 6.53 (d, 4H, $J_{HH} = 7.6$ Hz, H_j), 6.15 (d, 4H, $J_{HH} = 8.2$ Hz, H_l), 1.92 (s, 6H, H_k). ^{13}C NMR (150 MHz, C_6D_6 , 298 K): δ 160.69, 151.19, 146.27, 142.97, 142.93, 137.30, 131.11, 130.92, 129.17, 128.22, 127.92, 127.55, 127.52, 127.37, 126.39, 125.57, 124.26, 95.51, 20.72.

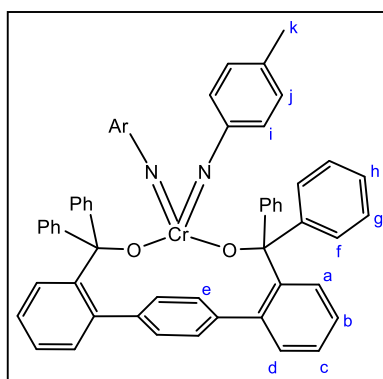


Figure 6. Assignment of 1H NMR signals for **3** (see previous paragraph for details).

$Cr[OO]^{Ph}(N(4-CH_3OC_6H_4))_2$ (4). A solution of 4-azidoanisole (0.023 g, 0.15 mmol in THF) was added to a 5 mL THF solution of $Cr_2([OO]^{Ph})_2$ (0.050 g, 0.038 mmol). Color changed from light green to brown with release of N_2 and the reaction was stirred for 24 h. The solvent was removed under vacuum and the resulting residue was recrystallized from ether/THF mixture at $-35\text{ }^{\circ}C$ to give brown solid which was washed with ether to afford the product in 54% yield (0.54 g, 0.043 mmol). 1H NMR (600 MHz, C_6D_6 , 298 K): δ 7.57–7.61 (m, 10H, H_a and H_i), 7.44 (s, 4H, H_e), 7.10–7.12 (m, 2H, H_b), 7.02–7.08 (t, 8H, $J_{HH} = 7.0$ Hz, H_g), 7.01–7.03 (t, 4H, $J_{HH} = 7.0$ Hz, H_h), 6.97 (m, 4H, H_c and H_d), 6.31 (d, 4H, $J_{HH} = 8.8$ Hz, H_j), 6.27 (d, 4H, $J_{HH} = 8.8$ Hz, H_l), 3.07 (s, 6H, H_k). ^{13}C NMR (150 MHz, C_6D_6 , 298 K): δ 158.54, 157.54, 151.30, 146.41, 143.00, 131.08, 130.95, 129.21, 127.92, 127.71, 127.54, 127.52, 127.31, 126.32, 126.13, 125.54, 112.79, 95.07, 54.91.

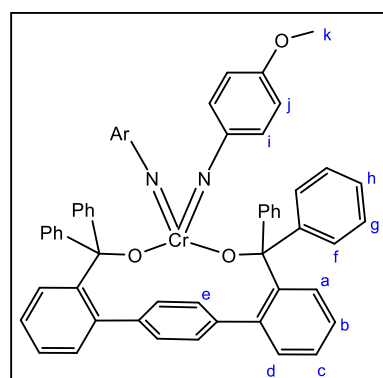


Figure 7. Assignment of 1H NMR signals for **4** (see previous paragraph for details).

Cr[OO]^{Ph}(N(3,5-Me₂C₆H₃))₂ (5). A solution of 3,5-dimethylphenyl azide (0.022 g, 0.15 mmol) in THF) was added to THF solution (5 mL) of Cr₂([OO]^{Ph})₂ (0.050 g, 0.038 mmol). Color changed from light green to brown with release of N₂ and the reaction was stirred for 24 h. The solvent was removed under vacuum and the residue was recrystallized from ether-THF at – 35 °C to form brown solid which was washed with ether to afford the product in 57% (0.038 g, 0.043 mmol). ¹H NMR (600 MHz, C₆D₆, 298 K) δ 7.57 - 7.61 (m, 10H, H_a and H_i), 7.42 (s, 4H, H_e), 7.09 - 7.11, (2H, t, J_{HH} = 6.4 Hz, H_b), 7.00 - 7.08 (m, 12H, H_g and H_h), 6.93 (t, 2H, J_{HH} = 7.6 Hz, H_c), 6.90 (d, 2H, J_{HH} = 8.8 Hz, H_d), 6.31 (s, 2H, H_k), 5.84 (s, 4H, H_j), 1.82 (s, 12H, H_i). ¹³C NMR (150 MHz, C₆D₆, 298K): δ 162.5, 151.20, 146.26, 142.97, 136.83, 131.11, 130.94, 129.21, 129.14, 128.98, 128.19, 127.92, 126.96, 126.75, 126.44, 126.20, 125.55, 121.99, 95.52, 20.37.

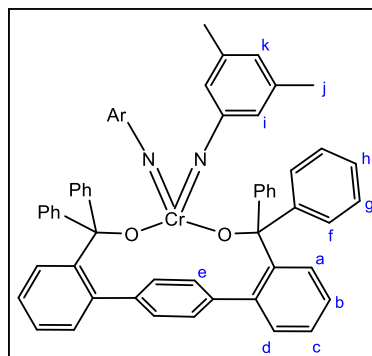


Figure 7. Assignment of ¹H NMR signals for **5** (see previous paragraph for details).

Cr[OO]^{Ph}(N₂CPh₂)₂ (6). A (5 mL) THF solution of Cr₂([OO]^{Ph})₂ (0.030 g, 0.023 mmol) was reacted with diphenyldiazomethane (0.018 g, 0.092 mmol) for 4 h. The light green color of the complex changed immediately to purple. The solution was stirred for 6 h at RT. The solvent was removed under vacuum and the residue was recrystallized from ether-THF mixture at -35 °C. Brown color crystals were isolated in 52% yield (0.025 g, 0.024 mmol). Calcd for C₇₀H₅₂CrN₄O₂×C₄H₈O×0.5C₆H₁₂: C, 80.60, H, 5.80. Found C, 79.52, H, 5.57.

6,6,12,12-tetraphenyl-6,12-dihydroindeno[1,2-b]fluorene (7). 1. Reaction of Cr₂([OO]^{Ph})₂ with (NO)(BF₄): A solution of (NO)(BF₄) (0.010 g, 0.093 mmol) in THF (5 mL) was added to a THF solution (5 mL) of Cr₂([OO]^{Ph})₂ (0.030 g, 0.023 mmol). The green color solution became cloudy and turned yellow over the course of 6 h. The solvent was removed under vacuum and the residue recrystallized with ether-THF mixture. Colorless crystals were obtained in 92% yield (0.023 g, 0.040 mmol). 2. Reaction of H₂[OO]^{Ph} with (NO)(BF₄): A solution of (NO)(BF₄) (0.012 g, 0.1 mmol) in THF (5 mL) was added to a THF solution (5 mL) of H₂[OO]^{Ph} (0.030 g, 0.051 mmol). The colorless solution turned light brown over a period of 6 h. The solvent was removed under vacuum and the residue recrystallized in CH₂Cl₂. Colorless crystals of **7** were obtained in 77% yield (0.021 g, 0.039 mmol). ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 7.81 (s, 2H, H_e), 7.71 (d, J_{HH} = 7.6 Hz, 2H, H_a), 7.38 (d, 2H, J_{HH} = 7.6, H_d), 7.32 (t, 2H, J_{HH} = 7.6 Hz, H_b), 7.26 (m, 22H, H_c, H_f, H_g, H_h). Related compound (lacking the phenyl substituents) and its NMR characterization were previously reported [50]. ¹³C NMR (125 MHz, CD₂Cl₂, 298K): δ 151.48, 151.12, 145.92, 140.21, 139.93, 128.27, 128.13, 127.58, 127.48, 126.69, 126.07, 120.16, 117.81, 65.24. HRMS (m/z): Calcd, [C₄₄H₃₀]⁺ 558.2347, found 558.2333.

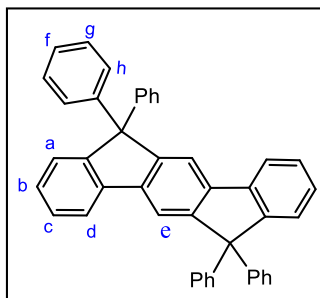


Figure 6. Assignment of ^1H NMR signals for **7** (see previous paragraph for details).

General Procedure for Catalytic Studies. C_6D_6 solution containing 20 equivalents of an organoazide, 24 equivalents of an isocyanide and 2 equivalents of 1,3,5-trimethoxybenzene (internal standard) was mixed with 2.5 mol% catalyst in C_6D_6 . The reaction was heated at 60 °C for 24 h. The products were identified and the yields were calculated using ^1H NMR spectroscopy.

3.3. X-ray Crystallographic Details

Structures of complexes **1**, **2**, **3**, and **6**, and 6,6,12,12-tetraphenyl-6,12-dihydroindeno[1,2-b]fluorene (**7**) were confirmed by X-ray structure determination; data collection and refinement details are given in Table 1. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. The structures of **1**, **3**, **6**, and **7** were collected using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at Wayne State University. The structure of **2** was collected using $\text{CuK}\alpha$ radiation ($1.54178 \text{ \AA}$) in the Center for Crystallographic Research in the Department of Chemistry, Michigan State University. The data were processed and refined using the APEX2 software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of **6** contained half a molecule of cyclohexane and a molecule of THF in the asymmetric unit. The structure of **7** co-crystallized with CH_2Cl_2 which was fully refined. The structure of **3** contained multiple severely disordered THF solvent molecules in the asymmetric unit, leading to the overall poor quality of the diffraction data. We had only limited success in modelling the disorder in THF solvent, thus, SQUEEZE program was applied to remove the disordered solvent. One of the *para*-tolyl groups in the structure of **3** was found to be disordered; the disorder was successfully modeled by finding two alternative conformations. The structure of **1** was also of relatively poor quality, due to the very small size of the crystals. Despite data collection at 60 s per frame, little diffraction was observed beyond $\sim 1 \text{ \AA}$. The structure of **1** contained several toluene molecules per asymmetric unit, one of which was found to be disordered over two conformations. The structure of **2** contained significant amount of highly disordered THF solvent, which was removed using SQUEEZE.

Table 1. X-ray crystallographic details for complexes 1-3, 6, and compound 7.

Complex	1	2	3	6	7
formula	C ₅₂ H ₄₆ CrO ₄ ×2.5C ₇ H ₈	2C ₈₈ H ₆₄ Cr ₂ O ₄	C ₅₈ H ₄₆ CrN ₂ O ₂	C ₇₀ H ₅₂ CrN ₄ O ₂ ×0.5C ₆ H ₁₂ ×C ₄ H ₈ O	C ₂₂ H ₁₅ ×CH ₂ Cl ₂
fw, g/mol	1020.25	2578.80	854.97	1147.34	364.27
crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 21/ <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.946(11)	13.9851(4)	17.38(15)	10.1831(6)	8.7464(5)
<i>b</i> (Å)	14.298(16))	19.4602(6)	13.03(11)	13.0107(7)	8.7610(5)
<i>c</i> (Å)	19.19(2)	30.4287(10)	28.58(19)	23.0961(13)	12.4072(7)
α (deg)	83.38(3)	81.683(2)	90.00	100.964(3)	76.995(2)
β (deg)	82.55(2)	77.609(2)	127.4(4)	101.580(3)	78.928(2)
γ (deg)	82.44(2)	74.125(2)	90.00	99.999(3)	70.505(2)
<i>V</i> (Å ³)	2668(5)	7747.2(4)	5142(71)	2870.7(3)	866.13(9)
<i>Z</i>	2	4	4	2	2
<i>d</i> _{calcd} , g/cm ³	1.270	1.1055	1.104	1.327	1.397
μ , mm ⁻¹	0.266	2.673	0.263	0.257	0.377
<i>T</i> (K)	100(2)	172.99	100(2)	100(2)	100(2)
2 θ , deg	49.00	128.14	47.44	52.96	55.02
<i>R</i> _{<i>I</i>} ^a [(<i>I</i> >2 σ)]	0.0981	0.0827	0.0727	0.0730	0.0388
<i>wR</i> ₂ ^b [(<i>I</i> >2 σ)]	0.2070	0.1875	0.1512	0.1710	0.0803
GOF ^c (F ²)	0.973	0.7573	0.881	1.037	1.041

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$. ^c GOF = $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

3.4. Computational Details

DFT calculations were performed using Gaussian 09 [52]. All calculations were performed at the BP86-D3/def2-SVP level of theory [53–57], employing density fitting, ultrafine grids [58], and Becke-Johnson damping for the dispersion corrections. Optimized structures were confirmed to be minima by ensuring all harmonic frequencies were real. All wavefunctions were verified to be stable. Orbital analyses were performed in GaussView 6.0.16 [59], and Mayer bond orders were calculated using Multiwfn 3.5 [60].

4. Conclusions

We have demonstrated that chelating bis(alkoxide) ligand [OO]^{Ph}, featuring terphenyl spacer between the alkoxide donors, forms mononuclear (Cr[OO]^{Ph}(THF)₂) or dinuclear (Cr₂[OO]^{Ph})₂ Cr(II) complexes, depending on the crystallization conditions. These results suggest that [OO]^{Ph} exhibits larger steric profile compared with two monodentate alkoxides [OC^{*t*}BuPh], which formed Cr₂(OC^{*t*}BuPh)₄ dimer invariably. Reactions with organoazides form diamagnetic Cr(VI) bis(imido) complexes, or paramagnetic Cr(IV) mono(imido) complexes. The outcome of the reaction depends on the sterics of organoazide: while mesityl azide formed Cr(IV) mono(imido), and 3,5-dimethylphenyl/4-methylphenyl azides formed Cr(VI) bis(imido) complexes. With diphenyldiazomethane, chromium bis(diphenylmethylenehydrazido) product forms. Treatment of the Cr(II) precursor with isocyanide likely forms a Cr(II) isocyanide adduct, whereas no reaction is observed with CO. Isoelectronic nitrosonium abstracts hydroxyl to induce cyclization producing 6,6,12,12-tetraphenyl-6,12-dihydroindeno[1,2-*b*]fluorene. Catalytic studies combining mixtures of isocyanides with organoazides enable carbodiimide formation only for bulkier (mono- or di-orthosubstituted) aryl azides. This finding is consistent with our previous report, that demonstrated that the C-N bond formation in carbodiimide is preceded by isocyanide coordination to the metal and thus occurs at Cr(IV) mono(imido) intermediate only. Our future studies will focus on the development of new chelating bis(alkoxide) ligands which could enable catalytic reactivity for wider range of substrates.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1: NMR, MS, UV-vis and IR spectra, cif files, and computational details. Cif files of the structures of **1-3**, **6**, and **7** were deposited at CCDC under the following numbers: 1970958-1970562.

Author Contributions: Conceptualization: SSK, RLL, SG; methodology: SSK, RJS, RLL, SG; writing—original draft preparation, SSK, RLL, SG; writing—review and editing, SSK, RLL; supervision: RLL, SG; funding acquisition: RLL, SG, RJS.

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Conflicts of Interest: The authors declare no conflict of interest.

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