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Synthesis, Characterization, and Catalytic Activity of Bimetallic Ti/Cr Complexes

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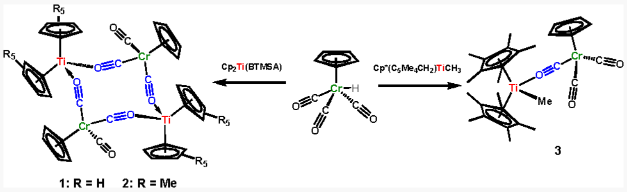
ABSTRACT: We report herein the reactions of the Rosenthal complexes, $Cp_2Ti(BTMSA)$ and $Cp^*_2Ti(BTMSA)$ (BTMSA: bis(trimethylsilyl)acetylene), with $CpCr(CO)_3H$. Those complexes are known to dissociate their alkyne ligands and to exhibit the reactivities of the putative titanocenes "Cp_2Ti" and "Cp^*_2Ti". Our reactions appear to proceed through the addition of $CpCr(CO)_3H$ to these titanocenes, giving rise to Ti^{IV}-H intermediates that lose H_2 to form the Ti^{III}−Cr complexes **1** and **2**. In the solid state, **1** and **2** both adopt a dimeric geometry, involving a 12-membered "Ti_2Cr_2" ring held together with Ti−O−C−Cr bridging carbonyls. The terminal carbonyls in **1** and **2** are trans. DFT calculations confirm that the loss of H_2 from the Ti^{IV}-H intermediate—forming the Ti^{III}-Cr dimer—is exergonic by 14.2 kcal mol^{-1} in the gas phase. The Bercaw compound Cp* $(C_5Me_4CH_2)TiCH_3$ reacts with $CpCr(CO)_3H$ to form a Ti^{IV}-CH_3 species with a coordinated $CpCr(CO)_3^-$ anion (**3**). The Ti-Cr dimer **1** is capable of catalyzing the hydrogenation of an epoxide to an anti-Markovnikov alcohol, avoiding the use of Cp_2TiX_2 (X = Cl$^-$ or mesylate), $NaCpCr(CO)_3$, and $HCpCr(CO)_3$ separately as in our previous catalyst system.



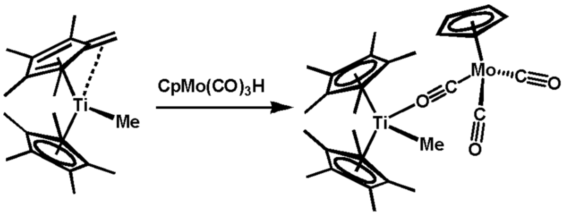
INTRODUCTION

Bimetallic complexes with bridging CO ligands are interesting because they often activate C≡O cooperatively.[1] Even though the earliest studies of these complexes emphasized their structure and bonding, bimetallic systems are now often used in catalysis. Examples include carbonylation of epoxides and aziridines,[2−6] carbonylative C-C coupling,[7] borylation of C−H bonds,[8,9] and hydrogenation of alkynes.[10] Advances in this area have been reviewed by Mankad et al.[11,12]

A number of groups have studied group 4 elements (Ti, Zr, and Hf) with coordinated carbonyl anions. Our own interests are centered in the reaction of group 4 methyls with group 6 metal hydrides. This reaction generally results in methane elimination and the synthesis of bimetallic compounds.[13] We have obtained a variety of Zr/M (M = Cr, Mo, and W) bimetallic complexes by the reaction of $Cp_2Zr(R)CH_3$ (R = methyl, acyl, or iminoacyl) with acidic metal hydrides. The rate of cleavage of the Zr−CH_3 bond depends on the nature of the adjacent R, and is significantly enhanced when R can act as a proton relay site.[14−18]

In 1981, Stucky et al. reported one of the earliest Ti/Mo bimetallic complexes via the reaction of $Cp^*(C_5Me_4CH_2)TiCH_3$[19] with $CpMo(CO)_3H$ (eq 1);[20] the product features a Ti^{IV} cation with $[CpMo(CO)_3]^-$. Later, Merola et al. prepared a Ti^{III}/Mo dimer by treating $(Cp)_2Ti(CO)_2$ with $[(C_5H_4CH_3)Mo(CO)_2]_2$ (eq 2).[21]

More recently, the Chirik group has isolated and characterized the monomers $(C_5Me_4SiMe_3)_2Ti(CO)CpCr(CO)_2$ and $(C_5Me_4SiMe_3)_2Ti(Cl)(CO)CpCr(CO)_2$ (eq 3).[22]



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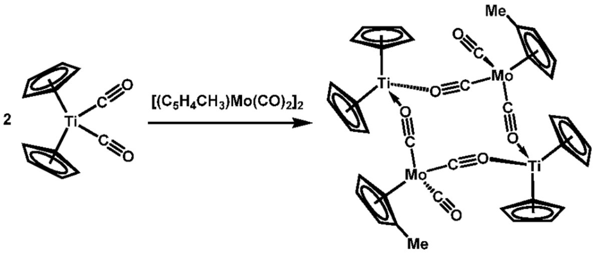

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They found that $CpCr(CO)_3H$ promotes hydrogen atom transfer from H_2 onto the NH_2 ligand of $(C_5Me_4SiMe_3)_2Ti(Cl)(NH_2)$ (eq 4).

Our group has demonstrated that the cooperative interaction of two different metals, Cp_2TiX_2 and CpCr-

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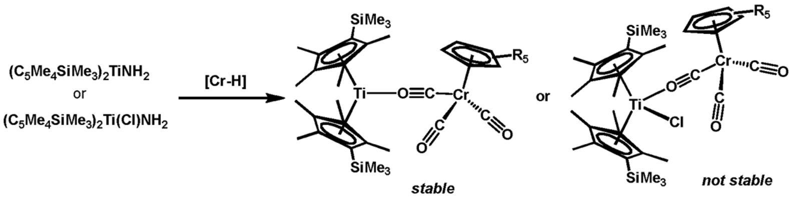

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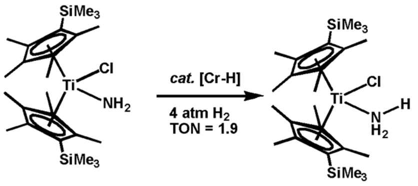


(4)

(CO)$_3$H, generates a catalytic system for the anti-Markovnikov epoxide hydrogenation. We believe that Ti^{III} opens the epoxide to generate a radical, CpCr(CO)$_3$· activates H_2, and CpCr(CO)$_3$H delivers an H· to the radical. Thus, at different points in the cycle, Cr delivers H·, H^+, and e^-.[23] In this process, the reaction or interaction between Ti and Cr complexes is especially important in understanding and optimizing the reaction. Here, we report the synthesis, characterization, and catalytic activity of Group IV−VI Ti/Cr heterobimetallic complexes. The reaction between Cp_2Ti(BTMSA) and CpCr(CO)$_3$H produced a dimeric species, which was found to be a competent catalyst for anti-Markovnikov epoxide hydrogenation.

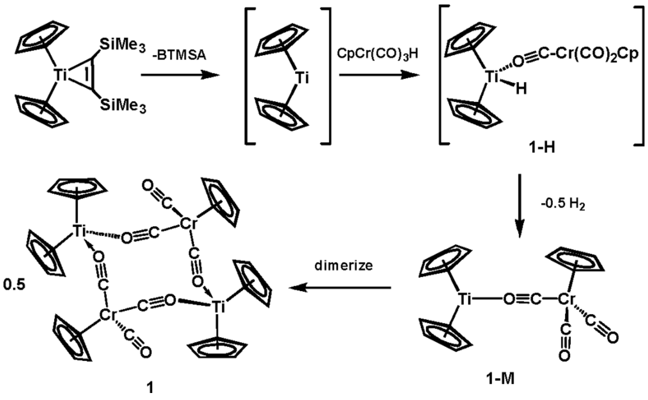
■ RESULTS AND DISCUSSION

Both the Chirik group[22] and our group[23] have demonstrated proton/hydrogen atom transfer from Cr hydrides to Ti$^{III/IV}$ complexes and have demonstrated that such a transfer plays an important role in catalytic processes such as nitrogen fixation and anti-Markovnikov epoxide hydrogenation. In Chirik's report, the Ti^{III} species $(C_5Me_4SiMe_3)_2$Ti(CO)Cp*Cr(CO)$_2$ is stable, while the Ti^{IV} compound $(C_5Me_4SiMe_3)_2$Ti(Cl)(CO)Cp*Cr(CO)$_2$ undergoes ligand redistribution and electron transfer at room temperature. These observations suggest that the stability of the Ti/Cr bimetallic systems is affected by the oxidation state of the Ti and have prompted us to study the reaction of CpCrCO$_3$H with a Ti^{II} species.

Titanocene "Cp_2Ti^{II}" is not stable; however, it can be generated by the well-known precursor Cp_2Ti(BTMSA) (BTMSA = bis(trimethylsilyl)acetylene).[24,25] Upon mixing equimolar solutions of Cp_2Ti(BTMSA) and CpCr(CO)$_3$H, we observed an immediate color change from brown to green, with gas evolution, followed by the precipitation of green crystals of **1** (Scheme 1). ^{1}H NMR indicated the formation of free BTMSA (δ 0.15) and H_2 (δ 4.47);[26] a broad signal at δ 5.40 (CpCr, $w_{1/2}$ = 42.5 Hz) and the absence of any Cp_2Ti signal suggested that the product was paramagnetic. The limited solubility of **1** and its paramagnetic nature prevented the acquisition of any useful ^{13}C NMR data. Dissolution of **1** in coordinating solvents such as CD_3CN results in breakdown of the dimeric structures and formation of a separated ion pair (*vide infra*). Magnetic measurements provide μ_{eff} = 1.77 μ_B (CD_3CN solution) which is close to the expected spin-only value for 1 unpaired electron (1.73 μ_B), and thus the monomer.

We were able to perform SC-XRD analysis on a crystal of **1** (Figure 1). In the solid state, **1** is a dimer, with a puckered 12-membered "Ti_2Cr_2" ring held together with bridging carbonyls and Ti-O-C-Cr interactions. The remaining two carbonyls in **1** are terminal and arranged in a trans fashion. The two TiCr units are related by an inversion center. The two bridging carbonyls are almost indistinguishable: (1) the Ti−O distances are 2.176(2) and 2.180(3) Å; (2) the Cr−C bonds are 1.780(3) and 1.775(4) Å; (3) the C−O distances are 1.189(5) and 1.199(4) Å. The structural features of **1** resemble those of the Ti_2Mo_2 ring reported by Merola.[21] On the basis of the aforementioned evidence, we concluded that **1** is the dimeric form of a Ti^{III} complex paired with the [CpCr(CO)$_3$]$^-$.

Scheme 1. Proposed Mechanism to Generate 1



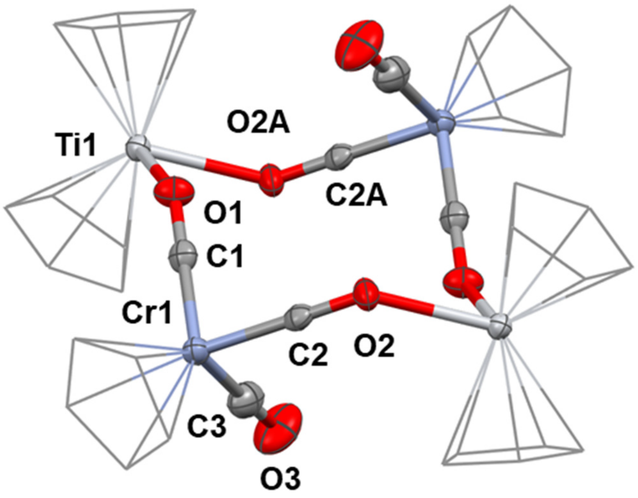


Figure 1. SC-XRD structure of **1** (hydrogen atoms on Cp have been omitted for clarity) at 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): Ti1−O1 2.180(3), Ti1−O2A 2.176(2), C1−O1 1.199(5), Cr1−C1 1.775(4), C2−O2 1.189(4), Cr1−C2 1.780(3), C3−O3 1.157(5), Cr1−C3 1.833(3); Ti−O1−C1 171.2(2), Ti−O2A−C2A 167.8(2).

We propose that the formation of **1** involves the sequence in Scheme 1. In the first step, the "Cp_2Ti", generated by ligand dissociation from $Cp_2Ti(BTMSA)$, reacts rapidly with Cr—H to form the transient $Cp_2Ti(H)(\mu\text{-}OC)Cr(CO)_2Cp$ (**1-H**). The Ti—H bond in the latter is probably weak, allowing it to evolve H_2 gas and decompose into the monomeric $Cp_2Ti(\mu\text{-}OC)Cr(CO)_2Cp$ (**1-M**). Density Functional Theory (DFT) results have suggested that decomposition of "$Cp_2Ti(H)Cl$" to Cp_2TiCl and dihydrogen is exergonic by 11 kcal/mol.[27] Calculations from our group indicate that loss of H_2 from **1-H**, forming **1-M** (Figure 2), is exergonic by 12.2 kcal/mol in the gas phase—consistent with our experimental observations. Full details of calculations can be found in the Supporting Information. The dimerization of **1-M** to **1** is further downhill, by 2 kcal per mol of **1-M**.

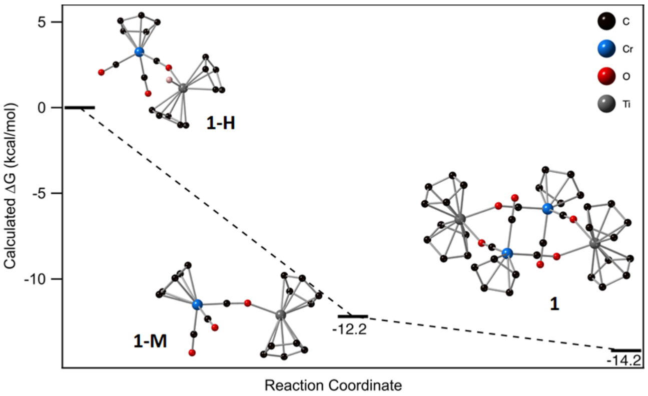
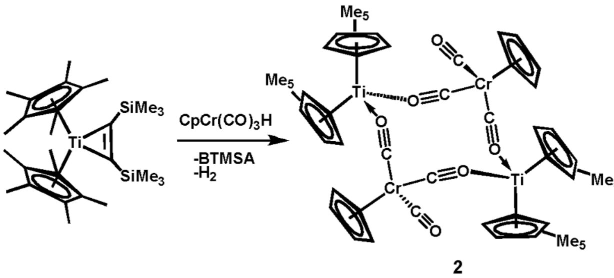


Figure 2. DFT-calculated formation of **1** from **1-H**.

It is also possible that H· transfer from $CpCr(CO)_3H$ (with a BDE of 62 kcal/mol)[28−30] to "Cp_2Ti" generates "Cp_2TiH", whose BDE has been computationally determined to be 71.7 kcal/mol.[31] If "Cp_2TiH" releases H_2 and regenerates "Cp_2Ti", combination with the $CpCr(CO)_3$· left after hydrogen atom transfer affords **1**. However, the reported dehydrogenation rate of "Cp_2TiH" is comparatively slow,[19,32] which does not agree with our observation of the rapid evolution of H_2. The reaction of $Cp_2Ti(BTMSA)$ with $Cp(CO)_3Cr\text{-}Cr(CO)_3Cp$, which is in equilibrium with $\cdot Cr(CO)_3Cp$, also provides compound **1**.

In order to improve the solubility of **1**, we decided to use $Cp^*_2Ti(BTMSA)$ as the Ti^{II} precursor. The reaction of $Cp^*_2Ti(BTMSA)$ with $CpCr(CO)_3H$ was much slower in benzene, without noticeable gas evolution (eq 5). X-ray quality crystals of **2** were obtained by layering pentane onto the benzene solution. In the solid state (SC-XRD, Figure 3), **2** also forms a 12-membered "Ti_2Cr_2" ring via Ti-O-C-Cr interactions with trans terminal COs. However, the ring in **2** is more planar than that in **1**.



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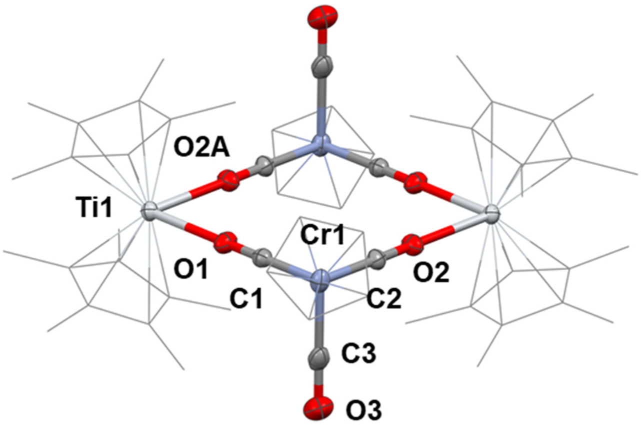


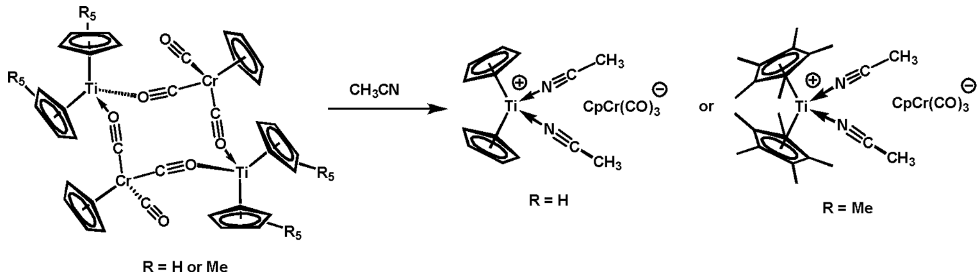
Figure 3. SC-XRD structure of **2** (hydrogen atoms on Cp and Cp* have been omitted for clarity) at 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): Ti1−O1 2.162(2), Ti1−O1 2.171(2), C1−O1 1.191(2), Cr1−C1 1.787(2), C2−O2 1.187(3), Cr1−C2 1.789(2), C3−O3 1.163(4), Cr1−C3 1.825(3); Ti−O1−C1 171.2(2), Ti−O2A−C2A 168.0(2).

Compound **2** is indeed more soluble in pentane and benzene. ^1H NMR in C_6D_6 shows a slightly broadened CpCr signal at δ 5.37 ($\Delta w_{1/2}$ = 45 Hz), along with $Cp^*_2Ti^{III}$ methyl signals shifted downfield to δ 11.43 and broadened substantially ($\Delta w_{1/2}$ = 1600 Hz)—indicating considerable spin density on the Cp* rings. Its EPR spectrum, in a mixture of CH_3CN and C_6D_6, shows g = 1.983 and hyperfine coupling from two nitrogens (I = 1, A_{iso} = 7.7 MHz, presumably from two acetonitriles coordinated to each Ti(III); see eq 6 below and Figure S9).

Magnetic measurements in CD_3CN showed a μ_{eff} of 1.64 μ_B per titanium, consistent with a single unpaired electron on each Ti. However, by carrying out SQUID magnetometry measurements directly on powders of **1** and **2**, we have been able to determine the magnetic coupling in the dimeric structures seen by X-ray crystallography. The temperature-corrected magnetic susceptibility ($\chi_M T$) of **1** is fairly constant at 0.57 cm^3 K/mol from 298 to 40 K. Below that temperature, the $\chi_M T$ of **1** decreases quickly, becoming nearly zero cm^3 K/mol by 6 K; it is clear that there is weak antiferromagnetic coupling between the two $S = {}^1/_2$ Ti^{III} centers. The behavior of $\chi_M T$ for **2** is similar to that for **1**, though the downturn begins at 50 K and finishes by 10 K, indicating that the antiferromagnetic coupling in **2** is slightly stronger than that in **1** (Figure S13).

A fit to the magnetic susceptibility data[33] of **1** and **2** as a weakly antiferromagnetically coupled system of 2 sites (A and B), both with $S = {}^1/_2$, gives $g_A = g_B$ = 1.77 for both, with J_{AB} = −12.4 cm^{-1} for **1** and J_{AB} = −20.4 cm^{-1} for **2** (Figure S13). While the g value of 1.77 is low, both **1** and **2** are quite air-sensitive and may have been partially oxidized as they were being transferred into the SQUID magnetometer. A fit to the observed $\chi_M T$ from 85% of the mass of the sample (with the remaining 15% assumed to have decomposed into a diamagnetic material) resulted in J values for **1** and **2** identical with those given above and g values of 1.92 for all Ti sites (Figure S14).

The solution structures of **1** and **2** depend on the coordinating ability of the solvent. In the solid state, **1** has an intense green color (Figure 4, inset a), and its solubility in benzene is limited (see the left of inset b). However, **1** can be dissolved in CH_3CN, resulting in a blue solution[34] (see the



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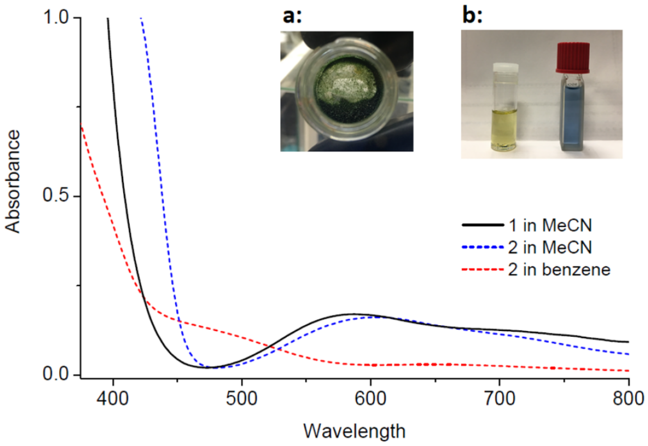
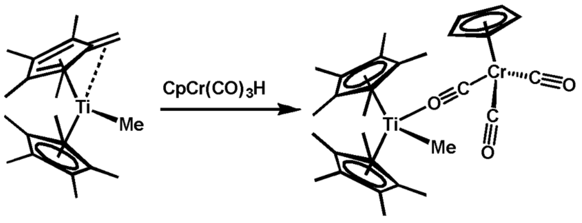


Figure 4. UV–vis spectra of **1** in acetonitrile (black) and **2** in acetonitrile (blue dashes) and in benzene (red dashes). Inset: (a) solid of **1**; (b) **1** in benzene (left) and acetonitrile (right).

right of inset b) with absorption features centered at 575 and 719 nm (Figure 4, black curve). The more soluble compound **2** provides a red-orange benzene solution (red dashes) blue-shifted relative to that of **1**, with features centered at 477 and 665 nm. Finally, **2** dissolved in CH_3CN provides a solution similar to that of **1** (593 nm, 725 nm). The solvatochromic shifts of those two compounds are surely due to the breakdown of the dimeric structures upon coordination of solvents such as CH_3CN (eq 6).[34] The absence of interaction between the cation and anion is confirmed by the ^1H NMR and ^{13}C NMR of data of both **1** and **2** in CD_3CN. The sharp ^1H signal at δ 4.46 for CpCr and only one ^{13}C signal at δ 246.1 for the carbonyl suggest the generation of free $[CpCr(CO)_3]^-$ (see SI).

We have also been able to prepare the heterobimetallic $Cp^*_2Ti(CH_3)$-(μ-OC)$Cr(CO)_2Cp$ (**3**) (eq 7) by adding



(7)

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$CpCr(CO)_3H$ to $Cp^*(C_5Me_4CH_2)TiCH_3$, a compound isolated by Bercaw and Brintzinger after methane elimination from $Cp^*_2TiMe_2$.[19] An analogous procedure was used by Stucky.[20] Presumably, the reaction involves transfer of a proton from $CpCr(CO)_3H$ to the methylene of the Ti compound, along with the coordination of one of the carbonyl oxygens of $[CpCr(CO)_3]^-$ to the Ti. Both the NMR spectra and single-crystal X-ray diffraction confirm the proposed structure. The sharpness of the ^1H signals at δ 4.76 (Cp), 1.73 (Me), and 0.57 (Cp*) is consistent with a diamagnetic product. ^{13}C NMR signals at δ 247.2 and 242.5 indicate the bridging and terminal carbonyl ligands.

A tightly bound Ti/Cr ion pair is again obvious upon SC-XRD analysis of **3** (Figure 5). The Ti–O distance (2.021(1) Å) is again increased in the μ-OC bridging carbonyl, but the Ti···O–C–Cr moiety is not linear, with a Ti···O–C angle of 156.3(2)° and an O–C–Cr one of 177.9(2)°. The comparison of selective bond distances and angles for the terminal and bridging CO in compounds **1**–**3** is given in Table 1.

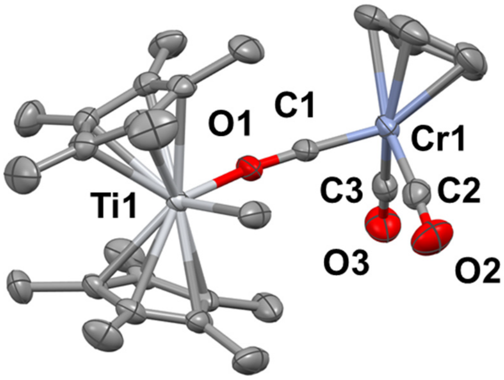

Figure 5. SC-XRD structure of **3** (the hydrogen atoms have been omitted for clarity) at 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): Ti1–O1 2.021(1), C1–O1 1.214(2), Cr1–C1 1.755(2), C2–O2 1.160(3), Cr1–C2 1.827(2), C3–O3 1.158(3), Cr1–C3 1.827(2); Ti–O1–C1 156.3(2).

We were now in a position to examine the catalytic ability of the new combinations (**1**, **2**, and **3**) of Ti and Cr. The Ti and Cr components are impressive catalysts *separately*: Nugent and

Table 1. Comparison of Selective Bond Distances (Å) and Angles (deg) in Compounds 1–3

		1	2	3
bridging CO	Ti–O	2.176(2) 2.180(3)	2.162(2) 2.171(2)	2.021(1)
	C–O	1.199(5) 1.189(4)	1.191(2) 1.187(3)	1.214(2)
	Cr–C	1.775(4) 1.780(3)	1.787(2) 1.789(2)	1.755(2)
	Ti–O–C	171.2(2) 167.8(2)	171.2(2) 168.0(2)	156.3(2)
terminal CO	C–O	1.157(5)	1.163(4)	1.160(3) 1.158(3)
	Cr–C	1.833(3)	1.825(3)	1.827(2) 1.827(2)

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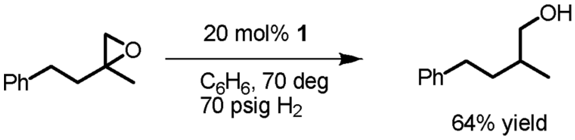
RajanBabu have demonstrated that stoichiometric amounts of Cp_2TiCl can open epoxides to carbon-centered radicals that can cyclize onto C=C double bonds;[35,36] the Gansäuer group has made the one-electron reduction of epoxides catalytic[37,38] and used a variety of H· donors, such as 1,4-cyclohexadiene,[38] Bu_3SnH,[36] thiols,[35] silanes,[39] or precious-metal hydrides,[40] to reduce the resulting carbon-centered radicals. Our group has shown that $CpCr(CO)_3H$, with a Cr−H bond dissociation energy of 62 kcal mol^{-1}, can transfer H· to different organic substrates[41−45] and be regenerated from $CpCr(CO)_3$· under H_2 pressure.[46]

We have successfully combined Ti and Cr in the dual cooperative catalyst mentioned at the end of the Introduction, which hydrogenates epoxides to anti-Markovnikov alcohols. The heterobimetallic Ti/Cr complexes we have just made can achieve catalytic activity comparable to the original system. In eq 8, the use of **1** avoids the need to add Cp_2TiX_2, $Na[CpCr(CO)_3]$, and $HCpCr(CO)_3$ separately, and gives a yield of anti-Markovnikov alcohol comparable to that achieved with our previous catalysts.



(8)

■ SUMMARY AND CONLUSIONS

We have found that the reactions of $CpCr(CO)_3H$ with Rosenthal complexes, $Cp_2Ti(BTMSA)$ and $Cp*_2Ti(BTMSA)$, afforded heterobimetallic compounds **1** and **2**. Our reactions appear to proceed through the addition of $CpCr(CO)_3H$ "Cp_2Ti" and "$Cp*_2Ti$", giving rise to Ti^{IV}-H intermediates that lose H_2 to form the Ti−Cr complexes **1** and **2** featuring paramagnetic Ti^{III} centers. In the solid state, **1** and **2** both adopt a dimeric geometry, which involved a 12-membered "Ti_2Cr_2" ring held together with Ti−O−C−Cr bridging carbonyls. The terminal carbonyls in **1** and **2** are trans. DFT calculations confirm that the loss of H_2 from the Ti^{IV}-H intermediate—forming the Ti^{III}-Cr dimer—is exergonic by about 14.2 kcal mol^{-1} in the gas phase. Upon dissolution in polar coordinating solvents such as acetonitrile, the dimers fall apart into separated ion pairs. Finally, we have successfully used compound **1** to catalyze the hydrogenation of an epoxide to the anti-Markovnikov alcohol.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all manipulations were carried out in an Ar-filled inert atmosphere box (O_2 < 1 ppm) or under Ar by standard Schlenk techniques. Glassware was flame- or oven-dried immediately prior to use. NMR spectra were recorded on a Bruker 400 or 500 MHz instrument. ^1H and ^{13}C NMR spectra are included in the Supporting Information. ATR FT-IR data were collected on a Bruker Alpha II FT-IR instrument. Solution samples for electronic spectroscopy were prepared under argon. Absorption spectra were recorded on a Cary 60 UV−vis. Absorption maxima were obtained by spectral deconvolution using Igor64. Elemental analyses were carried out at Midwest Microlab. EPR spectra were recorded on a Bruker EMX spectrometer at ambient temperature in deoxygenated acetonitrile and deuterated benzene solution in a 3 mm (inner diameter) quartz tube. EPR simulations were performed with Bruker's EasySpin software. Magnetic susceptibility measurements were performed using a Cryogenics S700X SQUID magnetometer. The loose polycrystalline sample was placed into a gel capsule and secured in place with eicosane, which was placed inside a plastic straw. Magnetization data at 100 K from 0 to 7 T were used as a ferromagnetic-free purity test. Direct current (dc) variable temperature magnetic susceptibility measurements were collected in the temperature range 3−295 K under an applied field of 0.1 T. The magnetism data were corrected for the small diamagnetic contribution of the gel capsule containing the sample and the straw and the diamagnetic contribution of the compounds. Magnetic susceptibility data were modeled in PHI.[33]

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection, and refinement parameters are summarized in the Supporting Information. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 2014/7).[47−49] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (CCDC 2032789−2032791). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Materials. Tetrahydrofuran and benzene were distilled from sodium/benzophenone ketyl under Ar. Pentane was stirred over sulfuric acid for several days to remove any olefins and then was distilled from sodium under Ar. Toluene was purified by the method of Grubbs.[50] Deuterated solvents (Cambridge Isotopes) were purified by vacuum transfer from the appropriate drying agent (potassium metal for benzene-d_6 and toluene-d_8 and P_4O_{10} for acetonitrile-d_3).

Synthetic Procedures. Bis(trimethylsilyl)acetylene (BTMSA) was purchased from Sigma-Aldrich Co. and used as received. Cp_2TiCl_2 and $Cp*_2TiCl_2$ were obtained as a gift from Boulder Scientific Co. and used as received. $Cp_2Ti(BTMSA)$, $Cp*_2Ti(BTMSA)$,[24,25] $Cp*(C_5Me_4CH_2)TiCH_3$,[19] and $CpCr(CO)_3H$[51−54] were prepared by literature methods. The hydrogenation reaction of the epoxide substrate was set up according to the literature procedure.[23]

$[Cp_2Ti\cdots(OC)Cr(CO)_2Cp]_2$ (1). $Cp_2Ti(BTMSA)_2$ (174.2 mg, 0.50 mmol) and $CpCr(CO)_3H$ (109.1 mg, 0.50 mmol) were loaded in a 20 mL vial and then dissolved in 2 mL of benzene in a glovebox. Immediate color change to green and evolution of H_2 were observed. Green crystals developed within minutes. The solution was left undisturbed overnight and then decanted. The crystals were washed with 5 mL of pentane and dried under vacuum. Yield: 160 mg (84%). ATR-FTIR: 1914, 1827, 1606 cm^{-1}. Anal. Calcd for $C_{36}H_{30}Cr_2O_6Ti_2$ (%): C, 57.02; H, 3.99. Found: C, 41.68; H, 3.96. The low C value might be due to the air/moisture sensitivity of **1** and carbide formation, as pointed out in the literature on a similar compound.[21]

$[Cp*_2Ti\cdots(OC)Cr(CO)_2Cp]_2$ (2). $Cp*_2Ti(BTMSA)_2$ (244.9 mg, 0.50 mmol) and $CpCr(CO)_3H$ (109.1 mg, 0.50 mmol) were loaded in a 20 mL vial and then dissolved in 2 mL of benzene in a glovebox. The resulting dark red solution was stirred overnight before layering 3 mL of pentane at room temperature. Dark red crystals were formed, isolated, and dried under vacuum. Yield: 210 mg (82%). ^1H NMR (500 MHz, C_6D_6, 298 K) δ 11.43 (br, C_5Me_5, 60H), 5.37 (br, Cp, 10H). ATR-FTIR: 1914, 1827, 1607 cm^{-1}. Anal. Calcd for $C_{56}H_{70}Cr_2O_6Ti_2$ (%): C, 64.74; H, 6.79. Found: C, 61.00; H, 6.78. The low C value might be due to the air/moisture sensitivity of **2** and carbide formation, as pointed out in the literature on a similar compound.[21]

$Cp*_2Ti(CH_3)\cdots(OC)Cr(CO)_2Cp_2$ (3). $CpCr(CO)_3H$ (109.1 mg, 0.50 mmol) in 2 mL of toluene was added dropwise to a toluene (2 mL) solution of $Cp*(C_5Me_4CH_2)TiCH_3$ (166.2 mg, 0.50 mol) in a 20 mL vial in a glovebox. The solution was layered with 4 mL of pentane and stored at −40 °C. Crystals of compound **3** grew, then were isolated, and dried under vacuum. Yield: 210 mg (76%). ^1H NMR (500 MHz, C_7D_8, 298 K) δ 4.76 (s, Cp, 5H), 1.37 (s, C_5Me_5, 30H), 0.57 (s, Ti-Me, 3H). ^{13}C NMR (126 MHz, C_7D_8, 298 K) δ 247.2, 242.5, 124.1, 85.1, 57.2, 11.5. ATR-FTIR: 1915, 1828, 1608 cm^{-1}. Anal. Calcd for $C_{29}H_{38}CrO_3Ti$ (%): C, 65.17; H, 7.17. Found: C, 65.37; H, 7.24.

NMR Reaction of $Cp_2Ti(BTMSA)_2$ with $CpCr(CO)_3H$ to Make $[Cp_2Ti\cdots(OC)Cr(CO)_2Cp]_2$ (1). A J. Young tube was loaded with $Cp_2Ti(BTMSA)_2$ (17.4 mg, 0.05 mmol), $CpCr(CO)_3H$ (10.9 mg, 0.05 mmol), and 0.6 mL of C_6D_6. ^1H NMR was taken immediately. The generation of H_2 and free BTMSA was evident from the signals at δ 4.47 and 0.15, respectively.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00645.

Cartesian coordinates (XYZ)

Full experimental details and additional figures (PDF)

Accession Codes

CCDC 2032789−2032791 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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