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chromatography through a short path of deactivated silica gel.⁹ Thermal reactions were carried out by following the same procedure but strictly excluding light.

In summary, a new stereoselective approach to vinyl ethers **3** starting from chromium carbenes having both alkyl and aryl substituents at the carbene carbon and stabilized sulfur ylides has been developed. This novel reaction provides an alternative strategy for constructing 2-acyl enol ethers directly in enolized form, in a process which formally results in the totally *site*-selective enolization of a β -keto ester or a β -diketone. Compounds **3** are in turn not available by using standard Wittig methodology, and the stereoselectivity of the process may be steric in nature. Efforts to extend this methodology to other chromium carbene complexes and to control the stereochemistry in the formation of compounds **3** are now in progress.

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Supplementary Material Available: Text describing the syntheses and giving full characterization and spectral data (¹H NMR, ¹³C NMR, IR, and analytical data) for compounds **3a-f** (4 pages). Ordering information is given on any current masthead page.

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Unexpected Carbon–Carbon Coupling between Organic Cyanides and an Isopropyl β -Carbon in a Hafnium Ene Diamide Complex

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Summary: A reaction sequence involving two hydrogen transfers and a C–C coupling on the β -carbon of an isopropyl group leads to formation of a new dianionic tridentate ligand in the reaction of the ene diamide complex $\text{Cp}^*\text{Hf}(\sigma^2, \pi\text{-iPr-DAB})\text{Cl}$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, iPr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene) with organic cyanides. The product $\text{Cp}^*\text{Hf}[\text{iPrNCH}=\text{CHNC}(\text{Me})=\text{CHC}(\text{tBu})=\text{NH}]\text{Cl}$ was structurally characterized (*Pbca*, $a = 13.454$ (1) Å, $b = 11.470$ (1) Å, $c = 31.297$ (2) Å, 100 K). The reaction sequence is probably initiated by the transfer of the iPr α -H atom to a coordinated cyanide. Such a hydrogen transfer was observed in the reaction of **1** with ketones, producing the ene imine alkoxide complexes $\text{Cp}^*\text{Hf}[\text{iPrNCH}=\text{CHN}=\text{CMe}_2](\text{OCHR}_2)\text{Cl}$, which were identified by NMR spectroscopy.

One of the most interesting and useful aspects of transition-metal centers in organometallic chemistry is that they can induce unusual transformations in coordinated organic ligands. C–C bond-forming reactions and reactions involving C–H bonds have attracted special attention in this respect and have found application in metal-directed organic synthesis.¹ Here we wish to report a unique sequence of consecutive C–H activation and C–C coupling on an iPr group in an ene diamide ligand observed in the

reaction of a hafnium ene diamide complex with organic cyanides.

Recently we reported the use of 1,4-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB) as an ancillary ligand for early-transition-metal centers to prepare various organohafnium complexes of the type $\text{Cp}^*\text{Hf}(\text{iPr-DAB})\text{R}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{Cl}$ (**1**), Me , $\text{C}\equiv\text{CMe}$, $\text{C}(\text{O})\text{Me}$, H).² In these complexes the ligand assumed a nonplanar σ^2, π ene diamide structure and acted in preliminary reactivity studies as an inert ancillary ligand, yielding thermally robust compounds. The π -donation from the nitrogen lone-pair electrons makes the metal center in these complexes significantly less electron-deficient than in the isostructural 14-electron butadiene complex $\text{Cp}^*\text{Hf}(\sigma^2, \pi\text{-2,3-dimethyl-1,3-butadiene})\text{Cl}$ (**2**).³

1

2

Despite this relative electron richness, complex **1** still exhibits some Lewis-acidic behavior and forms isolable

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Figure 1. X-ray structure of $\text{Cp}^*\text{Hf}(\text{iPr})\text{NCH}=\text{CHNC}(\text{Me})=\text{CHC}(\text{tBu})=\text{NH}]\text{Cl}$ (4). Selected interatomic distances (Å) and angles (deg) (standard deviations in parentheses) are as follows: Hf–Cl = 2.450 (1), Hf–N(1) = 2.107 (3), Hf–N(2) = 2.231 (4), Hf–N(3) = 2.135 (4), N(1)–C(3) = 1.473 (7), N(1)–C(4) = 1.379 (6), N(2)–C(5) = 1.427 (7), N(2)–C(6) = 1.343 (7), N(3)–C(9) = 1.336 (7), C(4)–C(5) = 1.331 (7), C(6)–C(8) = 1.375 (8), C(8)–C(9) = 1.405 (8); Cl–Hf–N(1) = 89.5 (1), Cl–Hf–N(2) = 140.0 (1), Cl–Hf–N(3) = 84.2 (1), N(1)–Hf–N(2) = 75.8 (2), N(1)–Hf–N(3) = 128.6 (2), N(2)–Hf–N(3) = 77.2 (2).

stoichiometric adducts with isocyanides such as $\text{Cp}^*\text{Hf}(\text{iPr-DAB})\text{Cl-CN}_{xy}$ (3) (eq 1).⁴ The inertness of the Hf– $\text{Cp}^*\text{Hf}(\text{iPr-DAB})\text{Cl} + xy\text{NC} \rightarrow$

$xy = 2,6\text{-dimethylphenyl}$

ene diamide bond relative to the Hf–butadiene bond is demonstrated by the fact that up to 150 °C no further reaction of 3 takes place, whereas for diene complex 2 insertion of the isocyanide into the Hf–diene bond has been observed.⁵

No isolable adduct of 1 with the organic cyanide $t\text{BuCN}$ was observed, but heating the reactants in toluene to 120 °C in a vacuum-sealed Pyrex tube produced an intensely orange solution, from which orange crystals were obtained. Spectroscopic⁶ and single-crystal X-ray⁷ diffraction data

(4) 3: ^1H NMR (δ , C_6D_6) 6.73 (t, 7.3 Hz, 1 H, xy p -CH), 6.58 (d, 7.3 Hz, 2 H, xy m -CH), 5.55 (s, 2 H, $=\text{CHN}$), 3.97 (sp, 6.6 Hz, 2 H, $i\text{Pr}$ CH), 2.09 (s, 6 H, xy Me), 2.06 (s, 15 H, Cp^*), 1.26 and 1.11 (d, 6.6 Hz, 6 H each, $i\text{Pr}$ Me); IR ν_{CN} 2070 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{HfClN}_3$: C, 52.26; H, 6.50; Cl, 5.71; Hf, 28.76. Found: C, 52.38; H, 6.56; Cl, 5.80; Hf, 29.26.

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(6) 4: ^1H NMR (δ , C_6D_6) 8.15 (br, 1 H, NH), 6.94 and 6.48 (d, 4.0 Hz, 1 H each, $=\text{CHN}$), 5.45 (d, 2.2 Hz, 1 H, $=\text{CH-}$), 4.59 (sp, 6.6 Hz, 1 H, $i\text{Pr}$ CH), 2.01 (s, 3 H, Me), 1.84 (s, 15 H, Cp^*), 1.33 and 1.22 (d, 6.6 Hz, 3 H each, $i\text{Pr}$ Me), 0.99 (s, 9 H, $t\text{Bu}$ Me); ^{13}C NMR (δ , C_6D_6) 10.80 (q, 126.6 Hz, Cp^* Me), 22.99 and 26.59 (q, 125.5 Hz, $i\text{Pr}$ Me), 23.46 (q, 126.6 Hz, Me), 29.61 (q, 125.5 Hz, $t\text{Bu}$ Me), 38.36 (s, $t\text{Bu}$ C), 54.13 (d, 139.3 Hz, $i\text{Pr}$ CH), 99.81 (d, 156.5 Hz, $=\text{CH-}$), 108.63 (d, 174.0 Hz, d, 10.4 Hz, $=\text{CH-}$), 120.53 (s, Cp^* ring), 129.15 (d, 162.3 Hz, d, 10.4 Hz, $=\text{CH-}$), 155.40 (s, $=\text{CN}$), 173.88 (s, $\text{C}=\text{N}$); IR ν_{NH} 3335 cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{40}\text{HfClN}_3$: C, 48.42; H, 6.71; Cl, 6.21; Hf, 31.29. Found: C, 48.92; H, 6.68; Cl, 6.31; Hf, 31.33.

(7) Crystallographic data for 4: space group $Pbca$, $a = 13.454$ (1) Å, $b = 11.470$ (1) Å, $c = 31.297$ (2) Å (100 K), $Z = 8$, $d_{\text{calc}} = 1.569$ g cm^{-3} . Data were collected on an Enraf-Nonius CAD4 diffractometer (Mo $K\alpha$, Zr filtered, 100 K) and corrected for Lp and absorption (DIFABS, $\mu = 44.1$ cm^{-1}); the structure was solved using Patterson methods (SHELXS-86) and refined (SHELXL-76) to $R = 0.032$ ($R_w = 0.031$) for 4102 unique reflections with $I > 2.5\sigma(I)$ and 258 parameters. The H atom on N(3) was located in a difference Fourier map and refined isotropically. The other H atoms were introduced at calculated positions and included in the refinement riding on their carrier atoms ($\text{C-H} = 1.02$ Å).

indicate that the product can be formulated as $\text{Cp}^*\text{Hf}[\text{N}(\text{iPr})\text{CH}=\text{CHNC}(\text{Me})=\text{CHC}(\text{tBu})=\text{NH}]\text{Cl}$ (4). The X-ray structure of this compound is represented in Figure 1. It shows that the Cp^*HfCl complex of a new dianionic tridentate ligand is formed by an apparent insertion of the cyanide into an $i\text{Pr}$ β -C–H bond, accompanied by the loss of two H atoms. The ligand can be described as a bis(imine) derivative of a substituted acetylacetonate in which one of the N atoms (N(2)) is also part of an ene diamide moiety. It is only slightly folded along the Hf–N(2) axis (torsional angle C(4)–C(5)–N(2)–C(6) = 160.7 (3)°). The ene diamide section of the ligand is planar, and the absence of interaction of the Hf center with the C(4)–C(5) bond is indicated by the short (1.331 (7) Å) C=C distance and the obtuse fold angle between the Hf, N(1), N(2) and N(1), C(4), C(5), N(2) planes of 161.7°. In $[\text{Cp}^*\text{Hf}(\text{iPr-DAB})\text{Hf}(\mu\text{-H})]_2$, the C=C distance and fold angle are respectively 1.375 (7) Å and 138.8°. The Hf center displays distorted-square-pyramidal coordination. The π -electrons in the section of the ligand between N(2) and N(3) seem to be considerably delocalized and may be described by two resonance states as in acetylacetonate type complexes. It is hard to determine whether the difference of 0.1 Å in Hf–N bond length between N(2) and N(3) is due to a preferred resonance state, the rigidity of the ligand geometry, or the different degrees of substitution for the two N atoms. The Hf–Cl distance of 2.450 (1) Å is rather long, which may suggest a relatively electron-rich metal center due to the presence of three nitrogen ligands that all have the possibility of π -interaction with the d^0 metal center.

Monitoring the reaction by ^1H NMR spectroscopy showed that 1 is converted quantitatively into 4 and that 0.5 mol of neopentylamine is formed per mole of Hf. The reaction sequence thus involves reduction of some of the cyanide, accounting for the loss of two H atoms from the organometallic product (eq 2). A similar reaction was

observed to occur with phenyl cyanide to produce the red phenyl analogue of 4. The reaction is rather slow when stoichiometric amounts of the reagents are used (several days at 120 °C for completion) but can be speeded up considerably by using an excess of cyanide. No intermediates in the sequence were observed by NMR spectroscopy, but a possible reaction route may be inferred by comparison with the reaction observed between 1 and ketones.

Complex 1 reacts with various ketones $RR'C=O$ ($R, R': tBu, Me; Ph, Ph$) to form intensely yellow solutions. Although we could not obtain single crystals suitable for X-ray diffraction, NMR spectra⁸ of the products are consistent with the reaction shown in Scheme I. This reaction involves transfer of an *iPr* α -H to the carbonyl carbon through a six-membered transition state to produce the ene imine alkoxide complexes $Cp^*Hf[iPrNCH=CHN=CMe_2](OCHRR')Cl$ (**5a**, $R, R' = Me, tBu$; **5b**, $R, R' = Ph, Ph$). This type of H-atom transfer is known from reactions between ketones and metal alkoxides, such as the Meerwein-Ponndorf-Verley (MPV) reactions between ketones and Al-isopropoxide complexes, where the *OiPr* α -H atom is transferred to the ketone.⁹ One example involving an *iPr*-DAB ligand was reported in the reaction of $Fe_2(CO)_6(iPr-DAB)$ with $MeO_2CC\equiv CCO_2Me$, where after initial coordination of the alkyne to the metal centers, the *iPr* α -H atom is transferred to the alkyne moiety.¹⁰ The process may also be related to reductions of polar unsaturated molecules by orthoamides and dihydropyridines, found to be mediated by electropositive cations such as Mg^{2+} and Zn^{2+} .¹¹

(8) **5a** ($R, R' = Me, tBu$): 1H NMR (δ , C_6D_6) 6.67 and 5.46 (d, 4.4 Hz, 1 H each, $=CH-$), 4.72 (sp, 6.6 Hz, 1 H, *iPr* CH), 3.95 (q, 6.6 Hz, 1 H, OCH), 2.03 (s, 15 H, Cp^*), 1.99 and 1.48 (s, 3 H, each, $N=CMe_2$), 1.29 (d, 6.6 Hz, 3 H, OCHMe), 1.20 and 1.16 (d, 6.6 Hz, 3 H each, *iPr* Me), 0.93 (s, 9 H, *tBu*); ^{13}C NMR (δ , C_6D_6) 11.89 (q, 126.6 Hz, Cp^* Me), 19.18, 22.63, and 25.96 (all q, 126 Hz, *iPr* Me and OCHMe), 26.63 (q, 126.6 Hz, *tBu* Me), 28.16 and 29.93 (q, 126 Hz, $N=CMe$), 36.67 (s, *tBu* C), 54.43 (d, 138.1 Hz, *iPr* CH), 84.71 (d, 138 Hz, OCH), 105.28 (d, 175 Hz, $=CH-$), 121.03 (s, Cp^* ring), 142.49 (d, 157 Hz, $=CH-$), 157.38 (s, $N=C$). In the reactions two isomers are observed in approximately a 3:1 ratio. The resonances reported are for the majority isomer.

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A possible relation between the reaction of 1 with ketones and with cyanides is shown in Scheme II. After initial formation of the ene imine intermediate 6 another H-transfer can occur (possibly through a 1,3-H shift and transfer of the hydrogen from one nitrogen to another through a four-membered transition state as observed in $Cp^*_2CeNHtBu-NH_2tBu$ complexes¹²) to form the vinylamido imine complex 7. Exchange of the imine by another cyanide can then lead to a C-C coupling reaction between the vinylamido $=CH_2$ group and the cyanide carbon atom. The possibility of such a coupling between cyanides and transition-metal vinylamides was demonstrated by Bercaw et al. in the reaction between $Cp^*_2ScN=C(R)Me$ and RCN ($R = p-MeC_6H_4$).¹³ A 1,3-H shift then produces the ligand as observed in the structure of 4. It is interesting to note that we have found no evidence for the presence of the aldimine $tBuCH=NH$ or its decomposition products, finding instead 0.5 equiv of neopentylamine. In most reduction reactions of organic cyanides the intermediate aldimine is more easily reduced than the parent cyanide.¹⁴ This may suggest that once formed, the aldimine is more efficient in its reaction with another molecule of 1 than the parent cyanide.

We have observed that, although generally 1,4-diisopropyl-1,4-diaza-1,3-butadiene acts as an inert ancillary σ^2, π -ene diamide ligand for hafnium in $Cp^*Hf(iPr-DAB)R$ complexes, the isopropyl groups are activated to exhibit reactivity through six-membered transition states. In the reaction with organic cyanides this leads to a unique sequence of C-H activations and a C-C coupling, showing that *N*-isopropyl ene amide ligands can be used in the formation of new multidentate ligand systems.

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Supplementary Material Available: Text giving experimental and spectroscopic data for the compounds described and text giving details of the structure determination and refinement and tables of crystallographic data, positional and thermal parameters, bond distances, bond angles, and torsion angles for 4 (14 pages). Ordering information is given on any current masthead page.

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