Reaction of Ketones with 1,4-Diaza-1,3-diene Zirconium and Hafnium Complexes: First Example of a 1,3-Dipolar Cycloaddition Reaction of 1,4-Diaza-1,3-diene Complexes of Early Transition Metals

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The novel complexes M[O(R)PhCH{CH=N(*t*Bu)}N(*t*Bu)]$_2$ [M = Zr, R = Me (**4a**), R = Ph (**4b**) and M = Hf, R = Me (**5a**), R = Ph (**5b**)] have been prepared in almost quantitative yield by reaction of (*t*Bu-DAD)$_2$Zr (**1**) and (*t*Bu-DAD)$_2$Hf (**2**) [*t*Bu-DAD = (*t*Bu)N=CHCH=N(*t*Bu)] with 2 equiv of the ketones MeCOPh (**3a**) or PhCOPh (**3b**). The reaction proceeds via a 1,3-dipolar cycloaddition of the C=O bond across the M−N−C unit of the DAD complexes. The molecular structures of the complexes **4a** and **5b** have been determined by a single-crystal X-ray diffraction study (**4a**, triclinic, space group $P\bar{1}$; $a = 10.395(2)$ Å, $b = 10.865(2)$ Å, $c = 16.842(3)$ Å, $\alpha = 93.80(3)°$, $\beta = 99.84(3)°$, $\gamma = 106.12(3)°$, $V = 1787.4(6)$ Å^3, $Z = 2$, R1 = 0.035 (wR2 = 0.101) for 6963 reflections with $I > 2\sigma(I)$; **5b**, monoclinic, space group $P2_1/c$, $a = 19.961(4)$ Å, $b = 10.482(2)$ Å, $c = 20.150(4)$ Å, $\beta = 91.30(1)°$, $V = 4215(1)$ Å^3, $Z = 4$, R1 = 0.036 (w*R*2 = 0.097) for 4650 reflections with $I > 2\sigma(I)$). The metal atoms in **4a** and **5b** adopt a pseudooctahedral coordination sphere consisting of four nitrogen and two oxygen atoms. The distortion is a consequence of the [2.2.1] bicyclic structure of the newly formed tridentate ligands which are not able to span three regular octahedral positions.

In the last years much research has been carried out on the preparation and reactivity of 1,4-*dia*za-1,3-*d*iene (DAD)[1] transition metal complexes.[2] An interesting aspect of the coordinated DAD ligand is the possibility to activate the imine carbon atom towards C−C coupling reactions. For instance, Frühauf et al. reported, that mononuclear (*i*Pr-DAD)FeL$_3$ complexes (L = CO, RNC), containing a chelating 4e σ-N, σ-N′-coordinated DAD ligand, react with organic substrates, e.g. activated alkynes to give different C−C coupling products.[3] The initial step in these reactions is described as a oxidative 1,3-dipolar [3 + 2] cycloaddition reaction of the dipolarophile to the 1,3-dipolar M−N=C fragment of the DAD complex resulting in the formation of a bicyclic intermediate. This unstable intermediate reacts further with a second dipolarophile to give a double cycloaddition product or reacts further by insertion of one CO or RNC ligand leading finally to a stable [2.2.2] bicyclic compound (Scheme 1).

With respect of their applicability these cycloaddition reactions are of importance because of their potential for use in the synthesis of organic heterocycles which cannot, or only in low yields, be prepared by classical organic pathways.

Since cycloaddition reactions are very sensitive to variations in the electron density at the reaction centres,[4] it was assumed that by changing the central metal and the dipolarophile the synthetical scope of the reaction could be extended. In order to study if this concept could be applied more generally to other DAD complexes we decided to use DAD complexes of early transition metals. The synthesis, properties and structures of different types of these DAD complexes have been described recently.[5] Most of these complexes bear a *s-cis* configurated DAD ligand that is doubly reduced by the metal to produce endiamido groups that can best be described as a σ^2,π-1,3-diaza-2-metallacyclopentene ("envelope structure"). In solution, these DAD complexes exhibit dynamic behavior, which may be attributed, on the basis of variable temperature ^{1}H NMR studies, to rapid ring inversion via a transitory planar metallacyclopentene species; it has been demonstrated for the homoleptic

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[1] Throughout this paper the 1,4-*diaza*-1,3-*dienes* of formula RN=CHCH=NR are abbreviated as R-DAD, hence (*t*Bu)N=CHCH=N(*t*Bu) is abbreviated as *t*Bu-DAD.

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[4] (a) Huisgen, R. *Angew. Chem.* **1963**, *75*, 604−637. (b) Huisgen, R. *Angew. Chem.* **1963**, *75*, 742−754. (c) Houk, K. H.; González, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81−90.

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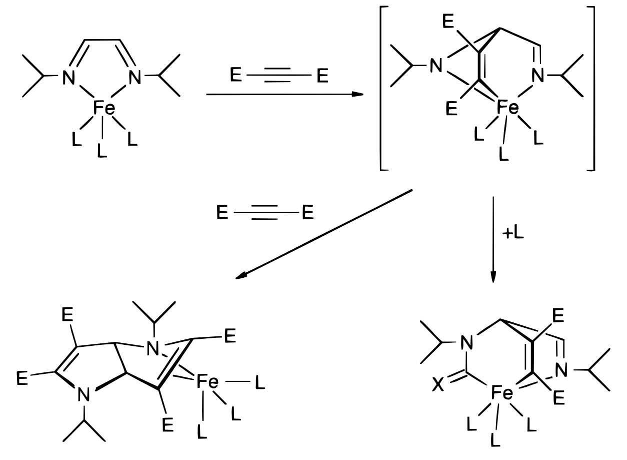
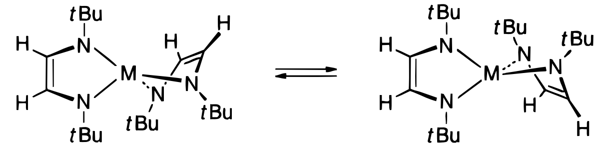
Scheme 1



Scheme 2



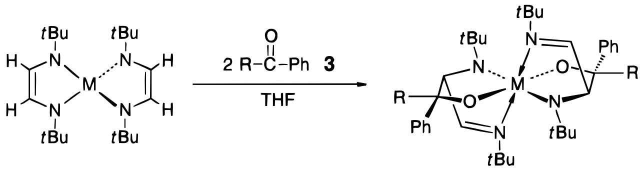
DAD complexes of the type (tBu-DAD)$_2$M (M = Ti, Zr, Hf) (Scheme 2).[6]

In this paper we present the reaction of these homoleptic DAD complexes (tBu-DAD)$_2$M [M = Zr (**1**), Hf (**2**)][7] with ketones as dipolarophiles. To our knowledge it is the first example of an [3 + 2] cycloaddition reaction of DAD complexes of early transition metals.

Reaction of the DAD complexes **1** and **2** with 2 equiv of acetophenone (**3a**) proceeded smoothly at −20 °C in THF to give the cycloaddition products **4a** and **5a** which were isolated as pale yellow crystals in 70−80% yield. In an analogous manner we examined the reaction of **1** and **2** with benzophenone (**3b**). The solution becomes dark green initially and gradually lightens to pale yellow. Colorless crystals of the new complexes **4b** and **5b** could be obtained in 85% yield upon cooling the solution. The new crystalline, air-sensitive cycloaddition products **4a**,**b** and **5a**,**b** are stable at room temperature and very soluble in THF but only sparingly so in diethyl ether and toluene.

The NMR spectroscopic data of **4a**,**b** and **5a**,**b** are listed in the experimental Section. The ^{1}H NMR spectra of the acetophenone addition products **4a** and **5a** and that of the benzophenone addition products **4b** and **5b** are very similar and are consistent with the structures depicted in Scheme 3. Most interesting are the resonances of the imine protons NCH of the DAD ligands. In all new compounds the signal of one of the former imine protons is shifted ca. 0.5−1.5 ppm upfield in comparison to those of the parent complexes which are at δ 5.68 (**1**) and 5.63 (**2**). The other imine proton signal is strongly shifted downfield (δ 7.89−8.24). These signal shifts reflect the change in the bonding feature of the DAD ligand, due to the 1,3-dipolar cycloaddition of the ketone. The ^3J coupling between the neighbouring imine protons is 2.8−3.0 Hz, which is in the usual range of $^3J_{\mathrm{H,H}}$ coupling constants of vicinal protons in CH−CH=N units whose C−H bonds are twisted against each other.[8] Since **4a** and **5a** contain two independent chiral centers, the former imine C atoms C2/C4 and the bridgehead C atoms C5/C6, they may exist in two diastereomeric configurations. However, only one set of resonances is observed in the ^{1}H and ^{13}C NMR spectra of both complexes pointing to the presence of only one diastereomer.

Scheme 3



1, **2**

4, **5**

	M	R
4a	Zr	Me
4b	Hf	Me
5a	Zr	Ph
5b	Hf	Ph

In the ^{13}C NMR spectra of **4a** and **5a** the chemical shift values of the imine carbon centers C1/C3 and C2/C4 of the DAD backbone are quite different. The resonances of C1/C3 are observed at δ 180.04 and 181.53, whereas the C−C coupled former imine carbon atoms C2/C4 give rise to signals at δ 70.99 and 68.78. The high δ-value of C1/C3 is in agreement with chemical shifts of imine carbon atoms of DAD's, which are bonded as σ-N donor ligands in complexes with strong Lewis acids, e.g $ZrCl_4\cdot[N(Me\text{-}4\text{-}C_6H_4){=}CPhCPh{=}N(Me\text{-}4\text{-}C_6H_4)]$ (δ 177.3).[9] The large upfield shift of C2/C4 reflects the change in hybridization from sp^2 to sp^3, resulting from the C−C coupling of the former imine carbon atom C2/C4 and the carbonyl carbon atom of the ketone C5/C6. The former imine carbon atoms C2 and C5 in **4b** and **5b** are chiral and so the phenyl groups of the OCPh$_2$ building block are diastereotopic and give rise to two independent absorptions.

In order to establish the structural details of these [3 + 2] cycloaddition products single-crystal X-ray analyses of **4a** and **5b** were carried out. The molecular structures of **4a** and **5b** are depicted in Figures 1 and 2, relevant bond distances, bond angles, and torsional angles are listed in Tables 1 and 2. The crystallographic data are summarized in Table 3.

Compound **4a** crystallizes in the triclinic space group $P\bar{1}$. The solid state structure of **4a** is consistent with the solution NMR data and clearly shows that two molecules acetophenone **3a** have been cycloadded over the bonds Zr−N(2)−C(2) and Zr−N(4)−(C4). The zirconium atom adopts a pseudooctahedral coordination sphere comprised of four nitrogen and two oxygen atoms. The distortion is caused by the fact, that as a

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(5) (a) Cloke, F. G. N.; de Lemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1344−1345. (b) Chamberlain, L. R.; Durfee, L. D.; Fanwick, Ph. E.; Kobriger, L. M.; Latesky, St. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068−6076. (c) Hessen, B.; Bol, J. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1276−1277. (d) Scholz, J.; Dlikan, M.; Ströhl, D.; Dietrich, A.; Schumann, H.; Thiele, K.-H. *Chem. Ber.* **1990**, *123*, 2279−2285. (e) tom Dieck, H.; Rieger, H. J.; Fendesak, G. *Inorg. Chim. Acta* **1990**, *177*, 191−197. (f) Scholz, J.; Dietrich, A.; Schumann, H.; Thiele, K.-H. *Chem. Ber.* **1991**, *124*, 1035−1039. (g) Herrmann, W. A.; Denk. M.; Scherer, W.; Klingan, F.-R. *J. Organomet. Chem.* **1993**, *444*, C21−C24. (h) Hubert-Pfalzgraf, L. G.; Zaki, A.; Toupet, L. *Acta Crystallogr.* **1993**, *C49*, 1609−1611. (i) Goddard, R.; Krüger, C.; Hadi, G. A.; Thiele, K.-H.; Scholz, J. *Z. Naturforsch.* **1994**, *49B*, 519−528.

(6) Activation barrier for M(NC=CN) ring inversion. (a) (tBu-DAD)$_2$Ti, $\Delta G^{\#}_{(-52\,^{\circ}\mathrm{C})} = 45.3$ kJ·mol^{-1}: Scholz, J. Unpublished results. (b) (tBu-DAD)$_2$Zr (**2**), $\Delta G^{\#}_{(-65\,^{\circ}\mathrm{C})} = 42.9$ kJ·mol^{-1}: Reference 7. (c) $Ti[N(Ph)C(Me){=}C(Me)N(Ph)]_2$, $\Delta G^{\#}_{(-70\,^{\circ}\mathrm{C})} = 42.5$ kJ·mol^{-1}: Reference 5h.

(7) Trompke, C. Ph.D. Thesis, Universität Hamburg, **1992**.

(8) Günther, H. *NMR-Spektroskopie*, 2. Auflage; Georg-Thieme-Verlag: Stuttgart, Germany, 1983; p 105.

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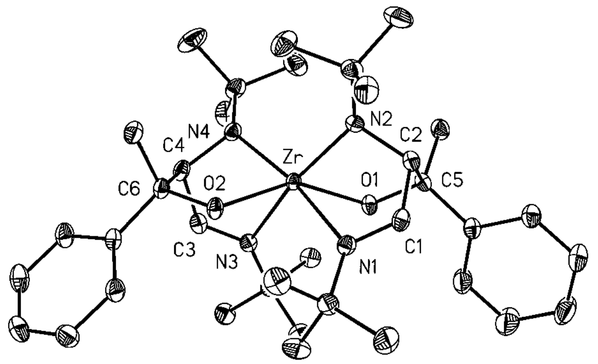

Figure 1. Molecular structure of **4a**. Thermal elipsoides are shown at the 50 % probability level, and hydrogen atoms are omitted for clarity.

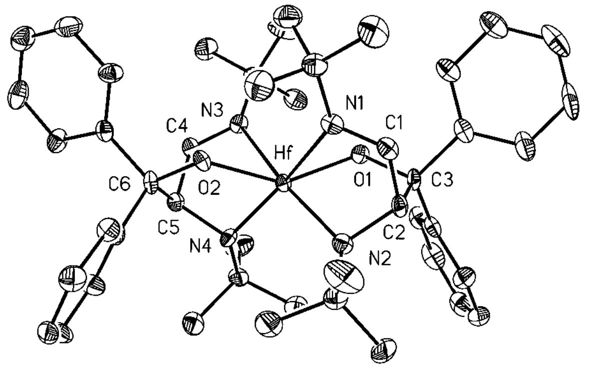

Figure 2. Molecular structure of **5b**. Thermal elipsoides are shown at the 50 % probability level, and hydrogen atoms are omitted for clarity.

Table 1. Selected Intramolecular Distances (Å) and Angles (deg) for **4a**

Zr−O1	2.041(2)	O1−C5	1.409(2)
Zr−O2	2.034(2)	O2−C6	1.413(2)
Zr−N1	2.521(2)	N1−C1	1.264(3)
Zr−N2	2.089(2)	N2−C2	1.468(3)
Zr−N3	2.529(2)	N3−C3	1.266(3)
Zr−N4	2.093(2)	N4−C4	1.476(3)
C1- C2	1.520(3)	C2−C5	1.573(3)
C3−C4	1.516(3)	C4−C6	1.565(3)
O1−Zr−O2	148.31(6)	N1−Zr−O1	78.79(6)
N1−Zr−N2	71.72(7)	N2−Zr−O1	80.62(7)
N3−Zr−N4	71.25(7)	N3−Zr−O2	80.08(6)
N4−Zr−O2	80.72(7)	Zr−O1−C5	115.6(1)
Zr−O2−C6	115.6(1)		
H1−C1−C2−H2	−22.6	H3−C3−C4−H4	−24.8
	Sum of Angles		
at N1	359.9	at N2	354.4
at N3	359.9	at N4	354.9

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) for **5b**

N1−Hf−N2	72.5(2)	N3−Hf−O2	80.0(2)
N3−Hf−N4	73.1(2)	N4−Hf−O2	81.2(2)
N1−Hf−O1	78.1(2)	Hf−O1−C3	115.6(4)
Hf−O2−C6	115.1(4)		
Hf−O1	2.022(4)	O1−C3	1.418(7)
Hf−O2	2.024(4)	O2−C6	1.415(7)
Hf−N1	2.495(5)	N1−C1	1.267(9)
Hf−N2	2.069(5)	N2−C2	1.475(8)
Hf−N3	2.511(5)	N3−C4	1.269(8)
Hf−N4	2.073(5)	N4−C5	1.473(8)
C1−C2	1.527(10)	C2−C3	1.580(10)
C4−C5	1.519(10)	C5−C6	1.552(10)
O1−Hf−O2	147.3(2)	N2−Hf−O1	82.1(2)
H1−C1−C2−H2	22.2	H4−C4−C5−H5	15.1
	Sum of Angles		
at N1	359.8	at N2	352.0
at N3	360.0	at N4	350.4

Table 3. Crystallographic Data and Details of Data Collection and Refinement of **4a** and **5b**

	4a	**5b**
chemical formula	$C_{36}H_{56}O_2N_4Zr$	$C_{46}H_{60}N_4O_2Hf$
mol wt	668.1	879.5
cryst dimens (mm^3)	0.40 × 0.39 × 0.36	0.40 × 0.38 × 0.38
cryst habit	yellow, needles	colorless, needles
cryst syst	triclinic	monoclinic
space group	$P1$ (No. 2)	$P2_1/c$ (No. 14)
temp (K)	183	183
cell params		
a (Å)	10.395(2)	19.961(4)
b (Å)	10.865(2)	10.482(2)
c (Å)	16.842(3)	20.150(4)
α (deg)	93.80(3)	90.0
β (deg)	99.84(3)	91.30(1)
γ (deg)	106.12(3)	90.0
vol (Å^3)	1787.4(6)	4215(1)
no. of formula units Z	2	4
D_c (g·cm^{-3})	1.24	1.39
abs coeff μ (Mo Kα) (cm^{-1})^a	3.43	25.2
2θ range (deg)	2−55	2−55
no. of unique tot. data	7585	5339
no. of obsd data with $I > 2\sigma(I)$	6963	4650
no. of variables	642	478
R1^b	0.035	0.036
wR2^c	0.101	0.097
rest electron density [eÅ^{-3}]	0.94	1.88

[a] An empirical absorption correction (Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56) was applied to **5b** (maximum and minimum transmission, 1.095 and 0.728; largest diff. peak and hole, 1.228 and 1.271 e Å^{-3}). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

consequence of their [2.2.1] bicyclic structure the newly formed tridentate ligands are not able to span three regular octahedral positions, and that there are significant differences in the Zr—N distances. Thus, the distances from Zr to N(2) and N(4) [2.089(2), 2.093(2) Å] are slightly longer than expected for alkylamido ligands bound to Zr(IV) but comparable to that found in other *t*Bu-DAD zirconium complexes.[10] In contrast, the Zr—N(1) and Zr—N(3) bonds are much longer [2.521(2), 2.529(2) Å] and are representative of a weak dative bond.[11] The differenes in Zr—N bond length are in accordance with the corresponding N—C distances of the DAD skeleton: Whereas N(2)—C(2) and N(4)—C(4) are in the typical range of C—N single bonds [1.468(3), 1.476(3) Å],[12a] the N(1)—C(1) and N(3)—N(3) bonds are shortened [1.264(3), 1.266(3) Å] and are now comparable to the N=C distances of *t*Bu-DAD.[12b] The Zr—O(1) and Zr—O(2) bond lengths of 2.041(2) and 2.034(2) Å are close to that what would have been predicted on the basis of the sum of the respective covalent radii.[13] Due to the C—C

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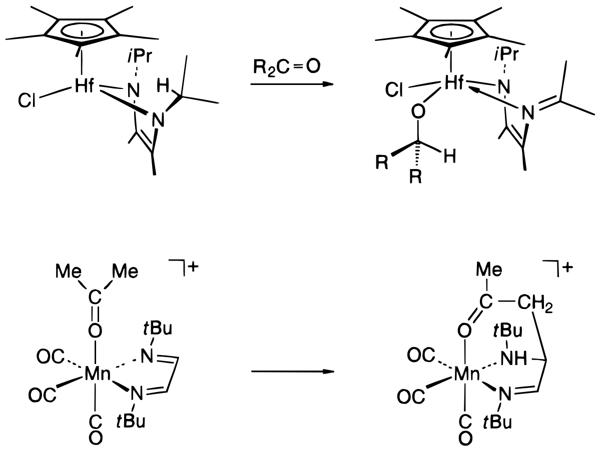
(10) Zr−N: (a) Cp′Zr(NMe$_2$)$_3$: 2.047(5)−2.067(4) Å. Antinolo, A.; Bristow, G. S.; Campbell, G. K.; Duff, A. W.; Hitchkock, P. B.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J.; Sarjudeen, N.; Winterborn, D. J. W.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *Polyhedron* **1989**, *8*, 1601−1606. (b) Cp*Zr(NH*t*Bu)$_3$: 2.002(10) and 2.015(11) Å. Bai, Y.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 825−831. Hf−N: (c) Cp*Hf[NH(*i*Pr$_2$-2,6-C$_6$H$_3$)$_3$: 2.041(4)−2.065(3) Å. Bai, Y.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 825−831. (d) Cp$_2$*Hf(H)NHMe: 2.027(8) Å. Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309−1312. (e) [Cp*Hf(*i*Pr-DAD)(μ-H)]$_2$: 2.058(4), 2.075(4) Å. Hessen, B.; Bol, J. E.; De Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1276−1277. (f) Cp$_2$Zr(*t*Bu-DAD): 2.105(3), 2.100(5) Å. Reference 7. (g) [CpZr(*t*Bu-DAD)Cl]$_2$: 2.080(1), 2.076(1) Å.

Scheme 4



coupling, the former C=O double bond of the carbonyl group of acetophenone is reduced to a C—O single bond [C(5)—O(1) 1.409(2), C(6)—O(2) 1.413(2) Å]. Moreover, the central double bonds of the former alkene units C(1)—C(2) and C(3)—C(4) have also been reduced to single bonds, which is reflected in bond distances of 1.520(3) and 1.516(3) Å.[12a]

Complex **5b** shows similar structural parameters around the central hafnium atom. The overall structure again may be described as distorted octahedral. The bond distances and interbond angles within the ligand cages are comparable to those found for **4a**, indicating that the cycloadded benzophenone **3b** does not alter the geometry of the remaining part of the coordination sphere. As expected, the nitrogen and carbon atoms of the starting enediamide skeleton, N—C=C—N, are not in the same plane and the observed N—C distances are shorter in the imine fragments than in the amide groups. Moreover, the structures also confirm that the newly formed (*t*Bu)N=CHCH-[C(Ph)RO]N(*t*Bu) ligands in **4a** as well as in **5b** coordinate in a tridentate fashion.

Apart from the papers of Frühauf et al. about 1,3-dipolar [3 + 2] cycloaddition reactions of Fe-, Ru-, or Mn(DAD) complexes with electron deficient alkenes or alkynes[3] there are reports of reactions of DAD complexes with other dipolarophiles. Teuben et al. have investigated the reaction of the hafnium complex Cp*Hf(*i*Pr-DAD)Cl with various ketones (Scheme 4, top). In contrast to our C—C coupling reaction they observed no C—C bond formation but instead H abstraction of one of the *i*Pr groups with transfer to the carbonyl carbon atom of the ketone to produce the eneimine alkoxide complex Cp*Hf-[(*i*Pr)NCH=CHN=CMe$_2$](OCHMe$_2$)Cl.[14] The intimate steps in these reactions are at present not completely clear. However, initial formation of the ketone-coordinated intermediate, which could not be isolated, seems plausible.

To the best of our knowledge, there is only one other example in which a C—C bond is formed by reaction of a ketone with a coordinated DAD (Scheme 4, bottom). Thus, Riera et al.[15] reported an intramolecular addition of acetone to an imine group of the DAD ligand in [(*t*Bu-DAD)Mn(CO)$_3$(MeCOMe)][ClO$_4$]. However, this reaction can't been discribed in terms of a 1,3-dipolar [3 + 2] cycloaddition reaction, because it happens by transfering a proton from the acidic methyl group to the imine nitrogen followed by an attack of the remaining acetonyl group, MeCOCH$_2$, to the imine carbon atom.

Conclusions

The synthesis of **4a**,**b** and **5a**,**b** has shown for the first time that the imine carbon atoms of DAD ligands bounded to early transition metals can selectively be substiuted or functionalized by electrophilic substrates. Moreover, it has been demonstrated that the reaction of ketones with DAD complexes of the type (DAD)$_2$M (M = Zr, Hf) can be used in the formation of new tridentate ligand systems. Decomplexations of these ligands can be accomplished. We are currently investigating possible applications for these new materials. With respect to the metallacyclic nature of the reaction products **4** and **5** and the relationship to the results of Frühauf et al. mentioned above[3] these reaction may be described as a 1,3-dipolar cycloaddition. Cycloadditions of 1,3-dipoles may occur by concerted or stepwise mechanisms.[4c] At this time, however, we do not have a detailed insight into the mechanism of our reaction. In order to better understand the factors influencing these reaction, further research on other metal complexes is necessary.

Experimental Section

All manipulations were performed under an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly distilled from sodium/benzophenone or lithium aluminium hydride and saturated with argon prior to use. Deuteriated THF-d_8 was treated with sodium/potassium alloy, then distilled, and stored under argon. The ^{1}H and the ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300.075 (^{1}H) and 75.462 MHz (^{13}C) with tetramethylsilane as reference. Elemental analyses were carried out at the Mikroanalytisches Laboratorium des Fachbereichs Chemie der Martin-Luther-Universität Halle-Wittenberg, Merseburg, Germany. ZrCl$_4$(THF)$_2$, HfCl$_4$(THF)$_2$,[16] and *t*Bu-DAD[17] were prepared according to literature procedures. All other chemicals used as starting materials were obtained commercially and were used without further purification.

X-ray Crystal Structure Determination of 4a and 5b. Crystals of **4a** and **5b** suitable for X-ray structure determination were grown from diethyl ether solutions at −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å). The unit cell parameters were obtained by a least-squares fit of 25 reflections. Three standard reflections were monitored every 2 h. No systematic variations in intensities were found. Data were corrected for Lorentz and polarization effects,[18] and an empirical absorption correction was applied to **5b**. The structures were solved by direct methods[19] and refined by full-matrix least-squares methods against F_o^2.[20] The hydrogen atoms were located from the difference map and for **4a** refined isotropically and for compound **5b** with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically. Cell constant and other pertinent data are recorded in Table 3.

Preparation of (*t*Bu-DAD)$_2$Zr (1) and (*t*Bu-DAD)$_2$Hf (2). **1** and **2** were prepared by reaction of ZrCl$_4$(THF)$_2$ or HfCl$_4$(THF)$_2$ with 2 eq

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(11) Dative Zr←N bonds: (a) ZrCl$_4$·dipy: 2.301(9), 2.297(9) Å. Troyanov, S. I.; Maso, G. N.; Rybakov, V. B. *Z. Neorg. Chim.* **1988**, *33*, 2798−2801. (b) ZrCl$_4$·[N(Me-4-C$_6$H$_4$)=CPhCPh=N(Me-4-C$_6$H$_4$)]: 2.360(2), 2.365(2) Å. Richter, B.; Scholz, J.; Neumüller, B.; Weimann, R.; Schumann, H. *Z. Anorg. Allg. Chem.*, **1995**, *621*, 365−372.

(12) (a) C—C 1.556 Å, C=C 1.321 Å, C—N 1.464 Å, C—O 1.426 Å. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1−S19. (b) *t*Bu-DAD: C—N 1.267(2) Å; C—C 1.467(2) Å. Huige, C. J. M.; Spek, A. L.; de Boer, J. L. *Acta Crystallogr.* **1985**, *C41*, 113−116.

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Li$_2$(*t*Bu-DAD) by methods previously reported for (*t*Bu-DAD)$_2$Ti.[5e] More details of the preparation of **1** and **2** have been described previously.[7]

1: orange yellow crystals; mp 148 °C dec. ^{1}H NMR (20 °C, THF-d_8): $\delta = 5.68$ (s, 4H, NC*H*=C*H*N), 1.18 (s, 36H, NC*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 104.43$ (dd, $^1J_{\mathrm{C,H}} = 164.6$ Hz, $^2J_{\mathrm{C,H}} = 9.8$ Hz, N*C*H=*C*HN), 56.42 (s, N*C*Me$_3$), 31.84 (q, $^1J_{\mathrm{C,H}} = 124.9$ Hz, NC*Me*$_3$).

2: yellow crystals; mp 180 °C dec. ^{1}H NMR (20 °C, THF-d_8): $\delta = 5.63$ (s, 4H, NC*H*=C*H*N), 1.18 (s, 36H, NC*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 102.60$ (dd, $^1J_{\mathrm{C,H}} = 167.1$ Hz, $^2J_{\mathrm{C,H}} = 9.0$ Hz, N*C*H=*C*HN), 56.20 (s, N*C*Me$_3$), 31.91 (q, $^1J_{\mathrm{C,H}} = 124.9$ Hz, NC*Me*$_3$).

General Procedure for the Preparation of 4a,b and 5a,b. A solution of the ketone **3a** or **3b** (11.69 mmol) in 20 mL of THF was slowly added to a stirred solution of the DAD complexes **1** (2.50 g, 5.84 mmol) or **2** (3.01 g, 5.84 mmol) in 50 mL of THF, which was cooled to −20 °C. The reaction mixture was warmed to room temperature and subsequently stirred for 24 h. After evaporation of the solvent the residue was extracted with 50 mL of diethyl ether. The solution was concentrated and stored at −20 °C. The complexes **4a**,**b** or **5a**,**b** precipitated as pale yellow or colourless crystals which were isolated by filtration and subsequently dried in vacuo. Crystals of **4a** and **5b** suitable for X-ray diffraction were prepared by slow crystallization at 0 °C from a saturated diethyl ether solution prepared at room temperature.

4a: pale yellow crystals; yield 78%; mp 122 °C. Anal. Calcd for $C_{36}H_{56}N_4O_2Zr$: C, 64.72; H, 8.45; N, 8.39. Found: C, 63.99; H, 8.52; N, 8.50. ^{1}H NMR (20 °C, THF-d_8): $\delta = 7.89$ (d, $^3J_{\mathrm{H,H}} = 2.8$ Hz, 2H; N=C*H*), 7.55 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 4H; *o*-Ph), 7.21 (t, $^3J_{\mathrm{H,H}} = 7.6$ Hz, 4H; *m*-Ph), 7.07 (t, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 2H; *p*-Ph), 4.24 (d, $^3J_{\mathrm{H,H}} = 2.8$ Hz, 2H; NC*H*), 1.85 (s, 6H; OC*Me*), 1.27 (s, 18H; C*Me*$_3$), 1.23 (s, 18H; C*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 180.04$ (d, $^1J_{\mathrm{C,H}} = 162.0$ Hz; N=*C*H), 150.31 (s; *i*-Ph), 128.15 (d, $^1J_{\mathrm{C,H}} = 157.5$ Hz; *o*-Ph), 126.64 (d, $^1J_{\mathrm{C,H}} = 156.4$ Hz; *m*-Ph), 126.17 (d, $^1J_{\mathrm{C,H}} = 159.3$ Hz; *p*-Ph), 85.98 (s; ZrO*C*), 70.99 (d, $^1J_{\mathrm{C,H}} = 137.5$ Hz, $^2J_{\mathrm{C,H}} = 11.2$ Hz; ZrN*C*H), 59.42 (s; *C*Me$_3$), 56.63 (s; *C*Me$_3$), 33.49 (q, $^1J_{\mathrm{C,H}} = 126.5$ Hz; OC*Me*), 31.67 (q, $^1J_{\mathrm{C,H}} = 126.7$ Hz; C*Me*$_3$), 30.03 (q, $^1J_{\mathrm{C,H}} = 126.2$ Hz; C*Me*$_3$).

4b: colorless crystals; yield 85%; mp 146 °C. Anal. Calcd for $C_{36}H_{56}N_4O_2Hf$: C, 57.24; H, 7.47; N, 7.42. Found: C, 57.10; H, 7.58; N, 7.63. ^{1}H NMR (20 °C, THF-d_8): $\delta = 8.07$ (d, $^3J_{\mathrm{H,H}} = 2.7$ Hz, 2H; N=C*H*), 7.79 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 4H; *o*-Ph), 7.64 (d, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 4H; *o*-Ph), 7.15 (m, 8H, *m*-Ph), 7.01 (m, 4H, *p*-Ph), 5.13 (d, $^3J_{\mathrm{H,H}} = 2.8$ Hz, 2H; NC*H*), 1.41 (s, 18H; C*Me*$_3$), 0.87 (s, 18H; C*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 179.96$ (d, $^1J_{\mathrm{C,H}} = 163.1$ Hz; ZrN=*C*H), 151.30 (s; *i*-Ph), 149.49 (s; *i*-Ph), 128.20 (d, $^1J_{\mathrm{C,H}} = 157.6$ Hz; *o/m*-Ph), 127.77 (d, $^1J_{\mathrm{C,H}} = 156.3$ Hz; *o/m*-Ph), 127.02 (d, $^1J_{\mathrm{C,H}} = 156.8$ Hz; *o/m*-Ph), 126.16 (d, $^1J_{\mathrm{C,H}} = 159.1$ Hz; *p*-Ph), 126.07 (d, $^1J_{\mathrm{C,H}} = 157.8$ Hz; *p*-Ph), 89.88 (s; ZrO*C*), 69.13 (dd, $^1J_{\mathrm{C,H}} = 138.1$ Hz, $^2J_{\mathrm{C,H}} = 11.4$ Hz; ZrN*C*H), 59.85 (s; *C*Me$_3$), 56.85 (s; *C*Me$_3$), 32.00 (q, $^1J_{\mathrm{C,H}} = 124.4$ Hz; C*Me*$_3$), 30.07 (q, $^1J_{\mathrm{C,H}} = 126.2$ Hz; C*Me*$_3$).

5a: pale yellow crystals; yield 80%; mp 130 °C. Anal. Calcd for $C_{46}H_{60}N_4O_2Zr$: C, 69.74; H, 7.63; N, 7.07. Found: C, 69.24; H, 7.60; N, 7.41. ^{1}H NMR (20 °C, THF-d_8): $\delta = 8.06$ (d, $^3J_{\mathrm{H,H}} = 3.1$ Hz, 2H; N=C*H*), 7.57 (d, $^3J_{\mathrm{H,H}} = 8.4$ Hz, 4H; *o*-Ph), 7.21 (t, $^3J_{\mathrm{H,H}} = 7.6$ Hz, 4H; *m*-Ph), 7.07 (t, $^3J_{\mathrm{H,H}} = 7.4$ Hz, 2H; *p*-Ph), 4.19 (d, $^3J_{\mathrm{H,H}} = 3.0$ Hz, 2H; NC*H*), 1.82 (s, 6H; OC*Me*), 1.27 (s, 18H; C*Me*$_3$), 1.24 (s, 18H; C*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 181.53$ (d, $^1J_{\mathrm{C,H}} = 162.6$ Hz; N=*C*H), 150.80 (s; *i*-Ph), 128.17 (d, $^1J_{\mathrm{C,H}} = 157.2$ Hz; *o*-Ph), 126.62 (d, $^1J_{\mathrm{C,H}} = 156.8$ Hz; *m*-Ph), 126.16 (d, $^1J_{\mathrm{C,H}} = 159.4$ Hz; *p*-Ph), 84.95 (s; HfO*C*), 68.78 (d, $^1J_{\mathrm{C,H}} = 132.4$ Hz, $^2J_{\mathrm{C,H}} = 11.0$ Hz; HfN*C*H), 59.63 (s; *C*Me$_3$), 56.69 (s; *C*Me$_3$), 33.59 (q, $^1J_{\mathrm{C,H}} = 127.7$ Hz; OC*Me*), 32.09 (q, $^1J_{\mathrm{C,H}} = 124.4$ Hz; C*Me*$_3$), 30.17 (q, $^1J_{\mathrm{C,H}} = 126.2$ Hz; C*Me*$_3$).

5b: colorless crystals; Yield 84% mp 154 °C. Anal. Calcd for $C_{46}H_{60}N_4O_2Hf$: C, 62.82; H, 6.88; N, 6.37. Found: C, 62.49; H, 6.93; N, 6.55. ^{1}H NMR (20 °C, THF-d_8): $\delta = 8.24$ (d, $^3J_{\mathrm{H,H}} = 2.9$ Hz, 2H; N=C*H*), 7.78 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 4H; *o*-Ph), 7.64 (d, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 4H; *o*-Ph), 7.14 (m, 8H, *m*-Ph), 6.99 (m, 4H, *p*-Ph), 5.10 (d, $^3J_{\mathrm{H,H}} = 2.9$ Hz, 2H; NC*H*), 1.42 (s, 18H; C*Me*$_3$), 0.84 (s, 18H; C*Me*$_3$). ^{13}C NMR (25 °C, THF-d_8): $\delta = 181.44$ (d, $^1J_{\mathrm{C,H}} = 163.2$ Hz; HfN=*C*H), 151.19 (s; *i*-Ph), 149.83 (s; *i*-Ph), 128.10 (d, $^1J_{\mathrm{C,H}} = 159.0$ Hz; *o/m*-Ph), 127.69 (d, $^1J_{\mathrm{C,H}} = 157.3$ Hz; *o/m*-Ph), 127.63 (d, $^1J_{\mathrm{C,H}} = 157.9$ Hz; *o/m*-Ph), 126.87 (d, $^1J_{\mathrm{C,H}} = 156.9$ Hz; *o/m*-Ph), 126.02 (d, $^1J_{\mathrm{C,H}} = 160.3$ Hz; *p*-Ph), 125.94 (d, $^1J_{\mathrm{C,H}} = 159.8$ Hz; *p*-Ph), 88.75 (s; HfO*C*), 66.75 (dd, $^1J_{\mathrm{C,H}} = 149.5$ Hz, $^2J_{\mathrm{C,H}} = 10.5$ Hz; HfN*C*H), 59.91 (s; *C*Me$_3$), 56.65 (s; *C*Me$_3$), 32.29 (q, $^1J_{\mathrm{C,H}} = 124.4$ Hz; C*Me*$_3$), 30.07 (q, $^1J_{\mathrm{C,H}} = 126.2$ Hz; C*Me*$_3$).

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Supporting Information Available: Tables of crystallographic data, fractional coordinates of the non-hydrogen and hydrogen atoms and isotropic thermal parameters, anisotropic thermal parameters of the non-hydrogen atoms, and complete bond distances and angles and figures showing structures with complete labeling (17 pages). Ordering information is given on any current masthead page.

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