Intramolecular Coupling of η^2-Iminoacyl Groups at Group 4 Metal Centers: A Kinetic Study of the Carbon–Carbon Double-Bond-Forming Reaction

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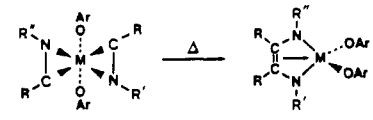
Abstract: The series of bis(η^2-iminoacyl) compounds of general formula $M(OAr)_2(\eta^2\text{-}R'NCR)_2$ (M = Ti, Zr, Hf; OAr = 2,6-diisopropyl- and 2,6-di-*tert*-butylphenoxide; R = CH_3, CH_2Ph; R′ = various substituted phenyls) undergo intramolecular coupling on thermolysis to produce the corresponding enediamide derivatives $M(OAr)_2[R'NC(R)=C(R)NR']$. A kinetic study of the reaction in hydrocarbon solvents has shown it to be first order. The reaction is metal dependent with the rate decreasing in the order Ti > Zr > Hf. The rate of the reaction is also dependent on the steric and electronic nature of the nitrogen substituent (R′). The use of the bulky aryl group 2,6-dimethylphenyl retards the reaction, while the use of various 3- and 4-substituted phenyls (3-F, 3-OMe, 4-OMe, 4-Cl, 4-NMe_2) shows the reaction to be accelerated by electron-withdrawing substituents. A σ plot based on kinetic data obtained at 67 °C and 77 °C yielded ρ values of 0.83 (R = 0.97) and 0.84 (R = 0.95), respectiely. Both the steric and electronic dependence of the reactivity on the nitrogen substituents is discussed mechanistically and used to rationalize the much more facile intramolecular coupling observed for the related η^2-acyl (η^2-OCR) functionalities.

The migratory insertion of carbon monoxide into high valent early transition metal, lanthanide, and actinide alkyl and hydride bonds has received considerable synthetic,[2-6] mechanistic,[2,7,8] and theoretical study.[9] The resulting η^2-acyl or η^2-formyl functional groups have also been the object of intense research effort. By far the most documented reactivity associated with these functionalities is their ability to undergo a range of carbon–carbon bond-forming reactions. In particular their inter- and intramolecular coupling to produce enediolate ligands appears to be an important characteristic.[10,11] These reactions can be included into a wider range of important carbon–carbon bond-forming reactions involing the transition-metal-mediated reductive coupling of carbon monoxide and isoelectronic molecules.[12-14] However, despite insightful synthetic and theoretical studies of the intramolecular coupling of η^2-acyls at these metal centers, to date no stable bis(η^2-acyl) precursor has been isolated prior to coupling. We have recently demonstrated that the isoelectronic η^2-iminoacyl group formed by the migratory insertion of organic isocyanides into group 4 and group 5 metal alkyl bonds exhibits directly related reactivity.[15] The intramolecular coupling of two η^2-iminiacyls as well as the cross-coupling of η^2-acyl and η^2-iminoacyls has been shown to yield the corresponding enediamide and enamidolate moieties.[15,16] Although the mixed acyl, iminoacyl precursors could not be isolated prior to coupling, the bis(η^2-iminoacyl) compounds are sufficiently stable to be obtained in high yield.[17] Both a series of such compounds as well as the product enediamide and enamidolate derivatives have been structurally and spectroscopically characterized.[16,17] The availability of the bis(η^2-iminoacyl) pre-

Scheme I



Reactant → Product	M	OAr	R	R′	R″
(1a) → (2a)	Ti	OAr-2,6-Pr^i_2	CH_2Ph	Bu^t	C_6H_5
(1b) → (2b)	Ti	OAr-2,6-Pr^i_2	CH_2Ph	Bu^t	C_6H_3-2,6-Me_2
$(3)^H \rightarrow (4)^H$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_5
$(3)^{3F} \rightarrow (4)^{3F}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_4-3F
$(3)^{3OMe} \rightarrow (4)^{3OMe}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_4-3OMe
$(3)^{4OMe} \rightarrow (4)^{4OMe}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_4-4OMe
$(3)^{4Cl} \rightarrow (4)^{4Cl}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_4-4Cl
$(3)^{4NMe_2} \rightarrow (4)^{4NMe_2}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_4-4NMe_2
$(3)^{2,6Me_2} \rightarrow (4)^{2,6Me_2}$	Zr	OAr-2,6-Bu^t_2	CH_3		C_6H_3-2,6-Me_2
(3a) → (4a)	Zr	OAr-2,6-Bu^t_2	CH_2Ph		C_6H_5
$(5)^H \rightarrow (6)^H$	Hf	OAr-2,6-Bu^t_2	CH_3		C_6H_5

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Table I. Estimated Barriers for the Ring Inversion of Ene–Diamido Complexes $M(OAr)_2[R'NC(R)=C(R)NR'']$

compd	M	OAr	R	R'	R''	$\Delta G^{\ddagger}$ (T_c)[a]
2a	Ti	OAr-2,6-*i*-Pr_2	CH_2Ph	*t*-Bu	C_6H_5	15.6 (17)
2b	Ti	OAr-2,6-*i*-Pr_2	CH_2Pr	*t*-Bu	C_6H_3-2,6-Me_2	17.1 (60)
4^H	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_5	15.5 (35)
4^{3F}	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_3H_4-3F	16.1 (45)
4^{3OMe}	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_4-4OMe	16.0 (45)
4^{4OMe}	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_4-4OMe	15.0 (25)
4^{4Cl}	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_4-4Cl	16.2 (45)
4^{4NMe_2}	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_4-4NMe_2	15.2 (30)
$4^{2,6Me_2}$	Zr	OAr-2,6-*t*-Bu_2	CH_3		C_6H_3-2,6-Me_2	14.5 (0)
4a	Zr	OAr-2,6-*t*-Bu_2	CH_2Ph		C_6H_5	12.7 (−15)
6^H	Hf	OAr-2,6-*t*-Bu_2	CH_3		C_6H_5	14.2 (10)

[a] $\Delta G^{\ddagger}$ in Kcal mol^{-1}; T_c in deg Celcius.

cursors as well as the essentially quantitative nature of the intramolecular coupling reaction has promoted us to carry out a kinetic and mechanistic study in order to try to obtain some insights into this carbon–carbon double-bond-forming reaction at these early transition-metal centers.

Results and Discussion

Synthesis of Compounds. The compounds used in this study are shown in Scheme I. The bis(η^2-iminoacyl) substrates are obtained in high yield by the simple addition of organic isocyanides to the corresponding bis(alkyls).[17] We have focused the majority of our attention on derivatives of the compound $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(CH_3)_2$ (OAr-2,6-*t*-Bu_2 = 2,6-di-*tert*-butylphenoxide) obtained by using a series of meta- and para-substituted phenylisocyanides as well as the sterically more demanding 2,6-dimethylphenylisocyanide (Scheme I). A single hafnium compound has also been included for direct comparison with its zirconium analogue. In the case of titanium, alkyl compounds containing 2,6-di-*tert*-butylphenoxide ligands are found to undergo facile intramolecular CH bond inactivation.[18] Hence we have examined the rate of intramolecular coupling of η^2-iminoacyls containing 2,6-diisopropylphenoxide ancillary lgation. Even with these sterically less demanding ligands, it is only possible to study those bis(η^2-iminoacyl) compounds shown (Scheme I) due to the rapidity of coupling typically observed at titanium metal centers.[15,16]

Thermolysis of the bis(η^2-iminoacyl) substrates in hydrocarbon solvents at temperatures of 30–130 °C leads to the clean formation of the corresponding enediamide complexes (Scheme I). The intramolecular coupling reaction is found to be accompanied by a slight color change, typically from pale yellow to yellow for the zirconium and hafnium series and from red to orange for the titanium derivatives. The solid-state structures of those enediamide compounds subjected to single-crystal X-ray diffraction analysis have shown the presence of a nonplanar, diazametallacyclopentene ring, resulting in nonequivalent aryloxide ligands.[16] This puckering of the chelate is also evident in the solution ^1H NMR spectra of these compounds. At ambient temperatures the aryloxide ligand signals are broad, resolving at lower temperatures into two equal intensity sets of resonances. Measurements of the coalescence temperature for this process allows an estimate of the activation energy for the ring flipping process. These are collected in Table I.

Kinetic Measurements. The rate of conversion of the bis(η^2-iminoacyl) compounds to the corresponding enediamide derivatives was obtained by ^1H NMR methods. This was achieved by monitoring the disappearance of the substrate and concomitant appearance of the product resonances for toluene-d_8 solutions in sealed 5-mm ^1H NMR tubes. For the majority of the compounds, thermolysis was carried out in the temperature-controlled probe of an NMR spectrometer. This has the added advantage that the probe temperature for thermolysis is well above the coalescence temperature of the ring inversion process for the product enediamides. Hence the spectra obtained contained sharp resonances for the aryloxide ligands in the products allowing easy integration. However, for compound $3^{2,6Me_2}$ containing the bulky 2,6-dimethylphenyl substituent on nitrogen the temperature needed for reaction was too high to be conveniently stabilized in an NMR probe. Hence for this compound the sealed tubes were thermolyzed by total immersion in a constant-temperature oil bath, the extent of reaction being measured by ^1H NMR at various times after rapid cooling. A typical set of data obtained is presented as a first-order plot in Figure 1.

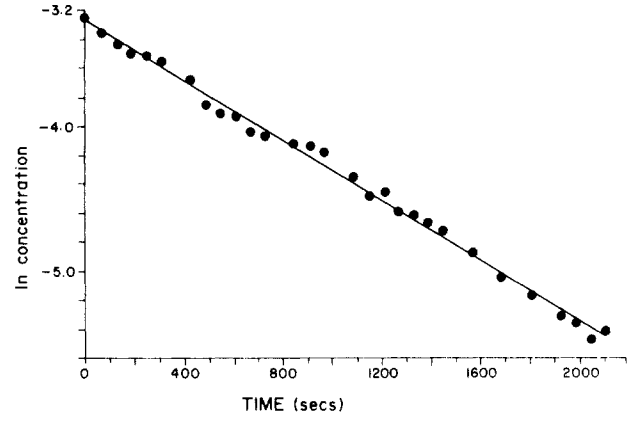

Figure 1. First-order plot for the disappearance of 3^{4OMe} at 94 °C.

Table II. Rate Constants for the Intramolecular Coupling of η^2-Iminoacyl Groups

reaction	T, °C	$10^4 k$ (s^{-1})	reaction	T, °C	$10^4 k$ (s^{-1})
1a → 2a	30	5.10 (30)	$3^{4Cl} \rightarrow 4^{4Cl}$	59	1.21 (67)
				67	2.61 (12)
1b → 2b	93	3.31 (15)		73	5.15 (30)
				77	8.97 (50)
$3^{3H} \rightarrow 4^{3H}$	67	1.78 (6)			
	73	2.51 (11)	$3^{4NMe_2} \rightarrow 4^{4NMe_2}$	67	0.417 (25)
	77	4.16 (25)		77	1.17 (6)
	86	9.56 (50)		86	3.27 (18)
				94	6.19 (30)
$3^{3F} \rightarrow 4^{3F}$	59	1.33 (8)			
	67	4.06 (20)	$3^{2,6Me_2} \rightarrow 4^{2,6Me_2}$	105	0.230 (15)
	73	7.38 (20)		114	0.493 (25)
	77	11.8 (50)		114	0.487 (25)
				121	1.02 (6)
$3^{3OMe} \rightarrow$	67	1.72 (7)		124	1.20 (7)
4^{3OMe}	73	2.65 (10)		135	2.67 (12)
	77	4.08 (25)			
	86	8.78 (45)	**3a → 4a**	67	0.598 (20)
				77	2.13 (15)
$3^{4OMe} \rightarrow$	67	0.729 (40)		86	4.35 (25)
4^{4OMe}	77	1.99 (10)		94	8.82 (45)
	86	4.24 (22)			
	94	10.4 (5)	$5^H \rightarrow 6^H$	77	0.513 (30)

Table III. Activation Parameters Obtained for the Intramolecular Coupling of η^2-Iminoacyl Groups

reaction	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	E_a [a]	log *A*
$3^H \rightarrow 4^H$	21.8 (9)	−12 (5)	22.6 (10)	10.7
$3^{3F} \rightarrow 4^{3F}$	27.7 (10)	6 (6)	27.9 (10)	14.5
$3^{3OMe} \rightarrow 4^{3OMe}$	21.0 (9)	−14 (7)	21.7 (10)	10.2
$3^{4OMe} \rightarrow 4^{4OMe}$	23.8 (8)	−8 (6)	24.5 (9)	11.6
$3^{4Cl} \rightarrow 4^{4Cl}$	24.9 (8)	−2 (5)	25.6 (8)	12.9
$3^{4NMe_2} \rightarrow 4^{4NMe_2}$	25.0 (7)	−5 (6)	25.7 (7)	12.1
$3^{2,6Me_2} \rightarrow 4^{2,6Me_2}$	24.4 (5)	−16 (5)	25.0 (6)	9.8
3a → 4a	24.2 (7)	−7 (5)	24.9 (7)	11.8

[a] Kcal mol^{-1}. [b] cal mol^{-1} K^{-1}.

The intramolecular coupling was found to be first-order in all cases. Furthermore, thermolysis of an equimolar mixture of $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}PhNCMe)_2$ $(3)^H$ and $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}PhNCCH_2Ph)_2$ (**3a**) resulted in products 4^H and **4a** containing only the symmetrical enediamide ligands as determined by NMR and mass spectrometric measurements. The rate constants and activation parameters obtained from the kinetic

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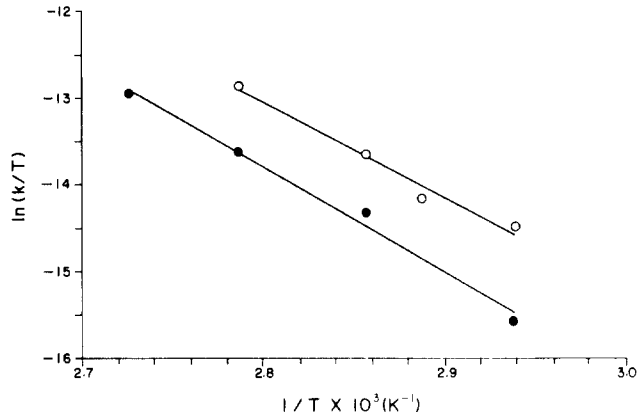

Figure 2. Activated complex theory (Eyring) plots for the intramolecular coupling reactions $3^{H} \rightarrow 4^{H}$ (○) and **3a** → **4a** (●).

measurements are collected in Tables II and III.

The general intramolecular coupling reaction outlined in Scheme I has a total of four variables: metal, aryloxide ligand, nitrogen substituent, and carbon substituent. The latter three have associated with them both steric and electronic components that can influence the reactivity. The data obtained in this study, Table II, indicate that the rate of intramolecular coupling decreases in the order Ti >> Zr > Hf. Although there are not available a pair of identical compounds to directly quantify the relative rates of reaction at titanium versus zirconium, the ability of the first-row metal to facilitate the carbon–carbon bond-forming reaction is evident from the fact that in the majority of cases the addition of organic isocyanides to $Ti(OAr)_2(R)_2$ compounds results in the immediate formation of coupled products. However, for the second- and third-row group 4 metals the compounds M(OAr-2,6-*t*-$Bu_2)_2(\eta^2$-PhNCMe)$_2$ (M = Zr, $(3)^{H}$, Hf, $(5)^{H}$) are both available for study, and kinetic measurements (Table II) show the zirconium derivative to couple ~8 times faster.

The origin of the more rapid intermolecular coupling associated wtih the titanium compounds is difficult to access. Sterically the smaller coordination sphere of Ti compared to Zr, Hf would be expected to hinder the adoption of a crowded transition state (vide infra). However, enthalpically the coupling reaction involves the breaking of two metal–carbon (iminoacyl) bonds and formation of a carbon–carbon double bond. All of the available thermodynamic data on bond disruption enthalpies indicate that the metal–carbon bond in Ti(IV) alkyls is signifncantly weaker than in Zr(IV) and Hf(IV) alkyls. This may, therefore, account for the greater potency of titanium for inducing these intramolecular coupling reactions.

Our work has not allowed us to extensively study the dependence of the coupling reaction on the steric and electronic properties of the aryloxide and carbon substituents. The rate of intramolecular coupling of compounds containing the ligands OAr-2,6-*t*-Bu_2 and its 4-methoxy derivative are identical within experimental error The use of 4-methoxy substituents has also been shown to have a negligible impact on the rates of cyclometalation of aryloxide ligands.[18] However, changing the carbon substituent from methyl to benzyl does lead to a slight decrease in the rate of the coupling reaction (Figure 2), but whether this effect is electronic or steric in origin cannot be determined.

However, we have been able to gain significant insight into the effect of the nitrogen substituent on the reaction. The most noticable effect is the dramatic retardation of the reaction on changing the nitrogen substituent from phenyl to 2,6-dimethylphenyl (cf. Figures 2 and 3 and Table II). The phenyl derivative Zr(OAr-2,6-*t*-$Bu_2)_2(\eta^2$-PhNCMe$)_2$ couples approximately 100 times faster than the more bulky xylyl analogue $3^{2,6Me_2}$. A similar retardation is noticable in the asymmetric titanium derivaties **1a** and **1b** where the replacement of the NC_6H_5 group by NC_6H_3-2,6Me_2 dramatically reduces the rate of intramolecular coupling. The introduction of electronically influencing substituents into the meta and para positions of this phenyl ring also modifies (albeit less dramatically) the rate of iminoacyl coupling

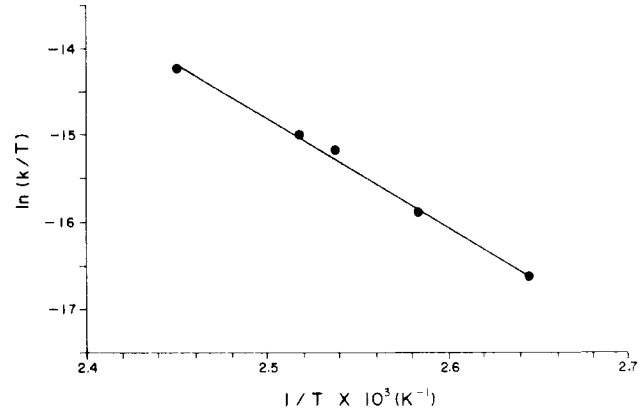

Figure 3. Activated complex theory (Eyring) plot for the intramolecular coupling reaction $3^{2,6Me_2} \rightarrow 4^{2,6Me_2}$.

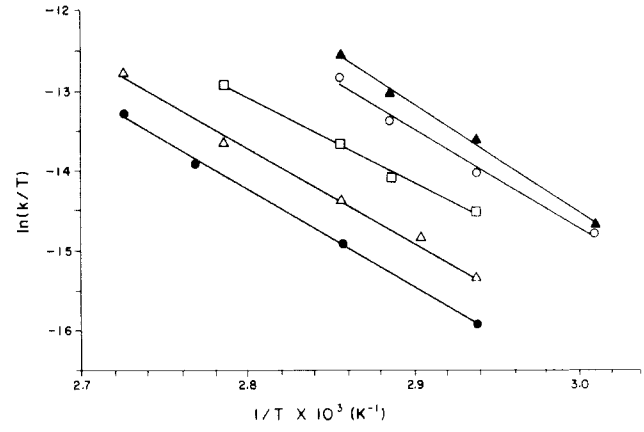

Figure 4. Activated complex theory (Eyring) plots for the intramolecular coupling reactions $3^{3F} \rightarrow 4^{3F}$ (▲); $3^{4Cl} \rightarrow 4^{4Cl}$ (○); $3^{3OMe} \rightarrow 4^{3OMe}$ (□); $3^{4OMe} \rightarrow 4^{4OMe}$ (△); $3^{4NMe_2} \rightarrow 4^{NMe_2}$ (●).

It can be seen (Figure 4) that electron-donating substituents (e.g., 4-NMe_2) retard the reaction, while electron-withdrawing substituents (e.g., 3-F) accelerate it. Comparison of kinetic data at the two common temperatures, 67 °C and 77 °C, shows a rate difference of ~10 between the two limiting substituents (4-NMe_2, 3-F) used.

Mechanistic Interpretations. A theoretical study of the intramolecular coupling of two η^2-acyl groups in the organoactinide compounds $Cp_2{}^*M(\eta^2$-RCO$)_2$ (M = Th, U) has recently been published.[19] The reaction pathway involving the coplanar coupling of the acyls to produce an enediolate chelate ring was found to be a symmetry disallowed, high energy process. Instead an initial twisting of the acyls from coplanarity prior to coupling was indicated to be the least energy pathway.[19] Although an analogous coupling reaction at group 4 metal centers has been observed upon carbonylation of Cp_2ZrR_2 and $Cp_2{}^*ZrR_2$ compounds, the intermediate bis(acyl) precursor is restricted in this case to only one of these groups being η^2-bound, i.e., $Cp_2M(\eta^2$-RCO$)(\eta^1$-RCO$)$.[9,19] The solid-state structure of the bis(η^2-iminoacyl) compounds used in this study shows both iminoacyls to be equally η^2-bound and to be oriented in a head-to-tail fashion parallel with each other (Scheme I).[17] ^{1}H NMR studies show rotation of the iminoacyl groups to be facile.[17] The simplest pathway one can envisage for the coupling reaction would be a rotation of both iminoacyls into a coplanar arrangement with cis carbon atoms followed by carbon–carbon bond formation In fact this exact coplanar arrangement of two η^2-iminoacyls has been structurally characterized in two compounds Zr(OAr-2,6-*t*-$Bu_2)(\eta^2$-*t*-BuNCH$_2$Ph$)_3$ and Ta(OAr-2,6-$Me_2)_2(CH_3)(\eta^2$-ArNCCH$_3)_2$.[17] However, preliminary theoretical calculations by Tatsumi et al.[20] on these coupling

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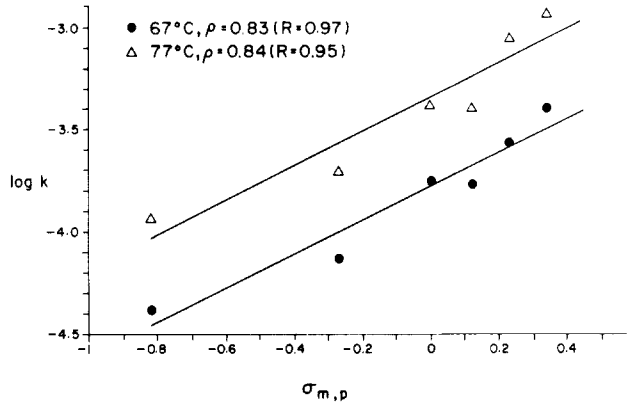
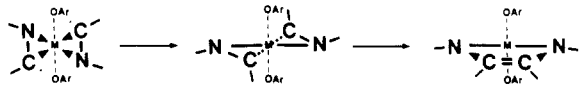


Figure 5. A plot of ln k for the intramolecular coupling of bis(η^2-iminoacyl) compounds at both 67 °C and 77 °C versus $\sigma_{m,p}$ values for the various substituted N-aryl groups.

Scheme II



reactions has shown the inplane pathway to be a high-energy, symmetry-disallowed process as it is for the $Cp_2^*M(\eta^2\text{-}RCO)_2$ actinide systems. Given the known ground-state structure and fluxionality of the bis(η^2-iminoacyl) derivatives it seems reasonable that a pathway analogous to that proposed for the actinide compounds is operative. This would involve a disrotatory motion of the η^2-iminoacyl C,N vectors so as to bring the two carbon atoms toward each other. The formation of the carbon–carbon bond would, however, begin before the two iminoacyls adopt a coplanar arrangement (Scheme II).[15a,16]

The difference in reactivities documented by us for η^2-acyl and η^2-iminoacyl groups appears to have both a steric as well as electronic component. The use of bulky substituents on the nitrogen atom retards the coupling reaction (Table II). This can be interpreted as being a result of the bulky substituents hindering the rotation of the iminoacyl groups, making the adoption of the correct configuration for carbon–carbon bond formation much more difficult. Previous studies have shown that rotation of η^2-iminoacyl groups is slowed down by the introduction of 2,6-dimethylphenyl substituent at nitrogen.[17,21] Electronically it can be seen that the use of electron-withdrawing substituents on nitrogen accelerate the reaction. This is hence electronically consistent with the fact that η^2-acyls, which contain the more electronegative oxygen atom versus NR, undergo facile coupling. Figure 5 shows a plot of ln k for the coupling reaction at 67 °C and 77 °C versus the σ value of the various phenyl substituents contained on nitrogen. The correlation can be seen to be poor, but monotonic, with a ρ value of +0.83 (2). Actually, the fact that the experimental data is based on a substitution at both nitrogens means that a case can be made that the effect of the substituents is one-half the magnitude indicated by this parameter. The correlation with σ^+ is significantly worse, Figure 6. Solid-state structural studies of both the bis(η^2-iminoacyl) substrates[17] and ene–diamide products[16] show phenyl substituents on nitrogen to be oriented perpendicular to the nitrogen–carbon bonds. Hence in both sets of compounds there should be little π-interaction between the nitrogen and its aryl substituent. If this ground-state orientation of the phenyl substituents is carried over to the transition state, then this would be consistent with the poorer correlation with σ^+ values.

In studying the ground electronic structure of high valent metal η^2-acyl compounds, Hoffmann et al. have identified the energy of the acyl π^*_{CO} orbital as being critical in determining its reactivity.[9] In particular, these studies of the intramolecular coupling of η^2-acyls at a C^*p_2U center indicated the energy of this orbital

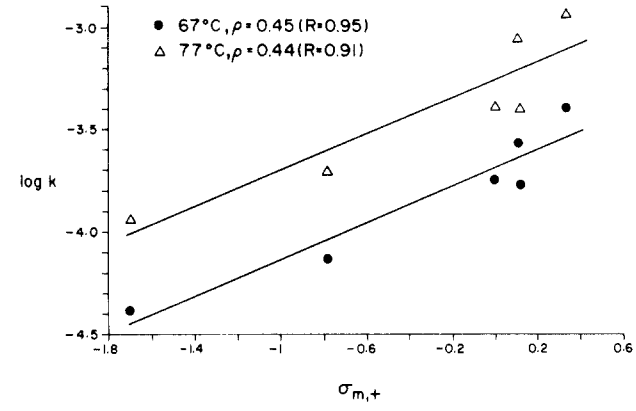


Figure 6. A plot of ln k versus $\sigma_{m,+}$ values for the intramolecular coupling of bis(η^2-iminoacyl) compounds.

to be an important factor in determining the barrier to C–C bond coupling.[19] This idea was used to rationalize the lack of intramolecular coupling observed for the corresponding bis(η^2-carbamoyl) (η^2-$CONR_2$) compounds.[19,22] The π-donation of the coplanar NR_2 substituent dramatically destabilizes the π^*_{CO} orbital and leads to a much higher barrier to carbon–carbon double bond formation. It seems reasonable to use a similar argument to explain the electronic inhibition observed here for the intramolecular coupling of η^2-iminoacyl groups compared to their more reactive oxygen counterparts. One would expect the π^*_{CN} orbital of an imioacyl group to lie at higher energy than the π^*_{CO} of an acyl function. This would, drawing direct analogy with the metallocene systems studies by Hoffmann,[19] result in an increased electronic barrier to carbon–carbon double bond formation. It can also be seen that the observed effect of various nitrogen substituents is also consistent with this picture. One would expect that electron-withdrawing substituents would result in a lowering of π^*_{CN} and, as is found, an acceleration of the rate of carbon–carbon bond formation. the retardation of intromolecular coupling by using electron-donating substituents on nitrogen and hence raising the π^*_{CN} orbital energy is simiarly consistent with this picture.

Experimental Section

Synthesis of Compounds. The synthesis and spectroscopic properties of the following compounds have been previously reported: **1a**, **2a**, **1b**, **2b**, $\mathbf{3}^H$, $\mathbf{4}^H$, $\mathbf{3}^{2,6me_2}$, $\mathbf{4}^{2,6Me_2}$, **3a**, **4a**, $\mathbf{5}^H$, and $\mathbf{6}^H$.[16,17] Of these $\mathbf{5}^H$, **2b**, and $\mathbf{4}^H$ have also been subjected to single-crystal X-ray diffraction study.[16,17] The synthetic strategies used to obtain the other compounds used in this work are essentially identical.[16,17] Hence only spectroscopic data for the new compounds is reported.

Zr(OAr-2,3-*t*-Bu$_2$)$_2$(η^2-MeCNC$_6$H$_4$-3F)$_2$ (3)^{3F}. IR (Nujol mull) $\bar{\nu}$ (C=N) = 1555 cm^{-1}, ^{1}H NMR ($C_6D_5CD_3$, 30 °C) δ 1.64 (s, *t*-Bu), 2.20 (s, NCCH_3), 6.9–7.3 (m, aromatics). Anal. Calcd for $ZrC_{44}H_{56}N_2O_2F_2$: C, 68.25; H, 7.30; N, 3.61; F, 4.90. Found: C, 67.82; H, 7.39,; N, 3.59; F, 5.13.

Zr(OAr-2,6-*t*-Bu$_2$)$_2$(η^2-MeCNC$_6$H$_4$-3OMe)$_2$ (3)^{3OMe}. IR (Nujol mull) $\bar{\nu}$ (C=N) = 1575 cm^{-1}; ^{1}H NMR ($C_6D_5CD_3$, 30 °C) δ 1.65 (s, *t*-Bu), 2.35 (s, NCCH_3), 3.20 (s, 30*Me*), 6.7–7.3 (m, aromatics). Anal. Calcd for $ZrC_{46}H_{62}N_2O_4$: C, 69.22, H, 7.84; N, 3.51. Found: C, 68.02; H, 7.71; N, 3.25.

Zr(OAr-2,6-*t*-Bu$_2$)$_2$(η^2-MeCNC$_6$H$_4$-4OMe)$_2$ (3)^{4OMe}. IR (Nujol Mull) $\bar{\nu}$ (C=N) = 1550 cm^{-1}; ^{1}H NMR ($C_6D_5CD_3$, 30 °C) δ 1.65 (s, *t*-Bu); 2.40 (s, NCCH_3), 3.20 (s, 40*Me*), 6.58 (d), 7.35 (d), 6.8–7.1 (m, aromatics). Anal. Calcd for $ZrC_{46}H_{62}N_2O_4$: C, 69.22; H, 7.84; N, 3.51. Found: C, 69.33; H, 7.91; N, 3.15.

Zr(OAr-2,6-*t*-Bu$_2$)$_2$(η^2-MeCNC$_6$H$_4$-4Cl)$_2$ (3)^{4Cl}. IR (Nujol Mull) $\bar{\nu}$ (C=N) = 1575 cm^{-1}, ^{1}H NMR ($C_6D_5CD_3$, 30 °C) δ 1.59 (s *t*-Bu), 2.22 (s, NCCH_3), 7.4 (d), 6.35, 6.8–7.0 (m, aromatics), ^{13}C NMR (C_6D_6, 30 °C) δ 246.1 (N*C*Me); 22.6 (NC*Me*); 35.5 (*C*Me$_3$); 31.6 (C*Me*$_3$). Anal. Calcd for $ZrC_{44}H_{56}N_2O_2Cl_2$: C, 65.47; H, 7.00; N, 3.47; Cl, 8.78. Found: C, 65.74; H, 6.86; N, 3.21; Cl, 9.18.

Zr(OAr-2,6-*t*-Bu$_2$)$_2$(η^2-MeCNC$_6$H$_4$-4NMe$_2$)$_2$ (3)^{4NMe_2}. IR (Nujol Mull) $\bar{\nu}$ (C=N) = 1600 cm^{-1}; ^{1}H NMR ($C_6D_5CD_3$, 30 °C) δ 1.66 (s,

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t-Bu), 2.40 (s, NC*Me*), 2.54 (s, 4N*Me*$_2$), 6.5 (d), 7.35 (d), 6.6–6.9 (m, aromatics); ^{13}C NMR (C_6D_6, 30 °C) δ 242.6 (N*C*Me), 22.7 (NC*Me*), 35.6 (*C*Me$_3$), 31.7 (C*Me*$_3$), 40.1 (N*Me*$_2$). Anal. Calcd for $ZrC_{48}H_{68}N_4O_2$: C, 69.92; H, 8.33; N, 6.78. Found: C, 69.39; H, 8.65; N, 6.79.

Zr(OAr-2,6-*t*-Bu$_2$)$_2$[3F-C$_6$H$_4$NC(CH$_3$)=C(CH$_3$)NC$_6$H$_4$-3F] (4)^{3F}. ^{1}H NMR ($C_6D_5CD_3$, −10 °C) δ 1.14 (s, *t*-Bu), 1.95 (s, NC*Me*), 6.8–7.1 (m, aromatics).

Zr(OAr-2,6-*t*-Bu$_2$)$_2$[3OMe-C$_6$H$_4$NC(CH$_3$)=C(CH$_3$)NC$_6$H$_4$3OMe] (4)^{3OMe}. ^{1}H NMR ($C_6D_5CD_3$, 0 °c) δ 1.19 (5), 1.51 (s, *t-Bu*) 2.09 (s, NC*Me*), 3.37 (s, 3O*Me*), 6.7–7.4 (m, aromatics).

Zr(OAr-2,6-*t*-Bu$_2$)$_2$[4OMe-C$_6$H$_4$NC(CH$_3$)=C(CH$_3$)NC$_6$H$_4$-4OMe] (4)^{4OMe}. ^{1}H NMR ($C_6D_5CD_3$, −5 °C) δ 1.24 (s), 1.58 (s, *t-Bu*), 2.09 (s, NC*Me*), 3.29 (s, 4O*Me*), 6.8–7.4 (m, aromatics).

Zr(OAr-2,6-*t*-Bu$_2$)$_2$[4Cl-C$_6$H$_4$NC(CH$_3$)=C(CH$_3$)NC$_6$H$_4$-4Cl] (4)^{4Cl}. ^{1}H NMR ($C_6D_6CD_3$, 0 °C, δ 1.13 (s), 1.47 (s, *t-Bu*), 1.94 (s, NC*Me*), 6.7–7.3 (m, aromatics).

Zr(OAr-2,6-*t*-Bu$_2$)$_2$[4NMe$_2$-C$_6$H$_4$NC(CH$_3$)=C(CH$_3$)NC$_6$4-4NMe$_2$] (4)^{4NMe_2}. ^{1}H NMR ($C_6D_5CD_3$, −10 °C) δ 1.29 (s), 1.61 (s, *t*-Bu), 2.10 (s, NC*Me*), 2.50 (s, NMe$_2$), 6.9–7.4 (m, aromatics). Anal. Calcd for $ZrC_{48}H_{68}N_4O_2$: C, 69.92; H, 8.33; N, 6.78. Found: C, 68.82; H, 8.55; N, 6.86.

Kinetic Measurements. The rate of intramolecular coupling of the bis(η^2-iminoacyl) compounds was determined by monitoring the changes in the ^{1}H NMR specra on thermolysis in the temperature-controlled probe of an NMR spectrometer. In nearly all cases the extent of reaction was obtained by integrating the ratio's of the *t*-Bu or *i*-Pr resonances of the aryloxide ligands in the starting material and enediamide product. In one case, **3**^{2,6Me_2}, thermolysis was carried out by total immersion of the sealed 5-mm ^{1}H NMR tube into a constant temperature oil bath The sample was then rapidly coled at various times, and the extent of reaction was determined by ^{1}H NMR. Both the rate constants and activation parameters were determined with the use of a linear least-squares fitting procedure.

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Registry No. 1a, 110316-44-4; **1b**, 110316-45-5; **2a**, 110316-36-4; **2b**, 110316-37-5; **3**^{H}, 105899-83-0; **3**^{3F}, 112320-06-6; **3**^{3OMe}, 112320-07-7; **3**^{4OMe}, 112320-08-8; **3**^{4Cl}, 112320-09-9; **3**^{4NMe_2}, 112320-10-2; **3**^{2,6Me_2}, 98065-02-2; **3a**, 110316-46-6; **4**^{H}, 110316-40-0; **4**^{3F}, 112347-47-4; **4**^{3OMe}, 112347-48-5; **4**^{4OMe}, 112347-49-6; **4**^{4Cl}, 112347-50-9; **4**^{4NMe_2}, 112347-51-0; **4**^{2,6Me_2}, 110316-38-6; **4a**, 110316-39-7; **5**^{H}, 105899-84-1; **6**^{H}, 110316-41-1.

Topological Kinetic Effects: Complexation of Interlocked Macrocyclic Ligands by Cationic Species

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Abstract: Complexation kinetic studies of various metal cations by a catenand have been performed. For comparison, the properties of some related open chain or monocyclic ligands have also been examined. Copper(I) and silver(I) catenate formation obeys a classical second-order rate law. The same is true for the model ligands examined, m-30 and dap. For Cu(dap)$_2^+$, the rate-limiting step corresponds to the formation of the bis-chelate complex from the monochelated one. On the other hand, Li^+, Cd^{2+}, Zn^{2+}, and Co^{2+} catenates are formed in two distinct steps. The first process is second order, and it is likely to be the binding of the metallic cation to one of the chelating subunits. The second step is more intriguing. It does not depend on the metal concentration, and it might correspond to the gliding motion of one ring within the other while the second chelate fragment attempts to coordinate to the metal center.

The fascinating properties of topologically novel molecules have been considered by several groups in the past. Interlocked rings were discussed several years ago, and synthetic approaches have now been developed.[1-5] In recent years a molecular Möbius strip has also been obtained as well as its cylindrical topological isomer.[6,7] Closed knotted cycles have also been envisaged,[2,3,8] although the preparation of such systems is still a challenge to synthetic chemists. [2]-Catenands consist of two interlocked macrocyclic ligands, and the first members of this new class of molecules have recently been reported.[9,10] The ligands are obtained by demetalation of their corresponding complexes, the catenates, the latter being synthesized from open chain ligands complexed to a transition-metal center (copper(I)) used as templating moiety.

Catenands represent a unique example of molecules displaying both topological novelty and the ability to interact with transition metals or other cationic species. In the complexation–decomplexation process the molecular system undergoes a complete rearrangement, which leads to drastic changes in shape (topography). However, since no covalent bond is cleaved within the catenand, the bond connectivity is obviously retained (topology)

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