Synthesis and Catalytic Activity of Cationic Allyl Complexes of Nickel Stabilized by a Single N-Heterocyclic Carbene Ligand

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*Summary: Cationic allylnickel complexes stabilized by a single N-heterocyclic carbene ligand (NHC) and a labile aquo or acetonitrile ligand ha*V*e been synthesized by protonation of aryloxide-containing precursors. These complexes catalyze the polymerization of 1,3-butadiene and styrene, mimicking the analogous phosphine-based system.*

N*-*heterocyclic carbene (NHC) ligands constitute a valuable alternative to phosphines in many types of catalytic processes.¹ For example, NHC-Ru complexes have found wide application in olefin metathesis catalysis^{1a,2} and have been successfully used in the metathesis polymerization of various types of olefins.³ However, examples of the application of NHC ligands in the addition polymerization of vinyl monomers remain scarce.4 Cavell has recently shown that Ni and Pd alkyls stabilized by NHC ligands undergo facile reductive elimination reactions leading to imidazolium salts, a process that may limit the applicability of such complexes to polymerization reactions.⁵ In addition, several nickel complexes containing NHC-based chelating ligands are moderately active as olefin polymerization catalysts.^{4b-d} The analogy between NHC and phosphine ligands⁶ suggested to us that the former could be applied in the design of new nickel catalysts for the polymerization of conjugated olefins such as 1,3-dienes and styrene. It is well-known that many phosphine complexes of nickel catalyze the polymerization of these monomers. "Naked" allylnickel complexes (i.e., those lacking strongly coordinating neutral or anionic ligands) range among the most active and stereoselective 1,3-butadiene

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polymerization catalysts, affording a polymer constituted largely of *cis*-1,4-butadiene units.^{7,8} Modification of the $[Ni(\eta^3-C_3H_5)]^+$ fragment by monodentate phosphines exerts a profound effect on the catalyst. Therefore, although appreciably less active, $[Ni(\eta^3-C_3H_5)L_2]^+$ complexes often display a completely different stereoselectivity and, for instance, the complex with $L =$ P(OPh)3 produces almost exclusively poly(*trans-*1,4-butadiene).9 Monodentate ligands also influence the polymerization of styrene by nickel allyls, and the addition of certain phosphines to the catalyst $[Ni(\eta^3-CH_2CMeCH_2)(cod)]^+$ improves its catalytic activity and the stereoregularity of the polymer.10 Experimental and theoretical investigations point to the monoligand species $[Ni(\eta^3\text{-allyl})L]^+$ and $[Ni(\eta^3\text{-benzyl})L]^+$ as the active intermediates in both butadiene and styrene polymerization, respectively.7,10,11 In general, such monophosphine *η*3-allyl or η ³-benzyl cationic derivatives cannot be isolated. However, the use of strongly binding NHC ligands provides an opportunity to prepare stable examples of coordinatively unsaturated monoligand allylnickel complexes, $[Ni(\eta^3$-allyl)(NHC)]^+$, or the chemically equivalent surrogates, [Ni(*η*3-allyl)(NHC)L′]⁺ (where L' is a neutral and labile ligand, such as diethyl ether, acetonitrile, or water), which could mimic the activity of the phosphine-containing catalysts. Several examples of palladium complexes of this type have been already described,¹² but the analogous Ni compounds remain hitherto unreported.

As a continuation of our previous work on nickel allyl aryloxide complexes, 8 we have explored the reactivity of the dimer **1** toward the carbene ligands 1,3,4,5-tetramethylimidazol-2-ylidene (I-Me,Me) and 2,5-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (I-DiPP). As shown in Scheme 1, these reactions afford the corresponding mononuclear adducts **2a**,**b**.

These compounds are thermally stable and can be readily isolated in high yield. They have been fully characterized, and their spectral properties and crystal structures will be presented elsewhere. As the metal-oxygen bond of nickel alkoxide and aryloxide complexes is easily cleaved by protic acids, complexes

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Scheme 1. Synthesis of Cationic Allylnickel Complexes

2 appear as promising sources of the target cationic compounds. Indeed, they react with the acid $[H(OEt₂)]^+[BAr^F₄]⁻$ in diethyl ether at -20 °C. The products formed in these reactions display low thermal stability in solution at room temperature, but the I-DiPP derivative **3** is stable enough to be isolated in a pure form. The NMR spectra of this compound show no evidence for the expected Et_2O ligand, but instead its analytical and IR data are consistent with the presence of an aquo ligand. The formation of this product can be attributed to the extreme lability of diethyl ether as a ligand. This is probably replaced by traces of water found during the subsequent manipulations.

The room-temperature NMR spectra of 3 in CD_2Cl_2 show broad signals that indicate a fluxional behavior. For example, the 13 C resonances corresponding to the allylic CH₂ groups, which can be observed below -20 °C at δ 43.2 and 70.0 ppm, become lost in the baseline at room temperature. Although the thermal instability of **3** prevented us from observing the coalescence of these signals, this observation suggests an apparent rotation of the *η*-allyl ligand, which generates an effective symmetry mirror in the molecule. This process is probably originated by the reversible dissociation of the aquo ligand.¹³

Attempts to grow crystals of **3** suitable for X-ray diffraction have been thwarted by its limited thermal stability in solution; hence, we undertook the synthesis of the more stable acetonitrile adducts **4a**,**b**. As shown in Scheme 1, these are obtained when the protonation reaction is carried out in MeCN. Alternatively, **4a** can be prepared by adding MeCN to **3**. Both **4a** and **4b** are appreciably more stable in solution than **3**. Their NMR spectra are also temperature-dependent. The behavior of **4a** is analogous to that of **3**, but the symmetrization of the allyl ligand becomes evident at higher temperatures. Thus, the 13C resonances of the allylic methylenes, observed at *δ* 51.9 and 72.9 ppm at room temperature, coalesce at 55 °C into a single signal appearing at *δ* 62.2 ppm. In contrast, the allylic resonances of **4b** remain well resolved at the same temperature. The fluxionality of this compound is due to the restricted rotation of the I-Me,Me ligand.

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The effect of the NHC ligand rotation is particularly noticeable at room temperature, as the 1H signals of the N-bound Me groups are found close to coalescence (300 MHz instrument), indicating a rotation energy barrier of ca. 14 kcal mol^{-1} . These observations suggest that the auxiliary ligand $(H₂O)$ or MeCN) becomes increasingly labile in the order $4b < 4a < 3$. It is worthing noting that the electrospray mass spectra of **3** and **4a** consist of a single peak cluster with mass/charge relations and isotopic distributions consistent with the ions $[Ni(\eta^3-C_3H_5)-]$ $(NHC)⁺$, indicating that in these compounds the auxiliary ligands are readily lost in the gas phase.

The crystal structures of **4a**,**b** are shown in Figures 1 and 2.15 The cationic parts of these complexes exhibit classic pseudosquare-planar geometries characteristic of d^8 M(II) allyl complexes. As is frequently observed for the latter compounds, the central carbon atom of the allyl group is found disordered in two almost equally probable positions. The allyl group adopts a slightly distorted η^3 coordination mode, with the Ni-CH₂ placed trans to the strongly donor NHC ligand being significantly longer than the $Ni-CH₂$ opposite to acetonitrile. The asymmetry is more pronounced for $4b$, where the two $Ni-CH₂$ bonds differ by 0.088(3) Å, than for **4a** (0.043(3) Å). The

Figure 1. Cationic part of the crystal structure of **4a**.

Figure 2. Cationic part of the crystal structure of **4b**.

Table 1. Polymerization of 1,3-Butadiene (BD) and Styrene (ST)*^a*

run	cat. (amt (umol))	monomer (amt (mmol))	vield (%)	TOF (h^{-1})	$10^{-3}M_{\rm n}$	$M_{\rm n}$ / $M_{\rm w}$
	3(15)	BD (120)	30	400	45.4	2.9
2	4b(19)	BD (120)	0.8	19		
3	3(20)	ST (89)	52	323	8.0	2.5
4	4b(20)	ST (89)	72	748	h	

^a Reaction conditions: solvent, toluene (10 mL); 30 °C; 5 h. *^b* Schultz-Flory mixture of oligomers, $\alpha = 0.11$.

apparenly stronger trans influence of the I-Me,Me ligand may be correlated with the shorter Ni-NHC bond of **4b** (1.8780(2) Å) as compared to that of **4a** (1.909(3) Å). The most conspicuous difference between the two structures is the different orientations of the I-DiPP and I-Me,Me ligands, which lay in planes that form angles of 34.2 and 76.5°, respectively, with the mean coordination plane. These differences may be due to steric effects or to crystal packing forces and reveal a lack of preferential orientation for the NHC ligands, which contrasts with the strong tendency of most sp^2 -C-bound ligands to arrange perpendicularly to the coordination plane in square-planar complexes. The latter behavior is frequently explained as a consequence of the metal-to-ligand electron back-donation, an effect that is probably absent in the case of the NHC derivatives.6

We have investigated the catalytic activity of these cationic carbene ligands in the polymerization of 1,3-butadiene and styrene (Table 1). The aquo complex **3** is a moderately active catalyst for the polymerization of 1,3-butadiene and styrene, producing poly(*cis*-1,4-butadiene) and atactic polystyrene, respectively. Although the acetonitrile derivative **4a** turned out to be inactive under the same conditions, the I-Me,Me derivative **4b** catalyzes the oligomerization of styrene, affording a Flory-Schultz mixture of oligomers characterized by a low value of α (0.11) and predominantly composed of the head-to-tail dimer (ca. 85%). Compound **4b** also polymerizes 1,3-butadiene, but the catalytic activity is very low in this case. The NMR spectra of the polybutadienes produced by **3** and **4b** are very similar, showing that these polymers are largely constituted of poly- (*cis*-1,4-butadiene) (92%), containing only minor amounts of trans*-*1,4- and trans*-*1,2-inserted units (approximately 4% each). This composition is close to that of the polymers produced by "naked" nickel-allyl catalysts, suggesting that in this case the

polymer could originate from small amounts of highly active ligand-free allylnickel species. In contrast, the oligomerization of styrene observed for catalyst **4b** clearly indicates selectivity control by the NHC ligand. As opposed to ethylene and other α -olefins, styrene is rarely dimerized or oligomerized by nickel catalysts.14 Although the participation of "naked" catalysts cannot be ruled out in the polymerization of styrene by **3** (the polymer produced is ca. 84% atactic), it is not unreasonable to assume that also in this case the NHC ligand is coordinated to the active species, as many phosphine-containing catalysts (e.g. PPh_3) also produce essentially atactic polystyrenes.¹⁰ Thus, it appears likely that the strongly σ -donating and relatively smallsized I-Me,Me ligand favors the chain transfer over the monomer insertion steps, while the larger size of I-DiPP limits the chain termination rate, producing higher molecular weights. The yields of the products obtained with **3** and **4b** indicate that each metal center produces many molecules of product per metal center and, hence, *â*-elimination or direct chain transfer to the monomer dominate over other chain termination routes, leading to irreversible catalyst deactivation: e.g., reductive elimination of imidazolium salts.5

In summary, we have prepared the first examples of allylnickel complexes stabilized by a single N-heterocyclic carbene ligand and showed that these are active catalysts in the polymerization or oligomerization of conjugated olefins (1,3 butadiene and styrene).

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Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and CIF files giving crystallographic X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽¹⁵⁾ Crystal data for complexes $4a$,**b** are as follows. $C_{64}H_{56}BF_{24}N_3Ni$ (4a): $M_r = 1392.64, 0.78 \times 0.42 \times 0.28 \text{ mm}^3$, monoclinic, space group *P*2₁/*c* (No. 14), $a = 13.403(2)$ Å, $b = 26.561(4)$ Å, $c = 18.492(3)$ Å, $\beta =$ $106.155(3)$ °, $V = 6323.0(17)$ \mathring{A}^3 , $Z = 4$, $D_c = 1.419$ g cm⁻³, $F_{000} = 2840$, Mo Kα radiation, $λ = 0.71073$ Å, $T = 100$ K, $2θ_{\text{max}} = 50^{\circ}$, 63 247 reflections collected, 11 038 unique ($R_{int} = 0.043$), final GOF = 1.086, R1 $= 0.0470$, wR2 $= 0.1117$, *R* indices based on 8592 reflections with $I >$ $3\sigma(I)$ (refinement on F^2), 910 parameters, 0 restraints, Lp and absorption corrections applied, $\mu = 0.420$ mm⁻¹. C₄₄H₃₂BF₂₄N₃Ni (**4b**): $M_r = 1128.25$, corrections applied, $\mu = 0.420$ mm⁻¹. C₄₄H₃₂BF₂₄N₃Ni (**4b**): $M_r = 1128.25$, 0.25 × 0.18 × 0.07 mm³, monoclinic, space group $P2\sqrt{c}$ (No. 14) $a =$ $0.25 \times 0.18 \times 0.07$ mm³, monoclinic, space group $P2_1/c$ (No. 14), $a = 18.194(2)$ \AA $b = 12.0772(16)$ \AA $c = 21.616(3)$ \AA \AA \AA $= 90.556(3)$ ° $V =$ 18.194(2) Å, $b = 12.0772(16)$ Å, $c = 21.616(3)$ Å, $\beta = 90.556(3)$ °, $V = 4749.7(11)$ Å³ $Z = 4$, $D_c = 1.578$ σ cm⁻³, $F_{000} = 2264$, λ (synchrotron) = $4749.7(11)$ \AA^3 , $Z = 4$, $D_c = 1.578$ g cm⁻³, $F_{000} = 2264$, λ (synchrotron) = 0.689 40 Å, $T = 150(2)$ K, $2\theta_{\text{max}} = 50^{\circ}$, 28 400 reflections collected, 11 545 unique ($R_{\text{int}} = 0.0316$), final GOF = 1.056, R1 = 0.0563 for 9557 observed unique ($R_{int} = 0.0316$), final GOF = 1.056, R1 = 0.0563 for 9557 observed
reflections ($I > 2\sigma(I)$) wR2 = 0.1627 for all reflections (refinement on reflections $(I > 2\sigma(I))$, wR2 = 0.1627 for all reflections (refinement on F^2). I.p and absorption corrections applied $\mu = 0.494$ mm⁻¹ F^2), Lp and absorption corrections applied, $\mu = 0.494$ mm⁻¹.