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DRIFTS and NIR Raman investigations on unsupported and supported allyl–lanthanoid complexes — catalysts for the polymerization of butadiene

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Dedicated on the occasion of the 65th birthday of Prof. Dr. Helmut Knözinger.

Abstract

Unsupported and supported $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ and $\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$ complexes were investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Raman spectroscopy and temperature-programmed reaction spectroscopy (TPRS). The obtained results allow conclusions concerning the structure and thermal stability of metal complexes, as well as their bonding properties. A structural model was developed for such allyl compounds based mainly on the vibrational spectroscopy data. This model was used to interpret the structural changes of these allyl–lanthanide complexes after being supported on methylaluminoxan (MAO)-modified silica (WITCO). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DRIFTS; Raman spectroscopy; Vibrational theory; Allyl–lanthanide complexes; Catalysts; Polymerization

1. Introduction

Anionic and neutral allyl–lanthanide complexes with different donor ligands are active homogeneous catalysts for the liquid phase polymerization of butadiene. Their synthesis, structure and polymerization properties in solution were recently investigated by Taube et al. [1–3]. Usually, these complexes catalyze the trans-polymerization of butadiene. The addition of Lewis-acidic aluminum organic compounds results in a change of the selectivity to *cis*-polybutadiene [3]. The supporting of these complexes for

their application in the heterogeneous catalytic polymerization of butadiene to *cis*-polybutadiene in a gas phase process is of interest because of ecological and technological advantages of such a process compared to the homogeneous catalytic polymerization in the liquid phase [4,5]. The modification of the lanthanide complexes mentioned above with methylaluminoxan (MAO) and the fixation of the obtained complex/MAO adducts on silica were reported by Rühmer et al. [5]. It could be demonstrated that these heterogeneous catalysts are suitable for the gas phase polymerization of butadiene.

A structural characterization of these catalysts requires the application of advanced investigation methods because of the high sensitivity of the organometallic complexes toward oxygen and moisture. Diffuse reflectance infrared Fourier transform spec-

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trospectroscopy (DRIFTS) and temperature-programmed reaction spectroscopy (TPRS) under extremely anaerobic conditions have been proved as suitable to characterize the active species [6]. The present work is aimed at the investigation of neodymium and lanthanum allyl complexes by means of DRIFTS and Raman spectroscopy, and to develop a model of the structural interpretation of the infrared data, considering results of quantum chemical calculations (density functional theory; DFT). This model allows a simple but reliable structure characterization (e.g. bond strength and bond length) of the catalytically interesting allyl ligands by the wavenumber of one characteristic band. This will be demonstrated for the changes of the structure of $\text{Ln}(\text{C}_3\text{H}_5)_3$ complexes after their supporting.

2. Experimental

The metal complexes $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$, $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$ were prepared as reported in Ref. [2]. The preparation of supported catalysts was described in detail in Ref. [5].

Handling of the oxygen and moisture sensitive samples for DRIFTS and Raman spectroscopy was carried out in a glove box (GANUK) under argon purified by a copper catalyst. DRIFTS investigations were performed in a reaction chamber (Graceby Specac) optimized for maximal infrared beam intensity, as well as extremely inert conditions, and attached to a gas manifold system which allows a fast change of the gas atmosphere. The gas flow was controlled using mass flow controllers. The used gases, helium (6.0) and hydrogen (5.0; Messer–Griesheim), were additionally purified by Hydrosorb/Oxisorb (Messer–Griesheim). Diffuse reflectance spectra were recorded using a Mattson research spectrometer RS-1 with the “Selector” equipment (Specac/L.O.T.) for diffuse reflection at a resolution of 8 or 4 cm^{-1} . Special sample holders for the DRIFTS measurements were developed, because commercial sample holders were not suitable. A so-called “diamond pad” with a sample volume of about $1 \mu\text{l}$ was employed, in which the unsupported metal complexes were placed between diamond

splinters. In case of the supported complexes, the sample was filled in a “conned hole” with a volume of $28.3 \mu\text{l}$. Two hundred scans were accumulated to obtain a sufficient signal to noise ratio. The collection time of one spectrum was only 1 min when using an MCT detector.

In order to study the thermal stability and reactivity, the samples were heated in a helium flow (10 ml/min) from 298 up to 473 K in steps of 25 K using ramps with a heating rate of 5 K/min.

Raman experiments were carried out on a spectrometer IFS 66 v (Bruker) with a Raman equipment FRA 106 using a nitrogen-cooled DTGS detector. The samples were excited by a Nd:YAG laser at a wavelength of 1064 nm. A laser power at the sample position between 12.7 and 25.5 W cm^{-2} was applied. The spectra were recorded by accumulation of 1000 scans with a resolution of 4 cm^{-1} .

A conventional equipment for TPX investigations was used for TPRS of the lanthanide catalysts. The lanthanide complexes were decomposed by heating the samples in a helium flow (30 ml/min), starting from room temperature up to 673 K (heating rate = 5 K/min). Detection of the desorbed products was followed by a quadrupole mass spectrometer QMG-420C (Balzers) in multi-ion detection mode, as well as by a thermal conductivity detector (TCD). The observed peaks were calibrated by pulses of the respective chemical compounds, e.g. propene.

3. Results

DRIFT spectra of the allyl lanthanide complexes are shown in Fig. 1. The spectra are characterized by bands of the $\nu_{\text{as}}(\overline{\text{C}\dots\text{C}\dots\text{C}})$, $\nu_{\text{s}}(\overline{\text{C}\dots\text{C}\dots\text{C}})$, $\nu(\text{CH})$ and $\delta(\text{CH})$ vibrational absorptions of the allyl ligands (Table 1).

An intensity decrease of dioxane bands was observed during heating of the samples $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ and $\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$ in helium up to 348 K. At the final temperature, dioxane bands were not longer detected in the spectrum of both the compounds (Fig. 2). Furthermore, a new band or shoulder on the band of the $\nu_{\text{as}}(\overline{\text{C}\dots\text{C}\dots\text{C}})$ vibration between 1490 and 1500 cm^{-1} appeared. A corresponding band was observed in the spectrum

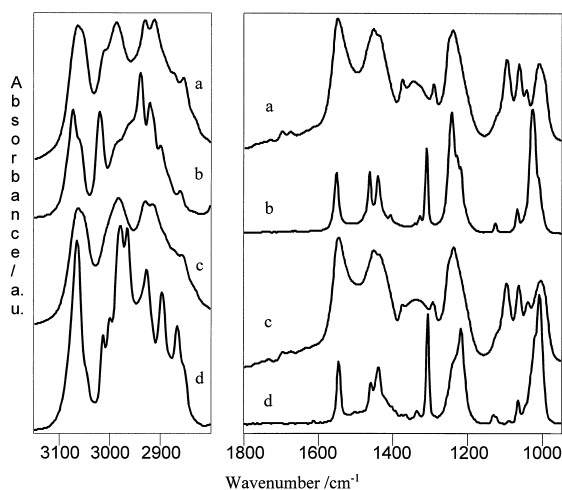


Fig. 1. Infrared and NIR Raman spectra of unsupported allyl complexes of neodymium and lanthanum (spectra normalized to 1): (a) DRIFT and (b) Raman spectrum of $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$, (c) DRIFT and (d) Raman spectrum of $\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$.

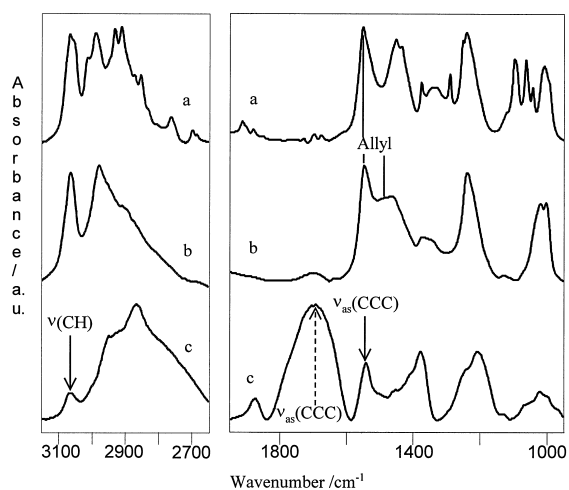


Fig. 2. DRIFT spectra of the thermal decomposition of $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ in a helium flow (10 ml/min) (spectra normalized to 1): (a) 30 min, 10 ml/min He flow, 298 K, (b) 30 min, 10 ml/min He flow, 348 K, (c) 30 min, 10 ml/min He flow, 373 K.

of $\text{Nd}(\text{C}_3\text{H}_5)_3$, synthesized in the absence of dioxane (Fig. 3). Infrared spectra of $\text{Li}[\text{Nd}(\text{C}_3\text{H}_5)_4]$, $\text{Li}[\text{La}(\text{C}_3\text{H}_5)_4]$, $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\text{Nd}(\text{C}_3\text{H}_5)_4]$ and $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\text{La}(\text{C}_3\text{H}_5)_4]$ also revealed a band between 1485 and 1496 cm^{-1} (Fig. 4).

The spectra of thermally formed $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{La}(\text{C}_3\text{H}_5)_3$ complexes are only slightly changed upon heating up to 348 or 373 K, respectively. A temperature increase up to 473 K resulted in a decrease of the intensity of the allyl vibrational band (at 1545–

1550 cm^{-1}) and a simultaneous appearance and increase of a broad band between 1680 and 1695 cm^{-1} (Fig. 2).

During TPRS investigations, the metal complexes were decomposed and the desorbed products were continuously analyzed. Mainly, propene ($m/e = 41, 42$) is formed via an α -H-elimination mechanism. Propene desorption from the unsupported complexes started at 353 ($\text{Nd}(\text{C}_3\text{H}_5)_3$) or 373 K ($\text{La}(\text{C}_3\text{H}_5)_3$), respectively. Maxima of the desorption peaks are

Table 1
Observed infrared and NIR Raman wavenumbers of characteristic allyl vibrations of the allyllanthanide complexes

Compound (vibration/wavenumber)	$\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ (DRIFTS/Raman)	$\text{Nd}(\text{C}_3\text{H}_5)_3$ (DRIFTS/Raman)	$\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$ (DRIFTS/Raman)	$\text{La}(\text{C}_3\text{H}_5)_3$
$\nu_{\text{CH}}/\text{cm}^{-1}$	3064/3071	3064/3066	3063/3064	3060
$\nu_{\text{a}}\text{CH}_2/\text{cm}^{-1}$	2986/3018	2976/–	2982/2978	2976
$\nu_{\text{s}}\text{CH}_2/\text{cm}^{-1}$	2930/2937	–/2941	2929/2927	2942
$\nu_{\text{as}}\text{CCC}/\text{cm}^{-1}$	1548/1549	1545/1544	1545/1544	1544
$\nu_{\text{s}}\text{CCC}/\text{cm}^{-1}$		1486/1491		1484
$\delta\text{CH}/\text{cm}^{-1}$	1239/1240	1238/1212	1237/1236	1237
$\delta^{(-)}\text{CH}_2/\text{cm}^{-1}$	1451/1460	1463/1460	1450/1458	1467
$\delta^{(+)}\text{CH}_2/\text{cm}^{-1}$	1344/1325	1352/–	1338/1335	1350
$\nu_{\text{s}}\text{CCC}/\text{cm}^{-1}$	1008/1009	1018/1020	1004/1009	1024
$\nu_{\text{s}}\text{CCC}/\text{cm}^{-1}$		1001/1008		1001

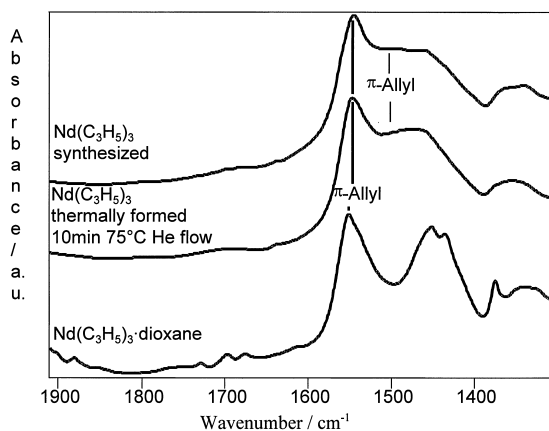


Fig. 3. DRIFT spectra of $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ synthesized and thermally formed $\text{Nd}(\text{C}_3\text{H}_5)_3$.

located at 388 and 411 K for $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{La}(\text{C}_3\text{H}_5)_2$, respectively.

Upon supporting, the metal complexes were first modified with MAO and then anchored on an MAO-loaded silicagel. In the DRIFT spectra of the supported trisallyl neodymium and lanthanum complexes (catalysts), a band at $1536\text{--}1538\text{ cm}^{-1}$ was observed after subtraction of the strong bands of the support (Fig. 5). Additionally, two strong and narrow

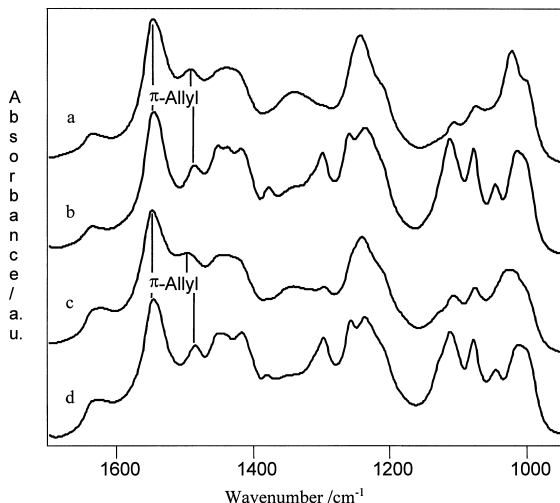


Fig. 4. DRIFT spectra of $\text{Li}[\text{Nd}(\text{C}_3\text{H}_5)_4]$ (a), $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\text{Nd}(\text{C}_3\text{H}_5)_4]$ (b), $\text{Li}[\text{La}(\text{C}_3\text{H}_5)_4]$ (c), and $[\text{Li}(\text{C}_4\text{H}_8\text{O}_2)][\text{La}(\text{C}_3\text{H}_5)_4]$ (d) (spectra normalized to 1).

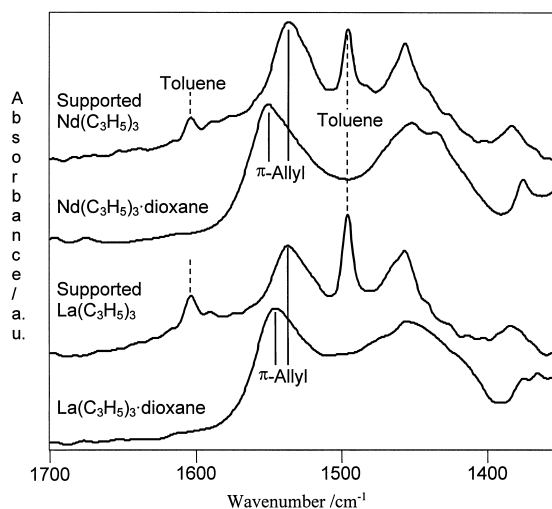


Fig. 5. Comparison of the DRIFT spectra of unsupported and supported allyl complexes of neodymium and lanthanum.

bands were detected at ca. 1605 and 1495 cm^{-1} (Fig. 5).

The WITCO support itself is characterized in the νOH region of the infrared spectrum by a band at 3650 cm^{-1} with a broad shoulder at lower wavenumbers. These bands remained nearly unchanged after heating in a helium flow up to 473 K. Two narrow bands at 1604 and 1495 cm^{-1} were detected in the region between 1800 and 1300 cm^{-1} . Heating results in a decrease of these bands. After a treatment at 373 K in helium, these bands were no longer observed in the DRIFT spectrum.

4. Discussion

The $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{La}(\text{C}_3\text{H}_5)_3$ metal complexes are characterized by absorption bands at $1545\text{--}1550$ and $1008\text{--}1024\text{ cm}^{-1}$ in the DRIFT spectra. These bands are assigned to the antisymmetric and symmetric stretching vibration of the CCC chain of π -allyl ligands, respectively [2,7,8]. These allyl ligands show only one $\nu_{\text{as}}(\text{CCC})$ and one $\nu_{\text{s}}(\text{CCC})$ band in the infrared spectrum because of a total π -charge compensation in the CCC-chain. Consequently, the bond length of both C–C bonds in π -allyl chains is equal.

Quantum chemical calculations (DFT method) have confirmed that the π -allyl ligands of nickel allyl complexes are the catalytic active sites in the butadiene polymerization. A mechanism for butadiene insertion and butadiene polymerization was suggested based on these results [9–12]. Consequently, the structural properties of π -allyl ligands in the investigated neodymium and lanthanum complexes are of special interest. Probably, they are the genuine catalytic active sites for the butadiene insertion and chain growth.

For interpretation of the structure and bonding relationships of these ligands of the allyl lanthanide complexes and their partial decomposition products, the chained molecule type $H_xC-CH_y-CH_z$ was selected (Fig. 6). This means a reduction of the vibrational spectrum into structure decisive CC stretching vibrations. The wavenumbers of these vibrations $\tilde{\nu}$, as well as CC valence force constants (f) were used for the following calculations. The force constant matrix is of second order and contains three force constants (Eq. 1). The terms F_{11} and F_{22} are stretching force constants, whereas F_{12} is the interaction force constant. Only two wavenumbers are available for the calculation of these three force constants, and infinitely real solutions exist for the valence force constants. All force constants can be directly calculated only from the axial symmetric molecule (C_{2v} symmetry) if F_{11} and F_{22} are equally. The use of matrix elements \mathbf{F} (matrix of force con-

stants) and \mathbf{G} (matrix of internal coordinates) results in Eqs. (1) and (2) [13].

$$\begin{vmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{vmatrix} \cdot \begin{vmatrix} F_{11} & F_{12} \\ F_{12} & F_{22} \end{vmatrix} - \lambda \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 0$$

$$\lambda = 5.89145 \times 10^{-7} \tilde{\nu}^2 \quad (1)$$

$$\begin{aligned} G_{11} &= \mu_x + \mu_y & G_{22} &= \mu_y + \mu_z & G_{12} &= \mu_y \cos \alpha \\ F_{11} &= f_{xy} & F_{22} &= f_{yz} & F_{12} &= f_{xy/yz} \end{aligned} \quad (2)$$

$1/\mu = 1/m_{CH_n}$ (reduced mass), $\tilde{\nu}$ = wavenumber (cm^{-1}).

A structure dependent mass correction (Eq. 3) for the hydrogen atoms bound to the carbon chain is necessary to get meaningful values for the reduced mass μ for the $H_xC-CH_y-CH_z$ model:

$$\begin{aligned} m_{CH_x} &= m_C + xm_H(1 - \cos \beta) \\ \beta &= \angle CCH_x, \\ m_{CH_y} &= m_C + ym_H(1 - \cos \gamma) \quad \gamma = \angle CCH_y, \\ m_{CH_z} &= m_C + zm_H(1 - \cos \delta) \quad \delta = \angle CCH_z, \\ (m_C &= 12.011 \text{ and } m_H = 1.0079). \end{aligned} \quad (3)$$

The relationship of Siebert [14] and Pauling [15] was used to calculate the bond strength (Pauling Bond Number BN) from the determined force constants (Eqs. 4 and 5):

$$BN_n = 0.57 f_n/f_1 + 0.43 \sqrt{(f_n/f_1)} \quad (4)$$

and

$$\begin{aligned} f_n/f_1 &= 0.2846 + 1.7544BN_n \\ &- \sqrt{0.0810 + 0.9984BN_n}. \end{aligned} \quad (5)$$

The force constant f_1 , being relevant for a single bond between the carbon atoms in the C_3 -chain amounts to 4.05 N cm^{-1} . Eqs. (4) and (5) can be transformed to Eqs. (6) and (7):

$$BN_{CC} = 0.1407 f_{CC} + 0.2137 \sqrt{f_{CC}} \quad (6)$$

$$\begin{aligned} f_{CC} &= 1.1534 + 7.1073BN_{CC} \\ &- \sqrt{1.3304 + 16.396BN_{CC}} \end{aligned} \quad (7)$$

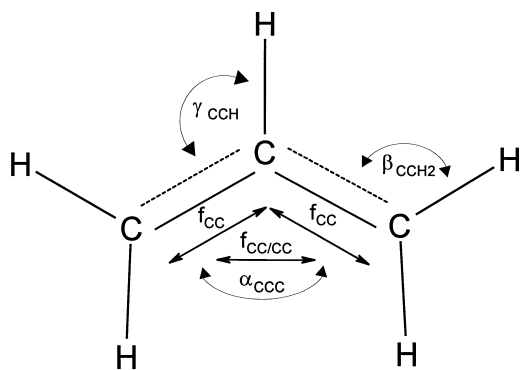


Fig. 6. Structure of a $CH_x-CH_y-CH_z$ molecule ($x = z = 2$, $y = 1$): f_{CC} — force constant between two C-atoms, $f_{CC/CC}$ — interaction force constant, α_{CCC} — angle between the three C-atoms, γ_{CCH} — angle between a C-atom and the CH group, β_{CCH_2} — angle between the central C-atom and a CH_2 group.

The bond number is related to the bond length by an empirical expression (Eq. 8) with a value d_1 for a C–C single bond of 154.4 pm:

$$\begin{aligned} d_{CC} &= d_1 - 71.0 \log \text{BN}_{CC} & (\text{BN}_n, \text{BN}_{CC} \geq 1) \\ d_{CC} &= d_1 - 60.0 \log \text{BN}_{CC} & (\text{BN}_n, \text{BN}_{CC} \leq 1) \end{aligned} \quad (8)$$

The structural data of different molecules with C₃-chains used for the “reduced vibration model”

are summarized in Table 2. Experimental values, as well as results of quantum chemical calculations of Bögel et al. [16], applying DFT method, were used for the calculations of the structure parameters. Only the quantum chemically determined values $\tilde{\nu}_{CC}$, f_{CC} , α , β , γ were needed for the described calculation. The bond numbers BN_{CC} were calculated by the derived model. Either wavenumbers $\tilde{\nu}_{CC}$ or force constants f_{CC} and the bonding angles, α , β , γ , are implied values. For further considerations, the sum

Table 2
Infrared and structure data of H_xC–CH_y–CH_z compounds

Structure	Name	Origin data			Calculated data		
		$\tilde{\nu}_{CC}$ (cm ⁻¹)	f_{CC} (N cm ⁻¹)	α_{CCC}	$f_{CC/CC}$	$\text{BN}_{CC}/\text{BN}_{CC}$	ΣBN_{CC}
<i>Experimental values of symmetrical CCC compounds</i>							
H ₃ C–CH ₂ –CH ₃	Propane	868/1053	4.211/4.211	112.4°	0.031	1.031/1.031	2.062
H ₂ C=CH–CH ₃	Propene	919/1647	4.467/10.291	124.3°	-0.925	1.080/2.133	3.214
HC≡C–CH ₃	Propine	926/2124	5.490/15.780	180.0°	0.491	1.273/3.069	4.342
H ₂ C=C=CH ₂	Allene	1071/1980	10.048/10.048	180.0°	0.131	2.091/2.091	4.182
C≡C≡C	Tricarbon	1225/2040	10.217/10.217	180.0°	0.401	2.121/2.121	4.242
<i>Quantum chemical calculated values of symmetrical CCC compounds (DFT method)</i>							
H ₃ C–CH ₂ –CH ₃	Propane	858/1042	4.267/4.267	113.0°	0.054	1.042/1.042	2.084
[H ₃ C–C–CH ₃] ²⁻	Isopropyliden(2 -)	842/972	4.007/4.007	103.7°	-0.021	0.992/0.992	1.983
[H ₂ C–CH ₂ –CH ₂] ²⁻	Propyliden(2 -)	768/933	3.103/3.103	122.0°	0.241	0.813/0.813	1.626
[H ₂ C–CH–CH ₂] ¹⁻	Allyl(1 -)	986/1547	6.638/6.638	132.8°	-0.508	1.485/1.485	2.969
[H ₂ CCCH ₂] ²⁻	Allyliden(2 -)	973/1248	5.145/5.145	119.9°	0.181	1.209/1.209	2.417
[HCCHCH] ³⁻	Allylidin(3 -)	857/1100	4.068/4.068	141.6°	0.658	1.003/1.003	2.007
[H ₂ C–CH–CH ₂] [*]	Allyl(*) radical	1015/1485	6.429/6.429	124.7°	-0.468	1.446/1.446	2.893
[H ₂ CCHCH ₂] ¹⁺	Allyl(1 +)	1034/1598	7.388/7.388	118.8°	-1.271	1.620/1.620	3.241
H ₂ C=C=CH ₂	Allene	1078/1991	9.928/9.928	180.0°	0.145	2.070/2.070	4.141
[HC=C=CH] ²⁻	Allenyliden(2 -)	1049/1672	7.410/7.410	173.9°	0.883	1.624/1.624	3.249
D ₃ C–CD ₂ –CD ₃	<i>d</i> ₈ -Propane	726/837	4.267/4.267	113.0°	0.244	1.042/1.042	2.084
[D ₂ C–CD–CD ₂] ¹⁻	<i>d</i> ₅ -Allyl(1 -)	818/1491	6.638/6.638	132.8°	-1.321	1.485/1.485	2.969
[D ₂ C–CD–CD ₂] [*]	<i>d</i> ₅ -Allyl(*) radical	836/1372	6.429/6.429	124.7°	-1.012	1.446/1.446	2.893
D ₂ C=C=CD ₂	<i>d</i> ₄ -Allene	866/1933	9.928/9.928	180.0°	-0.960	2.070/2.070	4.141
<i>Quantum chemical calculated values of asymmetrical CCC compounds (DFT method)</i>							
[H ₃ C–CH ₂ –CH ₂] ¹⁻	Propyl(1 -)	769/958	2.994/3.976	118.4°	0.316	0.791/0.986	1.777
H ₂ C=CH–CH ₃	Propene	910/1669	4.628/9.185	125.3°	-0.884	1.111/1.940	3.051
D ₂ C=CD–CD ₃	<i>d</i> ₆ -Propene	768/1599	4.628/9.185	125.3°	-0.884	1.111/1.940	3.051
[H ₂ C=C–CH ₃] ¹⁻	Isopropenyl(1 -)	853/1518	3.552/7.766	112.5°	-0.577	0.903/1.688	2.591
[HC=CH–CH ₃] ¹⁻	Propenyl(1 -)	863/1498	3.968/7.675	122.2°	-0.634	0.984/1.672	2.656
[H ₂ C–CH=CH] ²⁻	Propenyliden(2 -)	886/1411	3.834/6.413	137.6°	-0.393	0.958/1.444	2.401
[H ₂ CC=CH] ³⁻	Isopropenylididn(3 -)	714/1178	2.368/5.296	125.2°	0.173	0.662/1.237	1.899
HC≡C–CH ₃	Propine	927/2152	5.297/15.855	180.0°	0.411	1.234/3.082	4.315
DC≡C–CD ₃	<i>d</i> ₄ -Propine	821/2008	5.297/15.855	180.0°	0.411	1.234/3.082	4.315
[HC≡C–CH ₂] ¹⁻	Propargyl(1 -)	1073/1854	7.783/10.028	173.2°	-0.660	1.691/2.088	3.779
[H ₂ C–C≡C] ²⁻	Propinyliden(2 -)	868/1822	4.205/10.698	178.0°	-0.927	1.030/2.204	3.234

$\tilde{\nu}_{CC}$ — wavenumber [cm⁻¹], α_{CCC} — angle of the CCC chain, f_{CC} — force constant between two C-atoms [N cm⁻¹], $f_{CC/CC}$ — interaction force constant [N cm⁻¹], $\text{BN}_{CC}/\text{BN}_{CC}$ — bond numbers of both CC-chains, ΣBN_{CC} — sum of both bond numbers.

of both BN in a C₃-chain (ΣBN) was determined. The obtained sum of bond numbers of all compounds (Table 2) were used to derive an empirical correlation between $\Sigma\text{BN}_{\text{CC}}$ and the bond angle α_{CCC} (Eq. 9), as well as the interacting force constant $f_{\text{CC}/\text{CC}}$ (Eq. 10):

$$\Sigma\text{BN}_{\text{CC}} = 4.0536 - 2.4485 \left[5.086254 - (\log \alpha_{\text{CCC}})^2 \right]^2 (\pm 5.2\%) \quad (9)$$

$$f_{\text{CC}/\text{CC}} = -0.9293 + 0.021728 \left[(\Sigma\text{BN}_{\text{CC}})^2 - 10.7149 \right]^2 (\pm 9.7\%). \quad (10)$$

Especially, this empirical $f_{\text{CC}/\text{CC}}$ correlation was refined to allyl ligands (Eq. 11):

$$f_{\text{CC}/\text{CC}} = -0.5506 + 0.44868 \left[(\Sigma\text{BN}_{\text{CC}})^2 - 9.2241 \right]^2 (\pm 7.0\%). \quad (11)$$

With the help of these correlations, a method for the calculation of structure parameters from the wavenumber was given for the H_XC–CH_Y–CH_Z molecule model. This is, for example, illustrated by a bond number/wavenumber and force constant/

wavenumber nomograph for allyl ligands (Fig. 7). With this tool, the BN_{CC} value can certainly be determined by one wavenumber, e.g. of the antisymmetric $\nu(\text{CCC})$ vibration. All the other described structure parameters can be calculated from the bond number.

This procedure was applied to classify allyl compounds, e.g. allyl(1–) anions. The results summarized in Table 3 lead to the following conclusions. In the case of the dioxane containing trisallyl complexes, all the allyl ligands are bound in the same way because the bond strength and length are equal. Two different allyl ligands are observed in the case of the dioxane free complexes obtained by thermal treatment or by direct synthesis. The following structure is proposed for trisallyl compounds without dioxane: one allyl ligand is placed between two neodymium atoms (“bridged bonded allyl ligand”) after the removal of dioxane. π -charge compensation is furthermore present in these new-formed allyl ligands. A band between 1485 and 1496 cm⁻¹ was observed in the spectra of Li[La(C₃H₅)₄], Li[Nd(C₃H₅)₄], [Li(C₄H₈O₂)] [La(C₃H₅)₄] and [Li(C₄H₈O₂)] [Nd(C₃H₅)₄]. In these cases, crystal structure analysis has confirmed the proposed bridged bonded allyl ligand [17,18].

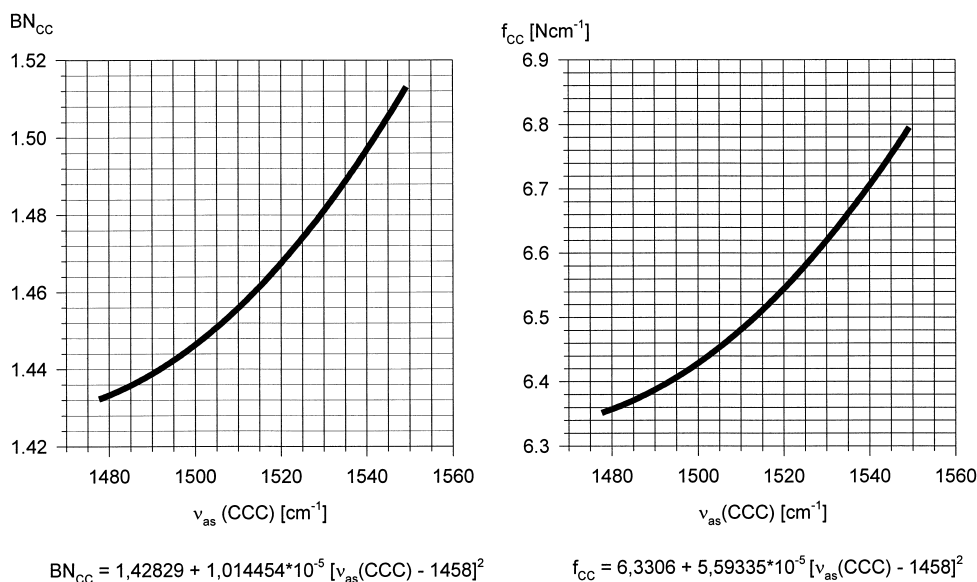


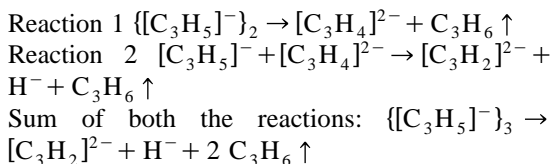
Fig. 7. C₃-angular chain vibrational model: π -allyl [H₂CCHCH₂]¹⁻ complex ligand nomographs for calculation of BN_{CC} and f_{CC} from $\nu_{\text{as}}(\text{CCC})$.

Table 3

From DRIFTS and NIR Raman results calculated structure parameters of the allyllanthanide complexes

Compound (structure parameter)	Nd(C ₃ H ₅) ₃ · dioxane	Nd(C ₃ H ₅) ₃ / (C ₃ H ₅) ₂ Nd(C ₃ H ₅)	La(C ₃ H ₅) ₃ · 1.5 dioxane	La(C ₃ H ₅) ₃ / (C ₃ H ₅) ₂ Nd(C ₃ H ₅)
BN _{CC}	1.50	1.51/1.44	1.49	1.51/1.43
ΣBN _{CC}	3.00	3.02/2.88	2.98	3.02/2.86
f _{CC} /N cm ⁻¹	6.71	6.75/6.37	6.68	6.78/6.41
d _{CC} /pm	141.9	141.8/143.2	142.0	141.7/143.3
α _{CCC} /°	128.7	128.9/126.6	128.5	129.1/126.4
β _{CCH2} /°	121.3	121.3/121.3	121.3	121.3/121.3
γ _{CCH} /°	115.6	115.5/116.7	115.7	115.4/116.8

Dioxane was removed by heating of the Nd(C₃H₅)₃ · dioxane and La(C₃H₅)₃ · 1.5 dioxane in a helium flow up to 348 K. The formed Nd(C₃H₅)₃ and La(C₃H₅)₃ were stable up to 348 and 373 K, respectively. Heating of the samples under helium from 348/373 up to 473 K resulted in an increasing decomposition of the allyl complexes with rising temperature. A new broad band with increasing intensity observed between 1680 and 1695 cm⁻¹ indicated the formation of compounds with a stronger bond between the C-atoms in the C₃-chain and with a lower hydrogen content, as compared to that of the allyl compounds. Propene and little amounts of propane were detected as decomposition products in the TPRS measurements. The maximum of the propene desorption peak was observed at 388 or 411 K for Nd(C₃H₅)₃ or La(C₃H₅)₃, respectively. The quantitative evaluation leads to the result that nearly two propene molecules were released from one trisallyl complex. Therefore, the following reaction pathways are proposed:



The release of propene can occur by an intramolecular or an intermolecular reaction. The formation of symmetric or of asymmetric [C₃H₂]²⁻ ligands, i.e. allenylidene or propynylidene seems to be possible. The assignment to allenylidene is more preferred because of the band at about 1370 cm⁻¹, which is characteristic for a δCH vibration. More-

over, a band for δCH₂ vibrations was not observed (Fig. 2). The bond number BN of the allenylidene ligand is 1.90 or 1.88 for the neodymium or the lanthanum complex, respectively. The calculated structure parameters are summarized in Table 4.

The commercial WITCO support contains toluene, resulting from its preparation. The bands at 1604 and 1495 cm⁻¹ in the infrared spectrum are typical for the ν_{as}(C...C) and for the δ(CH₃) vibration of toluene. Furthermore, hydroxyl groups are also observed by DRIFTS although the silicagel was loaded by MAO. That means that the hydroxyl groups on the silica surface are not completely removed by the pretreatment of silica gel upon production of this material.

After supporting the neodymium, as well as lanthanum complexes, a band at 1536–1538 cm⁻¹ assigned to ν_{as}(C...C...C) vibrations was observed in the DRIFT spectrum. The ν_s(C...C...C) band is superimposed by strong vibrational absorptions of the silica. The ν_{as}(C...C...C) band shifts ca. 10 cm⁻¹ to lower wavenumbers, pointing to interac-

Table 4

Calculated structure parameters of allenylidene complexes and supported trisallyllanthanide, resulting from DRIFTS results

Compound (structure parameter)	[HNdC ₃ H ₂] ²⁻	[HLaC ₃ H ₂] ²⁻	Supported Nd(C ₃ H ₅) ₃ and La(C ₃ H ₅) ₃
BN _{CC}	1.90	1.88	1.49
ΣBN _{CC}	3.80	3.76	2.98
f _{CC} /N cm ⁻¹	8.96	8.84	6.68
d _{CC} /pm	134.6	134.9	142.1
α _{CCC} /°	180.0	180.0	128.4
γ _{CCH} /°	120.0	120.0	

tions of the complex with the support (Fig. 5), particularly with the Lewis-acidic co-catalyst MAO. That means that only the electron density in the CCC allyl chain was slightly decreased. The π -bonding character in the allyl chain is still maintained. Obviously, the hydroxyl groups of the support have no influence on the main part of the structure of the neodymium complexes in the catalysts. Moreover, the catalysts also contain toluene as indicated by bands at 1605 and 1495 cm^{-1} .

Now, the influence of supporting on the structure has to be discussed in detail. By using the nomograph (Fig. 6) and Eqs. (7)–(11), the following structure changes (Table 4) are suggested. The bond number is reduced from 1.51 to 1.49 in comparison to the unsupported complex. Consequently, the valence force constant f_{CC} decreases from 6.75 to 6.68 N cm^{-1} and the bond length between the C-atoms d_{CC} increases from 141.8 to 142.1 pm. The bond angle of the C_3 -chain α_{CCC} is nearly unchanged. The calculated values certify the decrease of the electron density after anchoring of the complex on the Lewis-acidic support.

These results are the foundation of current characterizations of the unsupported and supported metal complexes during butadiene adsorption, which shall be published in the near future. Preliminary, the π -allyl ligands will be characterized as the active sites in unsupported and supported allyl complexes at which a polymerization of butadiene can start.

5. Conclusion

Combined DRIFTS and Raman measurements were used to develop a calculation model of structural parameters of various C_3 -chain containing compounds. This method allows the structural characterization of such compounds by only one wavenumber. The model was applied to trisallyl complexes of neodymium or lanthanum being active catalysts for butadiene polymerization. At first, the structure of these complexes was reduced in the model to their $\text{H}_2\text{C}\dots\text{CH}\dots\text{CH}_2$ allyl chain, which are the active sites in the catalysts. Structural parameters of the C_3 allyl chains, such as valence force constant (f_{CC}), bond length between the C-atoms (d_{CC}) and the

bond angle of the C_3 -chain (α_{CCC}) were calculated from only the wavenumber of the $\nu_{\text{as}}(\text{C}\dots\text{C}\dots\text{C})$ vibration. The calculated values were used to interpret the changes in the allyl chain caused by supporting of metal complexes on a strongly Lewis-acidic commercial support. Complex/support interaction results in a reduced electron density in the C_3 -chain.

The thermal stability of $\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot \text{dioxane}$ and $\text{La}(\text{C}_3\text{H}_5)_3 \cdot 1.5 \text{ dioxane}$ were investigated by DRIFTS and TPRS. During heating, dioxane is first removed; subsequently, about two propene molecules were released from one trisallyl complex. Dioxane removal results in the following proposed structure. One allyl ligand is placed between two neodymium atoms (“bridged bonded allyl ligand”), instead of dioxane. Propene release results in formation of proposed symmetric $[\text{C}_3\text{H}_2]^{2-}$ ligands (allenylidene).

Forthcoming, the interaction of the trisallyl complexes of neodymium or lanthanum with butadiene will be investigated based on the presented structural calculations.

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