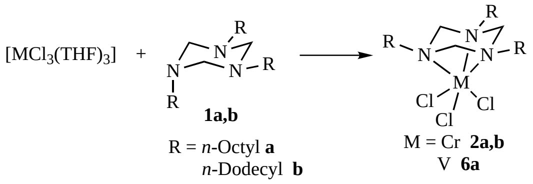
Selective Trimerization of α-Olefins with Triazacyclohexane Complexes of Chromium as Catalysts**

Randolf D. Köhn,* Matthias Haufe, Gabriele Kociok-Köhn, Siegfried Grimm, Peter Wasserscheid, and Wilhelm Keim

Dedicated to Professor Herbert Schumann
on the occasion of his 65th birthday

CrO_3/SiO_2-based heterogeneous Phillips catalysts[1] for the polymerization of ethene produce a large fraction of the world production of high-density polyethylene (HDPE).[2] Under certain conditions the CrO_3/SiO_2-based catalysts show an unusual selectivity for the trimerization of ethene to 1-hexene and homogeneous systems based on a mixture of chromium complexes, pyrrols, and alkylaluminum compounds have been optimized to produce the trimer selectively.[3, 4] Contrary to the Ziegler–Natta systems, very little is known about the mechanism and nature of the active species in these chromium systems although some model systems suggest a route via metallacycles.[5, 6] Another homogeneous system $[Cp^*TiMe_3]/B(C_6F_5)_3$ ($Cp^* = C_5Me_5$) has recently been found that can also trimerize ethene and "cotrimerize" styrene with ethene.[7] So far, none of these systems has been able to selectively trimerize α-olefins.

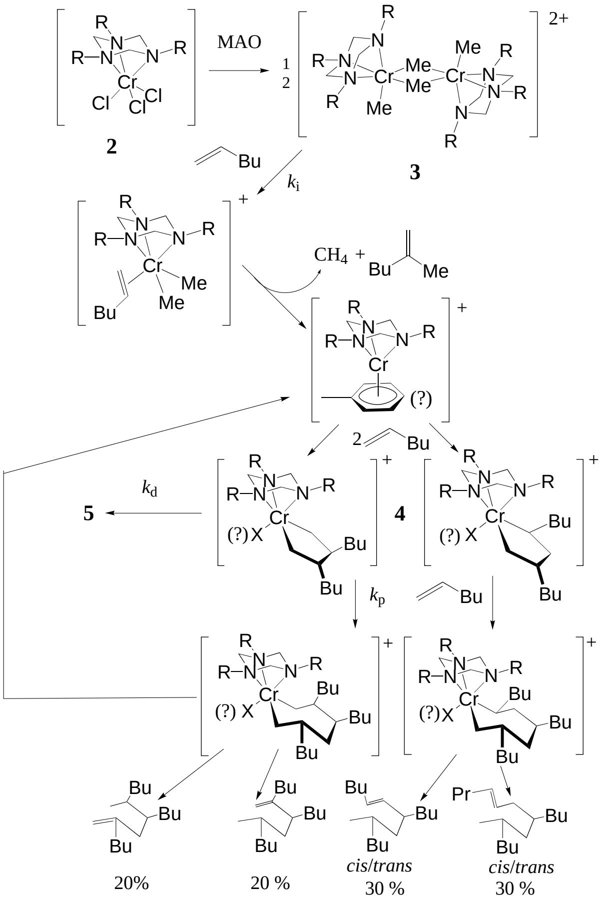
For several years we have been investigating the coordination chemistry of 1,3,5-triazacyclohexanes **1**. We were able to isolate $CrCl_3$ and alkylchromium(III) complexes as well as cationic alkylzinc complexes[8a–e] with ligands having very small steric demand due to the small N-metal-N angle. The toluene-soluble *n*-octyl- and *n*-dodecyl-substituted complexes **2a**, **b** can be prepared according to Scheme 1.[8e]



Scheme 1. Syntheses of the complexes **2** and **6**.

Activation of **2** with methylaluminoxane (MAO) gives a yellow-green solution that can polymerize ethene and also shows some trimerization activity.[8e] Now, we have found that α-olefins (propene, 1-hexene, and styrene) can be transformed in a new catalytic reaction selectively to a mixture of isomers of the trimers.[9] At room temperature, the catalytic trimerization ceases after a few hours at up to 80% conversion (at maximal chromium concentration of approximately 10 mM) or about 1000 turnovers (in neat hexene). At 0 °C, this catalyst decomposition can be avoided and trimerization to > 90% conversion is possible after several days in the refrigerator. The system is highly selective for α-olefins. Internal olefins (*cis* or *trans*) and conjugated dienes are not trimerized. Donor-functionalized olefins as well as donor solvents deactivate the system.

We have investigated the reaction with 1-hexene in more detail and our observations are in agreement with the mechanism shown in Scheme 2 which is similar to that proposed and supported by Briggs and Jolly.[3, 5] Compound **2** is alkylated by MAO and a methyl/chloride anion is abstracted to give a cationic complex **3**. After insertion of the first olefin, β-H and reductive alkane elimination gives a Cr^I complex. Oxidative addition of two olefins gives the metallacyclic steady-state complex **4**. The rate-determining insertion of a third olefin molecule into one of the Cr–C bonds of **4**



Scheme 2. Proposed mechanism for the trimerization and distribution of the major isomers.

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gives a metallacycloheptane which is unstable towards β-H and reductive alkane elimination to the Cr^{I} complex and finally **4** after oxidative addition of two more olefin molecules to complete the cycle. Compound **4** slowly decomposes to give an inactive complex **5**.

Besides unreacted 1-hexene the trimer can be isolated in high selectivity. The formation of the major isomers can be explained according to Scheme 2. Dimers and tetramers are found in less than 1%. Small amounts of methane and 2-methyl-1-hexene can be identified by NMR spectroscopy as the products of the initiation.

The homogeneous reaction can be monitored by UV/Vis and NMR spectroscopy. The UV/Vis spectrum of **2** (720 and 510 nm) changes to a new set of absorptions for **3** typical for Cr^{III} (at 600 and 430 nm) after addition of 100 equivalents of MAO. Compound **3** reacts within several minutes with added 1-hexene to give a new complex **4** (620 and 430 nm) which decomposes over several hours to give a complex **5** with absorptions at 550 and < 400 nm.

The paramagnetism of the chromium complexes does not allow a useful observation of the complexes by ^{1}H or ^{13}C NMR spectroscopy. However, the ring-deuterated complex $[D_6]$-**2a** is observable by ^{2}H NMR spectroscopy. η^3-coordinated $[D_6]$-**1a** shows a set of two signals of equal intensity for the two different deuterium atoms in the triazacyclohexane ring. The paramagnetically shifted and broadened signal pair at $\delta = 28$ and 5 for $[D_6]$-**2a** moves to $\delta = 65$ and 5 for **3** after addition of 100 equivalents of MAO. Addition of 1-hexene gives a new signal pair at $\delta = 50$ and 5 for **4**. Then, a slow decomposition can be observed with the appearance of equal amounts of **5** with a signal pair at $\delta = 140$ and 5 and a diamagnetic triazacyclohexane **1** with a sharp signal at $\delta = 3.6$ indicating decomplexation.

The kinetics of the 1-hexene consumption can be determined by ^{1}H NMR spectroscopy and can be described by the rate law given in Equation (1) (based on Scheme 2), with the rate constant for the olefin insertion into **4** of $k_p = 1 \times 10^{-2}\,s^{-1}M^{-1}$ and the decomposition rate constant of $k_d = 2 \times 10^{-4}\,s^{-1}$ at room temperature. Matching kinetics observed by the UV/Vis and NMR investigations of the complexes show that a triazacyclohexane complex **4** carries the trimerization and that the ligand is partially lost only upon decomposition.

$$\ln\{[\text{hexene}]/[\text{hexene}]_0\} = -3k_p[\text{Cr}]_0/k_d(1-\exp(-k_d t)) \qquad (1)$$

During the NMR studies, the average magnetic moment can be determined by the Evans method.[10] By using the concentrations of the individual chromium complexes from the kinetic investigations, the magnetic moments can be determined: 3.9 μ_B for **2**, 3.1 μ_B for **3**, 4.1 μ_B for **4**, and 3.3 μ_B for **5**. The magnetic moments for **2** and **4** are typical for mononuclear Cr^{III} complexes, while the reduced magnetic moments for **3** and **5** are in the range of bridged, dinuclear Cr^{III} complexes.

So far, there is only spectroscopic evidence for Cr^{III} complexes, and the Cr^{I} complex proposed in Scheme 2 is mostly based on the observation of the products of reductive elimination. The analogous V^{III} system **6a**/MAO also polymerizes ethene but does not react with 1-hexene under the same conditions. Usually analogous V^{III} complexes show similar reactions when no redox reaction is involved. Additionally, the isomer distribution of the trimers depends on the substitution patterns of the arene solvent used and may indicate a direct involvement of the solvent.

X-ray crystallography on crystals of **2a** at 110 K allowed the structure determination without disorder in the octyl substituents (Figure 1).[11]

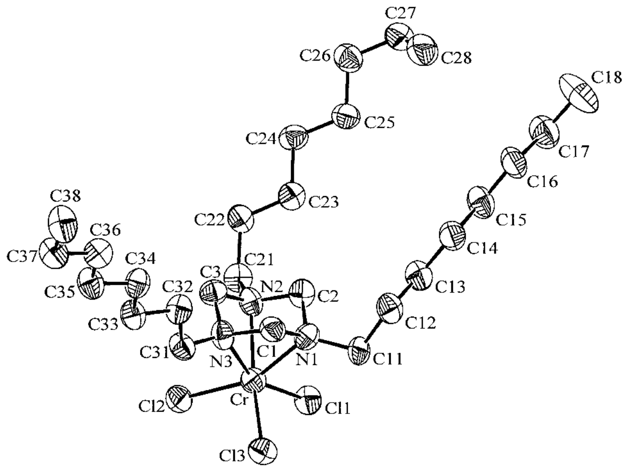

Figure 1. ZORTEP plot of the molecular structure of **2a** (thermal ellipsoids for 50% probability). Selected bond lengths [Å] and angles [°]: Cr-N1 2.095(7), Cr-Cl1 2.288(3), N1-Cr-N2 65.9(3), Cl1-Cr-Cl2 99.74(10), Cr-N1-C11 128.0(5), C1-N1-C11 114.6(7), C1-N1-C2 110.6(7).

The Cr–N bond length is at the lower limit of the range observed in other Cr^{III} – triazacyclohexane complexes (2.10 – 2.30 Å).[8b,c, 12] This Cr–N bond is also shorter than that in an analogous tri-*n*-butyl-substituted 1,4,7-triazacyclononane complex (2.15 Å).[13] This comparison shows that the much lower steric demand of triazacyclohexanes can overcome the electronic weakening of the bond caused by the nearly 30° mis-directed nitrogen lone pairs. Analogous methyl-substituted triazacyclononane or -dodecane complexes are not able to trimerize 1-hexene under the same conditions. This shows the importance of the low steric demand of the triazacyclohexane complexes for the reactivity towards α-olefins.

This unprecedented selective trimerization of α-olefins by the system **2**/MAO should allow access to new products from simple α-olefins. We are currently investigating the influence of the N substituents and the solvent on the isomer ratios.

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[1] J. P. Hogan, R. L. Banks (Phillips Petroleum), US-A2825721, **1958** [*Chem. Abstr.* **1958**, *52*, 8621h].

[2] M. Rätzsch, *Polymerwerkstoffe '98* (Merseburg, Germany), September 23 – 25, 1998; M. Rätzsch, *Kunststoffe* **1996**, *86*, 6; R. Messere, A. F. Noels, P. Dournel, N. Zandona, J. Breulet, *Proc. Metallocenes '96* (Düsseldorf, Germany), March 6 – 7, 1996, pp. 309 – 322.

[3] J. R.Briggs, *J. Chem. Soc. Chem. Commun.* **1989**, 674 – 675.

[4] M. E. Lashier (Phillips Petroleum Company), EP0 780 353, **1995** [*Chem. Abstr.* **1997**, *127*, P50277g].

[5] K. H. Theopold, *Eur. J. Inorg. Chem.* **1998**, 15 – 24.

[6] R. Emrich,O. Heinemann, P. W. Jolly, C. Krüger, G. P. J. Verhovnik, *Organometallics* **1997**, *16*, 1511 – 1513.

[7] C. Pellecchia, D. Pappalardo, L. Oliva, M. Mazzeo, G.-J. Gruter, *Macromolecules* **2000**, *33*, 2807–2814.

[8] a) M. Haufe, R. D. Köhn, G. Kociok-Köhn, A. C. Filippou, *Inorg. Chem. Commun.* **1998**, *1*, 263–266; b) R. D. Köhn, G. Kociok-Köhn, *Angew. Chem.* **1994**, *106*, 1958–1960; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1877–1879; c) R. D. Köhn, G. Kociok-Köhn, M. Haufe, *J. Organomet. Chem.* **1995**, *501*, 303–307; d) M. Haufe, R. D. Köhn, R. Weimann, G. Seifert, D. Zeigan, *J. Organomet. Chem.* **1996**, *520*, 121–129; e) R. D. Köhn, M. Haufe, S. Mihan, D. Lilge, *Chem. Commun.* **2000**, 1927–1928.

[9] Experimental details for the syntheses and analyses of new complexes and the trimerization are available in the Supporting Information.

[10] D. H. Grant, *J. Chem. Educ.* **1995**, *72*, 39–40.

[11] Crystal data of **2a**: crystal dimensions $0.57 \times 0.57 \times 0.01$ mm, monoclinic, $P2_1/n$ (no. 14), $Z=4$; $a=6.933(2)$, $b=36.796(8)$, $c=12.760(4)$ Å, $\beta=95.32(4)^\circ$, $V=3241.3(16)$ Å^3, $\rho_{calcd}=1.193$ g cm^{-3}, $F(000)=1260$, $T=110(2)$ K, Stoe IPDS area detector, $2.31^\circ \leq \theta \leq 26.34^\circ$, ($\lambda(Mo_{K\alpha})=0.71073$ Å, $\mu=0.609$ mm^{-1}), 22969 reflections collected, 6499 unique ($R_{int}=0.2330$), 6456 observed reflections ($I>2\sigma(I)$), empirical correction for absorption effects (ABSCOR, min. 0.254, max. 1.445) Patterson and Fourier synthesis (SHELXS-86 and SHELXL-97), 308 parameters, $R=0.1155$, $wR_2=0.2469$, GOF = 1.193, max./min. residual electron density $0.870/-0.951$ e Å^{-3}. $\chi=0.0042(13)$ for secondary extinction. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134609. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] M. V. Baker, D. H. Brown, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **2000**, 763–768.

[13] S.-J. Wu, G. P. Stahly, F. R. Fronczek, S. F. Watkins, *Acta Crystallogr. C* **1995**, *51*, 18–20.

Identification of a New Sex Pheromone from the Silk Dragline of the Tropical Wandering Spider *Cupiennius salei*[**]

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Ewald Gingl, and Rudolf Ehn

*Dedicated to Professor Wittko Francke
on the occasion of his 60th birthday*

The chemistry of pheromones of arachnids and particularly spiders has not received the same attention as that of the pheromones of insects,[1] despite the widespread distribution of spiders, their importance in many ecosystems, and their species-rich taxon. The silk is known to play a role as substrate for pheromones in various spiders,[2] but so far only one pheromone has been identified.[3] The large tropical wandering spider *Cupiennius salei* (Ctenidae) uses its silk dragline as a chemical signpost, which it leaves behind in the environment. A single thread of a female initiates courtship behavior in conspecific males. The males recognize the inherent chemical signal by examining the silk thread with their pedipalps and send vibratory signals through the substrate which are returned by the female.[4] In the current study we report on the identification and synthesis of the female courtship-inducing pheromone.

Silk can be obtained from the spiders by using an electrically driven reeling machine which draws the silk thread out of the silk glands of an immobilized, but awake spider. About 5–10 mg silk can be obtained in a week from a single individual. A bioassay was developed to guide in the identification of the active principle. In short, the spiders wandered along a glass duct covered with filter paper and encountered natural or chemically modified silk threads on their way. The characteristic vibratory courtship behavior could be elicited by silk samples from adult females.[5] In contrast, silk from males or juvenile females was not active. Active silk was extracted with different solvents and the extracts were then applied on inactive silk from male spiders to test their activity. Methanol extracts showed good responses and were used for further analyses.

By use of GC-MS methods usually employed in pheromone research only methyl pyroglutamate could be identified, but both enantiomers did not evoke any response in the bioassay. We then analyzed extracts by NMR spectroscopy. Surprisingly, active extracts prepared with deuterated methanol showed the presence of only one prominent compound, which was absent in inactive silk samples (Figure 1). The spectrum showed two different CH_3 groups and two different CH_2 groups, each of them with diastereotopic H atoms. The spectrum is consistent with the structure of the asymmetric dimethyl citrate **1**. This ester, to the best of our knowledge not known from nature before, was then synthesized as racemate to confirm the assignment.[6]

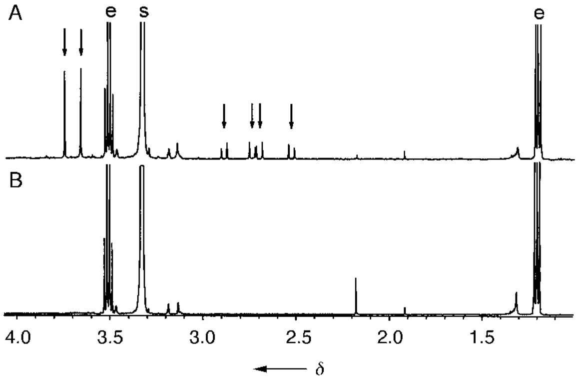

Figure 1. ^1H NMR spectrum of a silk extract (CD_3OD) from adult female (A) and male (B) *Cupiennius salei* spiders. Arrows indicate characteristic signals; e: ethanol (contaminant), s: solvent.

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