Note

Isolation and characterization of a monomeric, solvent coordinated ruthenium(II)carbene cation relevant to olefin metathesis

Peter Hofmann *, Martin A.O. Volland, S. Michael Hansen, Frank Eisenträger, Jürgen H. Gross, Katharina Stengel

Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Abstract

The isolation as well as spectroscopic and structural characterization of $[(\kappa^2\text{-}^t\text{Bu}_2\text{PCH}_2\text{P}^t\text{Bu}_2)\text{ClRu}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)_2\text{-}(\text{CH}_3\text{CN})]^+$ ($[\mathbf{5}^+]$), a solvent-coordinated monomeric ruthenium(II)carbene cation with a rigid *cis*-stereochemistry of two phosphines, are reported. Its relevance for the mechanism of olefin metathesis catalyzed by such complexes is discussed and distinct differences compared to complexes with the usual *trans*-phosphine stereochemistry are noted. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Carbene complexes; Metathesis; Homogenous catalysis; Density functional theory calculations

1. Introduction

Transition metal catalyzed formation of C–C bonds is of central importance in organic synthesis and polymer chemistry. Well defined molybdenum **1** [1] and ruthenium **2** [2] carbene complexes have found wide application as precatalysts for olefin metathesis reactions [3].

1 **2**
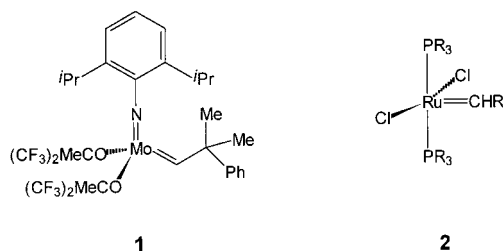
Due to their stability and functional group tolerance, research has focussed especially on Grubbs-type square pyramidal ruthenium(II)carbene complexes **2** with *trans*-phosphines. Attempts to improve their catalyst performance have aimed towards carbene [4] [5], phosphine [4]

or anionic ligand [6] variations, phosphine and chloro ligand replacement by chelating Schiff-bases [7], Lewis acid addition [8] and replacement of one [9] or both [10] of the *trans*-phosphines by Wanzlick–Arduengo type carbenes.

Recently, we introduced the first Grubbs type ruthenium(II)carbene complexes with a rigid *cis*-ligation of two electron-rich, sterically demanding phosphine centers **3** by using bis(di-*t*-butylphosphino)methane ($^t\text{Bu}_2\text{PCH}_2\text{-}\text{P}^t\text{Bu}_2$, dtbpm) [11]. Starting from these neutral precursors **3**, chloride abstraction has led to a novel class of dinuclear dicationic ruthenium(II)carbene complexes $[\mathbf{4}^{2+}][\text{OTf}^-]_2$ with high catalytic activity in ring-opening metathesis polymerization (ROMP) reactions [12].


3 a–d **[4 a–d]$^{2+}$**
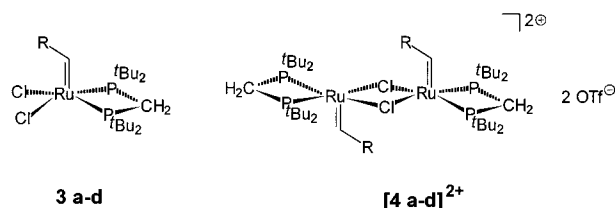
a = R = CH=C(CH$_3$)$_2$
b = R = CH=◇
c = R = CH=CPh$_2$
d = R = CH(CH$_3$)$_2$

* Corresponding author. Tel.: + 49-6221-548502; fax: + 49-6221-544885.

E-mail address: ph@phindigo.oci.uni-heidelberg.de (P. Hofmann).

As pointed out previously [12], monomeric solvent-coordinated cationic complexes [(κ^2-dtbpm)ClRu=CHR(solv)]$^+$, formed by dissociation of the dinuclear units [4^{2+}], presumably represent the catalytically active species. Here we report on the isolation and characterization of such a species, [(κ^2-^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)-ClRu=CH–CH=C(CH$_3$)$_2$(CH$_3$CN)](OTf) ([5^+][OTf$^-$]) (Fig. 1).

5$^+$
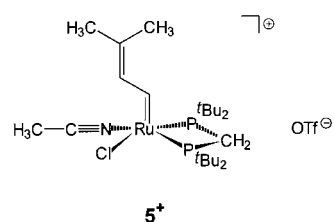
2. Results and discussion

The monomeric, solvent-coordinated complex [5^+][OTf$^-$] was obtained by addition of 2.8 equivalents of CH$_3$CN to a solution of [$4a^{2+}$][OTf$^-$]$_2$ in CD$_2$Cl$_2$. ^{1}H- and ^{31}P{^{1}H}-NMR spectra at 213 K clearly reveal the exclusive formation of the monomeric species.

As expected for the proposed structure, the ^{1}H-NMR spectrum of [5^+] displays four pseudodoublets for the ^{t}Bu-groups of the dtbpm ligand and the characteristic multiplet of the carbene proton at 16.68 ppm. The three protons of coordinated CH$_3$CN are shifted 0.6 ppm downfield with respect to noncoordinating excess CH$_3$CN. The ^{31}P{^{1}H}-NMR shows two doublets at $\delta = 13.2$ and 28.3 [^2J(P,P$'$) = 36 Hz] for the nonequivalent phosphorus nuclei. At ambient temperature an
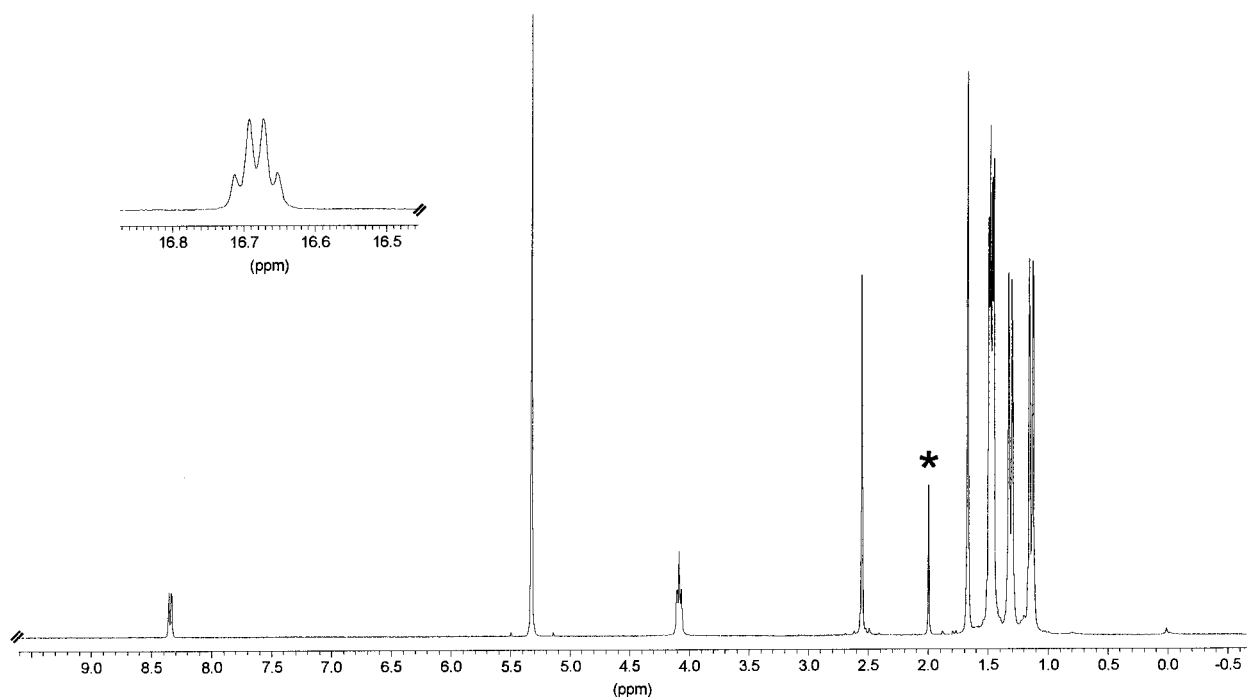

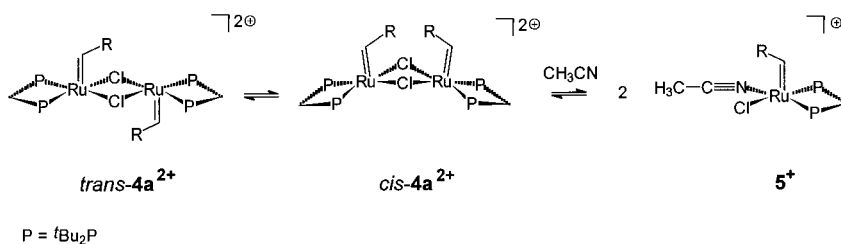Fig. 1. ^{1}H-NMR spectrum of [5^+][OTf$^-$] (CD$_2$Cl$_2$, 500.1 MHz, 213 K); excess CH_3CN shows singlet at 1.99 ppm (marked with *).

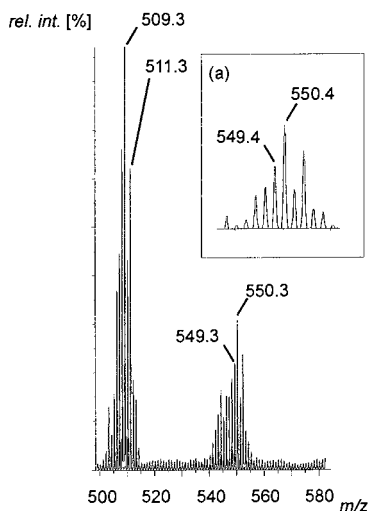*trans*-4a^{2+} *cis*-4a^{2+} 5$^+$

P = ^{t}Bu$_2$P

Scheme 1.

Fig. 2. Part of the positive-ion LT-FAB mass spectrum of [5^+] from a CH_2Cl_2 solution of [$4a^{2+}$][OTf$^-$]$_2$ containing stoichiometric amounts of CH_3CN. The insert (a) displays the isotopic pattern calculated for [$C_{24}H_{49}ClNP_2Ru$]$^+$ ([5^+]).
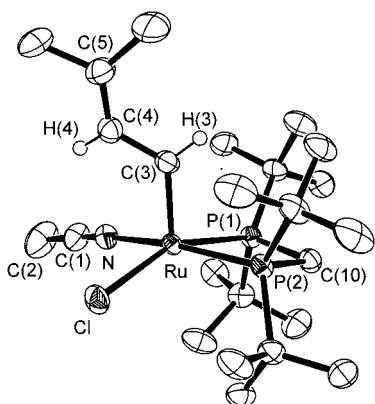

Fig. 3. Molecular structure of cation [5^+] in the solid state (ORTEP, 50% probability, hydrogen atoms except for H3 and H4 of the carbene moiety, triflate anion and cocrystalized noncoordinating CH_2Cl_2 are omitted for clarity). Selected distances (Å) and angles (°): Ru–P1 2.304(2), Ru–P2 2.353(2), Ru–Cl 2.379(2), Ru–N 2.117(5), Ru–C3 1.861(6), C3–C4 1.418(9), C1–N 1.124(8), P1–Ru–P2 73.63(5), Cl–Ru–N 88.10(15), Cl–Ru–P1 154.75(6), Cl–Ru–P2 97.36(6), N–Ru–P1 96.81(15), N–Ru–P2 167.66(16), C3–Ru–P1 97.8(2), C3–Ru–P2 95.4(2), C3–Ru–Cl 106.6(2), C3–Ru–N 93.6(2).

equilibrium of the *cis*- and *trans*-dinuclear dications [$4a^{2+}$] with [5^+] is observed in ^{1}H- and ^{31}P{^{1}H}-NMR spectra (Scheme 1).

First attempts to further characterize cation [5^+] from a solution of [$4a^{2+}$][OTf$^-$]$_2$ in pure CH_3CN by positive-ion low-temperature fast atom bombardment mass spectrometry (LT-FAB-MS) [13] and field desorption (FD) MS failed. Besides other fragments only the solvent-free ion [(κ^2-dtbpm)ClRu=CH–CH=C(CH$_3$)$_2$]$^+$

was detected. Even the 'soft' electrospray ionization (ESI) led to similar results. However, LT-FAB-MS with a CH_2Cl_2 solution of [$4a^{2+}$][OTf$^-$]$_2$ and stoichiometric amounts of CH_3CN resulted in detection of [(κ^2-^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)ClRu=CH–CH=C(CH$_3$)$_2$(CH$_3$CN)]$^+$ in the gas phase, as clearly apparent from the observed isotopic pattern (Fig. 2).

From a CH_2Cl_2–Et$_2$O–CH$_3$CN solution of [$4a^{2+}$]-[OTf$^-$]$_2$ at -20°C we were able to obtain crystals of [5^+][OTf$^-$] suitable for X-ray diffraction. The molecular geometry of cation [5^+] is displayed in Fig. 3. Violet crystals with dimensions $0.08 \times 0.20 \times 0.32$ mm^3, $C_{25}H_{49}ClF_3NO_3P_2RuS·CH_2Cl_2$, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.9749(2)$, $b = 23.5202(2)$, $c = 16.1425(1)$ Å, $\beta = 100.036(1)$°, $V = 3729.3(1)$ Å^3, $D_{calc} = 1.397$ g cm^{-3}, $2\theta_{max} = 55$°, radiation Mo–K$_\alpha$, $\lambda = 0.71073$ Å, 0.3°. ω-Scans with CCD area detector, $T = 200(2)$ K, 38 847 reflections measured, 8536 unique, 6563 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space, $\mu = 0.82$ mm^{-1}, $T_{min} = 0.81$, $T_{max} = 0.95$, structures solved by Patterson method and refined against F^2 with a full matrix least squares algorithm using the SHELXTL-PLUS (5.10) software package, 384 parameters refined, hydrogen atoms were treated using appropriate riding models except for H3 and H4, which were refined isotropically, final residual values $R(F) = 0.073$, $wR(F^2) = 16.9$ for observed reflections, residual electron density from -1.31 to 1.37 e Å^{-3}.

The ruthenium center of [5^+] is in a square pyramidal ligand environment, with the P atoms of the κ^2-dtbpm, the chloro and acetonitrile ligands in the basal plane and the carbene moiety in the apical position, nearly bisecting the P1–Ru–P2 angle. As in solution, the triflate anion does not coordinate to the metal center in the solid state.

Complex [5^+][OTf$^-$] efficiently polymerizes norbornene in CH_2Cl_2 at ambient temperature. It seems reasonable to assume that cation [5^+] initiates ROMP by exchange of the acetonitrile by the olefinic substrate. However, exclusion of the dinuclear dication [$4a^{2+}$] as a second ROMP initiator is not possible at this point, because it is also present in CH_2Cl_2 solution at ambient temperature.

To get some insight into the electronic structures and energetics of our systems, density functional theory (DFT) calculations (B3LYP/LANL2DZ) were carried out on the model cations 6^+, 7^+ and 8^+ [14]. As expected, the coordination of CH_3CN to 6^+ to form 7^+ in the gas phase is found to be quite exothermic (169 kJ mol^{-1}) at this level of theory.

6^+

7^+

8^+

9^+
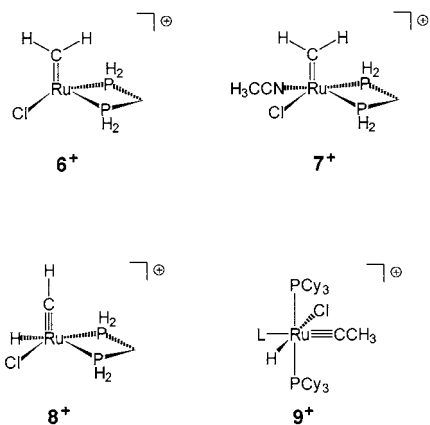
Different from cationic carbyne hydrido systems [9^+] of Werner et al. [15], where the carbene cation isomers cannot be detected, our complex [5^+] does not rearrange to a carbyne hydrido complex. This experimental observation is corroborated by a computational energy difference of 123 kJ mol^{-1} between models 6^+ and 8^+ in favor of the former.

In summary, the relevance of cationic solvent-coordinated monomeric ruthenium(II)carbenes [(κ^2-dtbpm)-ClRu=CHR(solv)]$^+$ in olefin metathesis catalyzed by our complexes has become clearer. Distinct differences compared to complexes with a *trans*-phosphine stereochemistry are apparent. Our results promise potential for tuning the catalytic properties of these systems by modifying the ligand set, the counterion and the carbene moiety.

3. Experimental

All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. NMR spectra were recorded using a Bruker DRX 500 spectrometer. Abbreviations used are: s = singlet, d = doublet, 'd' = pseudodoublet, t = triplet and 'qu' = pseudoquartet. A JEOL JMS-700 sector instrument equipped with a Xenon FAB gun was used for LT-FAB-MS. Complex [$4a^{2+}$][OTf$^-$]$_2$ was synthesized according to published procedures [11] [12].

NMR characterization of [5^+][OTf$^-$]: In a screw cap NMR tube 5.4 mg (4.1 μmol) [{(κ^2-dtbpm)-Ru=CH–CH=C(CH$_3$)$_2$}$_2$(μ_2-Cl)$_2$](OTf)$_2$ ([$4a^{2+}$][OTf$^-$]$_2$) are dissolved in 0.5 ml CD$_2$Cl$_2$ and treated with 0.6 μl (11.5 μmol, 2.8 eq) CH$_3$CN at ambient temperature. ^{1}H-NMR (CD$_2$Cl$_2$, 500.1 MHz, $T = 213$ K): $\delta = 1.14$ ('d', 9H, C(CH_3)$_3$), 1.31 ('d', 9H, C(CH_3)$_3$), 1.45 ('d', 9H, C(CH_3)$_3$), 1.48 ('d', 9H, C(CH_3)$_3$), 1.66 (s, 6H, CH=C(CH_3)$_2$), 2.55 (s, 3H, CH_3CN), 4.08 (t, ^2J(H,P) = 9.2 Hz, 2H, PCH_2P'), 8.34 (d, ^3J(H,H) = 10.4 Hz, 1H, CH=C(CH$_3$)$_2$), 16.68 ('qu', ^3J(H,H) = 10.4 Hz,

^3J(H,P) = 9.8 Hz, 1H, Ru=CH); ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, 202.5 MHz, $T = 213$ K) $\delta = 13.2$ (d, ^2J(P,P') = 36.0 Hz, PCH$_2$P'), 28.3 (d, ^2J(P,P') = 36.0 Hz, PCH$_2P'$). ^{1}H and ^{31}P{^{1}H}-NMR of the same sample at $T = 298$ K show the presence of cations *cis*- and *trans*-[$4a^{2+}$] [12] and [5^+].

4. Supplementary material

Crystallographic data for the structure reported here has been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 138352. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. Di-Mare, M. O'Regan, J. Am. Chem. Soc. 112 (1990) 3875.
[2] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974.
[3] (a) A. Fürstner (Ed.), Topics in Organometallic Chemistry: Alkene Metathesis in Organic Synthesis, vol. 1, Springer, Berlin, 1998. (b) M. Schuster, S. Blechert, Angew. Chem. 109 (1997) 2124; Angew. Chem. Int. Ed. Engl. 36 (1997) 2037.
[4] P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.
[5] J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus Jr., A.H. Hoveyda, J. Am. Chem. Soc. 121 (1999) 791.
[6] (a) Z. Wu, S.T. Nguyen, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 117 (1995) 5503. (b) E.L. Dias, S.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 119 (1997) 3887.
[7] S. Chang, L. Jones II, C. Wang, L.M. Henling, R.H. Grubbs, Organometallics 17 (1998) 3460.
[8] (a) E.L. Dias, R.H. Grubbs, Organometallics 17 (1998) 2758. (b) A. Fürstner, K. Langemann, J. Am. Chem. Soc. 119 (1997) 9130.
[9] (a) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674. (b) T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Angew. Chem. 111 (1999) 2573; Angew. Chem. Int. Ed. Engl. 38 (1999) 2416. (c) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247. (d) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953.

[10] T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. 110 (1998) 2631; Angew. Chem. Int. Ed. Engl. 37 (1998) 2490; Corrigendum: Angew. Chem. 111 (1999) 277; Angew. Chem. Int. Ed. Engl. 38 (1999) 262.

[11] S.M. Hansen, F. Rominger, M. Metz, P. Hofmann, Chem. Eur. J. 5 (1999) 557.

[12] S.M. Hansen, M.A.O. Volland, F. Rominger, F. Eisenträger, P. Hofmann, Angew. Chem. 111 (1999) 1360; Angew. Chem. Int. Ed. Engl. 38 (1999) 1273.

[13] (a) J.H. Gross, Rapid Commun. Mass Spectrom. 12 (1998) 1833. (b) H. Wang, W. Huang, Y. Lee, L. Chei, P. Huang, J. Shiea, J. Am. Soc. Mass Spectrom. 9 (1998) 1168. (c) J.H. Gross, S. Giesa, W. Krätschmer, Rapid Commun. Mass Spectrom. 13 (1999) 815.

[14] (a) For the DFT calculations the empirically parametrized B3LYP method within the GAUSSIAN-98 (Revision A.5) package was used: GAUSSIAN-98, Revision A.5, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, 1998. (b) All structures were geometry optimized and represent true minima on the potential energy surface (NIMAG = 0).

[15] W. Stüer, J. Wolf, H. Werner, P. Schwab, M. Schulz, Angew. Chem. 110 (1998) 3603; Angew. Chem. Int. Ed. Engl. 37 (1998) 3421.