ChemComm

Unusual formation of a hex-3-ene-1,5-diyne-3-yl ligand from a buta-1,3-diyne in the $Cp^*_2TiCl_2$–Mg system

Paul-Michael Pellny,[a] Frank G. Kirchbauer,[a] Vladimir V. Burlakov,[a] Anke Spannenberg,[a] Karel Mach[b] and Uwe Rosenthal*[a]

[a] *Institut für Organische Katalyseforschung an der Universität Rostock, Buchbinderstr. 5 - 6, D-18055 Rostock, Germany. E-mail: Uwe.Rosenthal@ifok.uni-rostock.de*

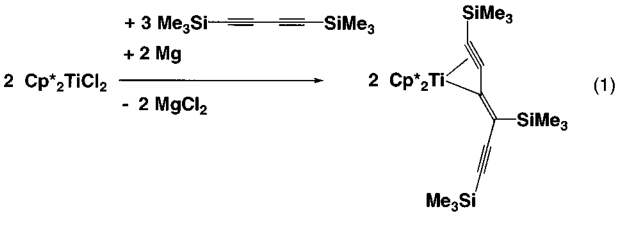
[b] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic*

Received (in Cambridge, UK) 20th August 1999, Accepted 10th November 1999

The reaction of [$Cp^*_2TiCl_2$] with equimolar amounts of magnesium in the presence of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ yields the first early transition metal η^3-enyne complex [$Cp^*_2Ti\{\eta^3\text{-}Me_3SiC_3{=}C(C{\equiv}CSiMe_3)SiMe_3\}$] 1 which is suggested to be an intermediate in early transition metal catalysed oligomerization reactions of alk-1-ynes.

Some years ago we found that $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ is cleaved[1a] by the [Cp_2TiCl_2]–Mg system in THF to give the dimeric titanium(III) complex [$\{Cp_2Ti(C{\equiv}CSiMe_3)\}_2$],[1] and, that in the presence of the [$Cp^*_2TiCl_2$]–Mg system with an excess of Mg, the paramagnetic [$\{Cp^*_2Ti(C{\equiv}CSiMe_3)_2\}\{MgCl(THF)\}$] tweezer-type compound was obtained.[2a] We have also described that when the diacetylide [$Cp^*_2Ti(C{\equiv}CSiMe_3)_2$] is irradiated by UV light it undergoes the reverse reaction, with a coupling of the acetylides to give the titanacyclopropene complex [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2{-}C{\equiv}CSiMe_3)$].[3a] This complex also forms from the above mentioned reduction of [$Cp^*_2TiCl_2$] in the presence of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ with an equimolar amount of Mg.[3b]

Here, we report the synthesis and the structure of the paramagnetic d^1 complex [$Cp^*_2Ti\{\eta^3\text{-}Me_3SiC_3{=}C(C{\equiv}CSiMe_3)SiMe_3\}$] **1** which arises from the [$Cp^*_2TiCl_2$]–Mg–$Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ system using the molar ratios indicated in eqn. (1).



1

Compound **1** is thus the third product, in addition to the above-mentioned titanacyclopropene and the tweezer complex, which has been obtained from this system under different stoichiometric conditions. The structure of the paramagnetic complex **1** was verified by elemental analysis, EPR, IR‡ and crystallography.

An X-ray crystal structure analysis of **1**§ (Fig. 1) revealed that a bent permethyltitanocene binds an unusual carbyl, 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl, in an η^3-mode. The Ti–C2, Ti–C3 and C2–C3 distances are consistent with a η^2-bonded triple bond and the Ti–C1 distance with a Ti–C σ bond. The alkenyl double bond is slightly elongated and the remote triple bond does not differ from the analogous bond in [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2{-}C{\equiv}CSiMe_3)$].[3a] The entire ligand moiety is nearly planar with the sums of the valence angles around the atoms C1 and C18 both being 360° and the silylalkynyl group is almost linear. The bite angle Cp1–Ti–Cp2 of nearly 140° (Cp = centroid of cyclopentadienyl ring) and the dihedral angle between the least-squares planes of the cyclopentadienyl rings of *ca.* 41° do not indicate a significant steric hindrance imposed by the hex-3-ene-1,5-diyne-3-yl ligand.

The solution EPR spectrum of **1** consists of a single line at $g = 1.991$ ($\Delta H = 1.7$ G). The absence of low-intensity satellites due to the interaction of d^1 electron with ^{49}Ti and ^{47}Ti isotopes ($I_N = 7/2$ and $5/2$, respectively) indicates that the unpaired electron is largely delocalized over the hex-3-ene-1,5-diyne-3-yl ligand. EPR measurements of the reacting mixtures showed the following succession of formed paramagnetic species: [Cp^*_2TiCl], [$\{Cp^*_2Ti(C{\equiv}CSiMe_3)_2\}\{MgCl(THF)\}$] and **1**.

Similar 1,4-substituted η^3-butenyne ligands coordinated to transition metals are known for *e.g.* Ru,[4a–d] Os,[4e] W[4f] and Fe,[4g,h] and their molecular parameters are essentially similar to those of the hex-3-ene-1,5-diyne-3-yl ligand in **1**. However, none of the known η^3-butenyne complexes is paramagnetic. Thus, compound **1** is the first early transition metal η^3-enyne complex and also the first paramagnetic complex of this type. While the above η^3-butenyne complexes are in many cases suggested to be intermediates in the catalysed dimerisations of alk-1-ynes, in early transition metal-based systems such intermediates like **1** have not yet been observed.[2b,5] Additionally, no such complex has been formed previously by cleavage of the central C–C single bond in a 1,3-butadiyne unit and coupling of the formed acetylide fragment with another buta-1,3-diyne.

The mechanism for the formation of complex **1** is yet not clear. On the basis of the starting materials {[$Cp^*_2TiCl_2$], Mg, $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$}, the intermediacy of [$Cp^*_2TiCl$] and

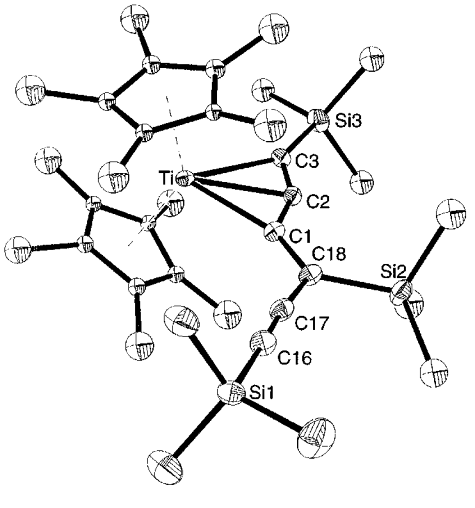


Fig. 1 Crystal structure of **1** with 30% probability level thermal ellipsoids. Hydrogen atoms and disordered groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–C2 2.302(4), Ti–C3 2.471(4), C2–C3 1.250(5), Ti–Cl 2.234(4), C1–C2 1.386(5), C1–C18 1.362(5), C16–C17 1.211(5), C17–C18 1.429(5); Si1–C16–C17 177.3(4), C16–C17–C18 173.2(4).

isolated products of this system {[{$Cp^*{}_2Ti(C{\equiv}CSiMe_3)_2$}{MgCl(THF)}], [$Cp^*{}_2Ti(\eta^2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)$] as well as other compounds which can reasonably be expected in the reaction mixture {*e.g.* [$Cp^*{}_2Ti(C{\equiv}CSiMe_3)_2$], [$Cp^*{}_2Ti(C{\equiv}CSiMe_3)$] and [$Mg(C{\equiv}CSiMe_3)Cl(THF)_n$] a variety of reaction pathways are possible.

In analogous zirconocene chemistry, Negishi and coworkers showed that [Cp_2ZrCl_2] reacts with 3 equiv. of the acetylides $LiC{\equiv}CR$ to yield, after hydrolysis, the enynes $RCH{=}CH\text{–}C{\equiv}CR$.[6] The mechanism of their formation suggested the presence of the 'ate' intermediates [{$Cp_2Zr(C{\equiv}CR)_3$}Li] and [{$Cp_2Zr(C{\equiv}CR)(\eta^2\text{-}RC_2\text{–}C{\equiv}CR)$}Li] which, however, were not isolated. Very recently this mechanism has been supported by Choukroun and Cassoux who succeeded in isolating and determining the crystal structure of the 'ate' complex [{$Cp_2Zr(C{\equiv}CPh)(\eta^2\text{-}PhC_2\text{–}C{\equiv}CPh)$}Li], generated from the reaction of [Cp_2ZrCl_2] with 3 equiv. of $LiC{\equiv}CR$.[7]

By taking into account these results one could assume that the isolated products, the titanacyclopropene [$Cp^*{}_2Ti(\eta^2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)$][3] or, alternatively, the tweezer compound [{$Cp^*{}_2Ti(C{\equiv}CSiMe_3)_2$}{MgCl(THF)}],[2] react with [$Cp^*{}_2Ti\text{–}C{\equiv}CSiMe_3$] or [$ClMg\text{–}C{\equiv}CSiMe_3$], resulting in the 'ate' complex [$Cp^*{}_2Ti(C{\equiv}CSiMe_3)(\eta^2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)$]$^-$[Y]$^+$ {[Y]$^+$ = [$Cp^*{}_2Ti$]$^+$ or [MgCl]$^+$}, both being similar to what has been discussed by Negishi and coworkers as non-isolable intermediates and to species which have recently been characterized by Choukroun and Cassoux. Since titanium is much less electropositive than zirconium and provides a considerably smaller coordination sphere, the diyne is inserted into the Ti–C acetylide bond (inter- or intra-molecularly) and complex **1** is formed.

Notes and references

† *General procedure* for the preparation of **1**: a suspension of [$Cp^*{}_2TiCl_2$] (792 mg, 2.04 mmol), Mg (48 mg, 1.97 mmol) and bis(trimethylsilyl)buta-1,3-diyne (593 mg, 3.05 mmol) in thf (10 mL) was stirred under argon for 5 days at 60 °C. The solution changed to dark-brown and all magnesium was dissolved. After filtration and standing at −78 °C for one day brown crystals formed which were separated and dried in vacuum to give 560 mg (46%) of **1**: mp 202–203 °C (decomp.). *m/z* 610 (M^+).

‡ *Spectral data* for **1**: EPR (THF, 220 °C): $g = 1.991$, $\Delta H = 1.7$ G; IR(Nujol)/cm^{-1}: 2109 ν(C≡C) (uncoordinated triple bond), 1868 cm^{-1} ν(C≡C) (coordinated triple bond). Anal. $C_{35}H_{57}Si_3Ti$ (M = 610.0): calc.: C, 68.92; H, 9.42. Found: C, 68.71; H, 9.32%.

§ *X-Ray structure analysis* of **1**: STOE-IPDS diffractometer, graphite monochromated Mo-Kα radiation, solution of structures by direct methods (SHELXS-86: G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467), refinement with full-matrix least-square techniques against F^2 (SHELXL-93: G. M. Sheldrick, University of Göttingen, Germany, 1993), triclinic, space group $P\bar{1}$; $a = 10.034(2)$, $b = 11.487(2)$, $c = 16.326(3)$ Å, $\alpha = 98.92(3)$, $\beta = 92.62(3)$, $\gamma = 90.55(3)°$, $V = 1856.8(6)$ Å^3, $Z = 2$, $D_c = 1.091$ g cm^{-3}; 5556 reflections measured, 5556 were independent of symmetry and 4084 were observed [$I > 2\sigma(I)$], $R = 0.060$, wR^2 (all data) = 0.161, 326 parameters. All atoms of the Cp* groups and the methyl groups at Si2 and Si3 are disordered. The atoms of the disordered fragments were refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. CCDC 182/1480. See http://www.rsc.org.suppdata/cc/1999/2505/ for crystallographic data in .cif format.

1 (*a*) U. Rosenthal and H. Görls, *J. Organomet. Chem.*, 1992, **439**, C36; (*b*) G. L. Wood, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1989, **28**, 382.

2 (*a*) S. I. Troyanov, V. Varga and K. Mach, *Organometallics*, 1993, **12**, 2820; (*b*) V. Varga, L. Petrusová, J. Cejka and K. Mach, *J. Organomet. Chem.*, 1997, **53**2, 251.

3 (*a*) F. G. Kirchbauer, Ph.D. Thesis, University of Rostock, 1999; (*b*) P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, W. Baumann, A. Spannenberg and U. Rosenthal, *J. Am. Chem. Soc.*, 1999, **121**, 8313.

4 (*a*) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa and F. Zanobini, *Organometallics*, 1996, **15**, 272; (*b*) C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani and A. Albinati, *J. Am. Chem. Soc.*, 1991, **113**, 5453; (*c*) G. Jia, A. L. Rheingold and D. W. Meek, *Organometallics*, 1989, **8**, 1379; (*d*) D. C. Liles and P. F. M. Verhoeven, *J. Organomet. Chem.*, 1996, **522**, 33; (*e*) J. Gotzig, H. Otto and H. Werner, *J. Organomet. Chem.*, 1985, **287**, 247; (*f*) A. K. McMullen, J. P. Selegue and J.-G. Wang, *Organometallics*, 1991, **10**, 3421; (*g*) M. Akita, S. Sugimoto, M. Terada and Y. Moro-oka, *J. Organomet. Chem.*, 1993, **447**, 103; (*h*) D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3151 and references therein.

5 (*a*) M. Horáček, I. Císařová, J. Čejka, J. Karban, L. Petrusová, and K. Mach, *J. Organomet. Chem.*, 1999, **577**, 103; (*b*) H. Akita, H. Yasuda and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 480; (*c*) A. D. Horton, *J. Chem. Soc., Chem. Commun.*, 1992, 185; (*d*) M. Yoshida and R. F. Jordan, *Organometallics*, 1997, **16**, 4508; (*e*) V. Varga, L. Petrusová, J. Čejka, V. Hanuš and K. Mach, *J. Organomet. Chem.*, 1996, **509**, 235; (*f*) P. Štěpnička, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta and K. Mach, *Organometallics*, 1999, **18**, 4869.

6 K. Takagi, C. J. Rousset and E. Negishi, *J. Am. Chem. Soc.*, 1991, **113**, 1440.

7 R. Choukroun and P. Cassoux, *Acc. Chem. Res.*, 1999, **32**, 494.

Commnication 9/06777I