Journal of Organometallic Chemistry, 438 (1992) 83–87
Elsevier Sequoia S.A., Lausanne
JOM 22809

Alpha-metalated diazoalkanes: synthesis of yttrium, lutetium and ytterbium trimethylsilyldiazomethyl complexes

Helmuth Siebald, Michèle Dartiguenave and Yves Dartiguenave
Laboratoire de Chimie Inorganique, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex (France)

(Received February 14, 1992)

Abstract

Reaction of $LiC(N_2)SiMe_3$ with $[MClCp^*_2]$ (M = Y, Lu, or Yb; Cp^* = pentamethylcyclopentadienyl) gives rise to the three new compounds $[M\{C(N_2)SiMe_3\}Cp^*_2(THF)]$ (M = Y, **1**; Lu, **2**; Yb, **3**) with a metal carbon σ bond. They are thermally sensitive hygroscopic solids which have been characterized by IR (for **1**, **2** and **3**) and ^1H NMR (for **1** and **2**) spectroscopy.

Diazoalkanes $RR'C(N_2)$ with various substituents R and R′ have been proven to be exceedingly useful in organic synthesis [1]. By comparison, metal-substituted diazoalkanes have been less investigated. Nevertheless, Na, Li, Mg, Hg, Sn diazoalkanes have been synthesized and used as diazo-transfer reagents [1]. Transition metal substituted diazoalkanes are even less known. Only Pd [2], Os [3], Rh [4], Ni [5] species have been prepared up to now and investigation of their chemical reactivity indicates that they behave as precursors of singlet carbene.

We report here the reactions of the lithium salt of trimethylsilyldiazoalkane with $[YClCp^*_2]$, $[LuClCp^*_2]$, and $[YbClCp^*_2]$ and show that they give rise to complexes with diazoalkane C-bonded to the transition metal. This is not unexpected, since Y and rare earth metals, although strongly electrophilic, give metal–carbon bonds when they react with lithium salts of organic moieties such as NaCp [6], $NaCp^*$ [7–9], $LiCH_3$ [10], $LiCH_2SiMe_3$ [11–13] and $LiCH(SiMe_3)_2$ [14]. However, the compounds are generally not stable and decompose readily [15].

$LiC(N_2)SiMe_3$ [16*] reacted for 30 min at −78°C with $YClCp^*_2$ prepared *in situ* by adding C_5Me_5Li to anhydrous YCl_3 in 30 ml THF. The temperature was then slowly increased to −25°C and the solution stirred at that temperature for 3 h. LiCl was filtered off. The temperature must be kept at −25°C during the whole synthesis in order to avoid decomposition. The yellow solution, concentrated *in*

Correspondence to: Dr. M. Dartiguenave.

* Reference number with asterisk indicates a note in the list of references.

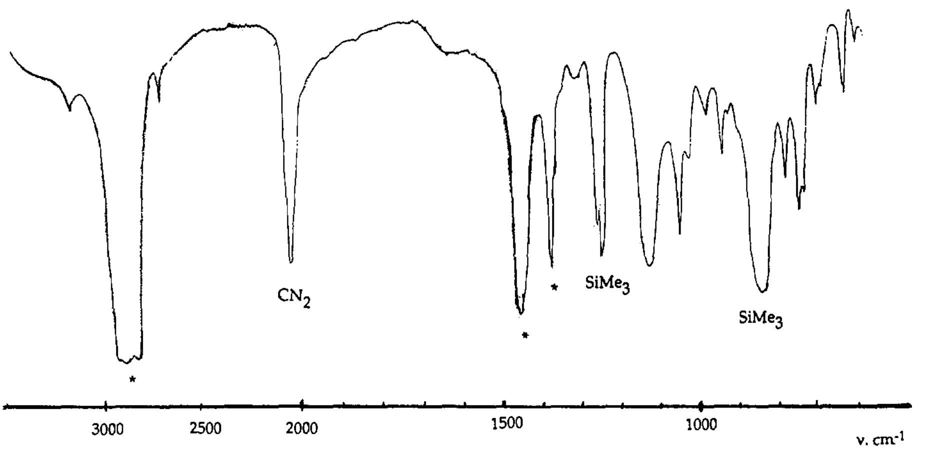


Fig. 1. Infrared spectrum (Nujol mull) of $[Cp_2^*Y\{C(N_2)SiMe_3\}(THF)]$ (1).

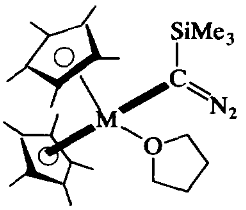
vacuo, gave a yellow oily material. Work up in ether, then in toluene, produced a yellow solution, which when kept overnight at −78°C gave a micro-crystalline air-sensitive powder. The compound was filtered, dried *in vacuo* and stored under argon [17].

Its IR spectrum (Fig. 1) Nujol mull, shows a strong $\nu(CN_2)$ at 2066 cm^{-1}, expected for C-coordinated $C(N_2)SiMe_3$. A slight high energy shift of this vibration is observed compared with the value of $HC(N_2)SiMe_3$ (2060 cm^{-1}), while low energy shifts (about 100 cm^{-1}) are reported when the diazoalkane is C-bonded to late transition metals. This agrees with the ionic character expected for the Y–C bond because of the electrophilicity of the electron-poor metal.

Bands arising from C_5Me_5 at 2719 cm^{-1} and $SiMe_3$ at 1275, 1246 and 844 cm^{-1} are also observed [18].

Coordinated THF is also apparent on the ^1H NMR spectrum (Fig. 2) from the triplet centred at 3.69 ppm (4 α-H) and a multiplet at 1.53 ppm (4 β-H) in the ratio 1 : 1. The singlet at 0.17 ppm is characteristic of the $SiMe_3$ group (9H). Two singlets are present in the range where the C_5Me_5 signal is expected, at 2.14 ppm (about 9H or 3Me) and 2.24 ppm (21H or 7Me). The spectrum is reproducible. Consequently, the dissymetry of the diazo-group may generate interactions with one of the Cp* ligands producing a slight high field shift for 3 of the Me groups. Such an effect has been observed previously in $[RhC(N_2)SiMe_3(PEt_3)_3]$ where the two phosphines are not magnetically equivalent in the solid [4b].

Thus a probable structure of the C-bonded trimethylsilyldiazomethyl complexes is as shown:



$M = Y^{3+}, Lu^{3+}, Yb^{3+}$

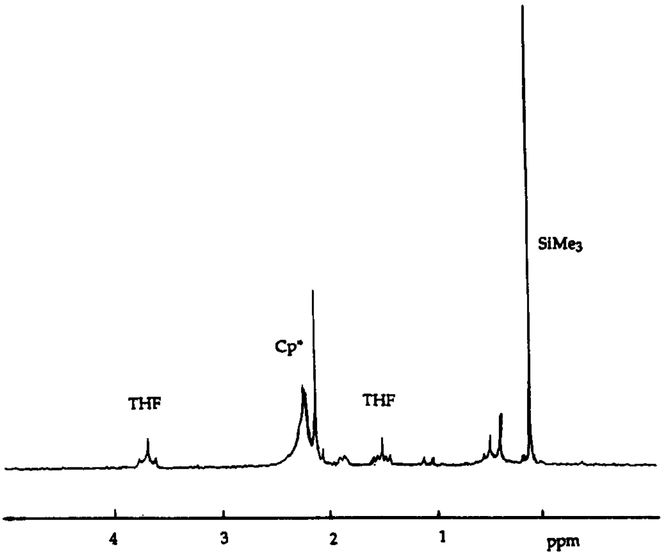


Fig. 2. ^{1}H NMR spectrum of [Cp$^*_2$Y{C(N$_2$)SiMe$_3$}(THF)] (1), in CD$_2$Cl$_2$, at 20°C. The low stability of 1 is illustrated by decomposition products in the range 0.2–1.2 ppm and at about 1.8 ppm.

The metal atom is located at the centre of a distorted tetrahedron formed by the two pentamethylcyclopentadienyl ligands, the diazo-carbon atom and the oxygen atom of the THF. Such a structure has been reported for [Cp$^*_2$LuCH$_2$SiMe$_3$(THF)] [19].

Compound **1** is unstable in solution at room temperature and decomposes into several unidentified species, as shown by the formation of three new signals in the SiMe$_3$ region on the ^{1}H NMR spectrum. A similar decomposition is observed when the solution is irradiated at 330 nm. This is not unexpected since, like lanthanide compounds, yttrium compounds cannot be stabilized through orbital interactions [20], as is usual for late transition metals, and observed for Rh and Ni C-bonded diazo-complexes.

Addition of tetramethylenediammine to the reaction mixture has no effect on the formation of **1**, which indicates that lithium was not trapped in the complex, as may happen in lanthanide chemistry [8,21].

Extending the reaction of LiC(N$_2$)SiMe$_3$ to [Cp$^*_2$LuCl] and [Cp$^*_2$YbCl] gives rise to [Cp$^*_2$Lu{C(N$_2$)SiMe$_3$}(THF)] (**2**), which is yellow and diamagnetic, and [Cp$^*_2$Yb{C(N$_2$)SiMe$_3$}(THF)] (**3**), which is dark red and paramagnetic; both are very air- and temperature-sensitive microcrystalline solids. Their IR spectra and the ^{1}H NMR spectrum of **2** [22*] are consistent with the formulations. They are less stable than **1**, both in solution and in the solid state [23*].

These reactions typify the Grignard-like reactivity of the lanthanide complexes as expected from the highly ionic character of the metal–carbon bonds.

Acknowledgements

This work was supported by the MEN (DRED) and CNRS (SDI). The Conselho Nacional de Desenvolvimento Cientifico e Tecnologico CNPq and the Department of Chemistry, Inorganic Chemistry Division of the Universidade Federal de Minas Gerais (Brazil) are gratefully acknowledged for financial support (HS).

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16 A solution of $LiC(N_2)SiMe_3$ (5.8 mmol) prepared from $HC(N_2)SiMe_3$ and LiBu in 10 ml of THF at -78°C just before use was added at that temperature to YCp_2^*Cl (5.74 mmol) in 30 ml THF.

17 A typical synthesis of $[Cp_2^*Y\{C(N_2)SiMe_3\}(THF)]$ (**1**): to a solution of 2.47 ml of C_5Me_5H (13.77 mmol) in 30 ml of THF were slowly added at -78°C, 8.6 ml of a 1.6 *M* solution of Li^nBu (13.76 mmol) in hexane. The temperature of the mixture was increased to 20°C and 1.12 g of YCl_3 (5.74 mmol) were added during 10 min. This suspension was then heated under reflux for 3 h, giving rise to $[YClCp_2^*]$ which was used *in situ*. To this solution, cooled to -78°C, was added 2.8 mmol of $LiCN_2SiMe_3$ [0.81 g (5.86 mmol.) of HCN_2SiMe_3 in 15 ml THF +3.7 ml of Li^nBu (1.6 *M* in hexane) (5.9 mmol) at -78°C, 25 min]. This suspension, protected from light, was stirred for 2 h at -78°C and then for 3 h at -25°C. Evaporation of the solvent under vacuum at -25°C and recrystallization from 20 ml of ether, then toluene gave **1** as a yellow powder, which was thermally sensitive and very hygroscopic. Yield: 60%. Anal. Found: C, 61.74; H, 8.7. $C_{28}H_{47}N_2OSiY$ calc.: C, 60.52; H, 9.0%.

18 The IR data are: **1**: 3177w, 2719w, 2066vs, 1303w, 1257vs, 1246vs, 1127vs, 1048s, 1021m, 974w, 936m, 918w, 844vs, 775m, 742m, 729m, 694w, 679w, 622m, 591w, 525m, 505m. **2**: 3183w, 2723w, 2069vs, 1302m, 1258vs, 1247vs, 1127s, 1048s, 1023s, 937w, 843vs, 776m, 742m, 729m, 693w, 621w, 600w, 536m, 503m. **3**: 3193w, 2723w, 2103vs, 1310s, 1258s, 1125s, 1078s, 1036s, 1022s, 969s, 930m, 860s, 840vs, 665m, 635m, 585m, 538w, 477m (vs = very strong, s = strong, m = medium, w = weak).

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22 The ^1H RMN spectrum of **2** is similar to **1**, but with more decomposition.

23 The experimental procedure used for the yttrium compound was extended to the lutetium and ytterbium species. $[Cp_2^*Lu\{C(N_2)SiMe_3\}(THF)]$: the reaction mixture obtained from the reaction of $LiC(N_2)SiMe_3$ and $[LuClCp_2^*]$ in THF at -78°C, gave rise, after filtration and work up at -25°C in

ether and toluene, to a yellow powder, which was thermally sensitive and very hygroscopic. No satisfactory elemental analysis could be obtained. Yield: 56%. IR: $\nu[C(N_2)]$: 2068 cm^{-1}, strong. ^1H NMR (CD_2Cl_2): 0.15 ppm ($SiMe_3$). $[Cp_2^*Yb\{C(N_2)SiMe_3\}(THF)]$: the reaction mixture obtained from the reaction of $LiC(N_2)SiMe_3$ on $YClCp_2^*$ in THF at −78°C, gave rise after filtration and work up and recrystallization at −25°C from ether and toluene to a red powder which was thermally sensitive and very hygroscopic. No satisfactory elemental analysis could be obtained. Yield: 52% IR: $\nu[C(N_2)]$: 2103 cm^{-1}.