Journal of Organometallic Chemistry, 288 (1985) C1—C5
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INSERTION OF CARBONYL COMPOUNDS INTO ACTINIDE—CARBON σ BONDS: REACTIVITY OF $[(Me_3Si)_2N]_2\overline{M{-}CH_2Si(Me)_2N}SiMe_3$

A DORMOND*, A. EL BOUADILI, A. AALITI and C. MOISE
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (U.A. 33), Faculté des Sciences, 6 bd Gabriel 21100 Dijon (France)

(Received February 13th, 1985)

Summary

The metallacycles $[(Me_3Si)_2N]_2\overline{M{-}CH_2Si(Me_2)N}SiMe_3$ (M = U, Th) were obtained in a quantitative one-step synthesis. Carbonyl compounds inserted into the actinide—carbon bond to give the six-membered metallacyles $[(Me_3Si)_2N]_2M{-}OC(RR')CH_2Si(Me_2)NSiMe_3$, which were identified by IR and NMR spectroscopy.

The four-membered metallacyles of thorium or uranium $[(Me_3Si)_2N]_2\overline{M{-}CH_2Si(Me_2)N}SiMe_3$ [1] have been obtained by γ-elimination of methane or hydrogen from $[(Me_3Si)_2N]_3MMe$ [2] or $[(Me_3Si)_2N]_3MH$ [3] at high temperature. As a consequence of the polarity of the actinide to carbon bond and of the ring strain in a four-membered metallacycle, these compounds are very reactive toward carbon monoxide, isocyanides, or cyanides [4].

The reactivity of the actinide—carbon σ bond of these metallacycles toward polar molecules suggested that they would have a rich organic chemistry. Although metal—carbon bond chemistry has been well developed for many elements hydrocarbyl-actinide [5] or lanthanide [6] chemistry has been little studied. In an effort to develop this area, we have studied the reactivity of the metallacycles toward C=O bonds.

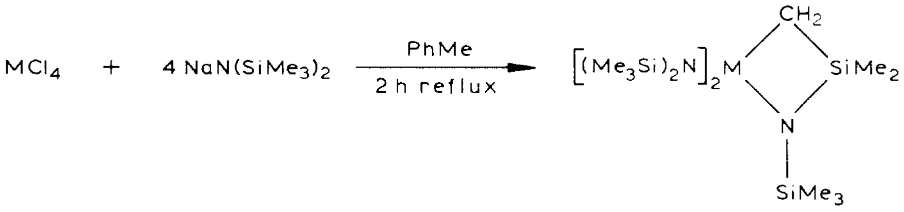
We describe below a quantitative one-step synthesis of the metallacycles and the facile insertion of ketones or aldehydes into the actinide—carbon bond of these compounds to give six-membered metallacycles containing both actinide—oxygen and actinide—nitrogen bonds.

The metallacycles 1a and 1b were obtained in high yield starting from MCl_4 and four equivalents of $NaN(SiMe_3)_2$ (or from $[(Me_3Si)_2N]_3MCl$ [2] and one $NaN(SiMe_3)_2$) in refluxing toluene.

---

*Author for correspondence.

0022-328X/85/$03.30



Yield > 95%

1a, M = U;

1b, M = Th)

Compounds **1a** and **1b** gave satisfactorily elemental analyses, and were found to be monomeric by cryoscopic measurement in benzene. They reacted with CO or $Me_3CC{\equiv}N$ to give quantitative yields of the insertion compounds previously described [4] (^1H and ^{13}C NMR data were identical with those previously reported). The structures of **1a** and **1b** are confirmed by their reaction with a stoichiometric amount of HCl (titrated THF solution), which gives a quantitative yield of the known $[(Me_3Si)_2N]_3MCl$ [2].

$$\mathbf{1a}, \mathbf{1b} \xrightarrow[\text{THF, RT}]{\text{HCl}} [(Me_3Si)_2N]_3MCl \quad \text{(yield 100\%)}$$

Surprisingly, the chemical shifts for the four sets of proton in the ^1H NMR spectrum of the paramagnetic **1a** and also to a lesser extend, that of the diamagnetic **1b**, showed major differences from those previously described*, and these differences cannot at present be explained. The shifts observed at 28° C for the four singlets respectively attributed to $N(SiMe_3)_2$, $NSiMe_3$, $SiMe_2$ and CH_2 protons, with literature values in parentheses, were: 1a: −13.03 (−23.3) + 9.62 (−9.90) + 11.23 (+ 2.08), −118.4 (−128.6); 1b: 0.35 (0.37), 0.33 (0.38), 0.63 (0.56), 0.92 (0.49). When the temperature was lowered, no significant broadening of the $NSiMe_3$ signal occurred, while the Me_2Si unit signal began to broaden at ca. −20° C and collapsed at −90° C, and in the limiting spectrum, at −105° C, the resonance of the two methyl group was split into two broad singlets at δ 35.1 and 18.3 ppm. The $N(SiMe_3)_2$ signal also began to broaden at −20° C and collapsed at −70° C; in the limiting spectrum, at −105° C, two sets of two broad singlets of equal intensity were present, at δ 6.5 and 1.5, −59.5 and −64 ppm, respectively. All the spectra changes were reversed when the temperature was raised and were independent of the concentration**.

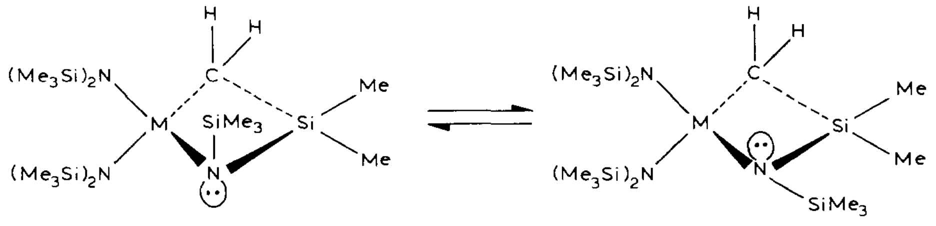
These observations were indicative of a slow $A \rightleftarrows B$ interconversion at low temperature***.

---

*The ^{13}C NMR spectra were identical with those previously reported.

**The behaviour of the CH_2 protons was not studied at low temperatures.

***No significant broadening at −80° C was observed by Andersen.



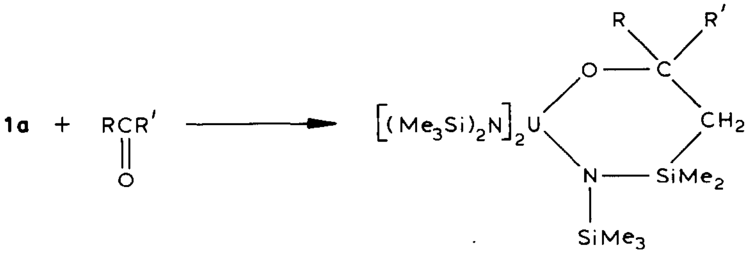
(A) (B)

The barrier to interconversion around the nitrogen atom can be estimated from the coalescence temperature of the signals of the Me groups in the $SiMe_2$ unit; viz. —90°C. The isotropic shifts of the resonances were found to obey an approximate Curie relationship (a plot of δ vs. i/T is linear) below the coalescence temperature, and extrapolation of the data yielded $\Delta\delta$ 1465 Hz and $\Delta G^{\neq}$, 31 ± 3 kJ mol^{-1}.

The splitting of each $N(SiMe_3)_2$ unit into two signals of equal intensity was indicative of restricted rotation around each nitrogen atom. This could arise from partial double bond character of the U—N bond due to interactions between the lone pair of the nitrogen atom and empty orbitals of the metallic nucleus. The barrier to rotation can be estimated from the coalescence temperature (—94°C) as $\Delta\nu$ 47.0 Hz, $\Delta G^{\neq}$ 34 ± 3 kJ mol^{-1}.

X-Ray crystallography would be required to reveal the full structural details, but we have so far been unable to isolate suitable single crystals.

When a stoichiometric amount of aldehyde or ketone was added to **1a** in benzene solution, a fast reaction occurred and the six-membered metallocycles **2** were obtained quantitatively. They were identified by NMR and IR spectroscopy*.



(**2a**, R = H, R' = CH_3; **2b**, R = H, R' = $C_5H_4FeC_5H_5$; **2c**, R = R' = CH_3; **2d**, R = R' = CD_3; **2e**, R = R' = C_6H_5; **2f**, R = CH_3, R' = $C_5H_4FeC_5H_5$)

The IR spectra (Nujol mulls) showed no carbonyl peaks in the range 1600—1700 cm^{-1}, but the stretching frequency of the uranium—oxygen single bond was present at around 480 cm^{-1} [8].

The ^1H NMR spectra of the insertion products are listed in Table 1. The

---

*A fast and probably analogous reaction occurred with esters, but the corresponding metallacycles could not be isolated.

paramagnetic shifts and the multiplicity of the signals provided important structural information.

Insertion into the uranium—methylenic carbon bond leads to marked deshielding of the methylene protons relative to those of the starting compound (ca. 140 ppm). The R and R′ protons were differently shifted relative to those in the initial diamagnetic ketones or aldehydes. The observed shift was closely related to the distance from the paramagnetic center, and it was thus possible to assign the signals of the *ortho*, *meta* and *para* phenyl protons and the α,α′ and β,β′ protons of the substituted cyclopentadienyl group. The $N(SiMe_3)_2$, $SiMe_2$ and CH_2 protons of **2a**, **2b** and **2c** were magnetically non-equivalent, as expected for chiral compounds.

The signals of $SiMe_2$ and CMe_2 protons of **2c** were assigned by comparison with the deutero compound **2d**. Both spectra showed a sharp singlet at 1.85 ppm corresponding to $SiMe_2$ protons, whereas the singlet at 1.20 ppm attributed to CMe_2 protons was absent for **2d**.

The broadening of the $N(SiMe_3)_2$ and phenyl signal of **2e** in the spectrum at 25°C seem to be due to restricted rotation of these groups in a sterically hindered molecule.

TABLE 1

^{1}H NMR SPECTRA OF THE SIX-MEMBERED METALLACYCLES 2 [a] (chemical shifts δ in ppm from tetramethylsilane; lw = linewidth)

Compound	$N(SiMe_3)_2$	$NSiMe_3$	$SiMe_2$	CH_2	R	R′
2a	−3.93 s(18)		5.56 s(8)	3.57 m [c] (1)		
R = H,		−14.97 s(9)			−3.6 [b]	11.92 d(3)
R′ = Me	−4.66 s(18)		3.12 s(8)	9.07 m [c] (1)		
2b	−3.78 s(18)		2.40 s(3)	2.42 m [c] (1)		
R = H,		−16.11 s(9)			−0.97 m(1)	2.40 s(5)
R′ = Fc	−4.77 s(18)		9.17 s(3)	10.59 m [c] (1)		α,α′: 0.6 m(1), 1.20 m(1) β,β′: 3.06 m(1), 3.20 m(1)
2c R = R′ = Me	−4.98 s(30)	−13.20 s(9)	1.85 s(6)	6.20 s(2)		1.20 s(6)
2d R = R′ = CD_3	−5.02 s(30)	−13.25 s(9)	1.84 s(6)	6.19 s(2)		
2e R = R′ = C_6H_5	−7.78 br(36) lw ≃75 Hz	−16.72 s(9)	3.77 s(6)	6.65 br(2) lw ≃20 Hz	*ortho*: 19.6 br(4); *meta-para*: 7.0 br(6 Hz) lw ≃ 350 Hz	
2e [d]	−6.74 s(36)	−14.74 s(9)	3.70 s(6)	6.23 s(2)	*ortho*: 16.97 br(4); *meta* 6.32 m(4) lw ≃40 Hz; *para* 6.23 t(2)	
2f	−4.56 s(18)		4.01 s(6)	3.32 d(1)		
R = Me,		−13.88 s(9)			−0.85 s(3)	2.85 s(5)
R′ = Fc	−6.23 s(18)		14.22 s(6)	8.08 d [e] (1)		α,α′: −0.20 m(1), −0.34 m(1) β,β′: 1.80 m(1), 109 m(1)

[a] Recorded on JEOL FX 100 or Brucker 400W in C_6D_6. [b] Detected by homodecoupling study. [c] Slightly broadened signals. [d] Recorded at 70°C. [e] *J* 14.6 Hz.

The high reactivity of the carbon—actinide bond of the four-membered metallacycles can be utilized in a large range of reactions, and further investigations along these lines are in progress.

References

1 S.J. Simpson, H.W. Turner and R.A. Andersen, Inorg. Chem., 20 (1981) 2991.
2 H.W. Turner, R.A. Andersen, A. Zalkin and D.H. Templeton, Inorg. Chem., 18 (1979) 1221.
3 H.W. Turner, S.J. Simpson and R.A. Andersen, J. Amer. Chem. Soc., 101 (1979) 7727.
4 S.J. Simpson and R.A. Andersen, J. Amer. Chem. Soc., 103 (1981) 4063.
5 (a) P.J. Fagan, J.M. Manriquez, T.J. Marks, in T.J. Marks, R.D. Fischer (Eds.), Organometallics of the *f* Elements, D. Reidel Publishing, Dordrecht, 1979, chaoter 4; (b) T.J. Marks, R.D. Ernst in G.W. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, chapter 21; (c) K.G. Molloy and T.J. Marks, J. Amer. Chem. Soc., 106 (1984) 7051; (d) G. Paolucci, G. Rossetto, P. Zanella, K. Yünlu and R.D. Fischer, J. Organomet. Chem., 272 (1984) 363; (e) A. Dormond, A. El Bouadili and C. Moise, J. Chem. Soc., Chem. Commun., (1984) 749.
6 (a) See also 5b; (b) P.L. Watson, J. Amer. Chem. Soc., 104 (1982) 337; J. Amer. Chem. Soc., 105 (1983) 6491; J. Chem. Soc., Chem. Commun., (1983) 276; (c) W.J. Evans, A.L. Wayda, W.E. Kunter and J.L. Atwood, J. Chem. Soc., Chem. Commun., (1981) 706 and refs. therein.
7 P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam and T.J. Marks, J. Amer. Chem. Soc., 103 (1981) 6650.
8 A. Dormond, B. Belkalem and R. Guilard, unpublished results.