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REACTIVITY OF THE METAL—CARBON BONDS IN THE METALLACYCLES $[(Me_3Si)_2N]\underline{MCH_2Si(Me)_2N}SiMe_3$*

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Summary

The metal—carbon bonds of the four-membered metallacycles $[(Me_3Si)_2N]_2\underline{MCH_2SiMe_2N}SiMe_3$ ($M \equiv U, Th$) reacts with carbonyl compounds to give the six-membered metallacycles $[(Me_3Si)_2N]_2\underline{M{-}OC(RR')\text{-}CH_2SiMe_2N}SiMe_3$. Acidic hydrogens reacts under mild conditions. Pyridine gives the *ortho*-metallated products from sp^2 activation, and metal hydrides give stable binuclear compounds with an isocarbonyl linkage whereas cyclopentadienes cleave the metal—nitrogen bond providing biscyclopentadienyl four-membered metallacycles.

1. Introduction

The actinide—carbon bond of the four-membered metallacycles $(Me_3Si)_2N_2MCH_2SiMe_2NSiMe_3$ ($M \equiv U, Th$), 1 [1, 2] show an enhanced reactivity due to the ring strain inherent in the four-membered ring and are known to insert 1- 2 dipolar organic molecules [2] and to react with hydrogen to yield a hydride derivative [1].

We report some new reactions of these metallacycles toward carbonyl compounds and toward "acidic" hydrogens in O—H, C—H, N—H and M—H bonds.

2. Experimental details

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

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3. Results and discussion

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}.

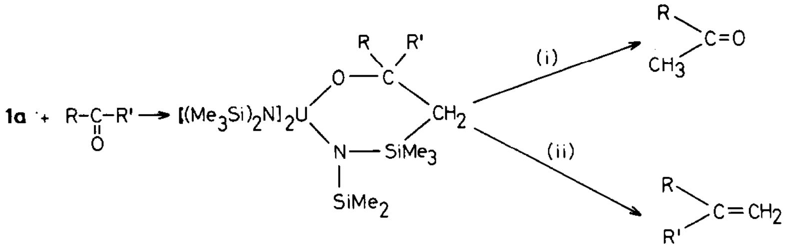
The ^1H NMR spectra of the insertion products are listed in Table 1. The paramagnetic shifts and the multiplicity of the signals provided important information.

Insertion into the uranium–methylenic carbon bond leads to marked deshielding of the methylene protons relative to those of the starting compound (about 140 ppm). The R and R$'$ protons were shifted differently relative to those in the initial diamagnetic carbonyl compounds. The observed shift was closely related to the distance from the paramagnetic center, and it was thus possible to assign 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 **2f** were nonequivalent, 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 the $SiMe_2$ 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.

Cleavage of the metallacycles **2** by aqueous HCl or a saturated solution of NH_4F afforded the corresponding vinyl compounds (from aldehydes or ketones) or the methylketones (from esters). These reactions are under investigation and the results will be published in a future paper.



2a - 2h

a, $R \equiv H$, $R' \equiv CH_3$; b, $R \equiv H$, $R' \equiv C_5H_4FeC_5H_5$; c, $R \equiv R' \equiv CH_3$; d, $R \equiv R' \equiv CD_3$; e, $R \equiv R' \equiv C_6H_5$; f, $R \equiv CH_3$, $R' \equiv C_5H_4FeC_5H_5$; g, $R \equiv C_6H_5$, $R' \equiv OEt$; h, $R \equiv C_5H_4FeC_5H_5$, $R' \equiv OEt$.

(i) $R' \equiv OEt$, $R \equiv C_6H_5$ or $C_5H_4FeC_5H_5$; (ii) R or $R' \equiv$ H, aryl, alkyl.

As shown in Scheme 1 the actinide to carbon σ-bonds undergo rapid protolysis [3]; thus **1** reacted rapidly with tertiary alcohols or sterically hindered phenols to produce alkoxy or aryloxy compounds, **3a, b**. H^1 NMR (C_6D_6) of **3a**, $R \equiv Bu^t$ (25 °C): δ −1.92 (s, 54 H, Me_3Si), 2.75 (s, 9H, Bu^t)

TABLE 1

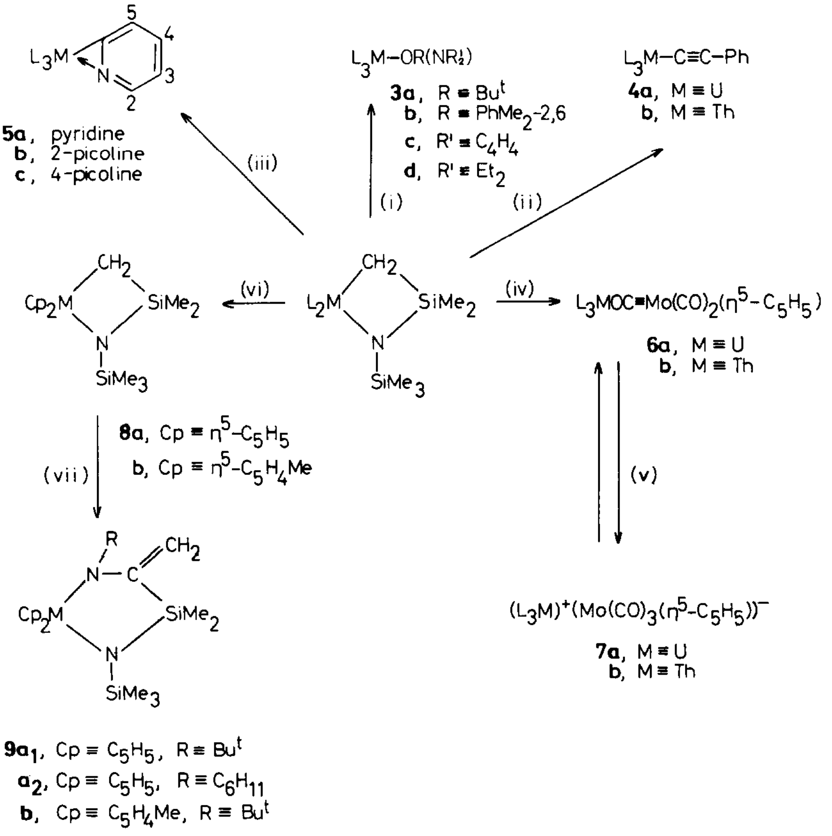
^{1}H NMR Data for the six-membered metallacycles 2^{a,b}

Compound	*N(SiMe$_3$)$_2$*	*NSiMe$_3$*	*SiMe$_2$*	*Protons*		
				CH$_2$	*R*	*R′*
2a	−3.93 s(18)		5.56 s(8)	3.57 m^{d} (1)		
R ≡ H, R′ ≡ Me		−14.97 s(9)			−3.6^{c}	11.92 d(3)
	−4.66 s(18)		3.12 s(8)	9.07 m^{d} (1)		
2b	−3.78 s(18)		2.40 s(3)	2.42 m^{d} (1)		
R ≡ H, R′ ≡ Fc		−16.11 s(9)			−0.97 m(1)	2.40 s(5)
	−4.77 s(18)		9.17 s(3)	10.59 m^{d} (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)	−13.26 s(9)	1.84 s(6)	6.19 s(2)		
2e R ≡ R′ ≡ C$_6$H$_5$	−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^{e}	−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, R′ ≡ F$_c$		−13.88 s(9)			−0.85 s(3)	2.85 s(5)
	−6.23 s(18)		14.22 s(6)	8.08 d^{f} (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 Brücker 400 W in C_6D_6. [b] s, singlet; d, doublet; t, triplet; m, multiplet; br, broad signal; lw, line width. [c] Detected by homodecoupling study. [d] Slightly broadened signals. [e] Recorded at 70 °C. [f] J = 14.6 Hz.

and of 3b, R ≡ $PhMe_2$-2,6 (70 °C): δ −5.58 (s, 54H, Me_3Si), 5.69 (s, 6H, Me_3), 9.04 (d, 2H, *m*-Ph), 8.70 (t, 1H, *p*-Ph). In the same manner, 1 reacts immediately at room temperature with secondary amines to give amido compounds, 3c, d. H^1 NMR (C_6D_6) of 3c, R ≡ C_4H_4: δ −2.35 (s, 54H, Me_3Si), −8.99 (s, 2H), −49.75 (s, 2H) and of 3d, R ≡ Et_2: δ −2.80 (s, 54H, Me_3Si), −1.07 (broad triplet, 6H, CH_3), 5.55 (broad, 4H, CH_2).

With phenylacetylene in benzene solution, a slow reaction occurred and the extremely sensitive and poorly stable hydrocarbyls 4 were obtained quantitatively. These compounds could not be isolated in a pure state, precluding elemental analysis and molecular weight measurements. Nevertheless, their structure was established unambiguously by H^1 NMR spectroscopy. 4a, (C_6D_6): δ −2.18 (br, lw = 33 Hz, 54H, Me_3Si), −12.90 (d, 2H, *o*-Ph), −3.10 (t, 2H, *m*-Ph), 3.41 (t, 1H, *p*-Ph). 4b, (C_6D_6): δ −0.47 (s, 54H, Me_3Si), 7.39 (m, 1H, *p*-Ph), 7.00 (m, 3H, *o*-Ph, *m*-Ph). The low stretching frequencies of



Scheme 1

Abbreviations: L ≡ $N(SiMe_3)_2$; M ≡ U unless specified. Reagents and solvents: (i) Bu^tOH, $PhMe_2$—2,6OH in benzene; (ii) H—C≡CPh in benzene, 4 h; (iii) pyridines in benzene, 4 h - 4 days; (iv) $HMo(CO)_3\eta^5C_5H_5$ in THF–pentane; (v) in THF; (vi) cyclopentadiene in benzene; (vii) Bu^t isocyanide or cyclohexylisocyanide in pentane.

the C≡C bonds (2069 cm^{-1}) and the $\Delta\nu$ C≡C = 42 cm^{-1} compared with the free alkyne suggested a dimeric structure for these complexes [4].

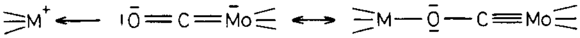
A facile activation of the sp^2 C—H bond of pyridine proceeded in two steps: the coordination of the pyridine gave an initial adduct, then a slow and quantitative reaction of metallation of the 2 position of the pyridine afforded 5 with both carbon and nitrogen coordinated to the uranium atom.

The kinetics of formation of 5 (monitored by NMR) showed no dependence on the excess of pyridine suggesting an intramolecular reaction [5]. The same *ortho*-metallation reaction took place but much more slowly when 2- or 4-picolines were used. A plausible explanation of the low reactivity of picolines could be that the presence of methyl donor substituents reduced the lability of the 2 and (or) 6 C—H bonds in the coordinated products. It is noteworthy that a similar *ortho*-metallation reported for Cp_2TiR complexes only occurs with 2-substituted pyridines and not for pyridine itself or 4-substituted pyridines [6].

The NMR spectra (Table 2) of 5 showed interesting trends concerning the structure of these compounds: the pyridine protons split in a range of about 120 ppm; the 5-protons appear at the high fields (about —25 ppm) as normally expected for a uranium aryl compound 3b, while the 2-protons are drastically deshielded at about 90 ppm (they appear at approximately 1.5 ppm in the adducts). This is indicative of a very short U–N distance and strong U–N bonding [7].

In THF solution at —30 °C, 1 reacted immediately with $HMo(CO)_3Cp$, in the molar ratio 1:1. When pentane was added to the THF solution, the binuclear compound 6 deposited immediately as microcrystalline powder.

The IR spectra of these compounds showed a very low carbonyl stretching frequency at about 1580 cm^{-1} indicative of an isocarbonyl linkage between both actinide and molybdenum atoms [8].



νCO(cm^{-1}), Nujol mulls were as follows: 6a (M ≡ U), 1929, 1820, 1579; 6b (M ≡ Th), 1920, 1820, 1586.

Compounds 6 were sparingly soluble in non-coordinating solvents such as toluene or hydrocarbons but highly soluble in THF. The IR spectra of THF solutions exhibit strong CO stretching peaks which are identical to those of the free carbonyl anions (1900, 1794, 1745 cm^{-1}), thereby suggesting a dissociation corresponding to an ionic structure, 7.

1 Reacted slowly with cyclopentadienes in benzene solution. Surprisingly, no cleavage of the metal—carbon bond was observed and the expected $[(Me_3Si)_2N]_3U\eta^5Cp$ compounds were not detected using an excess or a deficit of cyclopentadiene. The only compounds obtained were the biscyclopentadienyl metallacycles, 8[*], resulting from the cleavage of the two metal–dialkylamide bonds[†] and $HN(SiMe_3)_2$ was evolved.

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[*] The titanium analog was obtained from Cp_2TiCl_2 and $LiN(SiMe_3)_2$ [9].

[†] From $U(NEt_2)_4$, a similar reaction afforded $Cp_2U(NEt_2)_2$ [10].

TABLE 2

^{1}H NMR Data for compounds 5[a]

Compound	*SiMe$_3$*	*H$_2$*	*H$_3$*	*H$_4$*	*H$_5$*	*Me*
5a Pyridine	−8.76 (s, 54H)	91.45 (d, 1H)	33.21 (m, 1H)	9.55 (m, 1H)	−26.45 (d, 1H)	—
5b 2-Picoline	−8.56 (s, 54H)	—	22.70 (d, 1H)	6.02 (t, 1H)	−21.26 (d, 1H)	63.91 (s, 3H)
5c 4-Picoline	−8.96 (s, 54H)	94.47 (d, 1H)	34.53 (d, 1H)	—	−27.07 (s, 1H)	−4.23 (s, 3H)

[a] J 2, 3 = 5.3 Hz J 3, 4 = J 4,5 = 7.3 Hz.

TABLE 3

^{1}H NMR data for the biscyclopentadienyl compounds **8** and **9**

	Cp	*NSiMe$_3$*	*SiMe$_2$*	*CH$_2$*	*Me*	*N–R*
8a Cp ≡ C_5H_5	20.43 (s, 10H)	3.59 (s, 9H)	23.08 (s, 6H)	−71 (s, 2H)	—	—
8b Cp ≡ C_5H_4Me	α,α' −30.53 (m, 2H) −32.40 (m, 2H) β,β' −17.83 (m, 2H) −10.48 (m, 2H)	1.23 (s, 9H)	23.12 (s, 6H)	−72.7 (s, 2H)	−8.68 (s, 8H)	—
9a Cp ≡ C_5H_5 R ≡ Bu^t	−14.0 (s, 10H)	−1.12 (s, 9H)	−0.20 (s, 6H)	−5.26 (br, 2H, lw ≃70 Hz)		−18.69 (s, 9H)
9b Cp ≡ C_5H_5 R ≡ C_6H_{11}	−14.63 (s, 10H)	0.23 (s, 9H)	16.5 (s, 6H)	−2.62 (br, 2H, lw ≃25 Hz)		−22.61 (m, 2H) −21.96 (m, 2H) −7.76 (m, 2H) −6.05 (m, 1H) −4.42 (m, 2H) −4.03 (m, 1H) −7.1 (m, 1H)
9c Cp ≡ C_5H_4Me R ≡ Bu^t	α,α' −8.83 (m, 2H) −7.51 (m, 2H) β,β' −5.34 (m, 2H) −4.80 (m, 2H)	0.26 (s, 9H)	13.07 (s, 6H)	−8.44 (br, 2H, lw ≃10 Hz)	−16.5 (s, 6H)	−21.56 (s, 9H)

The structure of these metallacycles was established by NMR spectroscopy (Table 3): the spectrum of 8a consists of four sharp singlets, and the two substituted cyclopentadienyl rings of 8b exhibit four signals corresponding to the α, α' and β, β' protons [11].

The actinide carbon bond of 8 also possessed high reactivity: a rapid and quantitative reaction with isocyanides afforded the insertion compounds 9 (Table 3).

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