Reactivity of the Actinoid–Carbon σ Bond: Reaction of $[(Me_3Si)_2N]_2\overline{MCH_2Si(Me)_2N}SiMe_3$ with Acidic Hydrogen, Ready C–H Activation

Alain Dormond, Abdel Aziz El Bouadili, Claude Moïse

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (U. A. 33), Faculté des Sciences, 6 bd Gabriel, 21100 Dijon, France

The metal–carbon bond of the four-membered metallacycles $[(Me_3Si)_2N]_2\overline{MCH_2Si(Me)_2N}SiMe_3$ (M = U, Th) reacts under mild conditions with acidic hydrogens of alcohols, phenols, and alkynes, with pyridine to give the orthometallated products from sp^2 C–H activation, and with metal hydrides to give stable binuclear compounds with an isocarbonyl linkage, whereas cyclopentadienes cleave the metal–nitrogen bond providing biscyclopentadienyl four-membered metallacycles.

The actinoid–carbon bond of the four-membered ring metallacycles (1) $[(Me_3Si)_2N]_2\overline{MCH_2Si(Me)_2N}SiMe_3$, (M = U, Th)[1,2] shows an enhanced reactivity owing to the ring strain inherent in the four-membered ring and is known to insert 1,2 dipolar organic molecules[2,3] and to react with hydrogen to yield a hydride derivative.[1] We report some new reactions of

Table 1. ^{1}H N.m.r. data for (**4**).[a]

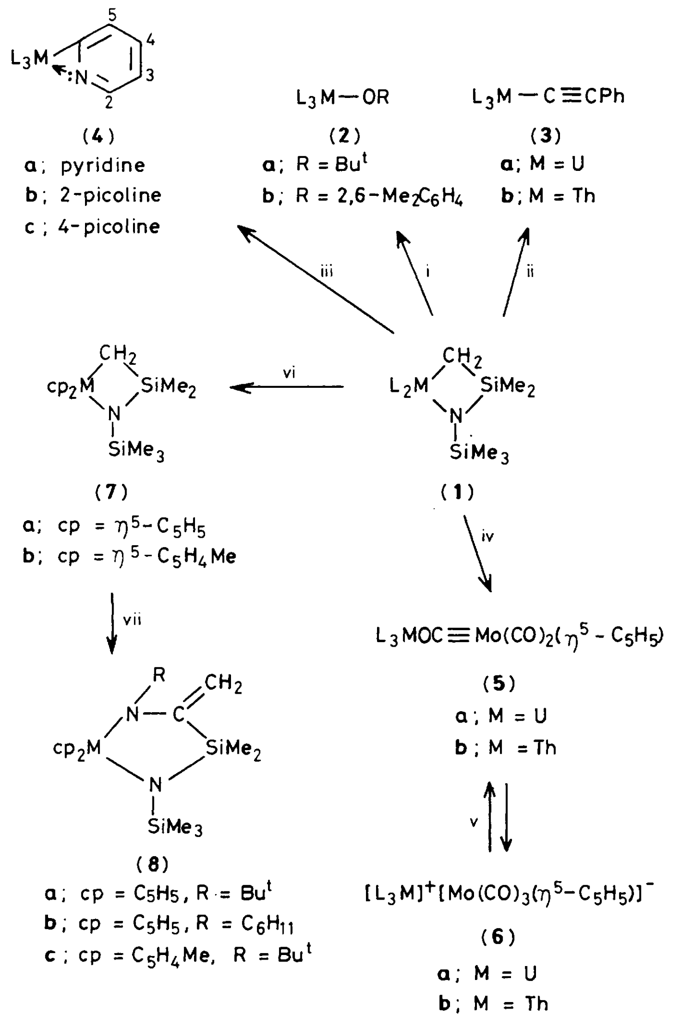
	$SiMe_3$	2-H	3-H	4-H	5-H	Me
(**4a**)	−8.76 (s, 54H)	91.45 (d, 1H)	33.21 (m, 1H)	9.55 (m, 1H)	−26.45 (d, 1H)	—
(**4b**)	−8.56 (s, 54H)	—	22.70 (d, 1H)	6.02 (t, 1H)	−21.26 (d, 1H)	63.91 (s, 3H)
(**4c**)	−8.96 (s, 54H)	94.47 (d, 1H)	34.53 (d, 1H)	—	−27.07 (s, 1H)	−4.23 (s, 3H)

[a] In C_6D_6, Me_4Si reference, $J(2,3)$ = 5.3, $J(3,4)$ = $J(4,5)$ = 7.3 Hz.

Table 2. ^{1}H N.m.r. data for (**7**) and (**8**).[a]

	cp	$NSiMe_3$	$SiMe_2$	CH_2	Me	N–R
(**7a**)	20.43 (s, 10H)	3.59 (s, 9H)	23.08 (s, 6H)	−71 (s, 2H)		
(**7b**)	α,α′ −30.53 (m, 2H) α,α′ −32.40 (m, 2H) β,β′ −17.83 (m, 2H) β,β′ −10.48 (m, 2H)	1.23 (s, 9H)	23.12 (3, 6H)	−72.7 (s, 2H)	−8.68 (s, 8H)	
(**8a**)	−14.0 (s, 10H)	−1.12 (s, 9H)	−0.20 (s, 6H)	−5.26 (br, 2H, *w* 70 Hz)		−18.69 (s, 9H)
(**8b**)	−14.63 (s, 10H)	0.23 (s, 9H)	16.5 (s, 6H)	−2.62 (br, 2H, *w* 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)
(**8c**)	α,α′ −8.83 (m, 2H) α,α′ −7.51 (m, 2H) β,β′ −5.34 (m, 2H) β,β′ −4.80 (m, 2H)	0.26 (s, 9H)	13.07 (s, 6H)	−8.44 (br, 2H, *w* 10 Hz)	−16.5 (s, 6H)	−21.56 (s, 9H)

[a] In C_6D_6, Me_4Si reference.



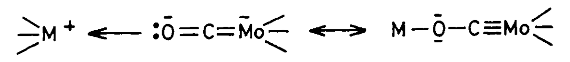
Scheme 1. L = $N(SiMe_3)_2$; when not specified M = U. *Reagents:* i, Bu^tOH, 2,6-MeC_6H_3OH in benzene; ii, HC≡CPh in benzene, 4 h; iii, pyridines in benzene, 4 h—4 days; iv, $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ in THF–pentane; v, THF; vi, cpH in benzene; vii, Bu^t isocyanide or cyclohexyl isocyanide in pentane.

these metallacycles toward 'acidic' hydrogens in O–H, C–H, or M–H bonds.

The actinoid–carbon σ-bonds undergo rapid protonation,[4] thus (**1**) reacted rapidly with tertiary alcohols or sterically hindered phenols to produce alkoxy or aryloxy compounds (**2**).† ^{1}H N.m.r. (C_6D_6) of (**2a**), R = Bu^t) (25 °C): δ −1.92 (s, 54H, Me_3Si) and 2.75 (s, 9H, Bu^t); (**2b**), R = $ArMe_2$-2,6 (70 °C): δ −5.58 (s, 54H, Me_3Si), 5.69 (s, 6H, Me_3), 9.04 (d, 2H, *m*-Ar), and 8.70 (t, 1H, *p*-Ar).

The n.m.r. spectrum of (**2b**) recorded at 25 °C showed a broadening of the signals indicative of restricted rotation due to the sterically bulky dimethylphenyl group. Cleavage of the metal–nitrogen bonds also occurred but was not competitive with attack on the metal–carbon bond.

With phenylacetylene and (**1**) in benzene solution, a slow reaction occurred and the extremely sensitive and unstable alkynyls (**3**) 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 ^{1}H n.m.r. spectroscopy. (**3a**) (C_6D_6): δ −2.18 (br, *w* 33 Hz, 54H, Me_3Si), −12.90 (d, 2H, *o*-H), −3.10 (t, 2H, *m*-H), and 3.41 (t, 1H, *p*-H); (**3b**) (C_6D_6): δ −0.47 (s, 54H, Me_3Si), 7.39 (m, 1H, *p*-H), and 7.00 (m, 4H, *o*-H, *m*-H). The low stretching frequencies of the C≡C bonds: 2069 cm^{-1} and the Δν C≡C 42 cm^{-1} compared with the free alkyne suggested a dimeric structure for these complexes.[5]



(A)

A ready activation of the sp^2 C–H bond of pyridine proceeded in two steps: the co-ordination of the pyridine gave an initial adduct, then a slow and quantitative metallation reaction at the 2-position of the pyridine afforded (**4**) with both C and N co-ordinated to the U atom.

The kinetics of formation of (**4**) (as monitored by n.m.r. spectroscopy) showed no dependence on an excess of pyridine suggesting an intramolecular reaction.[6] The same orthometallation 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 C–H bonds at the 2- and/or 6-positions in the co-ordinated products. It is noteworthy that a similar orthometallation reported for cp_2TiR (cp = C_5R_5, R = H or alkyl) complexes only occurs with 2-substituted pyridines and not for pyridine itself or 4-substituted pyridines.[7]

The n.m.r. spectra (Table 1) of (**4**) showed interesting trends concerning the structure of these compounds. The pyridine protons are split in a range of *ca.* 120 p.p.m., the 5-protons appear at high fields (*ca.* δ −25) as expected for a uranium aryl compound[4b] while the 2-protons are drastically deshielded at *ca.* δ 90 (they appear at *ca.* δ 1.5 in the adducts). This is indicative of a very short U–N distance and strong U–N bonding.[8]

In tetrahydrofuran (THF) solution at −30 °C, (**1**) reacted immediately with $HMo(CO)_3(C_5H_5)$, in the molar ratio 1 : 1. When pentane was added to the THF solution, the binuclear compound (**5**) deposited immediately as a microcrystalline powder.

The i.r. spectra of these compounds showed a very low carbonyl stretching frequency at *ca.* 1580 cm^{-1} indicative of an isocarbonyl linkage between both actinoid and Mo atoms[9] as in (A): ν(CO) (Nujol) (**5a**), (M = U) : 1929, 1820, and 1579 cm^{-1}; (**5b**), (M = Th): 1920, 1820, and 1586 cm^{-1}.

Compounds (**5**) were sparingly soluble in non-co-ordinating solvents such as toluene or hydrocarbons but highly soluble in THF. The i.r. spectra of THF solutions exhibit strong CO stretching peaks which are identical to those of the free carbonyl anions (1900, 1794, and 1745 cm^{-1}), thereby suggesting a dissociation corresponding to an ionic structure (**6**).

Metallacycle (**1**) reacted slowly with cyclopentadienes (cpH) in benzene. Surprisingly, no cleavage of the metal–carbon bond was observed and the expected $[(Me_3Si)_2N]_3U(\eta^5\text{-cp})$ compounds were not detected using an excess or a deficiency of cyclopentadiene. The only compounds obtained were the biscyclopentadienyl metallacycles (**7**)[10] resulting from the cleavage of the two metal–dialkylamide bonds[11] and $HN(SiMe_3)_2$ was evolved.

The structure of these metallacycles was established by n.m.r. spectroscopy (Table 2). The spectrum of (**7a**) consists of four sharp singlets and the two substituted cyclopentadienyl rings of (**7b**) exhibit four signals corresponding to the α,α′ and β,β′ protons.[12]

---

† All the complexes reported in this communication are isolated as brown (U) or white (Th) crystalline solids or powders, characterized by elemental analyses, i.r. and n.m.r. spectra.

The actinoid–carbon bond of (**7**) also possessed high reactivity: a rapid and quantitative reaction with isocyanides afforded the insertion compounds (**8**) (Table 2).

We thank Mr. D. Arnoult for technical assistance.

Received, 13th February 1985; Com. 189

References

1 S. J. Simpson, H. W. Turner, and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2991.
2 A. Dormond, A. Aaliti, A. El Bouadili, and C. Moïse, *J. Organomet. Chem.*, in the press.
3 S. J. Simpson and R. A. Andersen, *J. Am. Chem. Soc.*, 1981, **103**, 4063.
4 (a) P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam, and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650; (b) T. J. Marks, A. M. Seyam, and J. R. Kolb, *ibid.*, 1973, **95**, 5529; (c) T. J. Marks and W. A. Watcher, *ibid.*, 1976, **98**, 703.
5 R. D. Fischer and G. Bielang, *J. Organomet. Chem.*, 1980, **191**, 61 and references therein.
6 P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1983, 276.
7 F. Klei and J. H. Teuben, *J. Organomet. Chem.*, 1981, **214**, 53.
8 A. Dormond, A. Aaliti, and C. Moïse, unpublished results.
9 A. Dormond and C. Moïse, *Polyhedron*, 1985, **4**, 595.
10 C. R. Bennett and D. C. Bradley, *J. Chem. Soc., Chem. Commun.*, 1974, 29.
11 A. L. Arduini, N. M. Edelstein, J. D. Jamerson, J. G. Reynolds, K. Schmid, and J. Takats, *Inorg. Chem.*, 1981, **20**, 2470.
12 A. Dormond, C. Duval-Huet, and J. Tirouflet, *J. Organomet. Chem.*, 1981, **209**, 355.