Journal of Organometallic Chemistry, 192 (1980) C35—C38
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND STRUCTURE OF THE Nb^{IV} METALLOCYCLE $[M(\eta\text{-}C_5H_4SiMe_3)_2\{CH_2C_6H_4CH_2\text{-}o\}]$ (M = Nb, R = Me_3Si) AND REDUCTIVE CLEAVAGE OF d^0 ANALOGUES (M = Ti, Zr, OR Hf; R = H OR Me_3Si) BY $Na[C_{10}H_8]$

M.F. LAPPERT*, T.R. MARTIN, C.R.C. MILNE
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
J.L. ATWOOD*, W.E. HUNTER and R.E. PENTILLA
Department of Chemistry, University of Alabama, University, Alabama 35486 (U.S.A.)

(Received March 11th, 1980)

Summary

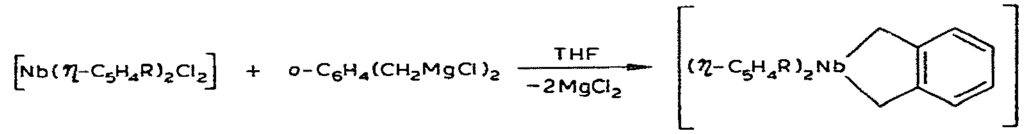
Reaction of $[Nb(\eta\text{-}C_5H_4R)_2Cl_2]$ with $o\text{-}C_6H_4(CH_2MgCl)_2$ in THF yields the metallocyclopentene $[Nb(\eta\text{-}C_5H_4R)_2\{CH_2C_6H_4CH_2\text{-}o\}]$ (Ia, R = Me_3Si; Ib, R = H), as confirmed by single crystal X-ray diffraction for Ia (average $\widehat{CNbC}$ = 72.4°); treatment of the isoleptic Zr compound (or Ti or Hf analogues) with $Na[C_{10}H_8]$ in THF gives $Na^+[CH_2C_6H_4\{CH_2M(C_5H_4R\text{-}\eta)_2\}\text{-}o]$ (M = Ti, Zr, or Hf).

We report (i) the preparation (eq. 1) of two niobium(IV) benzcyclopentenes (I), (ii) the crystal and molecular structure of one of these (Ia), and (iii) ESR data on complexes I and II (see eq. 2a).

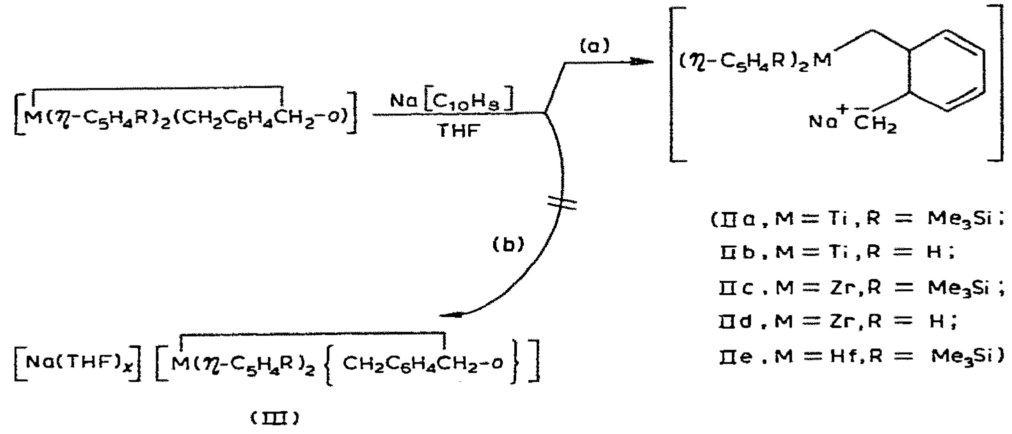
Compounds I appear to be the first examples of d^1 metallocycles. However, isoleptic d^0 analogues have recently been described and results on $[M(\eta\text{-}C_5H_4R)_2(CH_2C_6H_4CH_2\text{-}o)]$ (M = Ti, Zr, or Hf and R = Me_3Si; or M = Ti or Zr and R = H) [1] included X-ray data for $[Zr(\eta\text{-}C_5H_5)_2(CH_2C_6H_4CH_2\text{-}o)]$, (IV). The metallocycle Ia** is extremely air-sensitive like other niobocene(IV) alkyls [2]. The ESR spectra of complexes I (see Table 1) showed the expected ten line signal for a Nb^{IV} d^1 complex (^{93}Nb, $I = 9/2$, 100%). Coupling to α-H's was not observed, as had also been noted for $[Nb(\eta\text{-}C_5H_4R)_2R'R'']$ [2]. Isotropic $a(^{93}Nb)$ values were calculated from the second order spectra by a modification [3] of the Breit-Rabi equations. There is a correlation between $\widehat{LML'}$ angle θ for the d^1 complexes $[Nb(\eta\text{-}C_5H_4R)_2LL']$ and $a(^{93}Nb)$ [2,6]: (i) L = Cl = L′, R = H, θ = 85.0(1)°, a = 11.65 mT [5,6]; (ii) L = Cl, L′ = Me_3SiCH_2, R = Me_3Si, θ = 84.3(3)°, a = 9.80 [6]; (iii) L = $PhCH_2$ = L′, R = H, θ = 79.0° [6], a = 8.76 [2]; and (iv) LL′ = $o\text{-}C_6H_4(CH_2)_2$, R = Me_3Si, θ_{av} = 72.4(2)°, a = 7.72. The suggestion has been made that the HOMO for the d^1 complexes is primarily metal-

---

*Authors to whom correspondence should be addressed.
**M.p. 126—128°C.


(1)

(Ia, R = Me_3Si;
Ib, R = H)


(2)

(IIa, M = Ti, R = Me_3Si;
IIb, M = Ti, R = H;
IIc, M = Zr, R = Me_3Si;
IId, M = Zr, R = H;
IIe, M = Hf, R = Me_3Si)

centred [4]; this trend (i<ii<iii<iv), as well as the decrease in θ from 77.4° in IV [1] to 72.4° in Ia, is consistent with that view.

Addition of sodium naphthalide at ambient temperature to a d^0 metallobenzcyclopentene in THF causes reductive cleavage (eq. 2a) to yield the black (Ti) or brown (Zr or Hf) solution of the substituted benzyl carbanion (II). It may be that the metallate(III) complexes (III) (eq. 2b) are intermediates, but these were not detected by low temperature ESR experiments. Complexes II showed isotropic coupling to two equivalent α-H's (Table 1), and not to 4H's as required for III, or found for dialkyl analogues such as $[Zr(\eta\text{-}C_5H_4R)_2(CH_2Ph)_2]^-$ [7]*. We note that in the neutral precursor of the latter the $\widehat{CZrC}$ angle θ is expected to be in the range 94—97° [8], whereas in the d^0 metallocycle IV θ = 77.4° [1]; reduction of IV would still further lower the bite angle of the o-xylidene ligand and hence cause unacceptable steric strain.

TABLE 1

ESR DATA FOR THE NEW d^1 METAL ALKYLS AT 20°C

Complex	Solvent	$g_{av.}$	$a(^1H)$(mT)	$a(M)^a$(mT)
Ia^b	PhMe	1.999	c	7.72
Ib	PhMe	1.996	c	7.63
IIa	THF	1.985	0.475	1.09
IIb	THF	1.985	0.5	1.33
IIc	THF	1.986	0.5	1.5
IId^d	THF	1.985	0.55	1.48
IIe	THF	1.961	c	c

^{a} ^{47}Ti, $I = 5/2$, 17.3%; ^{49}Ti, $I = 7/2$, 5.5%; ^{91}Zr, $I = 5/2$, 11.3%; ^{179}Hf, $I = 9/2$, 13.7%. ^{b}Purple crystals, m.p. 126—128°C. ^{c}Not observed. ^{d}At −10°C.

---

*These d^1 Zr^{III} complexes were only identified by ESR, which shows four equivalent α-H's [7]; the possibility that a cyclopentadienyl anion has been cleaved cannot be ruled out.

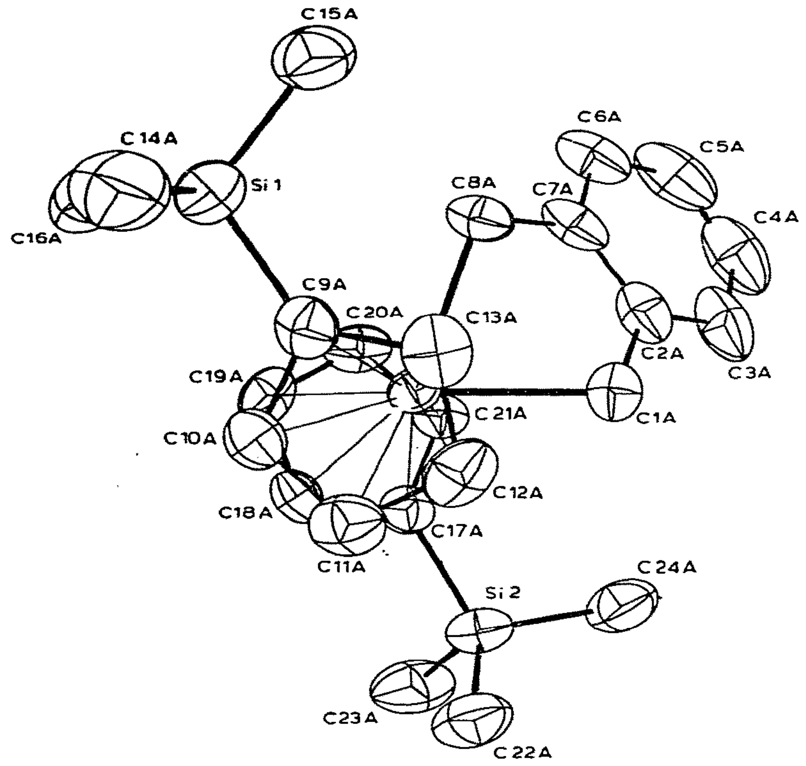


Fig. 1. ORTEP diagram of compound Ia.

The crystal of the title compound (Ia) was found to contain two molecules in the asymmetric unit, and the structure was refined to $R = 0.027$ based on 4667 observed reflections.

Crystal data. $C_{24}H_{34}Si_2Nb$, $M = 471.6$, triclinic, $a = 12.371(8)$, $b = 14.249(9)$, $c = 14.514(9)$ Å, $\alpha = 78.51(3)$, $\beta = 89.47(3)$, $\gamma = 73.67(3)°$, $\mu = 2403.1$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}, μ(Mo-K_α) = 5.93 cm^{-1}, $F(000) = 988$, λ(Mo-K_α) = 0.71069 Å, space group $P\bar{1}$. The niobium—carbon bond distances to the *o*-xylidene ligand are: Nb(1)—C(1a), 2.275(4) Å; Nb(1)—C(8a), 2.295(4) Å; Nb(2)—C(1b), 2.279(4) Å; Nb(2)—C(8b), 2.296(4) Å. The Nb—C(cyclopentadienyl) distances range from 2.407 to 2.443(4) Å and average 2.427 Å for Nb(1), while for Nb(2) the range is 2.392 to 2.458(4) Å, and the average, 2.426 Å. The Nb—C(*o*-xylidene) lengths can be compared to an average Nb—C(benzyl) distance of 2.304(3) Å in [Nb(η-C_5H_5)$_2$($CH_2C_6H_5$)$_2$] [2], to the Nb—C(ethyl) distance, 2.316(8) Å, in [Nb(η-C_5H_5)$_2$(C_2H_5)(C_2H_4)] [9], or to the Nb—C(trimethylsilylmethyl) length, 2.28(1) Å, in [Nb(η-$Me_3SiC_5H_4$)$_2$(CH_2SiMe_3)(Cl)] [6]. The most striking feature of the structure is the decrease in the bite angle for the *o*-xylidene ligand, C(1a)—Nb(1)—C(8a), 71.9(2)°, and C(1b)—Nb(2)—C(8b), 72.9(2)°, for this d^1 system, compared to the d^0 zirconocene *o*-xylidene analogue, 77.4(2)° in IV [1]. The Me_3Si-substituents appear to have been rotated so as to minimise their interaction. The independent values for the "angle of fold" (defined as that made by the plane of Nb, C(1a), and C(8a) with the extension of that of C(1a), C(2a), C(7a), and C(8a)) are 40.2 and

41.2°, compared to 53.1° in the Zr^{IV} analogue; and C(1a) and C(8a) are 0.07 Å out of the plane of the C_6 group.

Acknowledgements

We thank S.R.C. for the award of a studentship to T.R.M. and for other support, and the U.S.N.S.F. for partial support to J.L.A.

References

1 M.F. Lappert, T.R. Martin, J.L. Atwood and W.E. Hunter, J. Chem. Soc. Chem. Commun., in press.
2 P.B. Hitchcock, M.F. Lappert and C.R.C. Milne, J. Chem. Soc. Dalton, in press.
3 J. Roncin and R. Debuyst, J. Chem. Phys., 51 (1969) 577.
4 K. Prout, T.S. Cameron and R.A. Forder, Acta Cryst. B, 30 (1974) 2290.
5 R. Broussier, H. Normant and B. Gautheron, J. Organometal. Chem., 155 (1975) 335.
6 M.F. Lappert, C.R.C. Milne, J.L. Atwood and W.E. Hunter, to be published.
7 M.F. Lappert, P.I. Riley and P.I.W. Yarrow, J. Chem. Soc. Chem. Commun., (1979) 305.
8 J.L. Atwood, G.K. Barker, J. Holton, W.E. Hunter, M.F. Lappert and R. Pearce, J. Amer. Chem. Soc., 99 (1977) 6645.
9 L.J. Guggenberger, P. Meakin and F.N. Tebbe, J. Amer. Chem. Soc., 96 (1974) 5452.