Syntheses and Crystal Structures of the d^{0,1,2} Metallepins $[NbR_2(\eta\text{-}C_5H_5)_2][BF_4]$, $[NbR_2(\eta\text{-}C_5H_5)_2]$, and $[Na(18\text{-Crown-}6)(thf)_2][NbR_2(\eta\text{-}C_5H_5)_2]$ (thf = tetrahydrofuran); Reduction Product of $[ZrR_2(\eta\text{-}C_5H_5)_2][R_2 = (o\text{-}CH_2C_6H_4)_2{}^{2-}]$

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Reaction of $[Nb\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**1**) with $AgBF_4$ gives $[Nb\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (**2**) and with $Na[C_{10}H_8]$ in the presence of 18-crown-6, $[Na(18\text{-crown-}6)(thf)_2][Nb\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**3**) (thf = tetrahydrofuran), whereas reduction of $[Zr\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ results in a Zr–CH$_2$ cleavage; single crystal *X*-ray structure determinations on (**1**), (**2**), and (**3**), show a considerable variation in Nb–CH$_2$–C and CH$_2$–Nb–CH$_2$ angles, and in the torsion along the biphenyl axis, the angular changes at the niobium being in accordance with M.O. predictions [CH$_2$–Nb–CH$_2$, 106.3(1)° (d^0); 83.0° (d^1); 80(1) (d^2)].

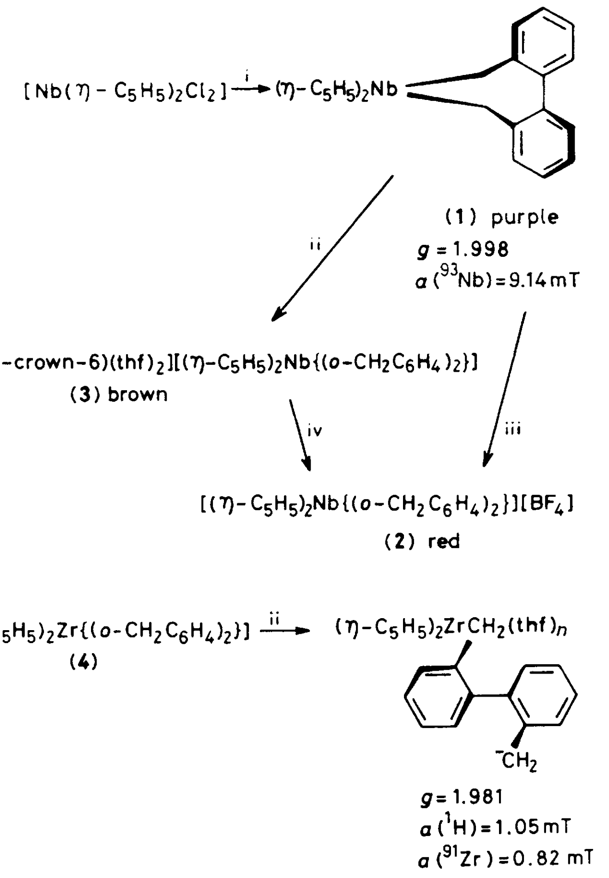
Recently we described a series of 5,7-dihydro-6*H*-dibenzo[*c,e*]-metallepins of Ti, Zr, Hf, and Sn, all derived from both an organodilithium complex, $[\{Li(tmeda)\}_2\{(o\text{-}CH_2C_6H_4)_2\}]$(tmeda = tetramethylethylenediamine) and a di-Grignard reagent.[1] We now report the syntheses and structures of the Group 5 d^{0,1,2} species $[Nb\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]^n$ ($n = 0, \pm1$) and the reduction of the neutral zirconium analogue; the d^1 niobium complex was found to be accessible using the di-Grignard reagent only. Principal features of interest include (i) the isolation of crystalline complexes for the sequence d$^{0-2}$, the anion of d^2 configuration being the first authenticated species of the type $[Nb(alkyl)_2(\eta\text{-}C_5H_5)_2]^{1-}$, and the conversion of (**3**) → (**2**) with the reagent $HBF_4{\cdot}OMe_2$; (ii) the complexes (**2**) and (**3**) are novel examples of niobocene metallepins of d^0 and d^2 configurations; (iii) the structures of (**1**) → (**3**) appear to be the first structurally characterized trio of complexes where the transition metal species are related by a sequential addition of a d electron, and (iv) the versatility of the ligand in accommodating a wide range of ligand 'bite' imposed by electronic constraints at the metal centre, *via* torsion along the biphenyl axis and variation in M–CH$_2$–C$_{Ar}$ angle.

Prior to this work the only d^2 niobocene dialkyl complex

Table 1. Selected structural details.

	Compound		
	(3),[a] d^2	**(1)**,[b] d^1	**(2)**,[a] d^0
Nb–CH_2	2.35(3), 2.30(3)	2.29_7	2.249(3), 2.251(4)
Nb–η-C	2.32(5)—2.50(6) <2.38>	2.37(2)—2.45(2) <2.41>	2.394(3)—2.441(4) $<2.41_8>$
Nb–Centroid	2.10, 2.06	2.10	2.10, 2.10
Nb · · · $C_β$	3.35(3), 3.39(3)	3.26(1)—3.29(1)	2.959(4), 2.960(4)
CH_2–Nb–CH_2	80(1)	83.0	106.3(1)
Nb–CH_2–C_{Ar}	123(2), 123(2)	118.7	103.1(2), 102.7(2)
Centroid–Nb–Centroid	136.0	135.3	131.0
Biphenyl torsion angle	59.6	62.4	78.4

[a] One complete niobium species in the asymmetric unit. [b] Results for the average of three molecules, one general and two on C_2 axes.



Scheme 1. *Reagents and conditions:* i, 0.08 M [{(thf)$_n$ClMgC$_6$H$_4$-CH$_2$-*o* }$_2$] (1 equiv.) in thf, 20 °C; ii, Na[$C_{10}H_8$] (1 equiv.), 18-crown-6 (1 equiv.), thf, 20 °C; iii, $AgBF_4$ (1 equiv.), thf, 20 °C; iv, $HBF_4{\cdot}OMe_2$ (2 equiv.), thf.

reported was [Nb($CH_2Ph)_2$(η-$C_5H_5)_2$]$^-$, studied electrochemically and not isolated.[2] The stability of (3) contrasts with chloride elimination on reduction of [Nb(CH_2SiMe_3)Cl(η-$C_5H_4Me)_2$].[3] As to the novelty of (2), the only other related d^0 species are [Nb($CH_2SiMe_3)_2$(η-$C_5H_5)_2$]$^+$ (ref. 4) and [Nb-($CH_2Ph)_2$(η-$C_5H_5)_2$]$^+$ (not isolated).[2]

Reduction of the d^0 zirconium derivative (4) results in heterolytic loss of CH_2- from the metal co-ordination sphere (Scheme 1). This is based on e.s.r. data (1 : 2 : 1 hydrogen hyperfine coupling pattern) and the fact that such a reaction has been proposed for the reduction of [$\overline{Zr(CH_2C_6H_4CH_2}$-*o*)(η-$C_5H_4R)_2$] (R = H, $SiMe_3$).[5]

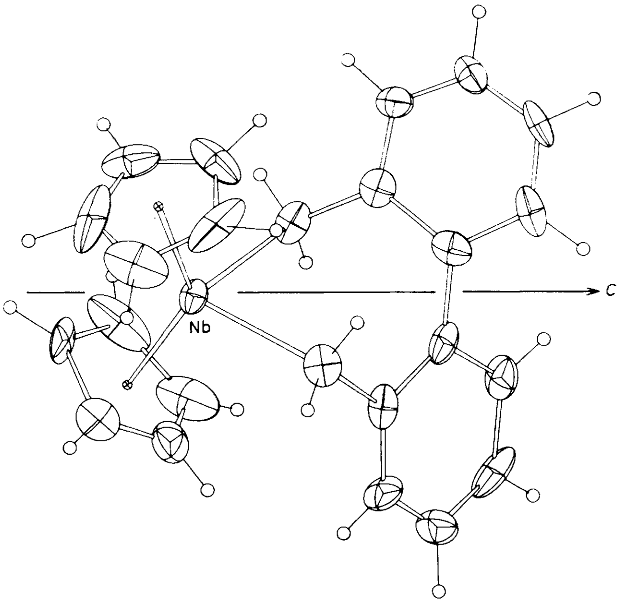


Figure 1. Molecular structure of [Nb{(*o*-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$]$^-$ showing an approximate C_2 symmetry axis.

The structures of **(1)**—**(3)**† offer a unique opportunity for comparing perturbations originating entirely from addition of d electrons. The most dramatic changes in structure are those of d^0 to d^1 rather than d^1 to d^2, borne out primarily by the Nb–CH_2–C and CH_2–Nb–CH_2 angles and the torsion angle of the biphenyl moiety (Table 1), features that clearly demonstrate the flexibility of the bidentate ligand. Variation of CH_2–Nb–CH_2 angle with d^n has a theoretical basis. Successive addition of a d electron to the a_1 LUMO of **(2)** should result

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† *Crystal data:* $C_{24}H_{22}Nb$ **(1)**, orthorhombic, *Pnn*2, $a = 31.985(9)$, $b = 10.875(3)$, $c = 10.527(3)$ Å, $Z = 8$; $C_{24}H_{22}BF_4Nb$ **(2)**, monoclinic, $P2_1/n$, $a = 13.602(6)$, $b = 12.934(5)$, $c = 12.623(5)$ Å, $\beta = 110.26(3)°$, $Z = 4$; $C_{44}H_{64}NaNbO_8$ **(3)**, triclinic, $P\bar{1}$, $a = 16.77(8)$, $b = 14.68(3)$, $c = 12.53(2)$ Å, $\alpha = 66.2(2)$, $\beta = 85.4(3)$, $\gamma = 66.2(3)°$, $Z = 2$. All structures were determined at room temperature [295(1) K] from 2326 [**(1)**], 4163 [**(2)**], and 3430 [**(3)**] independent 'observed' reflections (Mo-K_α radiation). *R* and R_w values for **(1)**, **(2)**, and **(3)** are respectively 0.045, 0.046; 0.040, 0.053; and 0.133, 0.178.

Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

in reduction of this angle.[6] While the angles in (**1**) and (**3**) are unexceptional and are therefore possibly determined by constraints imposed by populating the a_1 orbital, that of (**2**) is larger than usual for d^0 configurations, the origin of which may be an alkyl ligand interaction with the formally electron deficient metal centre. [The Nb–CH_2–C_β angle and Nb $\cdots$ C_β contact distances of (**2**) (Table 1) are significantly lower than those of (**1**) and (**3**).]

Two d^1 species related to (**1**), $[Nb(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$[7] and $[\overline{\text{Nb(CH}_2\text{C}_6\text{H}_4\text{C}}\text{H}_2\text{-}o)(\eta\text{-}C_5H_4SiMe_3)_2]$[4] possess CH_2–Nb–CH_2 angles respectively of 79 and 72.5° [*cf.* 83° in (**1**)] and have corresponding metal hyperfine coupling constants of 8.76 and 7.72 mT [*cf.* 9.14 mT in (**1**)]. Thus for these complexes there is a good trend of angular variation *vs.* $a(^{93}Nb)$, a feature which is consistent with the energy and degree of metal character of the HOMO being sensitive to the CH_2–Nb–CH_2 angle as noted recently for a wide variety of niobocene complexes.[7]

The sodium environments of two independent atoms in (**3**), both lying on crystallographic inversion centres, are hexagonal bipyramidal with the tetrahydrofuran (thf) oxygen atoms in the apical positions as in a dicyanophosphide salt[8] [Na–O(18-crown-6) 2.68(2)—2.80(3), Na–O(thf) 2.28(2)—2.32(4) Å].

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