Journal of Organometallic Chemistry, 175 (1979) 21—31
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ADDUCTS OF CYCLOPENTADIENYLSODIUM AND METHYLCYCLOPENTADIENYLSODIUM WITH OXYGEN BASES AND NITROGEN BASES: STRUCTURE OF CYCLOPENTADIENYLSODIUMTETRAMETHYLETHYLENEDIAMINE, $Na(C_5H_5)(Me_2NCH_2CH_2NMe_2)$

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(Received March 12th, 1979)

Summary

The capacity of cyclopentadienylsodium to form adducts with the following bases has been studied: diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, 1,4-dioxane, 1,3,5-trioxane, benzo-15-crown-5, triethylamine, tetramethylethylenediamine, pyridine, 4-dimethylaminopyridine, and 2,2′-bipyridyl. Most form extremely air- and moisture-sensitive 1 : 1 adducts $Na(C_5H_5)L$, where L = Lewis base. Similar adducts, $Na(C_5H_4Me)L$, of methylcyclopentadienylsodium have been prepared. Their infrared and ^1H NMR spectra are consistent with η^5-coordination of the cyclopentadienyl groups. In the crystal, the tetramethylethylenediamine adduct, $Na(C_5H_5)TMEDA$, adopts a puckered chain structure, with η^5-C_5H_5 rings bridging Na(TMEDA) units.

Introduction

In organolithium chemistry, the capacity of lithium atoms (or cations) to coordinate strongly to the π-systems of unsaturated hydrocarbon groups (or anions) has been amply illustrated during the past few years [1,2]. For example, X-ray crystallographic studies [2] have revealed the "π-complex" geometry of many organolithium compounds in which the lithium atoms, typically coordinated by a chelating base such as tetramethylethylenediamine (TMEDA), are also bonded to three or more carbon atoms of such unsaturated groups or anions as benzyl [3], triphenylmethyl [4], fluorenyl [5], (naphthalene)$^{2-}$ [6], (bifluorenyl)$^{2-}$ [7], indenyl [8], (anthracene)$^{2-}$ [9], and (hexatriene)$^{2-}$ [10]. In the indenofluorenide [11], $LiC_{19}H_{11}$, lithium atoms uncoordi-

TABLE 1

LIST OF ADDUCTS

Ligand, L	n	Compound number	M.p. (°C)	Crystal form	Thermal stability [a]	Solubility [b]		
						Benzene	Toluene	THF
Adducts of cyclopentadienylsodium, (I), $Na(C_5H_5)$, nL								
Diethyl ether	?	III	—	plates	c	c	c	a
THF	1	IV	—	needles	c	b	b	a
1,2-Dimethoxyethane	1	V	92— 95	plates	a	b	b	a
1,4-Dioxane	1	VI	—	plates	b	b—c	b—c	b
1,3,5-Trioxane	1	VII	159—160	plates	a	b	b	a
Benzo-15-crown-5	1	VIII	175—176	prisms	a	b—c	b—c	a
Triethylamine	?	IX	—	plates	c	b	b	a
TMEDA	1	X	135—138	plates	a	b	b	a
Pyridine	1	XI	105—107	needles	b	b	b	a
4-Dimethylaminopyridine	1	XII	203—205	prisms	a	b	b	a
2,2′-Bipyridine	1	XIII	136—139	needles	a	b—c	b—c	b
Adducts of methylcyclopentadienylsodium, (II), $Na(C_5H_4Me)$, nL								
THF	?	XIV	—	needles	c	b	b	a
TMEDA	1	XV		needles	a	a	a	a
Pyridine	?	XVI	—	plates	c	b	b	a
4-Dimethylaminopyridine	1	XVII	113—115	prisms	a	b	b	a
2,2′-Bipyridine	1	XVIII	127—130	needles [c]	a	b	a—b	a

[a] a, stable at 20°C, even under vacuum; b, isolable at 20°C, but dissociates at that temperature, particularly under reduced pressure; c, isolable at −78°C, but decomposes readily below +20°C. [b] a, dissolves 5 wt.% or more at 20°C; b, dissolves about 5 wt.% at the boiling point; c, very low solubility, or insoluble, at the boiling point. [c] Yellow; remaining adducts colourless.

nated by chelating nitrogen bases are sandwiched between two of the benzene rings of the ligands [11]. Similar strong interactions between the metal and various unsaturated organic ligands have been inferred from spectroscopic studies [12—16], and predicted (in the case of allyllithium) on theoretical grounds [17,18].

By contrast, organosodium systems, in which the metal—carbon bonding would be expected to be more ionic, have been much less fully studied, although π-type bonding interactions between bis(tetrahydrofuran)sodium units, $Na(THF)_2$, and the benzene rings of complex organoaluminate anions derived from naphthalene or anthracene have been found by X-ray crystallographic studies on the compounds $[Na(THF)_2]_2[Me_2AlC_{10}H_8]_2$ [19] and $[Na(THF)_2]_2[Me_2AlC_{14}H_{10}]_2$ [20]. In particular, before the present study no definitive structural work had been done on a sodium cyclopentadienide, even though cyclopentadienylsodium has been the subject of many vibrational and NMR spectroscopic studies [21—27] and is itself widely used as a reagent for the synthesis of transition metal cyclopentadienyl complexes [28,29]. Indeed, no systematic attempt to isolate coordination complexes of alkali metal cyclopentadienides had to our knowledge been reported. We therefore set out to explore the coordination chemistry of sodium cyclopentadienide, $Na(C_5H_5)$, and of its methyl derivative, $Na(C_5H_4Me)$, with two objectives: firstly, to find a compound or compounds suitable for X-ray crystallographic study, and so to establish the mode of coordination of the cyclopentadienyl group to sodium in one or more specific complexes; and secondly, to find out whether the vibrational and ^1H NMR spectra of complexes $Na(C_5H_5) \cdot nL$ might indicate any change in the mode of attachment of the cyclopentadienyl group to sodium as the number (n) and type of Lewis bases (L) were varied. By analogy with transition metal systems, decreasing hapticity of the cyclopentadienyl ligands with increasing n might have been expected if covalent metal—C_5H_5 ring interactions were important, though not if the Na—C_5H_5 bonding were essentially ionic.

A preliminary account of the structure of the TMEDA complex $Na(C_5H_5)$(TMEDA) has already been published [30]. This paper gives further information about this compound, and describes a series of related coordination complexes of cyclopentadienylsodium (I) and methylcyclopentadienylsodium (II).

Results and discussion

The normal method of preparation of cyclopentadienylsodium, which we have used in the present work, involves the reaction of the metal with cyclopentadiene in THF [28]. This affords a solution of $Na(C_5H_5)$ in THF from which uncoordinated $Na(C_5H_5)$ (I) can readily be obtained as a white powder by pumping off the solvent, only gentle heating (40°C) being needed to drive off the residual solvent of crystallisation. The low affinity of the cyclopentadienide for THF indicates it to have only feeble Lewis acidity, an indication supported by our study of its capacity to coordinate a range of ether and amine bases.

The results of our studies are summarized in Tables 1 and 2. Table 1 shows which Lewis bases, L, were found capable of forming adducts $Na(C_5H_4R) \cdot nL$ (R = H or Me) with $Na(C_5H_5)$ or $Na(C_5H_4Me)$, and in what proportion (n,

TABLE 2

ANALYTICAL DATA

Compound		Anal. (found (calcd.)) (%)			
		C	H	N	Na
I	$Na(C_5H_5)$	67.7	7.1	—	26.9
		(68.2)	(5.7)	—	(26.2)
II	$Na(C_5H_4Me)$	70.1	7.0	—	21.9
		(70.6)	(6.9)	—	(22.5)
V	$Na(C_5H_5)$(1,2-dimethoxyethane)	59.9	7.8	—	13.9
		(60.7)	(8.4)	—	(12.9)
VI	$Na(C_5H_5)$(1,4-dioxane)	61.8	7.5	—	11.6
		(61.4)	(7.4)	—	(13.1)
VII	$Na(C_5H_5)$(1,3,5-trioxane)	54.7	7.3	—	12.9
		(54.0)	(6.2)	—	(12.9)
VIII	$Na(C_5H_5)$(benzo-15-crown-5)	62.5	7.8	—	6.1
		(64.0)	(7.0)	—	(6.5)
X	$Na(C_5H_5)$(TMEDA)	64.0	9.6	13.4	11.7
		(64.6)	(10.3)	(13.7)	(11.3)
XI	$Na(C_5H_5)$(pyridine)	69.3	9.4	7.9	12.6
		(71.9)	(6.0)	(8.4)	(13.7)
XII	$Na(C_5H_5)$(4-dimethylaminopyridine)	66.9	7.1	12.6	10.8
		(68.1)	(7.1)	(13.3)	(11.0)
XIII	$Na(C_5H_5)$(2,2'-bipyridyl)	74.6	6.1	11.4	9.3
		(73.2)	(5.4)	(11.5)	(9.4)
XV	$Na(C_5H_5Me)$(TMEDA)	65.4	12.9	12.7	10.2
		(66.1)	(10.6)	(12.9)	(10.6)
XVII	$Na(C_5H_4Me)$(4-dimethylaminopyridine)	68.9	7.7	12.6	10.9
		(69.6)	(7.6)	(12.5)	(10.3)
XVIII	$Na(C_5H_4Me)$(2,2'-bipyridyl)	73.2	5.3	11.3	8.4
		(74.4)	(5.8)	(10.9)	(8.9)

which was invariably unity for the compounds that could be isolated and characterized). The melting temperatures, thermal stabilities and solubilities of the adducts are also indicated in Table 1. Table 2 gives analytical data for the compounds stable enough not to dissociate spontaneously at room temperature.

Some of the Lewis bases studied, e.g. THF, diethyl ether and triethylamine, coordinated only feebly to $Na(C_5H_5)$ and $Na(C_5H_4Me)$. Crystalline adducts of these bases, with the appearance given in Table 1, were apparently obtained by dissolving I or II in the base itself, and allowing the solutions to crystallise at low temperature (—40 to —78° C). When separated from the solvent and allowed to warm up under dry nitrogen, however, the crystals evolved base and crumbled to the powdery consistency characteristic of uncoordinated $Na(C_5H_4R)$. Analyses of the products showed them to retain only small and variable proportions of base.

Those bases that were found to form more stable adducts were added in 4- to 5-fold excess to solutions of $Na(C_5H_4R)$ in THF. These solutions were allowed to crystallize, and the crystals were separated, recrystallised twice from benzene, and then dried under vacuum. Although under these conditions the metal cyclopentadienide might have taken up two or more moles of base, the product was invariably the 1/1 adduct $M(C_5H_4R) \cdot L$, whether L was mono-, bi- or poly-dentate. Nevertheless, in view of the various potential hapticities of the

Lewis bases studied, these 1/1 adducts presumably have various numbers of coordination sites on sodium occupied by atoms of the ligand L, ranging from one site in the case of monodentate ligands like pyridine in compound XI to five sites in the case of the crown ether complex, compound VIII. It was thought that these various possible modes of attachment of L to the metal might in turn lead to various modes of attachment of the cyclopentadienyl groups to the metal. The infrared and ^1H NMR spectra of the adducts were recorded in a search for evidence of this, as the spectra of *mono-*, *tri-* and *penta-hapto* coordinated cyclopentadienyl groups, and of cyclopentadienyl anions, are well documented [21—27].

The frequencies of characteristic cyclopentadienyl group absorptions of selected adducts are given in Table 3, together with the frequencies of the corresponding bands in the spectra of the uncoordinated cyclopentadienides (which agree well with the literature values [22,24—27]. Fritz [21,25] has pointed out that five frequency regions can be used to characterise cyclopentadienyl ligands, four of which are employed in Table 3: the C—H stretching absorption, ν(C—H), at 3030—3080 cm^{-1}; the in-plane C—H bending mode, δ(C—H), at about 1000 cm^{-1}; the out-of-plane C—H bending mode, γ(C—H), at 700—730 cm^{-1}; and a metal—ring stretching absorption at about 300—330 cm^{-1}.

This last absorption, at 327 cm^{-1} for I, 300 cm^{-1} for II, provided a useful guide to the degree of conversion of uncoordinated $Na(C_5H_4R)$ into adduct $Na(C_5H_4R) \cdot L$, as it persisted, though with diminished intensity, in the spectra of adducts $Na(C_5H_4R) \cdot L$ contaminated by unreacted $Na(C_5H_4R)$ alongside the new band, characteristic of the adduct, at the higher frequencies listed in the final column of Table 3. This new band is probably attributable to Na—L stretching vibrations, as the $Na—C_5H_5$ interactions are expected to be weakened rather than strengthened by coordination of L to Na. Consistent with this, the new band occurs at ca. 400 cm^{-1} in the spectra of adducts of I with pyridine and 4-dimethylaminopyridine (both expected to be monodentate ligands), but at ca. 450 cm^{-1} in the spectra of the adducts with the bidentate chelating ligands TMEDA and bipyridyl. In the case of the crown ether complex (compound XI), if the sodium cation is surrounded, as seems likely, by the pentadentate crown ether, the resultant shielding of the metal by the ether must leave room for negligible metal—C_5H_5 ring bonding. The distinction between anionic $C_5H_5^-$ groups and ion-pairs incorporating such anions orientated *pentahapto* to the metal cations is slight, however, and the data in Table 3, while being consistent with η^5 ligand geometry for both the parent cyclopentadienides and their adducts, do not allow further structural conclusions to be drawn. The greater complexity of the spectra of the methylcyclopentadienyl compounds arises from the lower symmetry of the C_5H_4Me ring, and is not considered to reflect a different metal—ring geometry.

The ^1H NMR spectra of the adducts were also found to be consistent with *pentahapto* coordination of the cyclopentadienyl rings, in that the absorption attributable to the ring protons was invariably a singlet, even at —90° C, though the chemical shift of that singlet varied with the solvent and ligand. Table 4 illustrates the extent of that variation for the ligands THF, triethylamine, pyridine and TMEDA, using THF, benzene, acetonitrile and dimethylsulphoxide

TABLE 3

CHARACTERISTIC CYCLOPENTADIENYL GROUP ABSORPTIONS IN THE INFRARED SPECTRA OF THE SODIUM CYCLOPENTADIENIDES AND SOME OF THEIR ADDUCTS (AS NUJOL MULLS)

Compound number	Cyclo-pentadienide	Ligand L	Absorptions (cm^{-1})			Metal ring (or M—L)
			ν(C—H)	δ(C—H)	γ(C—H)	
I	Na(C_5H_5)	—	3070	998	715	327
VIII	Na(C_5H_5)	Benzo-15-crown-5	3060, 3040	1000	700	-
X	Na(C_5H_5)	TMEDA	3060	1010	720	(456)
XI	Na(C_5H_5)	Pyridine	3075	1005	720	(400)
XII	Na(C_5H_5)	4-Dimethylaminopyridine	3080	996	724	(404)
XIII	Na(C_5H_5)	2,2′-Bipyridyl	3065	999	720	(450)
II	Na(C_5H_4Me)	—	3050	1033, 1020	785, 715	300
XV	Na(C_5H_4Me)	TMEDA	3045, 3030	1032, 1020	770, 708	(420)
XVII	Na(C_5H_4Me)	4-Dimethylaminopyridine	3055, 3040	1035, 1020	780, 715	(410)
XVIII	Na(C_5H_4Me)	2,2′-Bipyridyl	3064, 3040	1039, 1029	780, 705	—

TABLE 4

CHEMICAL SHIFTS (p.p.m., RELATIVE TO BENZENE AS INTERNAL REFERENCE) OF THE CYCLOPENTADIENYL PROTONS IN THE ^{1}H nmr SPECTRA OF $Na(C_5H_5)$ AND SOME OF ITS ADDUCTS $Na(C_5H_5)L$ IN VARIOUS SOLVENTS

Compound number	Ligand L	Solvent			
		THF	Benzene	Acetonitrile	DMSO
I	—	1.94	—	1.63	1.79
VI	THF	1.94	—	1.64	—
XII	Et_3N	1.63	—	—	—
XIII	TMEDA	1.56	1.19	1.67	1.81
XIV	Pyridine	1.62	1.32	—	—

(DMSO) as solvents. The data in Table 4 suggest that all three amine ligands do coordinate to $Na(C_5H_5)$ in THF, even though the triethylamine adduct $Na(C_5H_5)NEt_3$ decomposed too readily at room temperature to be characterized. Moreover, they indicate that the anionic character of the C_5H_5 group in the adducts $Na(C_5H_5)L$ increases in the sequence $L = THF < Et_3N \sim$ pyridine $<$ TMEDA. The strongly coordinating solvents acetonitrile and dimethylsulphoxide, however, apparently displace THF, Et_3N and TMEDA from sodium when the adducts containing these bases are dissolved, since the chemical shifts of their solutions do not appear to vary significantly with the Lewis base.

The NMR results do not rule out the possibility of less symmetrical (η^1 or η^3) but fluxional coordination of the cyclopentadienyl groups to sodium in these adducts. Fluxional behaviour may be expected in compounds such as these in which the degree of covalency, and so directed nature of the bonding, is slight.

The ^{1}H NMR spectra of the methylcyclopentadienylsodium adducts $Na(C_5H_4Me)L$ were also consistent with *pentahapto* coordination. Methylcyclopentadienylsodium in THF gave only a single resonance due to the ring protons [23] and its adducts also gave singlets, even though the substituent methyl group lowers the ring symmetry and renders the ring protons non-equivalent, and might be expected to influence the activation energy of fluxional processes.

The one definite piece of structural information to emerge from our study is the crystal structure of compound X, $Na(C_5H_5)$TMEDA, a preliminary report of which has already been published [30]. The crystals are orthorhombic, with a 1596.1, b 894.9, c 1840.8 pm, space group P_{cca}, with 8 formula units in the unit cell. The intensity data were collected on a Hilger and Watts four-circle diffractometer, using Zr-filtered Mo radiation, to a limit of $\theta = 20°$. The structure was solved by the symbolic addition method, and refined by least squares methods to R 0.087 for the 771 reflections with net counts $\geqslant \sigma$.

The structure is illustrated in Fig. 1. Table 5 gives the atomic coordinates, Table 6 the bond distances, and Table 7 the bond angles. The structure consists of puckered chains of sodium atoms, each with a chelating TMEDA molecule attached, linked by bridging *pentahapto* cyclopentadienyl groups inclined at 88° to, and bisecting, the Na—Na axes, which are displaced 11 pm from the ring centres. This slippage from the ideal η^5 geometry is attributable to non-

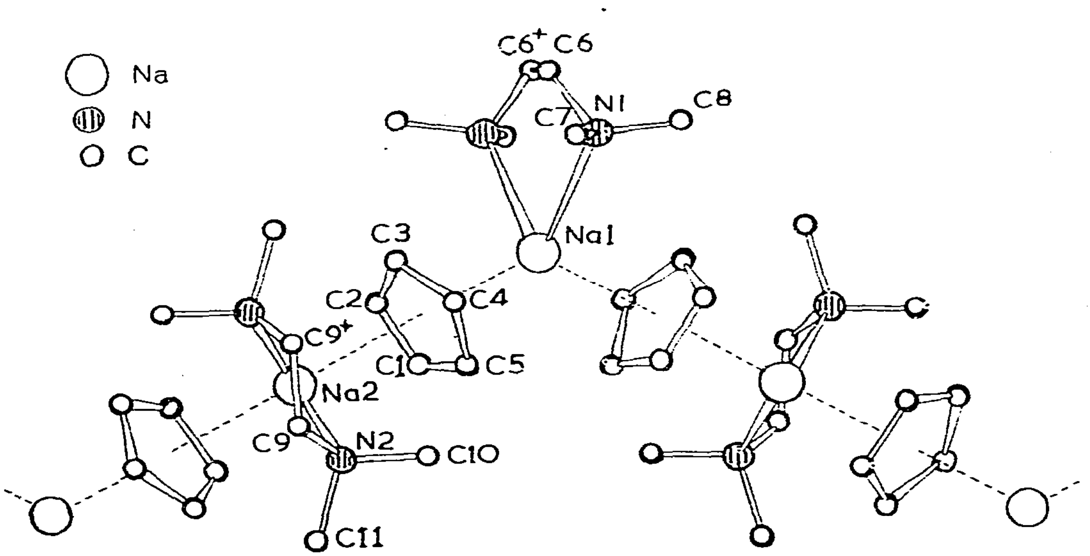

Fig. 1. Structure of compound X, $Na(C_5H_5)TMEDA$.

bonded repulsions between adjacent C_5H_5 rings.

The $-M(C_5H_5)M(C_5H_5)M(C_5H_5)-$ chain structure resembles those of $In(C_5H_5)$ [31], $Tl(C_5H_5)$ [31] and $Pb(C_5H_5)_2$ [32]. The degree of puckering of the chain (there are two crystallographically distinct Na—Na—Na angles of 128 and 119°) reflects the distorted tetrahedral coordination of the metal atoms (in $In(C_5H_5)$, the In—In—In angle is 137° [31] whereas in $Pb(C_5H_5)_2$, the Pb—Pb—Pb angles are 118 and 121° [32]). The chelating TMEDA groups have N—N distances of 308 and 305 pm, and both subtend an N—Na—N angle at the metal of only 72° illustrating the limited "bite" of this ligand and so underlining the importance of the size of the metal atom in determining

TABLE 5

ATOMIC COORDINATES OF $Na(C_5H_5)$ TMEDA

Atom	*x/a*	*y/b*	*z/c*
Na(1)	0.2500	0.0000	0.1237(2)
Na(2)	0.0000	0.3013(5)	0.2500
N(1)	0.3059(6)	0.1366(9)	0.0076(5)
N(2)	0.0457(5)	0.5409(7)	0.3224(4)
C(1)	0.1263(9)	0.0724(14)	0.2301(7)
C(2)	0.0811(6)	0.0798(16)	0.1658(9)
C(3)	0.1056(7)	0.2077(15)	0.1303(5)
C(4)	0.1661(7)	0.2767(10)	0.1708(8)
C(5)	0.1782(7)	0.1934(17)	0.2345(6)
C(6)	0.2535(12)	0.0798(12)	−0.0524(5)
C(7)	0.2888(8)	0.2966(15)	0.0108(7)
C(8)	0.3946(8)	0.1145(13)	−0.0024(6)
C(9)	0.0012(9)	0.6661(9)	0.2888(5)
C(10)	0.1360(7)	0.5551(12)	0.3184(6)
C(11)	0.0226(7)	0.5363(11)	0.3992(6)

TABLE 6

BOND DISTANCES IN $Na(C_5H_5)$ TMEDA

Bond	Distance (pm)	Bond	Distance (pm)
Na(1)—N(1)	261.8(9)	Na(2)—N(2)	262.8(7)
Na(1)—C(1)	285.6(15)	Na(2)—C(1)	289.7(14)
Na(1)—C(2)	289.4(10)	Na(2)—C(2)	282.9(14)
Na(1)—C(3)	296.3(12)	Na(2)—C(3)	289.8(11)
Na(1)—C(4)	294.6(10)	Na(2)—C(4)	303.3(12)
Na(1)—C(5)	290.9(13)	Na(2)—C(5)	301.7(11)
N(1)—C(6)	147.7(10)	N(2)—C(9)	146.3(12)
N(1)—C(7)	145.9(9)	N(2)—C(10)	144.9(13)
N(1)—C(8)	144.2(15)	N(2)—C(11)	146.0(13)
C(6)—C(6^{II})	143.2(15)	C(9)—C(9^{IV})	142.9(12)
C(1)—C(2)	138.7(20)	C(1)—C(5)	136.6(19)
C(2)—C(3)	137.5(19)	C(3)—C(4)	137.6(19)
C(4)—C(5)	140.2(18)		

whether TMEDA chelates (as in this case) or bridges (as in the potassium fluorenyl complex $KC_{13}H_9$(TMEDA) [2]). The cyclopentadienyl rings of Na(C_5H_5)TMEDA incidentally subtend an angle of only 47° at the metal (their carbon atoms lie on circles of radius 117 pm and are 292 pm from the metal atoms).

This structure is consistent with an ionic model of the bonding in terms of Na(TMEDA)$^+$ cations and $C_5H_5^-$ anions and may be contrasted with the structures of $[GaMe_2(C_5H_5)]_n$ [33] and $[ZnMe(C_5H_5)]_n$ [34], which also have —M(C_5H_5)M(C_5H_5)M(C_5H_5)— chain structures with, however, a greater degree of covalency in the metal—ring bonding as shown by the distortions from η^5-geometry in the gallium and zinc compounds. The metal—carbon distances (average 292 pm) in X are nevertheless short enough to allow a degree of covalency similar to that in the Grignard complex Mg(C_5H_5)Br($Et_2NCH_2CH_2NEt_2$) [35], for which Mg—C is 255 pm and Mg—N 226 pm, difference 29 pm (cf. Na—C 292 pm, Na—N 262 pm, difference 30 pm in X). The failure of X to take up a second TMEDA molecule, to form $Na(TMEDA)_2^+$-$(C_5H_5)^-$, indicates the strength of the metal—ring bonding.

A further structural indication of the anionic character of the cyclopenta-

TABLE 7

BOND ANGLES IN $Na(C_5H_5)$ TMEDA

	Angle (°)		Angle (°)
N(1)—Na(1)—N(1^{I})	70.5	N(2)—Na(2)—N(2^{I})	70.5
C(6)—N(1)—C(7)	105.1(9)	C(6)—N(1)—C(8)	114.4(9)
C(7)—N(1)—C(8)	108.9(9)	C(9)—N(2)—C(10)	113.2(7)
C(10)—N(2)—C(11)	107.6(7)	C(9)—N(2)—C(11)	107.9(7)
C(2)—C(1)—C(5)	109.1(10)	C(1)—C(2)—C(3)	107.3(10)
C(2)—C(3)—C(4)	108.5(10)	C(3)—C(4)—C(5)	108.2(11)
C(4)—C(5)—C(1)	106.8(11)	N(1)—C(6)—C(6^{II})	112.8(11)
N(2)—C(9)—C(9^{IV})	115.8(8)		

dienyl groups in X is the ring C—C distance of 138 pm (average), shorter than is usual for metal cyclopentadienides (cf. 142.5 pm for various beryllium compounds $Be(C_5H_5)X$ [36—38], 143 pm for $Fe(C_5H_5)_2$ [39] and $Ni(C_5H_5)_2$ [40], and 142 pm for $Mg(C_5H_5)_2$ [41]).

Compound X probably dissolves as the monomer, $Na(C_5H_5)$TMEDA, in benzene, toluene and THF, though its solubility in cold benzene was too low to confirm this by cryoscopic measurements. In these solutions it probably retains a *pentahapto* ring geometry, though when coordinating to only one metal atom, the cyclopentadienyl group may well form somewhat shorter Na—C bonds than occur in the crystal. The solutions and crystals of X, indeed of all the compounds in Table 1, are exceedingly sensitive to air and moisture; crystals of X rapidly turn brown and then black on exposure to air.

In conclusion, the extremely air- and moisture-sensitive adducts of $Na(C_5H_5)$ and $Na(C_5H_4Me)$ listed in Tables 1 and 2 have been isolated and characterised. Their infrared and ^1H NMR spectra are consistent with *pentahapto* coordination of their cyclopentadienyl groups. In crystalline $Na(C_5H_5)$TMEDA, η^5-C_5H_5 groups bridge Na(TMEDA) units in a puckered chain structure.

Experimental

Standard vacuum line or inert atmosphere (dry nitrogen) techniques were used for manipulations. The sodium cyclopentadienides I and II were prepared by thermal cracking of the cyclopentadiene dimers and reaction of the monomers, C_5H_6 and C_5H_5Me, with a dispersion of sodium in THF [23,28,29]. The resulting solutions were filtered and evaporated to dryness or treated with an excess of the base as appropriate.

Carbon, hydrogen and nitrogen were determined by combustion analysis using a Perkin—Elmer Model 240 Elemental Analyzer. Sodium was determined using an atomic absorption spectrophotometer (Perkin—Elmer Model 403). Infrared spectra in the range 4000—600 cm^{-1} were recorded using Nujol mulls between KBr disks on a Perkin—Elmer 457 instrument, and in the range 600—200 cm^{-1} between CsI discs protected by polyethylene film on a Perkin—Elmer 577 instrument. ^1H NMR spectra were recorded at 60 MHz on a Varian A56/60D spectrometer.

The bases and solvents used were rigorously dried and (where volatile) were vacuum-distilled before use.

Acknowledgement

We thank S.R.C. for financial support (to T.A.).

References

1 B.J. Wakefield, The Chemistry of Organolithium Compounds, Pergamon, Oxford, 1974, p. 11.
2 G.D. Stucky, Advan. Chem. Ser., 130 (1974) 56.
3 S.P. Patterman, I.L. Karle and G.D. Stucky, J. Amer. Chem. Soc., 92 (1970) 1150.
4 J.J. Brooks and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 7333.
5 J.J. Brooks, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 7339.
6 J.J. Brooks, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 7346.

7 M. Walczak and G.D. Stucky, J. Organometal. Chem., 97 (1975) 313.
8 W.E. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 97 (1975) 737.
9 W.E. Rhine, J. Davis and G.D. Stucky, J. Amer. Chem. Soc., 97 (1975) 2079.
10 S.K. Arora, R.B. Bates, W.A. Beavers and R.S. Cutler, J. Amer. Chem. Soc., 97 (1975) 6271.
11 D. Bladauski, H. Dietrich, H.-J. Hecht and D. Rewicki, Angew. Chem., 89 (1977) 490.
12 L.D. McKeever and R. Waack, J. Organometal. Chem., 28 (1971) 145.
13 W.H. Glaze, J.E. Hanicak, M.L. Moore and J. Chaudhuri, J. Organometal. Chem., 44 (1972) 39.
14 J.B. Smart, R. Hogan, P.A. Scherr, M.T. Emerson and J.P. Oliver, J. Organometal. Chem., 64 (1974) 1.
15 M. Tomoi, T. Yoneyama and H. Kakiuchi, Bull. Soc. Chem. Jap., 48 (1975) 1285.
16 B. Lundgren, G. Levin, S. Claesson and M. Szwarc, J. Amer. Chem. Soc., 97 (1975) 262.
17 J.F. Sebastian, J.R. Grunwell and B. Hsu, J. Organometal. Chem., 78 (1974) C1.
18 E.R. Tidwell and B.R. Russell, J. Organometal. Chem., 80 (1974) 175.
19 D.J. Brauer and G.D. Stucky, J. Amer. Chem. Soc., 92 (1970) 3956.
20 D.J. Brauer and G.D. Stucky, J. Organometal. Chem., 37 (1972) 217.
21 H.P. Fritz, Chem. Ber., 92 (1959) 780.
22 H.P. Fritz and R. Schneider, Chem. Ber., 93 (1960) 1171.
23 S. McLean and P. Haynes, Can. J. Chem., 41 (1963) 1231.
24 H.P. Fritz and L. Schaefer, Chem. Ber., 97 (1964) 1829.
25 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 240.
26 W.T. Ford, J. Organometal. Chem., 32 (1971) 27.
27 N.M. Sergeyev, Progr. Nucl. Magn. Resonance Spectrosc., 9 (1973) 71.
28 R.B. King and F.G.A. Stone, Inorg. Synth., 7 (1963) 99.
29 J. Birmingham, Advan. Organometal. Chem., 2 (1964) 367.
30 T. Aoyagi, H.M.M. Shearer, K. Wade and G. Whitehead, J. Chem. Soc. Chem. Commun., (1976) 164.
31 E. Frasson, F. Menegus and C. Panattoni, Nature, 199 (1963) 1087.
32 C. Panattoni, G. Bombieri and U. Croatto, Acta Cryst., 21 (1966) 823.
33 K. Mertz, F. Zettler, H.D. Hausen and J. Weidlein, J. Organometal. Chem., 122 (1976) 159.
34 T. Aoyagi, H.M.M. Shearer, K. Wade and G. Whitehead, J. Organometal. Chem., 146 (1978) C29.
35 C. Johnson, J. Toney and G.D. Stucky, J. Organometal. Chem., 40 (1972) C11.
36 A. Haaland, Acta Chem. Scand., 22 (1968) 3030.
37 D.A. Drew and A. Haaland, Acta Chem. Scand., 26 (1972) 3079, 3351.
38 A. Haaland and D.P. Novak, Acta Chem. Scand., A28 (1974) 153.
39 R.K. Bohn and A. Haaland, J. Organometal. Chem., 5 (1965) 470.
40 L. Hedberg and K. Hedberg, J. Chem. Phys., 53 (1970) 1228.
41 A. Haaland, J. Lusztyk, D.P. Novak, J. Brunvoll and K.B. Starowieyski, J. Chem. Soc. Chem. Commun., (1974) 54.