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Bulky Metal Aryloxides, Arylamides, and Sulphur and Phosphorus Analogues. Part 1. Synthetic and Chemical Studies of Titanium and Zirconium Aryloxides†

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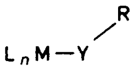
The synthesis and characterisation of several classes of aryloxides (OR) of Ti^{IV}, Ti^{III}, Zr^{IV}, and Li are described. Those of Ti^{IV} are of eight distinct classes: $[Ti(OR)_4]$, $[TiCl_2(OR)_2]$, $[TiCl_2(OR)_2(thf)_2]$, $[Ti(NMe_2)_2(OR)_2]$, $[Ti(OMe)_2(OR)_2]$, $[TiCl(OR')(OR)_2]$, $[TiCl(R')(OR)_2]$, and $[TiCl(\eta\text{-}C_5H_5)(OR)_2]$ (R′ = alkyl, thf = tetrahydrofuran); the Ti^{III} complexes are of types $[\{TiCl(OR)_2\}_n]$ and $[Ti(\eta\text{-}C_5H_5)_2(OR)]$; the Zr^{IV} complexes are of seven types: $[ZrCl_2(OR)_2]$ and $[Zr(\eta\text{-}C_5H_5)_2(OR)X]$, with X = OR, Cl, NMe_2, OMe, $OC(O)NMe_2$, or $N(Ph)C(O)NMe_2$; the new lithium aryloxides have formula $[Li(OR)(OEt_2)]_n$. Most of the results relate to the ligands $2,6\text{-}Me_2C_6H_3O^-$, $2,6\text{-}Pr^i{}_2C_6H_3O^-$, $2,6\text{-}Bu^t{}_2C_6H_3O^-$, $4\text{-}Me\text{-}2,6\text{-}Bu^t{}_2C_6H_2O^-$, $2,4,6\text{-}Bu^t{}_3C_6H_2O^-$, $3,5\text{-}Bu^t{}_2C_6H_3O^-$, and $2,4\text{-}Bu^t{}_2C_6H_3O^-$. The new complexes are readily soluble in diethyl ether and many also in hydrocarbons. Synthetic procedures include the following systems: (*i*) $LiBu^n\text{–}ROH\text{–}OEt_2$, for Li aryloxides; (*ii*) Ti^{IV}, Ti^{III}, or Zr^{IV} chlorides with $[Li(OR)(OEt_2)]_n$; (*iii*) for Ti^{III}, a redox reaction of type (*ii*) using a Ti^{IV} chloride as precursor; (*iv*) a Ti^{IV} or Zr^{IV} dimethylamide and ROH; and (*v*) for the Zr^{IV} carbamate or Zr^{IV} urea, a CO_2 or PhNCO insertion into the appropriate Zr^{IV} dimethylamide.

This series will deal with metal complexes derived from bulky α-aryl-substituted O-, S^{II}-, N-, and P^{III}-centred ligands. Much attention will be devoted to 2,6-disubstituted-aryl derivatives, especially those containing the bulky $C_6H_3Bu^t{}_2\text{-}2,6$ moiety (R). Among prominent ligands will be those of formula $\bar{Y}C_6H_2Bu^t{}_3\text{-}2,4,6$ (Y = O, S, NH, or PH). The 2,6-di-t-butylphenols (ROH) are cheap and readily available by virtue of their use as antioxidants, a property which derives from the persistent nature of the appropriate radical $\dot{O}R$.

Features which we believe to be of interest will include the prospect of obtaining metal complexes which will be (*i*) highly lipophilic, convenient for studying their chemistry in an inert hydrocarbon solvent; (*ii*) crystalline, and hence suitable for study by *X*-ray diffraction; (*iii*) monomeric; (*iv*) in a variety of cases, of unusual metal co-ordination number or oxidation state; (*v*) hindered with respect to M₮Y and/or Y₮R bond rotation; (*vi*) capable of existing in tautomeric forms of structure **(I)** (the more usual) or **(II)** (substituents on the aromatic ring being omitted); and (*vii*) part of a ring system, *e.g.* **(III)** (from $YC_6H_3Bu^t{}_2\text{-}2,6$), resulting from a C–H activation step.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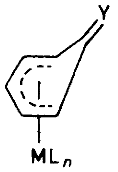
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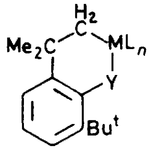
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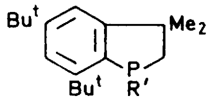
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Our first publication in this area was in 1980,[1] and further preliminary communications have dealt with (*a*) 2,6-di-t-butylaryloxides of Li,[1] Na, Mg,[2] Ti^{III},[3] Rh^I [the tautomer **(II)**], Ge^{II},[4] Sn^{II}, Pb^{II}, P^{II},[5] Th^{IV},[6] U^{IV}, Sc^{III},[7] Y^{III}, La^{III}, Pr^{III},[8] Nd^{III}, Dy^{III}, Ho^{III}, Er^{III}, or Yb^{III}; (*b*) 2,6-di-isopropyl- and 2,4,6-tri-t-butyl-arenethiolates of Li,[8] Ge^{II}, Sn^{II}, and Pb^{II}; and (*c*) 2,4,6-tri-t-butylanilides of Li[9] and B.[10]

The present paper is concerned with the synthesis and characterisation of (i) Ti^{IV} aryloxides belonging to eight distinct classes (R = aryl, R′ = alkyl): $[Ti(OR)_4]$, $[TiCl_2(OR)_2]$, $[TiCl_2(OR)_2(thf)_2]$ (thf = tetrahydrofuran), $[Ti(NMe_2)_2(OR)_2]$, $[Ti(OMe)_2(OR)_2]$, $[TiCl(OR')(OR)_2]$, $[TiCl(R')(OR)_2]$, and $[TiCl(\eta\text{-}C_5H_5)(OR)_2]$; (ii) two types of Ti^{III} aryloxides: $[\{TiCl(OR)_2\}_n]$ and $[Ti(\eta\text{-}C_5H_5)_2(OR)]$ (see also ref. 3); (iii) seven types of Zr^{IV} aryloxides: $[ZrCl_2(OR)_2]$, $[Zr(\eta\text{-}C_5H_5)_2(OR)_2]$, $[ZrCl(\eta\text{-}C_5H_5)_2(OR)]$, $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR)]$, $[Zr(\eta\text{-}C_5H_5)_2(OMe)(OR)]$, $[Zr(\eta\text{-}C_5H_5)_2\{OC(O)NMe_2\}(OR)]$, and $[Zr(\eta\text{-}C_5H_5)_2\{N(Ph)C(O)NMe_2\}(OR)]$; and (iv) some new lithium aryloxides, used in the preparation of some of the compounds in (i)—(iii), of formula $[Li(OR)(OEt_2)]_n$. In Part 2,[11] the *X*-ray structures, as well as the results of variable temperature n.m.r. study, of some of these compounds will be described.

The complex chemistry of 2,6-di-t-butylaryloxides can be traced back to the report of Shobatake and Nakamoto[12] in 1970 on the dimeric nature in benzene solution of $LiOR^4$-(thf) ($OR^4 = OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4$). Later studies, apart from our own, dealt with related aryloxides of Be,[13] Mg,[14] Al,[15] Ti^{IV},[16,17] Cr^{II},[18] Mn^{II},[19] Cu^I,[20] Zr^{IV},[16,17] Hf^{IV},[21] Ta^V,[22,23] and W^{VI}.[24] A particular notable observation, by Rothwell and co-workers,[17,22,23] was that C–H activation of a t-butyl group was possible, either thermally or photochemically, from a (2,6-di-t-butylaryloxo)tantalum(v) hydrocarbyl, to yield a metallacycle of type **(III)** (Y = O); there is evidence for a related reaction using a W^{VI} analogue.[24] Such C–H activation is also established in a formally rather different system: from $PCl(C_6H_2Bu^t{}_3\text{-}2,4,6)R'$ and $LiBu^n$ to give **(IV)** [$R' = CH(SiMe_3)_2$].[25]

The chemistry of metal aryloxides was reviewed in 1982.[26,]†

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† No reprints available.

† Bibliographic details pertaining to refs. 27—30,33 of the present paper are quoted incorrectly in ref. 26.

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The titanium and zirconium compounds referred to therein were the homoleptic M^{IV} complexes $[Ti(OPh)_4]$ (a dimer by cryoscopy in C_6H_6), $[Zr(OPh)_4]$, $[Ti(OC_6H_4Cl)_4]$, and some of their adducts with neutral ligands [for Ti: PhOH, ClC_6H_4OH, NH_3, α-$C_{10}H_7NH_2$, PhCOMe, or PhOCOMe; for Zr: PhOH, 2py (pyridine), bipy (2,2′-bipyridine), phen (1,10-phenanthroline), 2pyO (pyridine *N*-oxide), or bipyO (2,2′-bipyridine *N*,*N*′-dioxide)]. *X*-Ray data[27] showed that the phenol adduct is $[\{Ti(\mu\text{-}OPh)(OPh)_3(HOPh)\}_2]$; heteroleptic compounds mentioned were $[TiCl(OPh)_3]$, $[Ti(OBu^t)_2(OPh)_2]$ [and its thermal decomposition products $Ph\{OTi(OBu^t)(OPh)\}_4OPh$ and $Ph\{OTi(OBu^t)(OH)\}_4OH$],[26] $TiCl(OPh)_3(HOPh)$, and $[Ti(OR')_n(OPh)_{4-n}]$ (R' = Et or Pr^i, n = 1 or 2; these compounds gave symmetric products on heating),[28] and $[\{TiCl(\mu\text{-}OPh)(OPh)_2\}_2]$ (structure deduced from *X*-ray data on the crystal,[29] as well as cryoscopy in C_6H_6 and variable-temperature ^1H n.m.r.[30]).

Other phenoxotitanium compounds to have been described are $H\{Ti(OPh)_2\}_3$, $H\{Ti(OPh)_2\}_2(N_2)$, $H\{TiCl(OPh)_2(thf)_2\}_2$, $K_{11}Ti_3(OPh)_7$, $\{TiMe(OPh)_2\}_n$, $Ti_5Cl_2(OPh)_8$, $Ti_5(OPh)_8(SiMe_2)$, and $[Ti(CH_2SiMe_3)_2(OPh)_2]$.[30] Recently, it was shown that excess of 2,4,6-tri-t-butylphenol (R^5OH) with $[M(NMe_2)_4]$ at 120 °C afforded $[M(NMe_2)_2(OR^5)_2]$ (M = Ti or Zr);[16] *X*-ray data on the titanium compound revealed a distorted tetrahedral co-ordination geometry around the metal. The complex $[TiCl_2(OR^5)_2]$ was obtained by treating the dimethylamide with $SiClMe_3$. Based on another bulky phenol, 2,6-$Bu^t_2C_6H_3OH$ (R^3OH), the Zr and Hf complexes $[MCl(OR^3)_3]$ were obtained from MCl_4 and an excess of $LiOR^3$ in benzene or diethyl ether; the *X*-ray structure of the hafnium complex was determined.[21] Each of these chloro(aryloxide) complexes was resistant to further Cl^-/R^3O^- or $Cl^-/SiMe_3CH_2^-$ exchange, but using methyl-lithium in diethyl ether $[HfMe(OR^3)_3]$ was obtained.

Since the submission of this paper, Rothwell and co-workers[31] have reported on $[Ti(OR^3)_2X_2]$ (X = Cl or Br), $[MCl(OR^3)_3]$ (M = Ti, Zr, or Hf), and $[Ti(OR^3)_3X]$ (X = Br or I), which are monomers in benzene and show n.m.r.-inequivalent Bu^t groups at low temperature; *X*-ray data were provided for $[TiI(OR^3)_3]$ and $[HfCl(OR^3)_3]$, and cyclic voltammetry showed that the Ti^{IV} dihalides undergo reversible one-electron reduction to the monoanions, while the monohalides tend to afford $[Ti(OR^3)_3]$.

Results and Discussion

Seven different phenols were employed in the present study: 2,6-$Me_2C_6H_3OH$ (R^1OH), 2,6-$Pr^i_2C_6H_3OH$ (R^2OH), 2,6-$Bu^t_2C_6H_3OH$ (R^3OH), 4-Me-2,6-$Bu^t_2C_6H_2OH$ (R^4OH), 2,4,6-$Bu^t_3C_6H_2OH$ (R^5OH), 3,5-$Bu^t_2C_6H_3OH$ (R^6OH), 2,4-$Bu^t_2C_6H_3OH$ (R^7OH).

The new data relate mainly to the 2,6-dialkylphenols R^1OH—R^5OH. The phenols R^6OH and R^7OH were chosen to provide comparative data; the derived ligands R^6O^- and R^7O^- do not have such stringent steric requirements and yet each has two Bu^t substituents which were expected to provide metal complexes of good hydrocarbon solubility.

The new compounds here described are aryloxides of titanium(IV), **(1a)**—**(1j)**, titanium(III), **(1k)** and **(1l)**, zirconium(IV), **(2a)**—**(2m)**, and lithium, **(3a)**—**(3c)**. The lithium derivatives of these phenols were often required as aryloxide transfer reagents. Four of these were already known: obtained from R^1OH, R^3OH, R^4OH, and R^5OH; but for one of them, $[Li(OR^1)(OEt_2)]_n$, an improved synthesis is reported, equation (i) (R^1OH = 2,6-$Me_2C_6H_3OH$).

$$LiBu^n + R^1OH \xrightarrow{OEt_2,\ 0\,^\circ C} \tfrac{1}{n}[Li(OR^1)(OEt_2)]_n + C_4H_{10} \qquad (i)$$

It is our practice to use crystalline lithium compounds $[LiX(L)]_n$ of established analytical purity as X^- transfer reagents;[32] among the advantages that this offers are (*i*) confidence with regard to reaction stoicheiometry, requiring merely accurate weighing, and (*ii*) ease of manipulation. As for (*ii*), this arises because the incorporation of a ligand L produces a low degree of molecular aggregation (n is generally 2) and hence usually [but not invariably, see compound **(3c)**, below] the availability of a non-polar solvent, often a hydrocarbon or OEt_2, as the reaction medium. In this work $X^- = R^1O^-$—R^7O^- and L = OEt_2, and each of the compounds $[Li(OR^x)(OEt_2)]_n$ was readily soluble in diethyl ether. By analogy with the *X*-ray data available for $[Li(\mu\text{-}OR^4)(OEt_2)]_2$,[1] it is likely that each of the lithium aryloxides **(3a)**—**(3c)** has a similar solid-state structure.

Titanium(IV) *and Titanium*(III) *Aryloxides, Compounds* **(1a)**—**(1l)**.—Reaction of $[TiCl_4]$ with $[Li(OR^4)(OEt_2)]_2$ in diethyl ether proceeded rapidly at 0 °C or room temperature to give a high yield of $[TiCl_2(OR^4)_2]$ **(1d)** [equation (ii), M = Ti, R^4O = 4-Me-2,6-$Bu^t_2C_6H_2O$]. Further reaction of the titanium(IV) dichloro(aryloxide) **(1d)** with excess of the lithium reagent did not occur, even after several hours at reflux. This is attributed to steric hindrance imposed about titanium by the four *o*-Bu^t groups; the incomplete replacement of all the chlorides of a transition metal chloride MCl_m by 2,6-di-t-butylaryloxo-ligands has precedent for M = Ta^V,[23] Th^{IV},[6] U^{IV} (and even Ti^{IV} [23d] and Zr^{IV}).

$$MCl_4 + [Li(OR^4)(OEt_2)]_2 \longrightarrow [MCl_2(OR^4)_2] + 2LiCl \qquad (ii)$$

(1d), M = Ti
(2a), M = Zr

Attempts to prepare **(1d)** by reaction of the parent phenol R^4OH with $[TiCl_4]$ led mainly to substantial quantities of impure oily products. One preparation in diethyl ether gave a material considered to be $[TiCl_3(OR^4)(HOR^4)]$, on the basis of its ^1H n.m.r. spectrum. There are several examples in the literature of aryloxometal complexes containing hydrogen-bonded phenol.[27,33]

Complex **(1d)** is a deep red-brown crystalline solid which displays a limited moisture sensitivity; it may be handled briefly in air. Analogous titanium(IV) alkoxides are colourless.[34] An *X*-ray crystal structure determination[11] of **(1d)** has revealed it to be monomeric, and also showed that the aryloxide ligands are σ-bound [*i.e.*, as in **(I)** rather than **(II)**]; thus **(1d)** is an eight-electron complex. The ^1H (Table 2) and ^{13}C (Table 3) n.m.r. spectra of the new aryloxides of Ti^{IV} or Zr^{IV} are entirely consistent with the view that the RO^- ligands are invariably present as O-centred σ, rather than C_5-centred η^5, ligands.

Aspects of the chemistry of Ti^{IV} and Ti^{III} 2,6-di-t-butyl-4-methylaryloxides are summarised in Scheme 1, which focuses particularly on **(1d)**. Treatment of **(1d)** with two equivalents of a sodium alkoxide gave the bis-methoxide, **(1f)**, but only the mono-ethoxide, **(1g)**, or mono-t-butoxide, **(1h)**, using the bulkier homologues. Such well characterised mixed alkoxide/aryloxide derivatives, as far as we are aware, are unprecedented, and might have been expected to redistribute to symmetrical products; their stability is probably of kinetic origin, the bulky R^4O^- ligands making the possibility of an associative transition state for redistribution energetically unfavourable.

There was no evidence for adduct formation upon treatment of **(1d)** with pyridine. By contrast, the less hindered $[\{TiCl_2(OPh)_2\}_2]$ readily formed adducts such as $[TiCl_2(OPh)_2(py)_2]$.[26,29]

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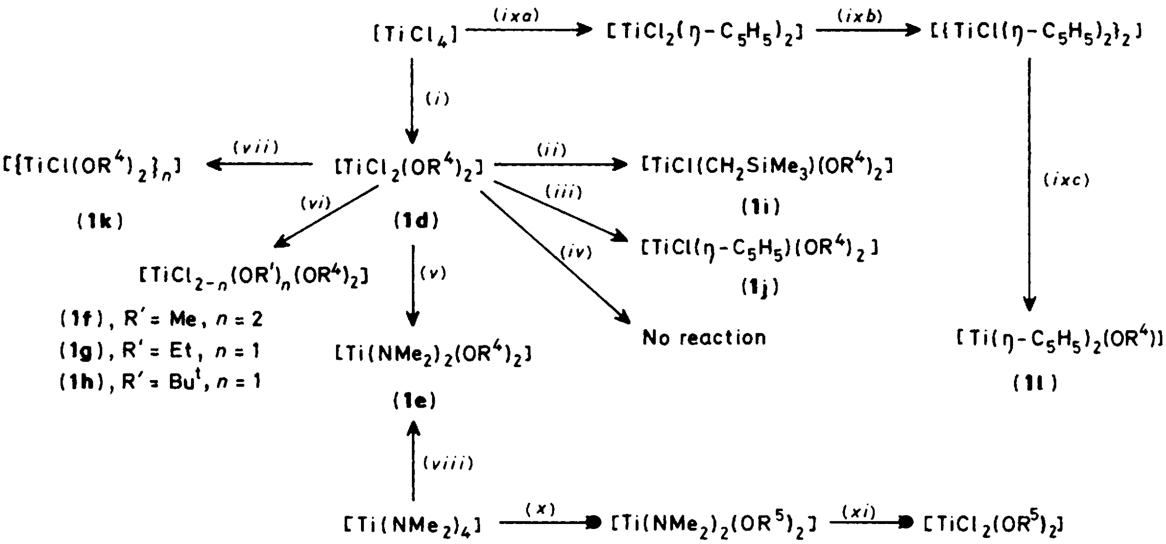
Table 1. Yields, colours, melting points, and analytical data for the new aryloxides of Ti^{IV}, (**1a**)—(**1j**), Ti^{III}, (**1k**), Zr^{IV}, (**2a**)—(**2m**), and Li, (**3a**)—(**3c**)[a]

	Compound	Yield[b] (%)	Colour	M.p. (°C)[c]	Found (required) (%) C	H	N
(**1a**)	$[Ti(OR^2)_4]$	50	Yellow	> 330[d]	76.2 (76.2)	8.95 (9.05)	
(**1b**)	$[TiCl_2(OR^1)_2(thf)_2]$	71	Rust-red		57.1 (57.0)	6.85 (6.80)	
(**1c**)	$[\{TiCl_2(OR^1)_2\}_n]$	67	Red	64—66	53.4 (53.2)	5.10 (5.00)	
(**1d**)	$[TiCl_2(OR^4)_2]$	93	Red-brown	176—177.5	64.6 (64.6)	8.45 (8.30)	
(**1e**)	$[Ti(NMe_2)_2(OR^4)_2]$	50	Orange	198	71.3 (71.1)	9.90 (10.0)	4.85 (4.85)
(**1f**)	$[Ti(OMe)_2(OR^4)_2]$	36	Yellow	170—174	69.8 (69.8)	9.90 (9.90)	
(**1g**)	$[TiCl(OEt)(OR^4)_2]$	16	Orange	121—123.5	67.6 (67.8)	9.35 (9.05)	
(**1h**)	$[TiCl(OBu^t)(OR^4)_2]$	47	Yellow-orange	183—184.5	69.4 (68.6)	9.30 (9.30)	
(**1i**)	$[TiCl(CH_2SiMe_3)(OR^4)_2]$	61	Yellow-tan	169—170	66.0 (67.0)	9.65 (9.45)	
(**1j**)	$[TiCl(\eta\text{-}C_5H_5)(OR^4)_2]$	45	Red-brown	193 (decomp.)	71.4 (71.6)	8.75 (8.75)	
(**1k**)	$[\{TiCl(OR^4)_2\}_n]$[e]	41	Green	130 (decomp.)	69.0 (69.0)	9.40 (8.90)	
(**2a**)	$[ZrCl_2(OR^4)_2]$	53	White	185—186	60.2 (60.0)	7.85 (7.70)	
(**2b**)	$[ZrCl(\eta\text{-}C_5H_5)_2(OR^2)]$	30	Beige	125—132	60.6 (60.9)	6.45 (6.25)	
(**2c**)	$[ZrCl(\eta\text{-}C_5H_5)_2(OR^3)]$	18	Pale yellow	185—190	62.6 (62.4)	6.90 (6.75)	
(**2d**)	$[ZrCl(\eta\text{-}C_5H_5)_2(OR^4)]$	68	Pale yellow	196—201	63.0 (63.1)	6.70 (7.00)	
(**2e**)	$[ZrCl(\eta\text{-}C_5H_5)_2(OR^5)]$	9	Pale yellow	141—143	64.7 (64.9)	7.60 (7.60)	
(**2f**)	$[Zr(\eta\text{-}C_5H_5)_2(OR^2)_2]$	47	White	180—182	71.1 (70.9)	7.65 (7.70)	
(**2g**)	$[Zr(\eta\text{-}C_5H_5)_2(OR^6)_2]$	27	White	153—159	68.3 (72.2)	8.00 (8.30)	
(**2h**)	$[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^3)]$	64	Yellow	169—172	66.2 (66.3)	7.90 (7.90)	2.75 (3.00)
(**2i**)	$[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^4)]$	19	Yellow	204—208	66.0 (66.9)	7.65 (8.10)	2.45 (2.90)
(**2j**)	$[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^5)]$[f]	—					
(**2k**)	$[Zr(\eta\text{-}C_5H_5)_2(OMe)(OR^3)]$	11	Yellow	160—164	64.1 (65.6)	7.30 (7.45)	
(**2l**)	$[Zr(\eta\text{-}C_5H_5)_2\{OC(O)NMe_2\}(OR^3)]$	24	White	120—140	60.8 (62.9)	7.00 (7.20)	2.45 (2.70)
(**2m**)	$[Zr(\eta\text{-}C_5H_5)_2\{N(Ph)C(O)NMe_2\}(OR^3)]$	22	White	154 (decomp.)			
(**3a**)	$[Li(OR^2)(OEt_2)]_n$	97	White	120—170 (decomp.)			
(**3b**)	$[Li(OR^6)(OEt_2)]_n$	96	White	> 300	74.6 (75.5)	10.9 (10.9)	
(**3c**)	$[Li(OR^7)(OEt_2)]_n$	37	White	211 (decomp.)	76.8 (75.5)	10.6 (10.9)	

[a] Abbreviations: $OR^1 = OC_6H_3Me_2$-2,6; $OR^2 = OC_6H_3Pr^i{}_2$-2,6; $OR^3 = OC_6H_3Bu^t{}_2$-2,6; $OR^4 = OC_6H_2Bu^t{}_2$-2,6-Me-4; $OR^5 = OC_6H_2Bu^t{}_3$-2,4,6; $OR^6 = OC_6H_3Bu^t{}_2$-3,5; $OR^7 = OC_6H_3Bu^t{}_2$-2,4. [b] Yields are not optimised. [c] Melting points were determined on samples under argon or dinitrogen in sealed tubes and are uncorrected. [d] The compound was reversibly thermochromic, changing colour gradually to blood-red on heating. [e] E.s.r. spectrum showed a broad singlet, $g_{av.} = 1.9446$. [f] Not isolated; n.m.r. data in Table 2.



Scheme 1. Aspects of the chemistry of titanium(IV) and titanium(III) complexes derived from 4-methyl-2,6-di-t-butylphenol (R^4OH) and 2,4,6-tri-t-butylphenol (R^5OH). (*i*) $[Li(OR^4)(OEt_2)]_2$ in OEt_2; (*ii*) $Mg(CH_2SiMe_3)_2$ in light petroleum; (*iii*) $Li(C_5H_5)$ in thf–OEt_2; (*iv*) pyridine, or $[Li(OR^4)(OEt_2)]_2$, or photolysis in OEt_2; (*v*) $\frac{2}{n}[Li(NMe_2)]_n$ in OEt_2; (*vi*) $2NaOR'$ in OEt_2; (*vii*) sodium amalgam or zinc dust in OEt_2; (*viii*) $4R^4OH$ in C_6H_6; (*ix*) successive treatment with (*a*) $2Tl(C_5H_5)$, (*b*) Zn dust, and (*c*) $[Li(OR^4)(OEt_2)]_2$ (ref. 3); (*x*) excess R^5OH, 120 °C (ref. 16); (*xi*) $SiClMe_3$, reflux 3 d (ref. 16)

Reaction of complex (**1d**) with lithium dimethylamide afforded $[Ti(NMe_2)_2(OR^4)_2]$ (**1e**), among the first (see ref. 16) well characterised mixed aryloxo/amido complexes; although mixed alkoxide/amides, *e.g.* $[Ti(NMe_2)(OPr^i)_3]$, are known.[35] An alternative route (see also ref. 16) to (**1e**), phenolysis of $[Ti(NMe_2)_4]$, was also found to be effective.

The 2,6-di-t-butyl-4-methylaryloxide (**1d**) was examined as a potential precursor to alkyl- or cyclopentadienyl-titanium

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complexes. Thus *two* equivalents of $Li(C_5H_5)$ gave $[TiCl(\eta\text{-}C_5H_5)(OR^4)_2]$ **(1j)** and similarly dialkylated Ti^{IV} compounds have also not been obtained. With $Mg(CH_2SiMe_3)_2$, $[TiCl(CH_2SiMe_3)(OR^4)_2]$ **(1i)** was formed, but the more powerful reagents $Li(CH_2SiMe_3)$ or $MgCl(CH_2SiMe_3)$ effected not only alkylation but also reduction, *e.g.*, to afford from the former $[\{TiCl(OR^4)_2\}_n]$ **(1k)**.

Reduction of $[TiCl_2(OR^4)_2]$ **(1d)** to bright green **(1k)** was best effected with one equivalent of either sodium amalgam or metallic zinc dust (the Ti^{III} compound may have R^4O^- in the η^5-bonding mode). The former reagent is preferred, as it led to a cleaner synthesis. Use of excess zinc afforded the same product, **(1k)**, but its formation was accompanied by a yellow-brown contaminant, which was not identified, although it was shown to be diamagnetic. It may well be related to an orange by-product, thought to be a cluster, obtained during zinc reduction of $[\{TiCl_2(OPh)_2\}_2]$.[30] The e.s.r. spectrum of the Ti^{III} aryloxide **(1k)** consisted of a broad singlet, $g_{av.} = 1.9446$, with no evidence of titanium satellites. The lack of coupling to titanium is presumably due to extensive delocalisation of the odd electron within the $Ti(OR^4)_2$ moiety; the e.s.r. spectrum of $[\{TiCl(\eta\text{-}C_5H_5)_2\}_2]$ similarly displays no titanium hyperfine interaction.[36]

Photolysis of complex **(1d)** in diethyl ether, in the cavity of an e.s.r. spectrometer, showed no paramagnetic species. The $R^4O^{\bullet}$ radical is known to be persistent and has a characteristic e.s.r. spectrum;[37] it has been observed previously during the photolysis of $M(OR^4)_2$ (M = Ge, Sn, or Pb) or $PCl(OR^4)_2$.[38]

Bright red $[TiCl_2(OC_6H_3Me_2\text{-}2,6)_2(thf)_2]$ **(1b)** was formed during reaction of $[TiCl_4]$ with $(LiOR^1)_n$ in thf–OEt_2 (1:1), the less bulky aryloxide ligand permitting the inclusion of two molecules of thf within the co-ordination sphere of the metal. The compound $(LiOR^1)_n$ is insoluble in most common aprotic organic solvents except thf, in which it has a limited solubility. Direct phenolysis of $[TiCl_4]$ in diethyl ether gave the thf-free aryloxide **(1c)**, equation (iii).

No pure product was obtained from reaction of $[TiCl_2(\eta\text{-}C_5H_5)_2]$ with one equivalent of $[Li(OC_6H_3Bu^t\text{-}2,6)(OEt_2)]_2$ in either thf or 1,2-dimethoxyethane. With two equivalents of $[Li(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)(OEt_2)]_2$ and a catalytic amount of *N,N,N',N'*-tetramethylethylenediamine (tmen), reduction occurred and deep purple crystals of $[Ti(\eta\text{-}C_5H_5)_2(OR^4)]$ were isolated. This Ti^{III} complex had previously been obtained by an alternative procedure, equation (iv);[3] $g_{av.} = 1.9795$ at 20 °C in toluene, with again no indication of ^{47}Ti hyperfine structure.

Use of the amine elimination procedure, as a route to bis(cyclopentadienyl)titanium(IV) aryloxides, was thwarted in the case of di-isopropylphenol by the high lability of the cyclopentadienyl moieties. Thus, $[Ti(OC_6H_3Pr^i{}_2\text{-}2,6)_4]$ **(1a)** was unexpectedly obtained upon phenolysis of $[Ti(\eta\text{-}C_5H_5)_2(NMe_2)_2]$, as well as, more conventionally, by treatment of $[Ti(NMe_2)_4]$ with an excess of the phenol, equation (v). This contrasts with the behaviour of the more bulky phenol 4-Me-2,6-$Bu^t{}_2C_6H_2OH$, which reacted with $[Ti(NMe_2)_4]$ to afford the mixed amido–aryloxo-product $[Ti(NMe_2)_2(OR^4)_2]$ **(1e)**, Scheme 1. Complex **(1a)** was observed to be thermochromic, the yellow crystals gradually turning blood-red on heating to *ca.* 300 °C. A thf solution of **(1a)** reacted within 2 h with a stoicheiometric equivalent of sodium metal, but no pure product was isolated from the resultant deep green solution.

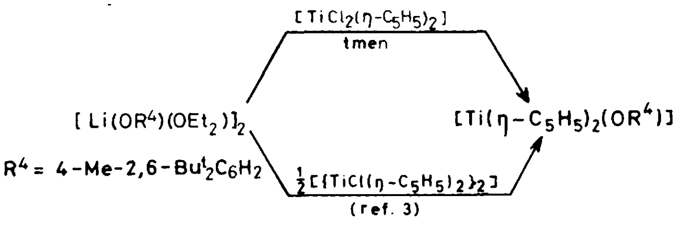
Zirconium(IV) *Aryloxides, Compounds* **(2a)**—**(2m)**.—The new compounds are $[ZrCl_2(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2]$ **(2a)** and 12 zirconocene(IV) aryloxides (for a summary, see Scheme 2).

The complex **(2a)** was prepared according to equation (ii) (M = Zr). It was surprisingly difficult to purify, requiring three fractional crystallisations before an analytically acceptable sample was obtained; this may have been due to inclusion of OEt_2 or thf. [No attempt was made to study the reaction of complex **(2a)** with either pyridine or a reducing agent.]

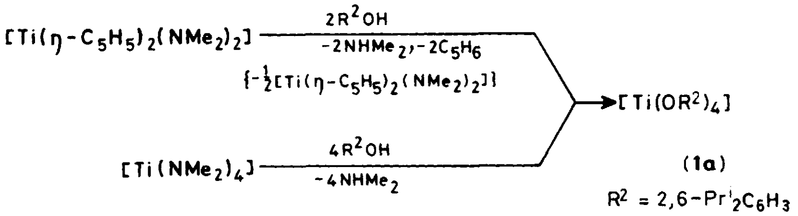
Chlorobis(cyclopentadienyl)zirconium(IV) aryloxides $[ZrCl(\eta\text{-}C_5H_5)_2(OR)]$ **(2b)**—**(2e)** were obtained as beige or pale yellow crystals upon treatment of $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ with the appropriate lithium reagent $[Li(OR)(OEt_2)]_2$ (R = R^2—R^5), equation (vi). The reactions were slow, requiring 2—4 d in refluxing thf to achieve reasonable conversions, but addition of tmen offered significant improvement. Thus, for example, $[ZrCl(\eta\text{-}C_5H_5)_2(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)]$ **(2d)** was obtained in 47% yield without tmen, but in 68% yield when tmen was added to the reaction mixture. In view of the relatively forcing conditions required to form compounds of the type $[ZrCl(\eta\text{-}C_5H_5)_2(OR)]$, it was not unexpected that the lithium aryloxides failed to react with $[ZrCl_2\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2]$, $[ZrCl_2(\eta\text{-}C_5H_4SiMe_3)_2]$, or $[ZrCl_2(\eta\text{-}C_5H_4Bu^t)_2]$;[39] starting materials

$$\underset{\textbf{(1b)}}{[TiCl_2(OR^1)_2(thf)_2]} \xleftarrow[\text{thf–OEt}_2]{\frac{2}{n}[Li(OR^1)]_n} [TiCl_4] \xrightarrow{2R^1OH} \underset{\textbf{(1c)}}{\tfrac{1}{n}[\{TiCl_2(OR^1)_2\}_n]} \qquad \text{(iii)}$$

$R^1 = 2,6\text{-}Me_2C_6H_3$



(iv)



(v)

$$[ZrCl_2(\eta\text{-}C_5H_5)_2] + \tfrac{1}{2}[Li(OR)(OEt_2)]_2 \xrightarrow{\text{tmen}} [ZrCl(\eta\text{-}C_5H_5)_2(OR)] + LiCl \qquad \text{(vi)}$$

R = $C_6H_3Pr^i{}_2$-2,6 **(2b)**, $C_6H_3Bu^t{}_2$-2,6 **(2c)**, $C_6H_2Bu^t{}_2$-2,6-Me-4 **(2d)**, or $C_6H_2Bu^t{}_3$-2,4,6 **(2e)**

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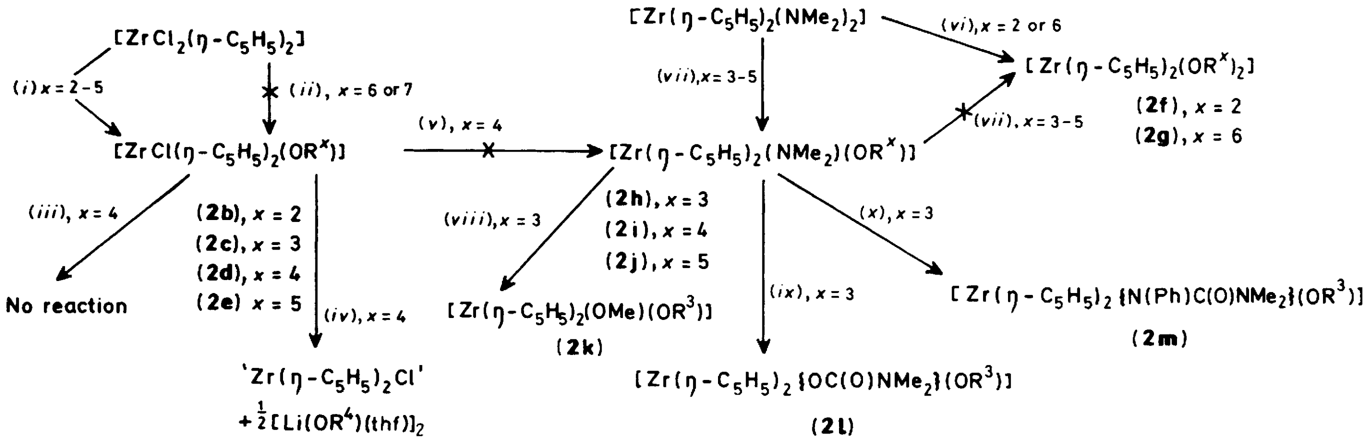

Scheme 2. Aspects of the chemistry of zirconocene(IV) aryloxides. Abbreviations: $OR^2 = OC_6H_3Pr^i{}_2$-2,6; $OR^3 = OC_6H_3Bu^t{}_2$-2,6; $OR^4 = OC_6H_2Bu^t{}_2$-2,6-Me-4; $OR^5 = OC_6H_2Bu^t{}_3$-2,4,6; $OR^6 = OC_6H_3Bu^t{}_2$-3,5; $OR^7 = OC_6H_3Bu^t{}_2$-2,4. (*i*) $[Li(OR^x)(OEt_2)]_n$ in thf (x = 2, 3, 4, or 5); (*ii*) $[Li(OR^x)(OEt_2)]_n$ in thf (x = 6 or 7); (*iii*) $[Li(OR^4)(OEt_2)]_2$ in thf (x = 4); (*iv*) Li powder in thf; (*v*) $Li(NMe_2)$ in C_6H_6; (*vi*) R^xOH in C_6H_6 (x = 2 or 6); (*vii*) R^xOH in C_6H_6 (x = 3, 4, or 5); (*viii*) MeOH in C_6H_6; (*ix*) CO_2 in n-C_6H_{14}; (*x*) PhNCO in n-C_6H_{14}

were recovered almost quantitatively from these experiments. No further substitution occurred when an excess of the lithium reagent was used. However, bis-aryloxides $[Zr(\eta\text{-}C_5H_5)_2(OC_6H_3Pr^i{}_2\text{-}2,6)_2]$ (**2f**) and $[Zr(\eta\text{-}C_5H_5)_2(OC_6H_3Bu^t{}_2\text{-}3,5)_2]$ (**2g**) were obtained by an alternative route $\{[Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2] + 2ROH\}$ (see below); perhaps because elimination of the volatile $NHMe_2$ is more facile than of LiCl. Rather surprisingly, in view of the results of equation (vi), the new aryloxides $[Li(OR)(OEt_2)]_n$ (R = R^6 or R^7) failed to react with $[ZrCl_2(\eta\text{-}C_5H_5)_2]$.

Bulky phenols reacted with $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2]$ to give zirconocene(IV) aryloxides as a consequence of amine elimination. Thus, when $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2]$ was treated with two equivalents of R^2OH or R^3OH in refluxing benzene for *ca.* 20 h, the appropriate white crystalline aryloxide $[Zr(\eta\text{-}C_5H_5)_2(OR)_2]$, (**2f**) or (**2g**), respectively, was obtained. The latter was not analytically pure, despite repeated recrystallisations, but it was readily identified by its ^1H n.m.r. spectrum. Use of one equivalent of R^2OH, in an attempt to prepare $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^2)]$, also led to isolation of the bis-aryloxide (**2f**). By contrast, even with an excess of the bulkier phenol R^3OH or R^4OH, only the yellow, air-sensitive crystalline monosubstituted compound $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR)]$, (**2h**) or (**2i**), respectively, was obtained. No product was isolated from the reaction of $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2]$ with two equivalents of R^5OH. However, from such an experiment carried out in a sealed n.m.r. tube in C_6D_6 at 80 °C, it was clear that the monosubstitution reaction proceeded cleanly, affording $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^5)]$ (**2j**). The difficulty in obtaining a crystalline material from the reaction mixture is attributed to the high solubility of the complex (**2j**). Similarly, a bis(cyclopentadienyl)(dimethylamido)zirconium(IV) aryloxide was not isolated from the analogous reaction of R^7OH with the Zr^{IV} bis-amide.

A small quantity of precipitate was formed when (**2d**), in thf, was stirred with sodium amalgam. The mixture did not exhibit an e.s.r. signal and no product was isolated. A thf solution of complex (**2d**) was reacted with lithium powder at room temperature, rapidly affording a deep purple solution. Instead of the expected chlorine atom abstraction and formation of $[Zr(\eta\text{-}C_5H_5)_2(OR^4)]$, the isolation of a large quantity of $[Li(OR^4)(thf)]_2$ indicated that the aryloxide (rather than Cl^-) was the better leaving group; a Zr product was, however, not identified. Dimethylamidolithium failed to react with complex (**2d**), either in diethyl ether at room temperature or in refluxing benzene.

The complex $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^3)]$ (**2h**) was chosen as being representative of the new class of compounds the bis(cyclopentadienyl)(dialkylamido)zirconium(IV) aryloxides, in order to examine some of their chemistry (Scheme 2); interest centred on amine eliminations and Zr–N insertions. Treatment of complex (**2h**) with one equivalent of methanol in refluxing benzene gave the unusual mixed Zr^{IV} aryloxide–alkoxide, $[Zr(\eta\text{-}C_5H_5)_2(OMe)(OR^3)]$ (**2k**). The corresponding reaction of complex (**2h**) with Bu^tOH was very slow. After refluxing in benzene for 4 d a ^1H n.m.r. spectrum of the crude reaction mixture showed that only 40% of the starting material had been consumed. When carbon dioxide was bubbled through a n-hexane solution of complex (**2h**), the yellow colour of the starting solution faded and white crystals of $[Zr(\eta\text{-}C_5H_5)_2\{OC(O)NMe_2\}(OR^3)]$ (**2l**) were precipitated. The carbamato-structure was confirmed by the observation of a C=O stretch at 1 620 cm^{-1} in the i.r. spectrum. Similarly, when complex (**2h**) was allowed to react with phenyl isocyanate for 8 d at room temperature, fine white crystals of the ureido derivative $[Zr(\eta\text{-}C_5H_5)_2\{N(Ph)C(O)NMe_2\}(OR^3)]$ (**2m**) were obtained and identified on the basis of their ^1H n.m.r. (Table 2) and i.r. (C=O stretch at 1 660 cm^{-1}) spectra. Such CO_2 (or PhNCO) insertion into zirconium–nitrogen bonds is well established.[35]

Lithium Aryloxides, Compounds (**3a**)—(**3c**).—The new lithium aryloxides (**3a**)—(**3c**) were obtained as white crystals by addition of n-butyl-lithium in n-hexane to cooled diethyl ether solutions of 2,6-di-isopropylphenol (R^2OH), 3,5-di-t-butylphenol (R^6OH), or 2,4-di-t-butylphenol (R^7OH), respectively. The complex $[Li(OR^2)(OEt_2)]_n$ (**3a**) precipitated from solution upon concentration; and the OR^7 analogue, (**3c**), was similarly obtained upon concentration and addition of n-pentane; whilst the OR^6 compound, (**3b**), was precipitated during the addition of the n-butyl-lithium solution to the phenol. All three complexes were isolated as etherates, $[Li(OR)(OEt_2)]_n$. Although their molecular weights were not determined, the high solubilities of (**3a**) and (**3c**) suggest that they are probably dimeric, with a pair of bridging R^xO^- ligands, like the lithium aryloxides formed from R^xOH (x = 3—5).[1] Complex (**3b**) displayed only slight solubility in diethyl ether, suggesting that it may be a higher aggregate. The aryloxide (**3c**) was insoluble in C_6D_6 and reacted fairly rapidly with $CDCl_3$; hence its n.m.r. spectrum was not recorded. The high $CDCl_3$ reactivity is unexpected, because the lithium aryloxides derived from 2,6-di-t-butylphenols are adequately inert towards $CDCl_3$ to allow their ^1H n.m.r. spectra to be observed.

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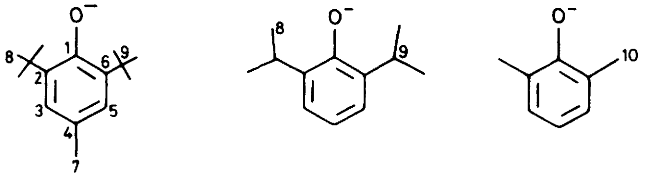
Table 2. Selected ^{1}H n.m.r. chemical shifts[a] for the new aryloxides

Compound	*o*-Substituent	*p*-Substituent	C_5H_5	Others	Solvent
(1a)	1.14 (d), 3.92 (sep)				*b*
(1b)	2.58 (s)[c]			thf at 1.50 (m) and 2.58 (m)	*d*
(1c)	2.18 (s)				*d*
(1d)	1.68 (s)	2.20 (s)			*d*
(1e)	1.48 (s)	2.32 (s)		NMe_2 at 3.40 (s)	*b*
(1f)	1.57 (s)	2.35 (s)		OMe at 4.32 (s)	*d*
(1h)	1.72 (s)	2.28 (s)		OBu^t at 1.54 (s)	*d*
(1i)	1.82 (s)	2.29 (s)		CH_2 at 3.66 (s), $SiMe_3$ at 0.53 (s)	*d*
(1j)	1.65 (s)	2.36 (s)	6.54 (s)		*d*
(2a)	1.62 (s)	2.18 (s)			*d*
(2b)	1.20 (d), 3.13 (sep)		6.32 (s)		*b*
(2c)	1.53 (d)		6.37 (s)		*b*
(2d)	1.52 (d)	2.33 (s)	6.37 (s)		*b*
(2e)	1.54 (d)	1.38 (s)	6.40 (s)		*b*
(2f)	1.38 (d), 3.50 (sep)		6.33 (s)		*b*
(2g)			6.26 (s)	Bu^t at 1.35 (s)	*b*
(2h)	1.42 (d)		6.10 (s)	NMe_2 at 2.80 (s)	*b*
(2i)	1.45 (d)	2.28 (s)	6.18 (s)	NMe_2 at 2.92 (s)	*b*
(2j)	*e*	*e*	5.91 (s)	NMe_2 at 2.89 (s)	*b*
(2k)	1.45 (d)		6.20 (s)	OMe at 3.84 (s)	*b*
(2l)	1.50 (d)		6.35 (s)	NMe_2 at 3.00 (s)	*b*
(2m)	1.32 (d)		6.35 (s)	NMe_2 at 2.42 (s), Ph at 6.00—7.15 (m)	*b*
(3a)	1.30 (d), 3.45 (sep)			OEt_2 at 0.75 (t) and 2.93 (q)	*d*
(3b)				Bu^t at 1.14 (s); OEt_2 at 1.10 (t) and 3.40 (q)	*b*

[a] Chemical shifts quoted in p.p.m. downfield from $SiMe_4$ as internal standard; s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet. [b] $CDCl_3$. [c] Coincident with thf resonance. [d] C_6D_6. [e] Assignments not made.

Table 3. Selected ^{13}C n.m.r. chemical shifts for some of the new aryloxides of Ti^{IV} and Zr^{IV}[a]



(A) (B) (C)

Compound	C^{10}	C^9	C^8	C^7	$C^{6,2}$	$C^{5,3}$	C^4	C^1	C_5H_5	Others
(1a)[b]		27.2	23.6		122.8	123.1	137.3	161.3		
(1b)	17.6				123.8[c]	128.6	128.4[c]	168.7		thf at 25.6 and 71.5
(1c)	16.8				124.9[c]	128.7	127.8[c]	167.8		
(1d)		35.7	32.1	21.5	133.7[d]	126.2	140.5[d]	170.0		
(1f)		35.4	31.2	21.5	129.5	125.9	139.6	163.6		OMe at 65.5
(1h)		35.6	32.1	21.5	131.2	126.2	139.9	166.0		$OC(CH_3)_3$ at 31.3[e]
(1i)		35.7	32.0	21.5	132.0	126.4	139.8	166.4		CH_2 at 110.6, $Si(CH_3)_3$ at 1.9
(1j)		36.1	32.8	21.2	130.2	126.4	139.0	169.2 169.5[f]	120.8	
(2a)		35.7	32.9	25.2	130.7	126.9	139.2	160.0		
(2b)[b]		26.2	23.9		120.2	123.3	136.0	159.5	114.6	
(2c)[b]		35.8	32.2 (d)						115.0	
(2d)[b]		35.6	32.2 (d)	20.8				164.6	114.9	
(2e)[b]		36.0	32.0 (d)					164.6	114.9	*p*-$C(CH_3)_3$ at 32.4
(2f)[b]		26.1	24.5		119.6	123.4	136.4	161.1	113.4	

[a] All spectra were ^{1}H-decoupled and, unless otherwise stated, recorded in C_6D_6. Shifts are quoted in p.p.m. relative to C_6D_6 (at 128.0 p.p.m.) or $CDCl_3$ (77.12 p.p.m.). The carbon numbering scheme is shown in (A)—(C). [b] In $CDCl_3$ solvent. [c] Tentative assignment. [d] The assignment of these resonances is based upon comparison of intensities with those of an 'off-resonance' spectrum of $[Li(OR^4)(OEt_2)_2]_2$. [e] $OC(CH_3)_3$ was not observed. [f] Two signals present, probably due to a trace of impurity.

Spectroscopic Data.—The n.m.r. spectra (Tables 2 and 3) of the new compounds are unexceptional. As noted earlier, no evidence was found in the spectra for η^5-binding of any of the aryloxide ligands in any of the new complexes. The most significant feature observed was the appearance of the *o*-Bu^t signals in the Zr^{IV} aryloxides **(2c)**—**(2e)**, **(2h)**, **(2i)**, and **(2k)**—**(2m)** as 1:1 doublets. This is attributed to restricted rotation about the carbon–oxygen bonds in these the most hindered aryloxides. A variable-temperature n.m.r. study of these complexes has been completed, and will be reported in Part 2 [along with structural data on some of the crystalline complexes **(1a)**, **(1d)**, and **(2h)**].[11] Temperature dependence was not observed in spectra of the other complexes.

The electron-impact mass spectra of the Ti aryloxides **(1b)**—

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(**1k**) showed parent ions in all but two cases, (**1b**) and (**1j**). The complex $[TiCl_2(OR^1)_2(thf)_2]$ (**1b**) displayed a highest ion corresponding to $(P - 2thf)^+$, whilst $[TiCl(\eta\text{-}C_5H_5)(OR^4)_2]$ (**1j**) fragmented with loss of Cl^- to give $(P - Cl)^+$. Elimination of chloride is attributed to weakness of the Ti–Cl bond due to steric crowding. An enhanced capacity to delocalise the charge within the $\eta^5\text{-}C_5H_5$ moiety may also be a contributory factor; we note that none of the other complexes examined contains good π-acceptor ligands.

Conclusions

Seven different di- or tri-substituted phenols R^1OH—R^7OH have been examined as sources of metal aryloxides, principally of Ti^{IV}, (**1a**)—(**1j**), or Zr^{IV}, (**2a**)—(**2m**), although two Ti^{III} complexes, (**1k**) and (**1l**), have also been obtained. Crystalline lithium aryloxides, as their 1:1 diethyl ether adducts, $[Li(OR)(OEt_2)]_n$ (**3**) ($n = 2$, except for $R = R^7$ where n is probably > 2; all such compounds were freely soluble in benzene), were also prepared; three of these ($R = R^2, R^6$, or R^7) are new compounds.

Two principal synthetic routes were employed: (*a*) Cl^-/RO^- exchange using $[Li(OR)(OEt_2)]_n$ as RO^- transfer agent, or (*b*) NMe_2^-/RO^- exchange from metal amide and ROH. As for reactions (*a*), the addition of tmen sometimes was found to enhance reactivity, possibly because of the absence of RO^- as bridging ligands in monomeric Li(OR)(tmen). Reactions (*b*) appeared to be more facile than (*a*), which may be due to the readier elimination of the volatile $NHMe_2$ in (*b*) rather than LiCl in (*a*); however, increased reactivity in system (*b*) was in one case accompanied by lower selectivity, see equation (v). Using $[TiCl_4]$ or $ZrCl_4$ and an excess of lithium 2,6-di-t-butylphenoxide, reaction (*a*) in OEt_2 gave only the di-substituted products $[MCl_2(OR)_2]$ {although, in refluxing C_6H_6, $[MCl(OC_6H_3Bu^t{}_2\text{-}2,6)_3]$ has been obtained[31]}. From the less bulky R^2OH, $[Ti(OR^2)_4]$ has been prepared by a reaction of type (*b*). A further aspect of reaction (*a*) is the propensity of $[Li(OR)(OEt_2)]_n$ to behave not only as a source of RO^- but also as a reducing agent ($Ti^{IV} \longrightarrow Ti^{III}$; Ti^{IV} being more readily reduced than Zr^{IV}), *e.g.*, in the conversion of $[Ti^{IV}Cl_2(\eta\text{-}C_5H_5)_2]$ to $[Ti^{III}(\eta\text{-}C_5H_5)_2(OR^4)]$.

Reduction of Ti^{IV} aryloxides has also been effected in other ways. Thus $[TiCl_2(OR^4)_2]$ (**1d**) gave $[\{TiCl(OR^4)_2\}_n]$ with $Li(CH_2SiMe_3)$, $MgCl(CH_2SiMe_3)$, Zn, or (best) with Na–Hg. Photolysis of (**1d**) gave no $R^4O^\bullet$. Treatment of $[ZrCl(\eta\text{-}C_5H_5)_2(OR^4)]$ with Li powder in thf gave reduction, but $[Li(OR^4)(thf)]_2$ was isolated, indicating that $R^4O^\bullet$ abstraction competes with that of Cl.

Steric effects have been used to good effect, in synthesising compounds such as $[Ti(OMe)_2(OR^4)_2]$ and $[TiCl(OR')(OR^4)_2]$ ($R' = Et$ or Bu^t), which are stable with respect to redistribution to symmetrical products.

Insertion reactions of CO_2 or PhNCO show that $NMe_2 >$ OR or $\eta\text{-}C_5H_5$ in migratory aptitude; *i.e.*, $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^3)]$ gave $[Zr(\eta\text{-}C_5H_5)_2\{OC(Y)NMe_2\}(OR^3)]$ (Y = O or NPh).

The vast majority of these Ti^{IV}, Ti^{III}, and Zr^{IV} bulky aryloxides were found to be crystalline, lipophilic, probably monomeric in hydrocarbon solution, and σ-*O*-bound to the metal.

Experimental

As the majority of the reagents used, and complexes isolated, were air- and moisture-sensitive, manipulations were carried out under an atmosphere of pure, dry dinitrogen or argon using standard Schlenk techniques. Experiments involving lithium powder were carried out under argon. All solvents were distilled from appropriate drying agents and thoroughly degassed before use. Throughout, the boiling point range of light petroleum was 40—60 °C.

Phenols R^1OH, R^4OH, and R^5OH were purified by passage of n-hexane or n-pentane solutions through basic alumina columns and subsequent removal of solvent under vacuum. The other phenols R^xOH (x = 2, 3, 6, or 7) were purified by distillation under reduced pressure. Methanol was distilled over magnesium methoxide, Bu^tOH over sodium, and phenyl isocyanate over phosphorus(v) oxide.

The following compounds were obtained according to literature methods: $[Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2]$,[35] $[Ti(NMe_2)_4]$,[35] and $[Li(OR^x)(OEt_2)]_2$ (x = 3, 4, or 5).[1] 2,6-Dimethylphenoxolithium was originally prepared by reaction of metallic lithium with the parent phenol,[12,40] a more convenient synthesis, using n-butyl-lithium, is described below.

Since the chlorobis(cyclopentadienyl)zirconium(IV) aryloxides (**2b**)—(**2e**) were prepared by a common experimental method, details of the synthesis of only one of them, (**2b**), are given. Similarly the procedure for obtaining bis(cyclopentadienyl)zirconium(IV) bis-aryloxides, (**2f**)—(**2g**), or bis(cyclopentadienyl)(dimethylamido)zirconium(IV) aryloxides (**2h**)—(**2i**) is illustrated by that for one of them, (**2h**); the Zr^{IV} bis-amide was added to the phenol in the case of (**2h**), but the phenol to the amide in the other instances.

Hydrogen-1 n.m.r. spectra were recorded on Varian T60 (60 MHz) or Perkin-Elmer R32 (90 MHz) spectrometers. Carbon-13 n.m.r. spectra were obtained on a JEOL PFT 100, and mass spectra with an AEI MS9, instrument. Infrared spectra in the range 4 000—400 cm^{-1} were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 597 spectrophotometer. Elemental analyses were performed in the Microanalytical Department of the University of Sussex by Mrs. A. G. Olney. Details on the new aryloxides of Ti^{IV}, (**1a**)—(**1j**), Ti^{III}, (**1k**), Zr^{IV}, (**2a**)—(**2m**), and Li, (**3a**)—(**3c**), are listed in Tables 1—3.

Synthesis of $[Ti(OC_6H_3Pr^i{}_2\text{-}2,6)_4]$ (**1a**).—(*a*) 2,6-Di-isopropylphenol, R^2OH (21.6 mmol), was added to tetrakis(dimethylamido)titanium (0.596 g, 2.7 mmol) in benzene (50 cm^3). After stirring at room temperature for 3 d and refluxing for 7 h, the deep green mixture was filtered and the filtrate was pumped to dryness. The solid residue was extracted with diethyl ether (60 cm^3) and filtered. Concentration and cooling of the extract afforded bright yellow crystals of the *product* (**1a**) (1.01 g, 50%), which were collected, washed with pentane (2 × 10 cm^3), and dried under vacuum.

(*b*) A mixture of $[TiCl_2(\eta\text{-}C_5H_5)_2]$ (2.1 g, 8.4 mmol) and dimethylamidolithium (0.91 g, 17.8 mmol) in toluene was heated to 80 °C for 16 h. The phenol R^2OH (4 cm^3, 21.6 mmol) was added and heating was continued for a further 22 h before filtration and evaporation of the dark green filtrate to dryness. The residue was extracted into diethyl ether (60 cm^3); the extract was filtered and then concentrated to *ca.* 30 cm^3. Cooling gave bright yellow crystals of the aryloxide (**1a**) (1.39 g, 45% based on R^2OH), which were filtered off, washed with n-pentane, and dried under vacuum. {The stoicheiometry employed was chosen so as to afford $[Ti(\eta\text{-}C_5H_5)_2(OR^2)_2]$.}

Synthesis of $[TiCl_2(OC_6H_3Me_2\text{-}2,6)_2(thf)_2]$ (**1b**).—A solution of titanium(IV) chloride (1.3 cm^3, 11.9 mmol) in n-hexane (*ca.* 10 cm^3) was added dropwise at −78 °C to a stirred suspension of 2,6-dimethylphenoxolithium, $LiOR^1$ (3.04 g, 23.7 mmol), in thf–OEt_2 (1:1, *ca.* 30 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for a further 15 h before removal of volatiles under vacuum. The resultant deep red solid was extracted into n-hexane (100 cm^3) and the extract was filtered. Concentration and cooling of the filtrate gave deep red crystals of the *product* (**1b**) (4.26 g, 71%),

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which were collected by decantation, washed with cold n-hexane, and dried under vacuum.

Synthesis of 2,6-*Dimethylphenoxolithium*.—To the phenol $\mathrm{R^1OH}$ (6.6 g, 54.0 mmol) in diethyl ether (25 $\mathrm{cm^3}$) cooled to 0 °C, was added dropwise a cooled (0 °C) solution of n-butyllithium in n-hexane (33.7 $\mathrm{cm^3}$ of a 1.6 mol $\mathrm{dm^{-3}}$ solution, 54.0 mmol) over 30 min. Precipitation of the white microcrystalline product began during the addition and continued for 2—3 h thereafter at room temperature. The precipitate was collected, washed with three aliquots of n-hexane at 0 °C, and dried under vacuum. The title compound $[\mathrm{Li(OR^1)(OEt_2)}]_n$ was thus obtained as a free-flowing, white, microcrystalline solid (3.5 g, 51%) (Found: C, 74.9; H, 7.15. Calc. for $\mathrm{C_8H_9LiO}$: C, 75.0; H, 7.10%), m.p. > 320 °C.

Synthesis of $[\mathrm{TiCl_2(OC_6H_3Me_2\text{-}2,6)_2}]$ (**1c**).—Titanium(IV) chloride (4.65 $\mathrm{cm^3}$, 42.4 mmol) was added to a solution of the phenol $\mathrm{R^1OH}$ (10.35 g, 84.7 mmol) in diethyl ether (100 $\mathrm{cm^3}$) at 0 °C. A bright red solution formed immediately, and was stirred overnight at room temperature. Volatiles were removed under vacuum and the residue was extracted with light petroleum (150 $\mathrm{cm^3}$). Filtration and then concentration and cooling of the red filtrate afforded bright red crystals of the *product* (**1c**) (10.21 g, 67%), which were washed with light petroleum and then dried under vacuum.

Synthesis of $[\mathrm{TiCl_2(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}]$ (**1d**).—4-Methyl-2,6-di-t-butylphenoxolithium(diethyl etherate) (11.74 g, 19.6 mmol) was suspended in diethyl ether (180 $\mathrm{cm^3}$) and cooled to 0 °C. A solution of titanium(IV) chloride (2.15 $\mathrm{cm^3}$, 19.6 mmol) in n-hexane (25 $\mathrm{cm^3}$) was added dropwise over 1 h to produce a deep red-brown suspension. After warming to room temperature and stirring for several hours, the suspended lithium chloride was removed by filtration. The resulting filtrate was concentrated to *ca.* 100 $\mathrm{cm^3}$ under vacuum and allowed to crystallise at −30 °C. Deep red-brown crystals of the *product* (**1d**) (10.2 g, 93%) were obtained; recrystallisation from diethyl ether at −30 °C gave the analytically pure sample.

Synthesis of $[\mathrm{Ti(NMe_2)_2(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}]$ (**1e**).—(*a*) Dimethylamidolithium (0.17 g, 3.3 mmol) was added to a solution of complex (**1d**) (0.93 g, 1.7 mmol) in diethyl ether (50 $\mathrm{cm^3}$) at room temperature. An orange suspension was instantly obtained. After several hours' stirring, the suspension was filtered. Concentration and cooling of the filtrate gave orange crystals of the *product* (**1e**) (0.82 g, 43%).

(*b*) 4-Methyl-2,6-di-t-butylphenol (5.84 g, 26.5 mmol) was added to tetrakis(dimethylamido)titanium (1.05 g, 4.7 mmol) in benzene (75 $\mathrm{cm^3}$). After stirring at room temperature for 2 d and refluxing (17 h), the mixture was filtered and evaporated to give a green-brown oil. Extraction into diethyl ether (75 $\mathrm{cm^3}$), filtration, then concentration of the filtrate to *ca.* 30 $\mathrm{cm^3}$ and cooling gave orange crystals. The crystals were collected, washed with pentane (3 × 15 $\mathrm{cm^3}$), and pumped dry; they were identified as the title compound (**1e**) (1.34 g, 50%).

Other Reactions of $[\mathrm{TiCl_2(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}]$ (**1d**).—(*a*) *With sodium methoxide.* The methoxide (0.30 g, 5.5 mmol) was added to a solution of (**1d**) (1.53 g, 2.8 mmol) in diethyl ether (30 $\mathrm{cm^3}$) at 0 °C. A bright yellow suspension was apparent after *ca.* 30 min at room temperature; the mixture was stirred for a further 15 h, and then filtered. The filtrate was pumped to dryness, extracted with light petroleum (10 $\mathrm{cm^3}$), filtered, concentrated, and cooled. Bright yellow crystals of the mixed $\mathrm{Ti^{IV}}$ alkoxide–aryloxide *compound* $[\mathrm{Ti(OMe)_2(OR^4)_2}]$ (**1f**) (0.55 g, 36%) were separated by filtration.

(*b*) *With sodium ethoxide.* The ethoxide (0.33 g, 4.8 mmol) was added to a solution of (**1d**) (1.34 g, 2.4 mmol) in diethyl ether (50 $\mathrm{cm^3}$). After stirring for 4 d at room temperature, the volatiles were removed under vacuum and the residue was extracted into light petroleum (100 $\mathrm{cm^3}$). Filtration gave an orange solution which was concentrated to *ca.* 5 $\mathrm{cm^3}$ and cooled to yield orange crystals of the *product* $[\mathrm{TiCl(OEt)(OR^4)_2}]$ (**1g**) (0.22 g, 16%).

(*c*) *With sodium t-butoxide.* The t-butoxide (0.89 g, 10.0 mmol) was added to a solution of (**1d**) (2.82 g, 5.0 mmol) in diethyl ether (40 $\mathrm{cm^3}$) at 0 °C. Volatiles were removed under vacuum, after stirring for 15 h at room temperature. Light petroleum (100 $\mathrm{cm^3}$) was added and the resultant suspension filtered. Concentration of the filtrate to *ca.* 20 $\mathrm{cm^3}$ and cooling afforded yellow-orange microcrystals of the *product* $[\mathrm{TiCl(OBu^t)(OR^4)_2}]$ (**1h**) (1.40 g, 47%). Recrystallisation from diethyl ether gave the analytically pure sample.

(*d*) *With bis*(*trimethylsilylmethyl*)*magnesium.* To a solution of (**1d**) (1.3 g, 2.3 mmol) in light petroleum (20 $\mathrm{cm^3}$) was added dropwise at 0 °C a n-hexane solution of the magnesium reagent (37.0 $\mathrm{cm^3}$ of a 0.063 mol $\mathrm{dm^{-3}}$ solution, 2.3 mmol). The reaction mixture, which immediately developed a tan colour, was allowed to warm slowly (*ca.* 4 h) to room temperature. Filtration, concentration of the filtrate to *ca.* 10 $\mathrm{cm^3}$, and cooling yielded yellow-tan crystals of the *product* $[\mathrm{TiCl(CH_2SiMe_3)(OR^4)_2}]$ (**1i**) (0.85 g, 61%), which were collected and recrystallised from light petroleum to give the analytically pure sample.

(*e*) *With cyclopentadienyl-lithium.* A solution of (**1d**) (1.00 g, 1.8 mmol) in diethyl ether (40 $\mathrm{cm^3}$) was cooled to −78 °C. A freshly prepared thf solution of the lithium reagent (12.8 $\mathrm{cm^3}$ of a 0.28 mol $\mathrm{dm^{-3}}$ solution, 3.6 mmol) was then added dropwise at −78 °C. The reaction mixture was allowed to warm slowly to room temperature, and was stirred for a further 48 h, refluxed for 6 h, and then allowed to cool. Filtration gave a clear filtrate which was cooled to yield deep red-brown crystals of the *product* $[\mathrm{TiCl(\eta\text{-}C_5H_5)(OR^4)_2}]$ (**1j**) (0.46 g, 45%), which were collected by decantation and dried under vacuum.

(*f*) *With sodium amalgam* (Na–Hg). A 1% sodium amalgam (0.3 g Na, 13.0 mmol) was placed under diethyl ether (60 $\mathrm{cm^3}$). Solid compound (**1d**) (3.43 g, 6.1 mmol) was added at room temperature. The mixture developed a deep green colour after stirring for *ca.* 30 min, and was stirred for a further 15 h. Filtration, concentration of the filtrate (to *ca.* 20 $\mathrm{cm^3}$), and cooling afforded deep green crystals of the *product* $[\{\mathrm{TiCl(OR^4)_2}\}_n]$ (**1k**) (1.33 g, 41%).

(*g*) *With metallic zinc.* To a stirred solution of (**1d**) (4.16 g, 7.5 mmol) in diethyl ether (60 $\mathrm{cm^3}$) was added zinc dust (1.93 g, 29.5 mmol) at room temperature. After 24 h the mixture was filtered, and the filtrate concentrated to *ca.* 30 $\mathrm{cm^3}$, and cooled to produce a mixture of deep green crystals and a golden yellow impurity. Repeated recrystallisations from n-hexane afforded the green compound free from the impurity; its e.s.r. spectrum was identical to that of compound (**1k**).

Reaction of $[\mathrm{TiCl_2(\eta\text{-}C_5H_5)_2}]$ *with* $[\mathrm{Li(OR^4)(OEt_2)}]_2$ *in the Presence of tmen.*—The lithium reagent (4.56 g, 7.6 mmol) was added in portions as a solid to titanocene(IV) chloride (1.70 g, 6.8 mmol) in thf (60 $\mathrm{cm^3}$). No reaction was apparent after stirring overnight. The amine tmen (1 $\mathrm{cm^3}$) was added, the mixture was refluxed for 3 d, and was then pumped to dryness. Extraction into benzene (75 $\mathrm{cm^3}$), filtration to remove LiCl, and evaporation to dryness were followed by extraction into diethyl ether (75 $\mathrm{cm^3}$). Concentration (to *ca.* 30 $\mathrm{cm^3}$) and cooling of the extract gave a crop of deep purple needles identified as $[\mathrm{Ti(\eta\text{-}C_5H_5)_2(OR^4)}]$ (**1l**) (0.70 g, 26%).

Preparation of $[\mathrm{ZrCl_2(OR^4)_2}]$ (**2a**).—To a suspension of freshly sublimed $\mathrm{ZrCl_4}$ (1.85 g, 7.9 mmol) in thf (*ca.* 40 $\mathrm{cm^3}$) was added solid 4-methyl-2,6-di-t-butylphenoxo(diethyl ether)-

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lithium, $[\mathrm{Li(OR^4)(OEt_2)}]_2$ (4.85 g, 8.1 mmol). Stirring was continued at room temperature for 15 h and the reaction mixture was then heated to reflux for 2 h. Volatiles were removed under vacuum to give an off-white oily residue, which was extracted into benzene (*ca.* 40 $\mathrm{cm^3}$), and filtered. The pale yellow filtrate was concentrated to *ca.* 20 $\mathrm{cm^3}$ and an equal volume of n-hexane was added. A white powder precipitated from solution on cooling. This was not collected; instead, the volatiles were removed under vacuum and the residue was extracted into n-hexane (40 $\mathrm{cm^3}$) at 50 °C. The extract was filtered and then cooled slowly to -30 °C to give white crystals of the *product* (**2a**) (2.53 g, 53%), which were collected and dried under vacuum. Recrystallisation from light petroleum gave the analytically pure sample as white concreted crystals.

Reaction of $[\{\mathrm{TiCl(\eta\text{-}C_5H_5)_2}\}_2]$ *with* $[\mathrm{Li(OR^4)(OEt_2)}]_2$.—The $\mathrm{Ti^{III}}$ chloride with the lithium reagent in equimolar proportions, on a 7.0 mmolar scale, in thf (35 $\mathrm{cm^3}$) were mixed at 20 °C and the mixture was heated under reflux for 1 d. Evaporation of the solvent and extraction into benzene (30 $\mathrm{cm^3}$) afforded on cooling and concentration the *product* $[\mathrm{Ti(\eta\text{-}C_5H_5)_2(OR^4)}]$ (**1l**) (50%), m.p. 167—169 °C, $g_{\mathrm{av.}} = 1.9795$ at 20 °C in PhMe, as purple crystals. The compound is a monomer in benzene (cryoscopy); for preliminary *X*-ray data, see ref. 3.

Preparation of $[\mathrm{ZrCl(\eta\text{-}C_5H_5)_2(OR^2)}]$ (**2b**).—$[\mathrm{Li(OR^2)(OEt_2)}]_n$ [3.35 g, 13.0 mmol (calculated for $n = 1$)] was added in portions as a solid to a solution of $[\mathrm{ZrCl_2(\eta\text{-}C_5H_5)_2}]$ (3.4 g, 11.6 mmol) in thf (75 $\mathrm{cm^3}$) at 0 °C. The amine tmen (1 $\mathrm{cm^3}$) was added and the mixture was refluxed for 4 d, and then evaporated to dryness. The residue was extracted into toluene (50 $\mathrm{cm^3}$) and filtered. The filtrate was evaporated to dryness and the residue extracted into diethyl ether (75 $\mathrm{cm^3}$). Concentration and cooling of the ether solution gave beige crystals which were washed with cold pentane. The filtrate and washings were combined to give a second crop of crystals. The total yield of the *product* (**2b**) was 1.49 g (30%).

Preparation of $[\mathrm{Li(OR^2)(OEt_2)}]_n$ (**3a**).—n-Butyl-lithium (115 $\mathrm{cm^3}$ of a 1.6 mol $\mathrm{dm^{-3}}$ solution in n-hexane, 184 mmol) was added dropwise to a solution of 2,6-di-isopropylphenol (30 $\mathrm{cm^3}$, 162 mmol) in diethyl ether (200 $\mathrm{cm^3}$). The solution was stirred overnight and then evaporated under vacuum to 100 $\mathrm{cm^3}$. Cooling afforded a heavy crop of white crystals which were collected and washed with cold n-hexane. After drying under vacuum, the *product* was identified as $[\mathrm{Li(OR^2)(OEt_2)}]_n$ (40.6 g, 97%).

Preparation of $[\mathrm{Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^3)}]$ (**2h**).—$[\mathrm{Zr(\eta\text{-}C_5H_5)_2(NMe_2)_2}]$ (1.97 g, 6.4 mmol) was added in portions as a solid to a solution of 2,6-di-t-butylphenol (3.50 g, 17 mmol) in benzene (75 $\mathrm{cm^3}$). The resultant bright yellow solution was refluxed for 20 h and evaporated under vacuum to give a yellow oil. The oil was extracted into diethyl ether, filtered, and the filtrate was concentrated and cooled. The yellow needles which formed were collected and washed with pentane at -78 °C. They were identified as *compound* (**2h**) (1.92 g, 64%).

Reactions of $[\mathrm{Zr(\eta\text{-}C_5H_5)_2(NMe_2)(OR^3)}]$ (**2h**).—(*a*) *With methanol.* Methanol (0.12 $\mathrm{cm^3}$, 3 mmol) was added to a solution of (**2h**) (1.40 g, 3 mmol) in benzene (70 $\mathrm{cm^3}$) to give a yellow solution, which was refluxed for 15 h and then evaporated under vacuum to give a yellow oily residue. The latter was extracted into diethyl ether, filtered, and the filtrate concentrated and cooled. The yellow crystals which formed were collected and washed with n-pentane at -78 °C, and identified as the *compound* $[\mathrm{Zr(\eta\text{-}C_5H_5)_2(OMe)(OR^3)}]$ (**2k**), (0.15 g, 11%).

(*b*) *With t-butyl alcohol.* The alcohol (0.4 $\mathrm{cm^3}$, 4.3 mmol) was added to a solution of (**2h**) (2.00 g, 4.3 mmol) in benzene (75 $\mathrm{cm^3}$) and the resultant solution was refluxed for 4 d. Volatiles were removed under vacuum and the oily yellow residue was extracted into diethyl ether; the extract was filtered. Concentration and cooling of the filtrate gave yellow crystals. A ^{1}H n.m.r. spectrum showed that the crystals contained *ca.* 60% starting material and 40% $[\mathrm{Zr(\eta\text{-}C_5H_5)_2(OBu^t)(OR^3)}]$.

(*c*) *With carbon dioxide.* Dry $\mathrm{CO_2}$ gas was bubbled through a solution of (**2h**) (1.05 g, 2.2 mmol) in n-hexane (75 $\mathrm{cm^3}$) for 1 h. The colour of the reaction mixture changed gradually from deep yellow to pale yellow and white crystals slowly separated. The passage of carbon dioxide was continued for another 1 h and then the mixture was cooled. The white precipitate, which was collected and recrystallised from n-hexane, was identified as the *compound* $[\mathrm{Zr(\eta\text{-}C_5H_5)_2\{OC(O)NMe_2\}(OR^3)}]$ (**2l**) (0.27 g, 24%).

(*d*) *With phenyl isocyanate.* The isocyanate (0.3 $\mathrm{cm^3}$, 3.8 mmol) in n-hexane (10 $\mathrm{cm^3}$) was added dropwise to a solution of (**2h**) (1.20 g, 2.6 mmol) in n-hexane (50 $\mathrm{cm^3}$). The yellow mixture was stirred at room temperature for 8 d. The fine white powder which separated was collected, dried under vacuum, and identified as the *compound* $[\mathrm{Zr(\eta\text{-}C_5H_5)_2\{N(Ph)C(O)NMe_2\}(OR^3)}]$ (**2m**) (0.33 g, 22%) from its ^{1}H n.m.r. and i.r. spectra.

Preparation of $[\mathrm{Li(OR^6)(OEt_2)}]_n$ (**3b**).—To a solution of 3,5-di-t-butylphenol (3.00 g, 14.5 mmol) in diethyl ether (75 $\mathrm{cm^3}$) was added n-butyl-lithium (10 $\mathrm{cm^3}$ of a 1.6 mol $\mathrm{dm^{-3}}$ solution in n-hexane, 16 mmol) at 0 °C. An immediate exothermic reaction ensued and a white precipitate formed. The mixture was stirred at room temperature overnight, and was then concentrated under vacuum and cooled. The white precipitate was collected, washed with n-pentane, dried, and identified as the *compound* (**3b**) (3.98 g, 96%).

Preparation of $[\mathrm{Li(OR^7)(OEt_2)}]_n$ (**3c**).—To a solution of 2,4-di-t-butylphenol (10.00 g, 48.5 mmol) in diethyl ether (250 $\mathrm{cm^3}$) was added n-butyl-lithium (35 $\mathrm{cm^3}$ of a 1.6 mol $\mathrm{dm^{-3}}$ solution in n-hexane, 56 mmol) at 0 °C. No precipitate formed on stirring overnight. Solvent was removed under reduced pressure and n-pentane was added to the greyish residue. The white precipitate which immediately formed was collected and washed with n-pentane. On recrystallisation from n-pentane it was identified as the *compound* (**3c**) (5.08 g, 37%).

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