Journal of

The Chemical Society,

Chemical Communications

NUMBER 7/1979 5 APRIL

New Approach to Anionic Transition Metal Alkyls; Synthesis and E.S.R. Characterisation of the d^1 Dialkylmetallate(III)'s $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$ (M = Ti, Zr, or Hf)†

By MICHAEL F. LAPPERT,* PAUL I. RILEY, and PAUL I. W. YARROW

(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary Sodium naphthalide in tetrahydrofuran (thf) smoothly converts a d^0 metallocene dialkyl $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]$ (M = Ti, Zr, or Hf; R^1 = H, Me, or Pr^i; R^2 = Me, $PhCH_2$, Me_3CCH_2, Me_3SiCH_2, or Ph_2CH) into the corresponding d^1 dialkylmetallate(III) $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$, characterised by e.s.r. spectroscopy [g_{av}, 1·991 ± 0·007; $a(^1H)$, 0·26 ± 0·09 mT; $a(^{47,49}Ti)$, 0·87 ± 0·16 mT; $a(^{91}Zr)$, 2·06 ± 0·34 mT; $a(^{177}Hf)$, not observed]; commercial samples of $HfCl_4$ contain 5—10% of the Zr analogue, as estimated by ^{13}C n.m.r. (on an organometallic derivative) or e.s.r. spectroscopy of the derived d^1 dialkylmetallate(III).

WE report a procedure for preparing paramagnetic anionic transition metal alkyls (**1**) which we expect to have some generality [equation (1)]. This is illustrated here for some d^1 dialkylmetallate(III)'s, $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$ (M = Ti, Zr, or Hf).

$$[ML_nR_m] + Na[C_{10}H_8] \xrightarrow{\text{thf}} \underset{(\mathbf{1})}{[Na(thf)_x][ML_nR_m]} \qquad (1)$$

Although the chemistry of alkyltitanium(III) complexes is well documented, there are few examples of Zr or Hf analogues.[1] The new compounds $[Na(thf)_x][M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]$ (**1**) are obtained as dark-brown, air- and moisture-sensitive solutions in thf upon titrating $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]$ against the green thf solution of $Na[C_{10}H_8]$. The anions of (**1**) are unambiguously characterised by their thf solution e.s.r. spectra at 20 °C (Table), and are indefinitely stable (not M = Hf) under these conditions. In the Figure is the spectrum of $[Zr(\eta\text{-}C_5H_5)_2(CH_2CMe_3)_2]^-$, featuring (i) the central 1,2,3,2,1-quintet due to four equivalent CH_2CMe_3 protons and (ii) the six ^{91}Zr satellites ($I = {}^5/_2$, 11·23% natural abundance).

TABLE. E.s.r. data on $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$ in thf at 20 °C[a]

$[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$			Multiplicity of central signal[b]	g_{av}	$a(^1H)$/ mT	$a(M)$/ mT
M	R^1	R^2				
Ti	H	Me	Septet[c]	1·986	0·360	0·720
Ti	H	$PhCH_2$	q	1·998	0·212	0·837
Ti	H	Me_3SiCH_2	q	1·985	0·275	1·025
Zr	H	$PhCH_2$	q	1·986	0·245	1·750
Zr	H	Me_3CCH_2	q	1·993	0·175	1·725
Zr	H	Ph_2CH	—[d]	1·987	—[e]	1·000
Zr	H	Me_3SiCH_2	q	1·984	0·300	2·375
Zr	Me	Me_3SiCH_2	q	1·987	0·350	2·400
Zr	Pr^i	Me_3SiCH_2	q	1·984	0·350	2·350
Hf	Pr^i	Me_3SiCH_2	q[f]	1·987	0·350	—[g]

[a] Obtained according to equation (1) from $[M(\eta\text{-}C_5H_4R^1)_2R^2{}_2]$ (ref. 7). [b] q = quintet. [c] Resolved only at −20 °C; ref. 5 cites (for OEt_2 solution) g_{av}, 1·990, and $a(^1H)$, 0·42 mT. [d] Broad signal. [e] Not resolved. [f] Part of an octet, overlapping with Zr analogue (see text). [g] ^{177}Hf ($I = {}^5/_2$, 18·5%)–^{179}Hf ($I = {}^5/_2$, 13·7%) hyperfine coupling was not observed.

Neutral d^1 metallocene(III) alkyls are known for Ti: $[Ti(\eta\text{-}C_5H_5)_2R]$ (R = aryl or $PhCH_2$, but not R = Me, Et, or Pr^i),[2] the methyl compound being stabilised as the tetramethylaluminate $[Ti(\eta\text{-}C_5H_5)_2Me_2AlMe_2]$.[3] However for Zr, only a single bulky alkyl is reported, as the dinitrogen complex $[Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}N_2)R]$ [R = $(Me_3Si)_2CH$].[4] Anionic

---

† No reprints available.

species were hitherto represented solely by $[Ti(\eta\text{-}C_5H_5)_2R_2]^-$ (R = Me, Et, or Pr) formed from the d^1 $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ and a large excess of RMgX.[5]

The e.s.r. spectra of thf solutions of $[Ti(\eta\text{-}C_5H_4R^1)_2R^2{}_2]^-$ show a central quintet for $R^2 = Me_3SiCH_2$ or $PhCH_2$ or a binomial septet for R^2 = Me, flanked by satellites originating from ^{47}Ti ($I = {}^5/_2$, 17·3%) and ^{49}Ti ($I = {}^7/_2$, 5·5%) (Table). For the Zr^{III} analogues, a noteworthy feature is the low ^{91}Zr hyperfine coupling constant for the benzhydryl complex $[Zr(\eta\text{-}C_5H_5)_2(CHPh_2)_2]^-$, probably due to substantial spin density being associated with the phenyl rings. The g_{av} values and isotropic ^{91}Zr coupling constants for the Zr^{III} anions are similar to those observed in $[Zr(\eta\text{-}C_5H_5)_2(PPh_2)_2]^-$ [g_{av}, 1·989; $a(^{91}Zr)$, 2·25 mT],[6] indicative of metal-centred radicals, but contrast with the high g value (2·0037) and low $a(^{91}Zr)$ (0·85 mT) found in $[Zr(\eta\text{-}C_5H_5)_2(\mu_2\text{-}N_2)\{CH(SiMe_3)_2\}]$ and attributed to extensive electron delocalisation onto the dinitrogen ligand.[4]

Upon $Na[C_{10}H_8]$–thf reduction of the compound believed to be $[Hf(\eta\text{-}C_5H_4Pr^i)_2(CH_2SiMe_3)_2]$ (on the basis of analytical, i.r., and ^1H n.m.r. data),[7] a weak spectrum assignable to the Zr analogue was observed after several hours. Repetition of the experiment and immediate scanning of the spectrum showed a central eight-line signal, which is assigned to the overlap of two quintets arising from a mixture of the anions $[M(\eta\text{-}C_5H_4Pr^i)_2(CH_2SiMe_3)_2]^-$ (M = Zr, 5—10%, g_{av} = 1·984; and M = Hf, g_{av} = 1·987). It appears that the Hf compound readily decomposes to diamagnetic product(s). Examination by ^{13}C n.m.r. spectroscopy of various samples of organohafnium compounds obtained from commercially available $HfCl_4$, such as $[Hf(\eta\text{-}C_5H_5)_2Cl_2]$ confirmed the presence of 5—10% of the Zr analogue.

The present results on d^1 alkylmetallates are complementary to those which we recently described[8] dealing with d^0 cationic metal alkyls from d^1 precursors. The ready availability of stable organometallic compounds in adjacent oxidation states is unusual. Further objectives are directed towards (i) obtaining crystalline complexes {solid, but not crystalline, $[Na(thf)_n][Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$ has been isolated}, (ii) synthetic applications of alkylmetallates, and (iii) paramagnetic alkylmetallates of later transition elements.

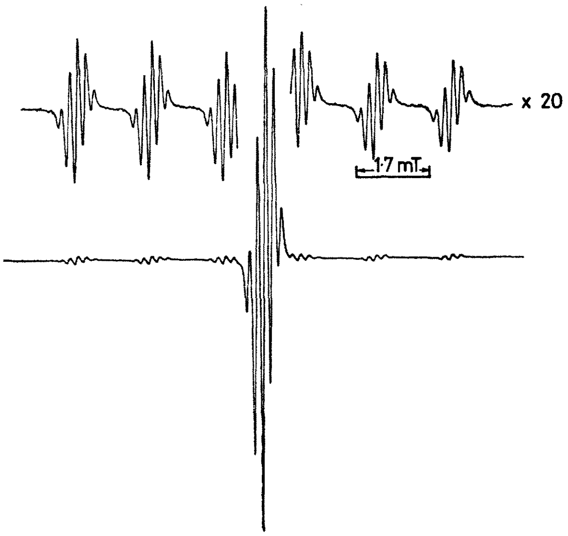

FIGURE. E.s.r. spectrum of $[Zr(\eta^5\text{-}C_5H_5)_2(CH_2CMe_3)_2]^-$ in thf at 20 °C.

We thank the S.R.C. for the award of a Fellowship (to P.I.R.) and, with I.C.I. Ltd. Corporate Laboratory, of a CASE studentship (to P.I.W.Y.), and Dr. J. Holton for his interest.

(*Received*, 13*th December* 1978; *Com.* 1326.)

---

[1] P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium and Hafnium,' Academic Press, New York, 1974; R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243.

[2] J. H. Teuben, *J. Organometallic Chem.*, 1974, **69**, 241.

[3] J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J.C.S. Dalton*, 1979, 45.

[4] M. J. S. Gynane, J. Jeffery, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1978, 34.

[5] H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1967, **89**, 6871.

[6] Unpublished data of J. Myatt (cited in ref. 4) (*cf.*, J. G. Kenworthy, J. Myatt, and P. F. Todd, *Chem. Comm.*, 1969, 263).

[7] Data on this and other neutral $[M^{IV}(\eta\text{-}C_5H_4R^1)_2R^2{}_2]$ complexes will be published by us in *J.C.S. Dalton*.

[8] M. F. Lappert and C. R. C. Milne, *J.C.S. Chem. Comm.*, 1978, 925.