A New Approach to Cationic Transition Metal Alkyls: $[M(\eta\text{-}C_5H_5)_2\text{-}(CH_2SiMe_3)_2]^+[Y]^-$ (M = Nb or Ta, Y = BF_4 or SbF_6) and their Conversion into the Alkylidene Complexes $[M(\eta\text{-}C_5H_5)_2(CHSiMe_3)(CH_2SiMe_3)]$†

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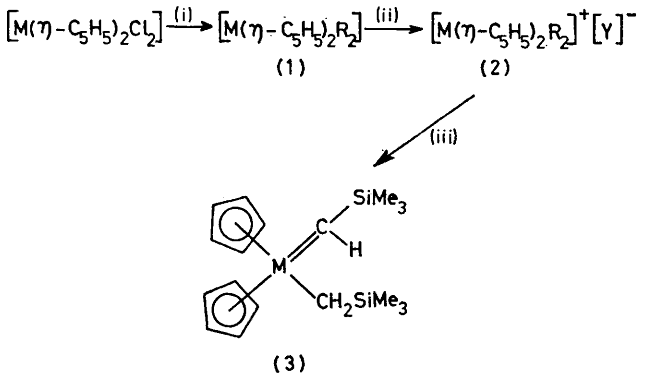
Summary The alkylmetal(IV) complex $[M(\eta\text{-}C_5H_5)_2R_2]$ (M = Nb or Ta, R = CH_2SiMe_3), obtained from $[M(\eta\text{-}C_5H_5)_2Cl_2]$ and LiR, is oxidised by AgY (Y = BF_4 or SbF_6) in MeCN at 25 °C to yield the thermally stable, crystalline, CH_2Cl_2-soluble cationic alkylmetal(V) complex $[M(\eta\text{-}C_5H_5)_2R_2]^+[Y]^-$, which may be deprotonated by reaction with $Li[N(SiMe_3)_2]$ in tetrahydrofuran (thf) to give the thermally stable, pentane-soluble, crystalline ylide $[M(\eta\text{-}C_5H_5)_2(CHSiMe_3)(CH_2SiMe_3)]$.

Cationic early transition metal alkyls are unusual,[1,2] probably because of the lack of a general synthetic route and, in many cases, the possibility[1] of a low activation energy decomposition pathway *via* loss of carbonium ion and/or a a bimolecular process involving nucleophilic attack either at the metal centre or resulting in proton abstraction.

We now report the synthesis of the cationic group 5 metal(V) alkyls, $[M(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]^+[Y]^-$ (M = Nb or Ta, Y = BF_4 or SbF_6), (**2**), from a neutral metal(IV) alkyl precursor, (**1**), using a silver salt as a one-electron oxidant [Scheme, reaction (ii)]. We further find that these salts are readily deprotonated [Scheme, reaction (iii)] (see also ref. 3) to yield the metal(V) ylide (**3**). Compounds (**3**) belong to a rare species, the transition metal ylide, discovered by Schrock, of which the following are in the literature:[3] $[Ta(CHCMe_3)(CH_2CMe_3)_3]$, $[Ta(\eta\text{-}C_5H_5)_2(CHPh)(CH_2Ph)]$, $[Ta(\eta\text{-}C_5H_5)_2(CX_2)(CX_3)]$ (X = H or D), and $[Ta(\eta\text{-}C_5H_4R)(\eta\text{-}C_5H_4Me)(CH_2)(CH_3)]$ (R = H or Me).‡ Data on compounds (**1**)—(**3**) are in the Table.



Scheme. Synthesis of metal(IV) dialkyls (**1**), dialkylmetal(V) salts (**2**), and metal(V) ylides (**3**) (M = Nb or Ta, Y = BF_4 or SbF_6, R = CH_2SiMe_3): (i) LiR, OEt_2, 0 °C; (ii) AgY, MeCN, 20 °C; (iii) $Li[N(SiMe_3)_2]$, thf, 20 °C.

The chemical shift of the α-hydrogen of the carbene carbon is at very low field (Nb < Ta) in the ^1H n.m.r. spectrum as expected for a secondary carbene hydrogen.[3,4] The cyclopentadienyl and the methylene proton resonances of the CH_2SiMe_3 group of the tantalum ylide (**3**, M = Ta) show inequivalences at room temperature due to restricted

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† No reprints available.

‡ See also R. R. Schrock and J. D. Sellmann, *J. Amer. Chem. Soc.*, 1978, **100**, 3359; L. W. Messerle and R. K. Schrock, *ibid.*, p. 3793, which appeared since submission of this paper.

TABLE. New organo-niobium or -tantalum complexes.[a]

Compound	Appearance	M.p. (° C)	^{1}H n.m.r. (τ) or e.s.r. parameters
(**1**), M = Nb[b]	Red-brown	128—130 (decomp.)	$g = 2{\cdot}037$, a (^{93}Nb) = 97 G[c]
(**1**), M = Ta	Red		$g = 2{\cdot}021$, a (^{181}Ta) = 98 G[c]
(**2**), M = Nb, Y = BF_4	Pale yellow	126 (decomp.)	3·44 (Cp), 8·01 (CH_2), 9·81 ($SiMe_3$)[d]
(**2**), M = Ta, Y = BF_4	White	158—160 (decomp.)	3·48 (Cp), 8·82 (CH_2), 9·87 ($SiMe_3$)[d]
(**3**), M = Nb	Pale yellow	71 (decomp.)	−2·57 (CH), 4·63 (Cp), 9·60 ($SiMe_3$), 9·70 ($SiMe_3$) 10·26 (CH_2)[e]
(**3**), M = Ta	Cream	90–92 (decomp.)	−0·21 (CH), 4·63 (Cp), 9·43 ($SiMe_3$), 9·57 ($SiMe_3$), 10·06 (CH_2)[e]

[a] The analogous Mo^V complex $[Mo(\eta\text{-}C_5H_5)_2Me_2]^+[SbF_6]^-$, $g = 2{\cdot}021$, $a(^1H) = 5{\cdot}7$ G, $a(^{95/97}Mo) = 29{\cdot}0$ G, was obtained from (**1**, M = Mo, R = Me) and Ag[SbF_6] (Dr. M. L. H. Green has obtained this by an alternative procedure). [b] See M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36. [c] In PhMe. [d] In CD_2Cl_2; Cp = cyclopentadienyl. [e] In C_6D_6.

rotation about the Ta=C bond (*cf.* ref. 5). Similar behaviour is observed for the niobium analogue, but interestingly only at lower temperatures. The chemical shift of the methylene hydrogen in complexes (**2**) are also at low field (Nb < Ta).

Well characterised cationic transition metal alkyls include the homoleptic $[MR_2]^+$ (M = Cu, Ag, or Au, and R is derived from a P or As ylide, *e.g.*, Me_3PCH_2),[6] $[Cr(CH_2SiMe_3)_2(bipy)_2]^+$,[7] and the d^2 $[M(\eta\text{-}C_5H_5)_2(L)R]^+$ (M = Mo or W, with, *e.g.*, L = C_2H_4 or PPh_3 and R = Me),[8] and most recently,[3] the d^0 $[Ta(\eta\text{-}C_5H_4R)(\eta\text{-}C_5H_4R')(Me)X]^+$ (X = Me, and R = R′ = H or Me, or R = H and R′ = Me; or X = Br and R = R′ = H). These compounds have a rich chemistry. Especially relevant, in the present context, is Schrock and Sharp's deprotonation of their Ta^V salts to yield Ta^V ylides,[3] the former being obtained by CH_3^--abstraction from a neutral Ta^V–CH_3 precursor using $[Ph_3C]^+[BF_4]^-$.

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