Electronic Absorption Spectra and Photochemical Reactivity of Group 5 Metal Alkyl Compounds: Photochemical α-Hydrogen Abstraction†

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The electronic absorption spectra as well as the electrochemical and photochemical behaviour of a number of niobium and tantalum alkyls of formula $[MX_2(CH_2R')_3]$ (X = Cl, OPr^i, $OC_6H_3Me_2$-2,6, $OC_6H_3Pr^i_2$-2,6, and $OC_6H_3Bu^t_2$-2,6; R′ = H, $SiMe_3$, or Ph) have been studied. The electronic spectra of these d^0 compounds are dominated by an intense ligand to metal charge transfer (l.m.c.t.) band, the energy of which is strongly dependent on X. Evidence is presented in support of the assignment of these bands as alkyl to metal in character. Furthermore, the observed photochemistry of these compounds, in some cases leading to the efficient and almost quantitative photosynthesis of alkylidene functional groups, has been investigated. For $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$ irradiation into the observed l.m.c.t. band at 313 nm produces the methylidene complex $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(=CH_2)(CH_3)]$ and methane with a quantum efficiency of 0.95 ± 0.1. Mechanistically, studies indicate that the reaction is concerted while for $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$ photogeneration of the corresponding alkylidene involves an intermediate alkyl radical which can be intercepted.

The field of organotransition metal photochemistry has developed over the last 20 years as both an interesting and important area of chemical research, leading to a better understanding of reactivity and electronic structure in organometallic chemistry.[1,2] For early transition metals (Groups 4 and 5) the most extensive photochemical work has involved studies of mixed cyclopentadienyl–alkyl[3] derivatives as well as some polyhydride complexes.[4] By far the best studied systems are the $[M(\eta\text{-}C_5H_5)_2R_2]$ (M = Ti, Zr, or Hf) derivatives and a number of important synthetic and mechanistic insights have resulted.[5,6] During our studies of the early transition metal organometallic chemistry associated with bulky aryloxide ligands, we have recently shown that for a number of compounds of stoicheiometry $[Ta(OC_6H_3R_2\text{-}2,6)_2(CH_2R')_3]$ it is possible photochemically to induce the formation of alkylidene functional groups which are thermally inaccessible, *e.g.* equation (1).[7,8]

$$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3] \longrightarrow [Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(=CH_2)Me] + CH_4 \quad (1)$$

This process of photochemical α-hydrogen abstraction has also been documented by Schrock and co-workers[9] in a number of cases and more recently by Fryzuk[10] for an iridium dialkyl system. Marks and co-workers[11] have demonstrated the photochemical induction of the related β-hydride abstraction process in a series of organo-actinide compounds. We wish to report here a more extensive study of the electronic structure and photochemistry of a series of tantalum alkyl compounds as well as some mechanistic conclusions concerning photochemically induced α-hydrogen abstraction in these derivatives.

Results and Discussion

Electronic Absorption Spectra.—We have examined the electronic spectra of a number of alkyl complexes of niobium and tantalum containing aryloxide, alkoxide, and chloride ligation. These data are collected in the Table. It can be seen that all of the complexes of stoicheiometry $[MX_2(CH_2R')_3]$ (M = Nb or Ta, X = aryloxide, OPr^i, or Cl) show at least one intense electronic absorption between 220 and 400 nm, the intensity and position of this band being strongly dependent on both the metal and ligation. These absorption bands have all of the characteristics of ligand to metal charge-transfer (l.m.c.t.) transitions occurring in these d^0 metal complexes. In particular the following features are worthy of note.

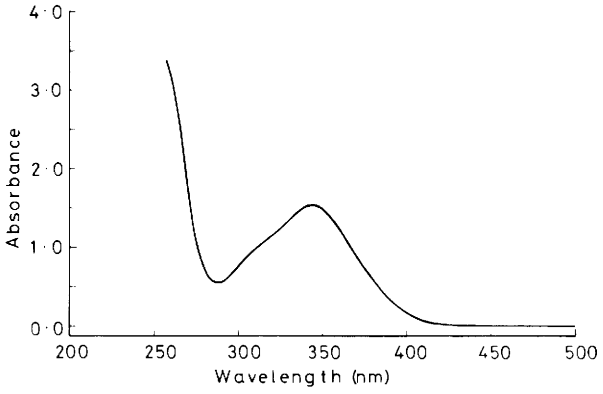

Figure 1. Electronic absorption spectrum of $[TaCl_2(CH_2SiMe_3)_3]$ in cyclohexane solution

For the trialkyls, $[MX_2(CH_2R')_3]$, it is assumed that the complexes consistently adopt a trigonal bipyramidal (t.b.p.) geometry with *trans*-axial X substituents. Both n.m.r. data and the available, structural information support this assumption.[8,12] In the dichloride, $[TaCl_2(CH_2SiMe_3)_3]$ (Figure 1) the strong absorption at 344 nm undergoes a dramatic blue shift on substituting OPr^i for chloride, to 239 nm in $[Ta(OPr^i)_2(CH_2SiMe_3)_3]$ (Figure 2). For pairs of compounds such as $[M(OPr^i)_2(CH_2SiMe_3)_3]$ (M = Nb or Ta) the band is red-shifted for the more easily reduced metal, Nb (Figure 2), consistent with the assignment of this band as l.m.c.t. In the case of the aryloxy compounds $[M(OC_6H_3R_2\text{-}2,6)_2(CH_2R')_3]$, the absorption falls between the position of the chloride and alkoxide bands, Table. However, consideration of the electronic spectra of the aryloxide derivatives has to bear in mind the possible interference of the lowest lying π–π* band (*B* band) of

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† *Non-S.I. unit employed:* Torr ≈ 133 N m^{-2}, eV ≈ 1.60 × 10^{-19} J.

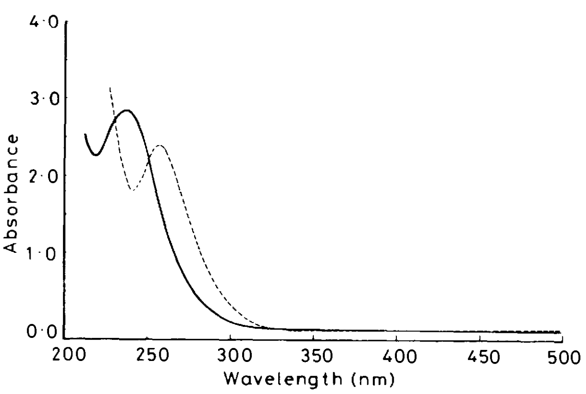


Figure 2. Electronic absorption spectra of $[Ta(OPr^i)_2(CH_2SiMe_3)_3]$ (——) and $[Nb(OPr^i)_2(CH_2SiMe_3)_3]$ (— — —) in cyclohexane solution

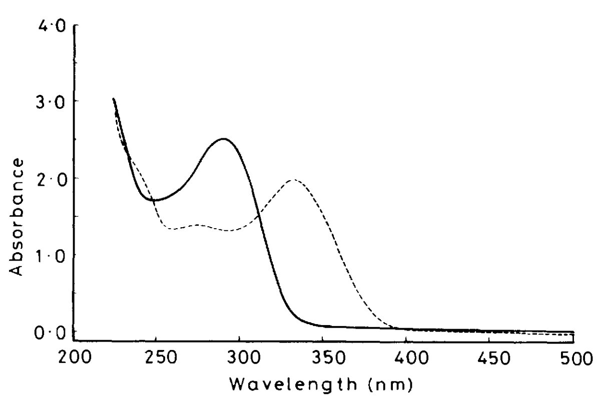


Figure 4. Electronic absorption spectra of $[Ta(OC_6H_3Me_2\text{-}2,6)_2Me_3]$ (——) and $[Nb(OC_6H_3Me_2\text{-}2,6)_2Me_3]$ (— — —) in cyclohexane solution

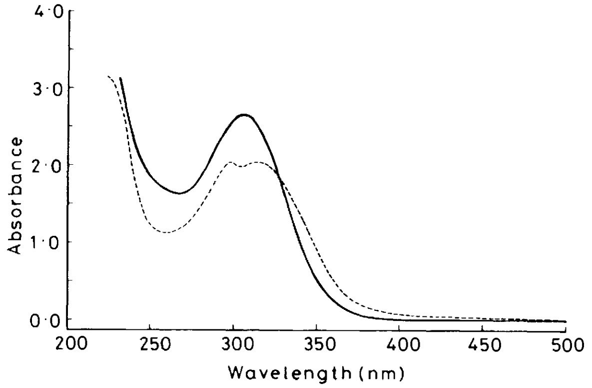


Figure 3. Electronic absorption spectra of $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$ (——) and $[Ta(OC_6H_2Bu^t_2\text{-}2,6\text{-}OMe\text{-}4)_2Me_3]$ (— — —) in cyclohexane solution

Table. Electronic absorption spectra and electrochemical behaviour

Compound	$\lambda_{max.}$/ nm($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})[a]	$E_{\frac{1}{2}}$(M/M$^-$)/ V[b]
$[TaCl_2(CH_2SiMe_3)_3]$	344 (5)	−1.34[c]
	318 (sh)	
$[Ta(OPr^i)_2(CH_2SiMe_3)_3]$	239 (10)	*d*
$[Nb(OPr^i)_2(CH_2SiMe_3)_3]$	257 (10)	*d*
$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$	307 (7)	−2.10[c]
$[Ta(OC_6H_2Bu^t_2\text{-}2,6\text{-}OMe\text{-}4)_2Me_3]$	318 (8)	−2.20[c]
$[Ta(OC_6H_3Me_2\text{-}2,6)_2Me_3]$	291 (7)	−2.47[e]
$[Nb(OC_6H_3Me_2\text{-}2,6)_2Me_3]$	332 (10)	−2.03[e]
	277 (6)	
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Me_3]$	295 (10)	
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$	302 (10)	−2.31[e]
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2Ph)_3]$	282 (10)	−2.44[e]
	325 (sh)	
$[Ta(OC_6H_3Me_2\text{-}2,6)_4Me]$	270 (16)	
$[Ta(OC_6H_3Me_2\text{-}2,6)_5]$	277 (20)	

[a] Recorded in cyclohexane solvent. Due to the high air- and moisture-sensitivity of these compounds the value of ε is approximate, estimated as ±10%. [b] Measured in 0.2 mol dm^{-3} $NBu^n_4PF_6$–thf solutions by cyclic voltammetric techniques; V *vs.* Ag quasi-reference electrode against which the $[Fe(\eta\text{-}C_5H_5)_2]^{+/0}$ couple lies at +0.47 V; $E_{p,a} - E_{p,c}$ = 90 mV. [c] $(E_{p,a} + E_{p,c})/2$ quoted at scan rate of 25 mV s^{-1}. [d] Outside solvent limit, < −2.5 V. [e] Irreversible reductions, $E_{p,c}$ quoted at scan rate of 25 mV s^{-1}.

the aromatic ring.[13] In simple phenols this band is found in the range 270—280 nm, typically with some fine structure especially in non-polar solvents.[13] For the conjugate base, phenoxide, this band intensifies slightly ($\varepsilon_{max.}$ from 1 500 to 2 600 dm^3 mol^{-1} cm^{-1}) and red-shifts by 15—20 nm. Hence it seems reasonable that this π–π^* transition of the 2,6-dialkylphenoxide complexes will lie in the region 270—300 nm of the electronic spectrum. This is close to the region where the strong absorption band is found in complexes $[Ta(OC_6H_3R_2\text{-}2,6)_2Me_3]$ (Figure 3). However, the following observations rule out this *B* band making more than a small contribution to this absorption. Firstly, addition of a *p*-methoxy substituent onto aromatic rings is known to increase the intensity of the *B* band and also cause it to red-shift by up to 25 nm.[13] A comparison of the spectra of the two complexes $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Me_3]$ and $[Ta(OC_6H_2Bu^t_2\text{-}2,6\text{-}OMe\text{-}4)_2Me_3]$ (Figure 3) shows the *B* band growing in as a shoulder at 298 nm for the *p*-methoxy derivative. Hence, this confirms that in the unsubstituted derivative this band probably lies around 275 nm and makes an insignificant contribution to the intense band centred at 307 nm. Conclusive evidence comes from a comparison of the spectra for $[M(OC_6H_3Me_2\text{-}2,6)_2Me_3]$ (M = Ta or Nb) (Figure 4). On going from tantalum to niobium the l.m.c.t. band moves from 291 to 332 nm, 'exposing' the much weaker *B* band of the two aryloxide ligands at 278 nm.

The question that now arises concerns the exact origin of these l.m.c.t. bands in complexes of type $[MX_2(CH_2R')_3]$: do these represent alkyl to metal or heteroatom (O,Cl) lone pair to metal charge-transfer bands, or a combination of both? On the basis of the observed photochemistry of these compounds (see below), their spectroscopic properties, and molecular orbital calculations we believe these intense transitions correspond to alkyl to metal charge-transfer processes. For a complex of the type $[MCl_2(CH_2R')_3]$ (M = Nb or Ta) assuming a pure D_{3h} symmetry (axial Cl) for the MCl_2C_3 core, the five metal–ligand σ bonds will involve primarily the s,d_{z^2} (both a_1'), p_z (a_2''), and d_{xy}, $d_{x^2-y^2}$ (e' mixed with p_x,p_y) sets of metal orbitals.[14] The lowest unoccupied molecular orbitals (l.u.m.o.s) for such a scheme would, therefore, be the d_{xz},d_{yz} (e'') set, capable of π-bonding with the lone pairs of the axial heteroatom, above which would lie the σ^* orbitals containing predominantly $d_{xy},d_{x^2-y^2}$ (e') and d_{z^2} (a_1') character. A qualitative molecular orbital diagram based on an extended Hückel calculation carried out on $[NbCl_2Me_3]$ confirms this idea.[14] Calculations on $[Nb(OH)_2Me_3]$ show the oxygen atom lone-pair electrons to lie even further below the three M–C σ bonds (Figure 5). This picture, therefore, indicates that alkyl to metal transitions should be significantly lower in energy than chlorine or oxygen to metal charge-transfer processes.

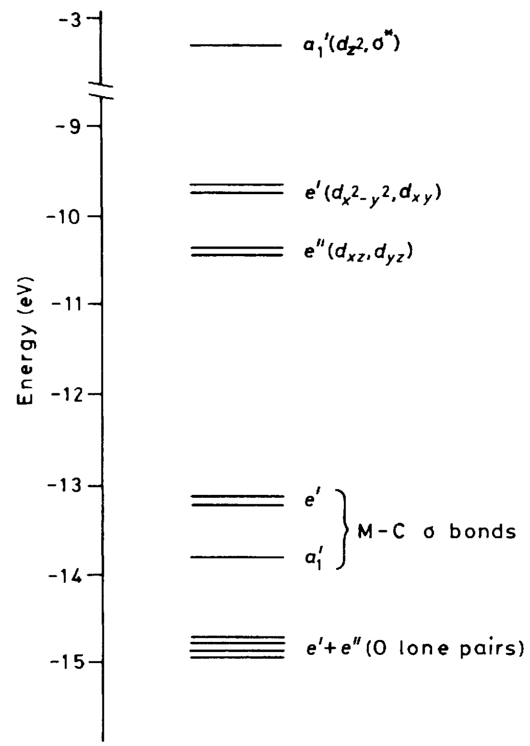


Figure 5. Qualitative molecular orbital diagram from extended Hückel calculation on $[\text{Nb(OH)}_2\text{Me}_3]$ with *trans*-axial hydroxide groups. The Nb–O–H angles are set at 180°, although reducing them to 150° has very little effect on the overall molecular orbital picture

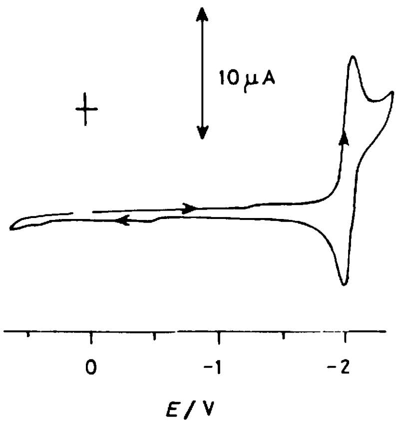


Figure 6. Cyclic voltammogram (scan rate 25 mV s^{-1} at a Pt disc electrode) of $[\text{Ta(OC}_6\text{H}_3\text{Bu}^t{}_2\text{-2,6)}_2\text{Me}_3]$ in 0.2 mol dm^{-3} $\text{NBu}^n{}_4\text{PF}_6$–thf

The electronic spectrum of the dichloride (Figure 1) shows, as well as the intense absorption centred on 344 nm, a shoulder at 318 nm. It seems reasonable, therefore, on the basis of the above argument to assign this slightly weaker transition as a chlorine to metal transition. For the alkoxide and aryloxide complexes, the oxygen to metal transitions presumably lie below 220 nm. However, for the complex $[\text{Nb(OC}_6\text{H}_3\text{Me}_2\text{-2,6)}_2\text{Me}_3]$ (Figure 4) there is a shoulder at 240 nm which may indeed be due to this transition. Substitution of aryloxide ligands for alkyl groups to give complexes of the type $[\text{Ta(OC}_6\text{H}_3\text{Me}_2\text{-2,6)}_4\text{Me}]$ and $[\text{Ta(OC}_6\text{H}_3\text{Me}_2\text{-2,6)}_5]$ shifts the absorption bands even further into the ultraviolet, so that now the π–π* band of the aryl ring becomes the dominant feature of the spectrum (Table).

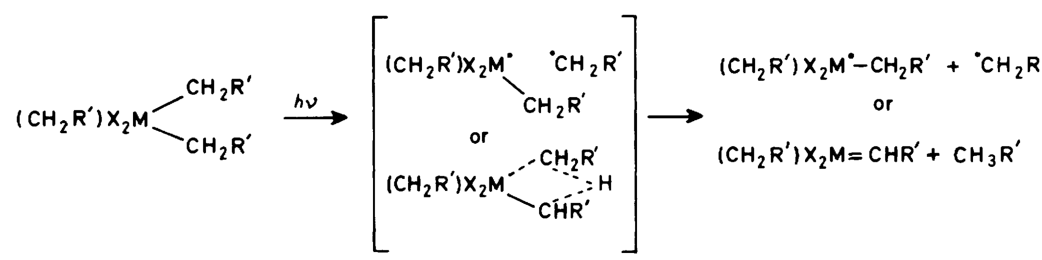
Electrochemical Measurements.—If one accepts that the lowest energy transitions in these systems originate from alkyl to metal charge-transfer processes, then the question arises as to the explanation of the observed progressive blue shifts in these bands on going from chloride to aryloxide to alkoxide axial substituents. This substituent effect clearly may reflect either a stabilization of the M–C σ bonds (lowering the highest occupied molecular orbitals, h.o.m.o.s), a raising in energy of the l.u.m.o.s or a combination of both. On going from chloride to alkoxide coligation a dramatic change in the π-donor capabilities of the axial heteroatom takes place.

Alkoxides are known to undergo significant oxygen *p* to metal *d*π-bonding, resulting in a number of both structural and reactivity effects.[15,16] For the axial $[\text{MX}_2(\text{CH}_2\text{R}')_3]$ complexes the l.u.m.o.s are expected to be primarily d_{xz} and d_{yz} metal-based orbitals. It is with these orbitals that one expects the most significant π-interaction from the axial heteroatom. One would predict that the more strongly π-donating alkoxide would lead to this orbital being pushed up in energy resulting in a widening of the h.o.m.o.–l.u.m.o. gap. The aryloxide substituent, which is known to be a weaker π-donor than alkoxide,[17] would be expected to have a slightly lesser impact. This picture of the axial substituents raising in energy the l.u.m.o.s is consistent with the observed electronic spectra. However, another way in which one might possibly gain information concerning the electronic structure of these compounds is electrochemistry. It has been argued that oxidation and reduction potentials of a series of related compounds can correlate with the relative energies of the h.o.m.o.s and l.u.m.o.s, respectively.[18] Oxidation is clearly not feasible for these d^0 metal complexes, but we have investigated reduction potentials by cyclic voltammetric methods. Most of the complexes exhibit an irreversible, one-electron reduction within the limits of the solvent system used; tetrahydrofuran (thf) with 0.2 mol dm^{-3} $\text{NBu}^n{}_4\text{PF}_6$ as supporting electrolyte. The potentials are given in the Table referenced against a Ag–AgCl quasi-reference electrode against which the $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^{+/0}$ couple lies at +0.47 V. In the case of $[\text{Ta(OC}_6\text{H}_3\text{Bu}^t{}_2\text{-2,6)}_2\text{Me}_3]$ the reduction wave appears reversible (Figure 6) as indicated by $i_{p,a}/i_{p,c} = 1$ for scan rates between 20 and 800 mV s^{-1}. It can be seen that the substitution of an alkoxide for a chloride results in the complex becoming dramatically more difficult to reduce, while aryloxide has an intermediate effect.

In other systems we have studied the substitution of $\text{OC}_6\text{H}_3\text{R}_2\text{-2,6}$ for Cl typically results in the reduction potential being made more negative by 300 mV per $\text{OC}_6\text{H}_3\text{R}_2\text{-2,6}$.[19,20] Clearly there is a correlation (albeit a poor one) between the energy of the lowest l.m.c.t. in these complexes and their one-electron reduction potentials, supportive of the idea that the position of the alkyl to metal transition is strongly dependent on the π-donor properties of the coligation attached to the metal.

Photochemical Reactivity.—All of the trialkyl compounds investigated in this study show photochemical reactivity on irradiation with a medium-pressure Hg lamp. However, only a few of the complexes show what can be considered 'clean' photochemistry and these will be considered first.

The complexes $[\text{Ta(OC}_6\text{H}_3\text{Bu}^t{}_2\text{-2,6)}_2\text{Me}_3]$ and $[\text{Ta(OC}_6\text{H}_2\text{Bu}^t{}_2\text{-2,6-OMe-4)}_2\text{Me}_3]$ undergo essentially quantitative conversion to the corresponding methylidene complexes on photolysis in benzene or cyclohexane solution.[12] Irradiation into the strong absorption band of these complexes using the isolated 313 nm line of the Hg spectrum leads to the observed photochemistry with a measured quantum efficiency at 15 °C of



Scheme. X = aryloxide, OPr^i, or Cl; R′ = H, Ph, or $SiMe_3$

0.95 ± 0.1 for $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Me_3]$. A similar reactivity is seen for the complex $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(CH_2SiMe_3)_3]$,[8] forming the corresponding trimethylsilylmethylidene function with an efficiency at 313 nm of 0.40 ± 0.1. Photolysis of the labelled compound $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2(CD_3)_3]$ at 313 nm resulted in the formation of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2({=}CD_2)(CD_3)]$ with the same efficiency as for the unlabelled complex. Hence, this photoreaction displays no photokinetic isotope effect.

In contrast, the photolysis of all of the other trialkyls results in the formation of a mixture of products, none of which appears to be an alkylidene complex. The trimethyl complex $[M(OC_6H_3Me_2\text{-}2,6)_2Me_3]$ (M = Nb or Ta) will generate a large amount of methane on photolysis, but the only identifiably metal-containing product is small amounts of $[Ta(OC_6H_3Me_2\text{-}2,6)_3Me_2]$ in the latter case. When photolysis is carried out in C_6D_6 or $C_6D_5CD_3$ only CH_4 is generated with no detectable CH_3D. Hence, it appears here that photochemical α-hydride abstraction is taking place, but the product methylidene complex is unstable. Similarly, the complex $[Ta(OC_6H_3Me_2\text{-}2,6)_2(CH_2SiMe_3)_3]$ generates $SiMe_4$, but the only identifiable product is $[Ta(OC_6H_3Me_2\text{-}2,6)_3(CH_2SiMe_3)_2]$. We believe the lack of formation of any stable alkylidene products in these cases is related to the steric size of the aryloxide ligation. Schrock and Sharp[21] have shown that a facile decomposition pathway for Group 5 alkylidene complexes is by intermolecular reaction. Hence, for the less bulky aryloxides bimolecular decomposition of the photogenerated alkylidenes is probably occurring.

In the case of the tribenzyl, $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(CH_2Ph)_3]$ only small amounts of toluene are generated on photolysis. Instead, large amounts of $PhCH_2CH_2Ph$ are produced in benzene or cyclohexane solution. The metal-containing product of this photolysis could not be identified. However, no signals corresponding to a Ta=CHPh functional group were ever detected. The formation of $PhCH_2CH_2Ph$ is consistent with the initial formation of benzyl radicals in solution which are sufficiently stable to build up in concentration and undergo dimerization.

These observations prompted us to investigate whether a common photochemical pathway involving the initial photogeneration of alkyl radicals was taking place for all of these metal systems. All of the alkyl complexes in this study when mixed in benzene solution with nitrosodurene ($C_6H_2Me_3NO$) and irradiated in the cavity of an e.s.r. spectrometer, generate spectra of the corresponding spin-trapped alkyl radicals.[22] However, this experiment is fraught with many problems, not least is the possible thermal reactivity of nitrosodurene with the alkyl complexes or the photogenerated products.[23] Quantitative analysis of the e.s.r. spectrum generated by photolysis of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Me_3]$ with nitrosodurene indicated that the spin-trapped radical represented $<1\%$ of the fate of the tantalum-methyl groups. A much more informative study involved the irradiation of the alkyl compounds in the presence of cyclohexa-1,4-diene (C_6H_8), a compound known to undergo ready hydrogen transfer to alkyl radicals. The most significant results from this study are as follows.

(*i*) The photochemical formation of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2({=}CH_2)(CH_3)]$ from the corresponding trimethyl complex is not quenched by the addition of cyclohexa-1,4-diene. Furthermore, the photochemical α-hydrogen abstraction to produce the methylidene can be carried out with this compound as the neat solvent. Only very small amounts of benzene are produced.

(*ii*) The photochemical production of $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2({=}CHSiMe_3)(CH_2SiMe_3)]$ can be reduced by adding cyclohexa-1,4-diene and totally quenched if enough of the reagent is added. Corresponding amounts of benzene and $SiMe_4$ are produced. The alkylidene complex once formed does not itself react with the diene.

(*iii*) Addition of cyclohexa-1,4-diene to solutions of $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(CH_2Ph)_3]$ stops the photochemical formation of $PhCH_2CH_2Ph$ and instead leads to the production of toluene and benzene. Again no metal-containing products could be identified.

Mechanistic Considerations.—All of the above results and considerations can be accommodated into the general reaction sequence shown in the Scheme. Initially, irradiation into the alkyl to metal charge-transfer band results in the homolytic cleavage of the metal–carbon bond to produce a reduced metal complex and an alkyl radical. Depending on the nature of the alkyl group and metal complex the following can then occur. In the case of the methyl and trimethylsilyl compounds, α-hydrogen abstraction from one of the remaining alkyl groups can take place to generate the alkylidene complex. For small substituents on the metal this compound is presumably unstable and goes onto other products. In the photochemical production of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2({=}CH_2)(CH_3)]$ the essentially 100% quantum efficiency, lack of a photokinetic isotope effect for photolysis of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2(CD_3)_3]$ and insensitivity to cyclohexa-1,4-diene implies either that the methyl radical never escapes the solvent cage or that the reaction is in fact more concerted. This latter pathway could involve a multicentre transition state. The photolysis of $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(CH_2SiMe_3)_3]$, however, must involve an intermediate CH_2SiMe_3 radical which can be intercepted prior to α-hydrogen abstraction by cyclohexa-1,4-diene. The reduced quantum efficiency for α-hydrogen abstraction in this case (0.4 ± 0.1) may indicate that reformation of the metal–carbon bond can occur. The use of benzyl ligands results in the formation of benzyl radicals which apparently show little tendency in these systems to abstract α-hydrogens. Instead the much less potent radical escapes into the bulk medium to undergo either dimerization or hydrogen atom abstraction from added cyclohexa-1,4-diene.

Experimental

General procedures for the manipulation of these air- and moisture-sensitive compounds have been described.[8]

Starting Materials.—The aryloxide derivatives[8] and [$TaCl_2(CH_2SiMe_3)_3$][24] were synthesized using reported procedures.

[$Ta(OPr^i)_2(CH_2SiMe_3)_3$]. To a solution of [$Ta_2(OPr^i)_{10}$][25] (2.1 g, 2.7 mmol) in benzene (30 cm^3) was slowly added $Li(CH_2SiMe_3)$ (6.4 g, 6.8 mmol) also in benzene (20 cm^3). The mixture was stirred for 1 h, filtered, and the solvent removed under vacuum. Sublimation of the residues at 80 °C (10^{-3} Torr) gave the product as a white solid. Yield 1.93 g, 66% (Found: C, 38.7; H, 8.95. $C_{18}H_{47}O_2Si_3Ta$ requires C, 38.55; H, 8.95%). ^1H n.m.r. (C_6D_6): δ 0.66 (s, 6 H, Ta-CH_2), 0.18 (s, 27 H, $SiMe_3$), 1.39 (d, 12 H, $CHMe_2$), 4.82 (spt, 2 H, $CHMe_2$). [$Nb(OPr^i)_2(CH_2SiMe_3)_3$] was obtained by essentially an identical procedure. ^1H n.m.r. (C_6D_6): 1.17 (s, 6 H, Nb-CH_2), 0.18 (s, 27 H, $SiMe_3$), 1.42 (d, 12 H, $CHMe_2$), 4.79 (spt, 2 H, $CHMe_2$).

Electronic Absorption Spectra.—Electronic spectra were run either on an IBM Instruments 9420 or a Hewlett-Packard HP8450A u.v.-visible spectrophotometer using CaH_2-dried cyclohexane as solvent. All complexes obeyed the Beer-Lambert law over a dilution factor of 10.

Electrochemical Measurements.—Cyclic voltammograms were obtained by using a BioAnalytical Systems, Inc. model CV-1A instrument. Potential control for coulometric experiments was performed with a potentiostat purchased from BioAnalytical Systems, Inc. A three-compartment (H) cell was used with a Pt disc or gauze working electrode, Pt wire auxiliary electrode, and Ag–AgCl quasi-reference electrode to which all potentials refer. Scan rates were 25 mV s^{-1}. Under these conditions, the [$Fe(\eta\text{-}C_5H_5)_2$]$^{+/0}$ couple was measured at +0.47 V, consistent to ±10 mV, with a separation between the anodic and cathodic waves of 90 mV.

Photochemical Studies.—Samples for photolysis were typically sealed under vacuum in 5-mm ^1H n.m.r. tubes. Radiation sources included a 450 W Ace/Hanovia medium-pressure Hg lamp housed in a water-cooled quartz jacket as well as an Oriel Corp. 1 000-W Hg–Xe lamp. The 313 nm line of the Hg spectrum was isolated by the use of an interference filter purchased from Oriel Corp. Quantum efficiencies were determined in benzene using the known *trans–cis* isomerization of stilbene.[26] Nitrosodurene was synthesized by literature methods[22] while cyclohexa-1,4-diene was obtained commercially and dried prior to use.

Acknowledgements

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