Polyhedron Vol. 9, No. 8, pp. 1051–1058, 1990
Printed in Great Britain

0277–5387/90 \$3.00+.00

THE CYCLOMETALLATION OF 2,6-DIPHENYLPHENOXIDE (OAr-2,6Ph_2) LIGANDS AT NIOBIUM(V) AND TANTALUM(V) METAL CENTRES: THE SOLID STATE STRUCTURES OF THE MONOCYCLOMETALLATED COMPOUNDS $Ta(OC_6H_3Ph$-$C_6H_4)(OAr$-$2,6Ph_2)_2(R)$ ($R = CH_3$, n-C_4H_9) AND $Nb(OC_6H_3Ph$-$C_6H_4)(OAr$-$2,6Ph_2)_2(Cl)$

ROBERT W. CHESNUT, JOYCE S. YU, PHILLIP E. FANWICK and IAN P. ROTHWELL*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, U.S.A.

and

JOHN C. HUFFMAN

Department of Chemistry, Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

(*Received* 5 *September* 1989; *accepted* 20 *November* 1989)

Abstract—The dimethyl compounds $M(OAr\text{-}2,6Ph_2)_3(CH_3)_2$ ($M = Nb$, Ta; OAr-2,6Ph_2 = 2,6-diphenylphenoxide) undergo the thermal loss of methane in hydrocarbon solvents to generate the monocylometallated compounds $M(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(CH_3)$ (M = Nb, **1**; Ta, **2**). Kinetic studies show the reactions to be first-order with activation parameters $\Delta H^{\ddagger} = 25.3 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15 \pm 5$ cal mol^{-1} K^{-1} for the tantalum compound. The use of the labelled compound $Ta(OAr\text{-}2,6Ph_2)_3(CD_3)_2$ shows no change in the rate of metallation and also the absence of a methylidene intermediate for the reaction. Attempts to generate a bis(n-butyl) compound by treatment of $Ta(OAr\text{-}2,6Ph_2)_3Cl_2$ with $LiBu^n$ (2 equivs) led instead to the immediate formation of the metallated compound $Ta(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(Bu^n)$ (**3**) along with butane. Thermolysis of the bis(p-methylbenzyl) compound $Ta(OAr\text{-}2,6Ph_2)_3(CH_2C_6H_4\text{-}4Me)_2$ also leads to a monocyclometallated compound (**4**) and p-xylene. However, attempts to obtain a corresponding niobium bis(p-methylbenzyl) compound by treatment of $Nb(OAr\text{-}2,6Ph_2)_3Cl_2$ with $Mg(CH_2C_6H_4\text{-}4Me)_2$ led instead directly to the monocyclometallated derivatives $Nb(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(Cl)$ (**5**) and $Nb(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(CH_2C_6H_4\text{-}4Me)$ (**6**). Single-crystal X-ray diffraction studies of **2**, **3** and **5** show the molecules to be similar in the solid state. A trigonal bipyramidal environment about the metal atom is observed with *trans*,axial oxygen atoms. The new M—C(aryl) bond is chelated to an oxygen atom in one of the axial positions. Crystal data for $TaC_{64}H_{50}O_3$; **2**·3/2C_6H_6 at −155°C: $a = 13.497(3)$, $b = 17.033(6)$, $c = 10.744(2)$ Å, $\alpha = 94.76(1)$, $\beta = 96.34(1)$, $\gamma = 79.80(1)°$, $Z = 2$, $d_{calc} = 1.444$ g cm^{-3} in space group $P\bar{1}$; for $TaC_{64}H_{53}O_3$; **3**·C_6H_6 at −130°C: $a = 18.202(5)$, $b = 17.930(3)$, $c = 15.282(3)$ Å, $\beta = 96.05(2)°$, $Z = 4$, $d_{calc} = 1.408$ g cm^{-3} in space group $P2_1/c$; for $NbC_{54}H_{38}ClO_3$; **5** at 20°C: $a = 18.830(4)$, $b = 11.2856(9)$, $c = 20.725(5)$ Å, $\beta = 102.8(1)°$, $Z = 4$, $d_{calc} = 1.335$ g cm^{-1} in space group $P2_1/c$.

One of the most exciting recent developments in early transition metal organometallic chemistry has been the recognition that high valent, d^0-metal alkyl and related functional groups have the ability to intra- and intermolecularly activate carbon–hydrogen bonds under mild conditions.[1–6] A common

---

* Author to whom correspondence should be addressed.

feature of these reactions has been the need to carry out careful labelling studies in order to determine the actual pathway leading to C—H bond activation.[1–6] During our studies of the early transition metal chemistry associated with sterically bulky aryloxide ligation we have characterized a number of reactions involving the cyclometallation of 2,6-di-*tert*-butylphenoxide ligands.[7] A series of mechanistic studies of the reaction at tantalum(V) has shown that these reactions may proceed via indirect and sometimes competing reaction pathways.[8,9] More recent work has focussed on the related cyclometallation chemistry of 2,6-diphenylphenoxide ligands at various *p*- and *d*-block metal centres.[10,11] In this paper we wish to report on the cyclometallation of this ligand at niobium(V) and tantalum(V) metal centres, focussing on the mechanistic aspects of the reactivity as well as the structure of the metallated products.

RESULTS AND DISCUSSION

The dimethyl compounds $M(OAr\text{-}2,6Ph_2)_3(CH_3)_2$ ($M = Nb, Ta$; $OAr\text{-}2,6Ph_2$ = 2,6-diphenylphenoxide) can be readily obtained in high yield from the corresponding dichloride.[12] Thermolysis of the alkyl compounds in hydrocarbon solvents at temperatures above 120°C leads to the formation of corresponding monocyclometallated compounds, **1** and **2**, and one equivalent of methane (Scheme 1). The reactions can be readily monitored in toluene-d_8 solution in sealed 5 mm NMR tubes by ^1H NMR spectroscopy. Although the aromatic region of the spectra is rather uninformative, the sharp $M—CH_3$ resonance of the dimethyl compound at δ +0.18 (Nb) and −0.21 ppm (Ta) is replaced by a new methyl resonance of **1** and **2** at δ −0.05 and −0.39 ppm, respectively, along with a corresponding peak for methane. In the ^{13}C NMR spectra of **1** and **2** highly characteristic resonances at δ 190.9 (Nb) and 199.9 ppm (Ta) can be assigned to the $M—C(ipso)$ carbon atom of the new metallacycle ring. A single-crystal X-ray analysis of **2** confirms the stoichiometry of the compound as well as its mononuclearity (Fig. 1). Some selected bond distances and angles are collected in Table 1. The environment about the metal atom in **2** can best be described as trigonal bipyramidal with two axial oxygen atoms. The oxygen atom of the six-membered metallacycle ring occupies one of the axial sites while the new Ta–C bond lies in an equatorial position leading to a chelate bite at the metal of 80.8(2)°. As with other six-membered metallacycle rings formed by cyclometallation of aryloxide ligands, this small bite angle is readily accommodated with little puckering of the six-membered ring due to the large Ta—O—C angle, in this case 141.4(4)°.[7] The Ta—O distances of 1.883(4)–1.909(4) Å and Ta—C distances of 2.125(7) (alkyl) and 2.215(5) Å (aryl) are well within the range reported for related aryloxyl alkyl or aryl derivatives of tantalum(V).[13] The overall structure of **1** bears a close resemblance to that found for the monocyclometallated compound $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr\text{-}2,6Bu^t_2)(Ph)_2$ ($OAr\text{-}2,6Bu^t_2$ = 2,6-di-*tert*-butylphenoxide).[9]

$$M(OAr)_3(CH_3)_2 \longrightarrow M(OC_6H_3Ph{-}C_6H_4)(OAr)_2(CH_3) + CH_4$$

M = Nb (1); Ta (2)

OAr = 2,6-diphenylphenoxide

Scheme 1.

A kinetic study of the formation of **2** was carried out by monitoring changes in the ^1H NMR spectrum in toluene-d_8 solution upon heating. The ring closure reaction was found to obey first-order kinetics over 3–4 half-lives yielding the following rate constants $10^5 k/s^{-1}$ at various temperatures (T/°C): 4.15(120); 10.1(130); 9.75(130); 18.0(139); 50.0 (151). These data yield activation parameters for the reaction of $\Delta H^{\ddagger} = 25.3(8)$ kcal mol^{-1} and

Table 1. Selected bond distances (Å) and angles (°) for $Ta(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph)_2(CH_3)$ (**2**)

Ta—O(3)	1.909(4)	Ta—O(2)	1.883(4)
Ta—O(41)	1.899(4)	Ta—C(2)	2.125(2)
Ta—C(21)	2.215(5)		
O(3)—Ta—O(22)	92.6(2)	O(3)—Ta—O(41)	168.9(2)
O(3)—Ta—C(2)	87.3(2)	O(3)—Ta—C(21)	80.9(2)
O(22)—Ta—O(41)	98.0(2)	O(22)—Ta—C(2)	109.7(2)
O(22)—Ta—Cl(2)	131.2(2)	O(41)—Ta—C(2)	92.0(2)
O(41)—Ta—C(21)	89.7(2)	C(2)—Ta—C(21)	118.1(2)
Ta—O(3)—C(4)	141.4(4)	Ta—O(22)—C(23)	146.6(4)
Ta—O(41)—C(42)	169.5(4)		

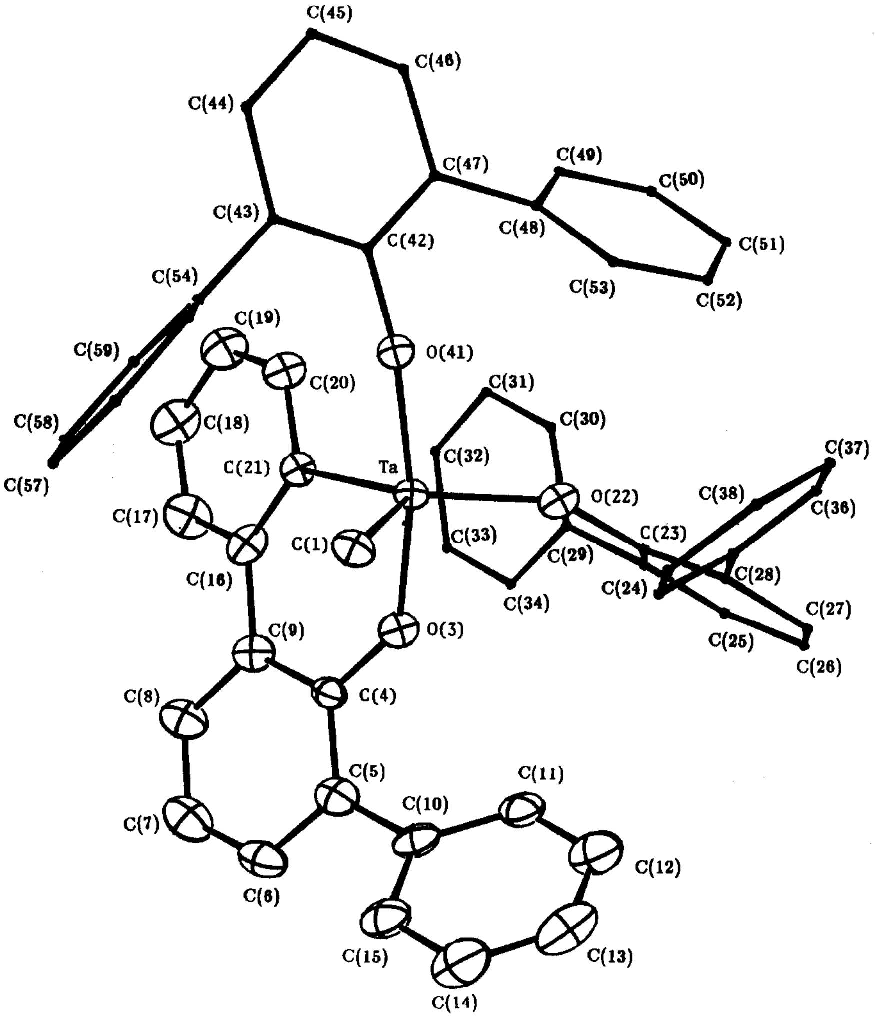


Fig. 1. ORTEP view of Ta(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(CH$_3$) (**2**) emphasizing the central coordination sphere.

$\Delta S^\ddagger = -15(5)$ cal mol^{-1} K^{-1} (Fig. 2). The moderately large and negative entropy of activation for the reaction compares favourably with the other values reported for related reactions and appears to be a consistent characteristic of such cyclometallation reactions.^{7}

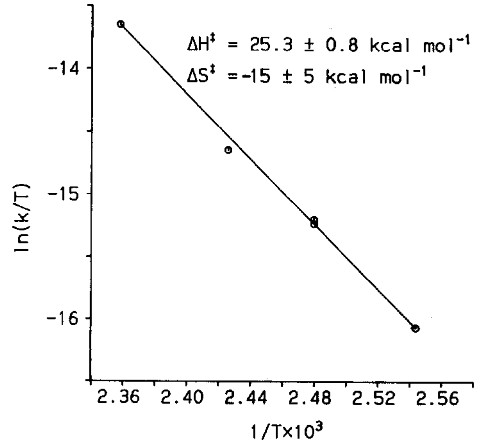
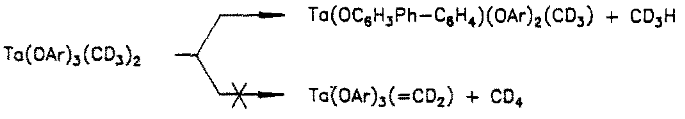


Fig. 2. Activated complex theory plot for the formation of **2** from Ta(OAr-2,6Ph$_2$)$_3$(CH$_3$)$_2$.

An important aspect of high-valent early transition metal alkyl chemistry is the possible formation of stable or intermediate alkylidene functional groups by α-hydrogen abstraction processes.^{5,8,14,15} It is possible that the formation of **2** from Ta(OAr-2,6Ph$_2$)$_3$(CH$_3$)$_2$ proceeds via initial formation of a methylidene intermediate, [Ta(OAr-2,6Ph$_2$)$_3$(=CH$_2$)], which then undergoes rapid addition of the aromatic C—H bond to the tantalum methylide double bond to generate the product. This pathway has to be taken seriously given the fact that alkylidene compounds of the type Ta(OAr)$_2$(X)(=CHR) (X = OAr, CH$_2$R) have been isolated^{13,16} and that a photogenerated tantalum methylidene intermediate was found to rapidly activate the aliphatic C—H bonds of OAr-2,6Bu$^t_2$ ligands.^{8,17} In order to check this possibility



OAr = 2,6–diphenylphenoxide

Scheme 2.

the compound Ta(OAr-2,6Ph$_2$)$_3$(CD$_3$)$_2$ was synthesized by reacting the dichloride with LiCD$_3$. Thermolysis of this compound in toluene was found to yield the monocyclometallated compound **2**. Analysis of this product by mass spectrometry clearly indicated the presence of only **2**-d$_3$. A simulation of the mass spectrum indicated $< 5\%$ of **2**-d$_2$, i.e. containing TaCHD$_2$, to be present. Hence, thermolysis of the labelled compound leads to loss of CD$_3$H and formation of only **1**-d$_3$. No loss of CD$_4$ to generate an intermediate [Ta(OAr-2,6Ph$_2$)$_3$(=CD$_2$)] was detected in this experiment. Hence, it appears that the methyl leaving group in these reactions combines directly with the hydrogen of the aromatic C—H bond to yield the product **2** (Scheme 2). On the basis of work by many groups this process is believed to occur via a four-centre, four-electron transition state.[1-7]

Attempts to isolate a bis-*n*-butyl compound by treatment of Ta(OAr-2,6Ph$_2$)$_3$Cl$_2$ with Bu^{n}Li (2 equivs) led instead to the isolation of the monocyclometallated compound Ta(OC$_6$H$_4$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(Bu^n) (**3**) in moderate yields. The dark brown reaction mixture contained numerous other unidentified components. Pale yellow crystals of **3** could be obtained from the reaction mixture by slow cooling of toluene solutions. The ^{13}C NMR spectrum of **3** clearly shows the Ta—*C*(*ipso*) resonance at δ 199.3 ppm along with the four non-equivalent Ta—*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$ resonances. However, the ^{1}H NMR spectrum of **3** appears very complicated in the aliphatic region. In particular, a series of overlapping multiplets are observed in the δ -0.5 to $+1.0$ ppm region. This complexity of the Bu^n resonances can be explained by the molecular structure of **3** which lacks a plane of symmetry through the Ta—Bu^n bond, hence making all of the three methylene groups diastereotopic.

A solid-state structural analysis of **3** by single-

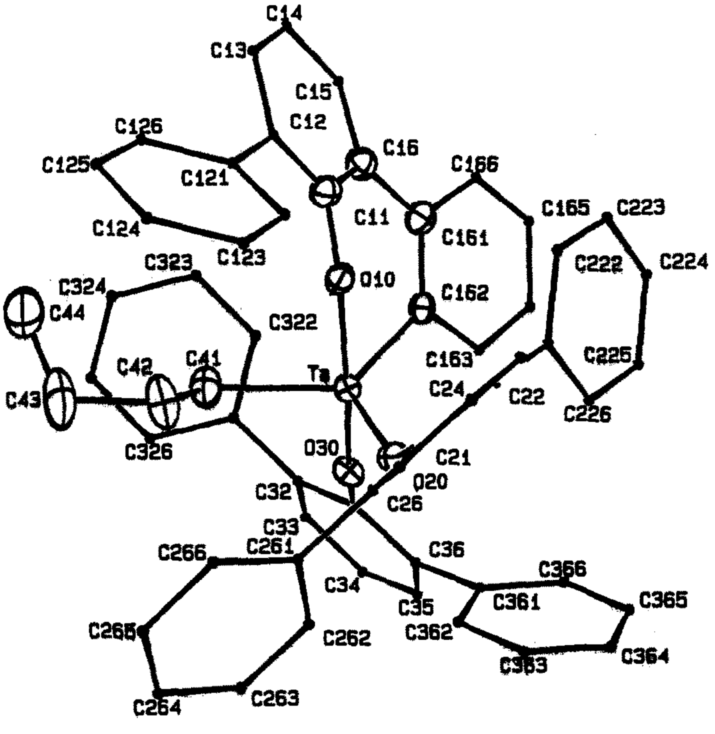


Fig. 3. ORTEP view of Ta(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(Bu^n) (**3**).

Table 2. Selected bond distances (Å) and angles (°) for Ta(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(Bu^n) (3)

Ta—O(10)	1.913(3)	Ta—O(20)	1.910(3)
Ta—O(30)	1.890(3)	Ta—C(41)	2.149(4)
Ta—C(162)	2.182(4)		
O(10)—Ta—O(20)	95.6(1)	O(10)—Ta—O(30)	164.5(1)
O(10)—Ta—C(41)	85.6(1)	O(10)—Ta—C(162)	81.4(1)
O(20)—Ta—O(30)	99.6(1)	O(20)—Ta—C(41)	110.9(2)
O(20)—Ta—C(162)	125.4(1)	O(30)—Ta—C(41)	91.9(2)
O(30)—Ta—C(162)	87.2(1)	C(41)—Ta—C(162)	123.0(2)
Ta—O(10)—C(11)	136.5(3)	Ta—O(20)—C(21)	136.9(3)
Ta—O(30)—C(31)	160.7(3)		

crystal X-ray diffraction methods shows a molecular geometry almost identical to that of **2** (Fig. 3). Some selected bond distances and angles are collected in Table 2.

Treatment of the dichloride Ta(OAr-2,6Ph$_2$)$_3$Cl$_2$ with Mg(CH$_2$C$_6$H$_4$-4Me)$_2$ (where CH$_2$C$_6$H$_4$-4Me = 4-methylbenzyl) allows the isolation of the corresponding dialkyl compound in high yield.[12] Thermolysis of this compound at 120°C also leads to the formation of a monocyclometallated compound Ta(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(CH$_2$C$_6$H$_4$-4Me) (**4**) along with one equivalent of *p*-xylene. In contrast, treatment of Nb(OAr-2,6Ph$_2$)$_3$Cl$_2$ with Mg(CH$_2$C$_6$H$_4$-4Me)$_2$ is found to initially yield the monocyclometallated chloro compound Nb(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(Cl) (**5**), which then undergoes further reaction to produce the *p*-methylbenzyl compound (**6**) (Scheme 3). Compounds **1**, **5** and **6** are of interest as they represent the first reported examples of cyclometallated aryloxide compounds of niobium. A single-crystal X-ray diffraction study of **5** was carried out for comparison with the related tantalum compounds (Fig. 4). Some selected bond distances and angles are collected in Table 3. Again a geometry about the central metal atom is found in **5** that is extremely close to those observed for **2** and **3**. In fact a comparison of the overall geometries of **2**, **3** and **5**, as well as the conformations adopted by the non-metallated OAr-2,6Ph$_2$ ligands, shows a close similarity (Figs 1, 3 and 4).

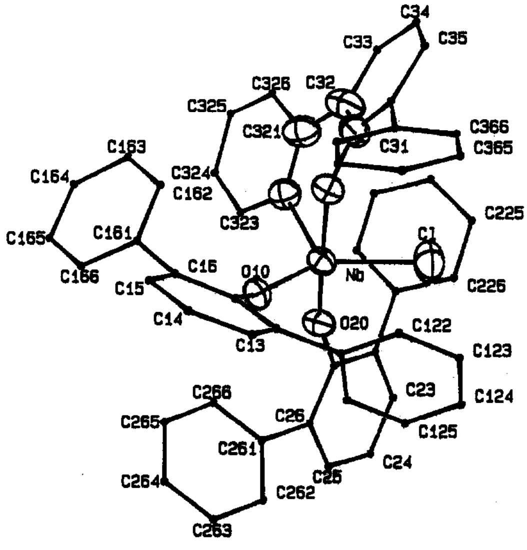
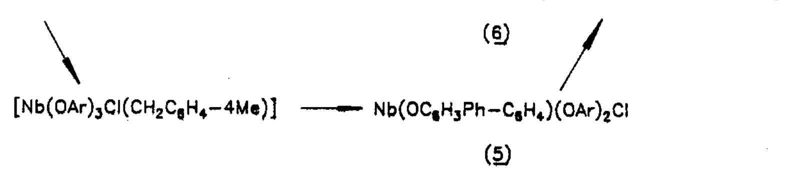


Fig. 4. ORTEP view of Nb(OC$_6$H$_3$Ph-C$_6$H$_4$)(OAr-2,6Ph$_2$)$_2$(Cl) (**5**).

Although variable-temperature analyses of the kinetics of the ring closure reactions of Nb(OAr-2,6Ph$_2$)$_3$(CH$_3$)$_2$ and Ta(OAr-2,6Ph$_2$)$_3$(CH$_2$C$_6$H$_4$-4Me)$_2$ were not carried out, first-order kinetics were found to be obeyed for the disappearance of both compounds at 120°C. Hence the following three half lives for the cyclometallation reactions are



OAr = 2,6-diphenylphenoxide

Scheme 3.

Table 3. Selected bond distances (Å) and angles (°) for $Nb(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(Cl)$ (**5**)

Nb—Cl	2.316(1)	Nb—O(20)	1.898(3)
Nb—O(10)	1.872(3)	Nb—O(30)	1.918(3)
Nb—C(322)	2.122(5)		
Cl—Nb—O(10)	136.8(1)	Cl—Nb—O(20)	91.3(1)
Cl—Nb—O(30)	86.4(1)	Cl—Nb—C(322)	113.0(1)
O(10)—Nb—O(20)	96.7(1)	O(10)—Nb—O(30)	89.4(1)
O(10)—Nb—C(322)	108.8(2)	O(20)—Nb—O(30)	173.1(1)
O(20)—Nb—C(322)	93.5(2)	O(30)—Nb—C(322)	81.4(2)
Nb—O(10)—C(11)	141.5(3)	Nb—O(20)—C(21)	163.9(3)
Nb—O(30)—C(31)	131.1(3)		

available for comparison:

Compound	Half-life (min at 120°C)
$Nb(OAr\text{-}2,6Ph_2)_3Me_2$	22(2)
$Ta(OAr\text{-}2,6Ph_2)_3Me_2$	280(20)
$Ta(OAr\text{-}2,6Ph_2)_3(CH_2C_6H_4\text{-}4Me)_2$	65(5)

Hence it can be seen that cyclometallation occurs much faster at niobium than at tantalum for the same set of ligands. The difference in rates between the two metals, more than an order of magnitude, is much more pronounced than that observed for the cyclometallation of 2,6-di-*tert*-butylphenoxide ligands at titanium and zirconium. In that study a rate difference of only three (Ti > Zr) was found.[7,18] It can also be seen from the data that benzyl ligands are superior leaving groups to methyl ligands at tantalum. This difference in the rate may be attributable to the fact that early *d*-block metal bonds to benzyl ligands have been consistently found to be weaker than corresponding metal–methyl bonds.[19] Furthermore, this and related observations[7,9] may explain why treatment of $Nb(OAr\text{-}2,6Ph_2)_3Cl_2$ with $Mg(CH_2C_6H_4\text{-}4Me)_2$ leads to monocyclometallated **5** (Scheme 3). This reaction will initially produce the mono(benzyl) compound $Nb(OAr\text{-}2,6Ph_2)_3(CH_2C_6H_4\text{-}4Me)(Cl)$. Presumably cyclometallation occurs rapidly in this compound before further substitution can take place. The fact that the niobium bis(methyl) and tantalum bis(benzyl) compounds are isolable must be due to the slower rates of cyclometallation. A very similar situation was found for the reaction of $Ta(OAr\text{-}2,6Bu^t_2)_2Cl_3$ with LiPh, where rapid formation of a monocyclometallated compound $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr\text{-}2,6Bu^t_2)Cl_2$ was followed by the formation of corresponding phenyl derivatives.[9]

EXPERIMENTAL

All operations were carried out either under a dry nitrogen atmosphere or *in vacuo* using a Vacuum Atmosphere Dri-Lab or by standard Schlenck techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone and stored under DRY nitrogen. The compounds $M(OAr\text{-}2,6Ph_2)_3Cl_2$, and $M(OAr\text{-}2,6Ph_2)_3(CH_3)_2$ (M = Nb, Ta) were prepared by reported procedures.[12]

$Nb(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(CH_3)$ (**1**)

A solution of $Nb(OAr)_3(CH_3)_2$ (0.20 g) dissolved in toluene (5 cm^3) was heated at 120°C for 2 h in a closed flask. Cooling and removal of solvent under vacuum yielded the product as a yellow powder. Yield = 0.18 g (90%). ^1H NMR (C_6D_6, 30°C): δ 6.60–7.85 (aromatics), −0.05 (s, Nb—CH_3). ^{13}C NMR (C_6D_6, 30°C): δ 190.9 (Nb—*C*), 62.0 (Nb—*C*H_3). Found: C, 78.4; H, 5.0. Calc. for $NbC_{55}H_{41}O_3$: C, 78.4; H, 4.9%.

$Ta(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(CH_3)$ (**2**)

A solution of $Ta(OAr)_3(CH_3)_2$ (0.25 g) in toluene (5 cm^3) was heated for 7 h at 120°C in a closed flask. Removal of solvent under vacuum yielded the product as a pale white powder. The crude product was dissolved in a minimum amount of benzene. Slow evaporation of the benzene solvent inside the Dri-lab yielded colourless crystals of the product suitable for X-ray analysis. Yield = 0.24 g (87%). ^1H NMR (C_6D_6, 30°C): δ 7.74, 6.90 d, 7.4–6.4 (aromatics), −0.39 (s, Ta—CH_3). ^{13}C NMR (C_6D_6, 30°C): δ 199.9 (Ta—*C*), 64.3 (*C*H_3). Found: C, 72.8; H, 5.3. Calc. for $TaC_{65}H_{50}O_3$: C, 73.4; H, 4.8%.

$Ta(OC_6H_3Ph\text{-}C_6H_4)(OAr\text{-}2,6Ph_2)_2(Bu^n)$ (**3**)

To a solution of 20 g (2.0 mmol) of $Ta(OAr)_3Cl_2$ dissolved in 10 cm^3 of benzene was added, 2.0 cm^3 of a 2.2 M *n*-BuLi solution in hexane over 10 min. The mixture was cooled with an ice bath throughout the n-BuLi addition. The reaction mixture was stirred for 40 min before being warmed to room temperature. A white precipitate that formed during stirring was filtered off, and the solvent was evaporated from the filtrate. The resulting crude solid was redissolved in a minimum amount of benzene, and crystals of product slowly formed over 24 h. Yield = 0.55 g (28.3%). Additional product could be obtained by concentrating the supernatant. ^{1}H NMR (C_6D_6, 30°C): δ 7.87 d, 7.82 d, 7.73 d, 7.35–6.20 (aromatics), 1.35 to −0.50 (m, Ta—C_4*H*$_9$). ^{13}C NMR: δ 199.3 (Ta—*C*), 87.3, 31.3, 28.8, 13.6 (Ta—C_4H_9). Found: C, 72.5; H, 4.9. Calc. for $TaC_{64}H_{53}O_3$ **3**·C_6H_6: C, 73.1; H, 5.1%.

$Ta(OC_6H_3Ph - C_6H_4)(OAr - 2,6Ph_2)_2(CH_2C_6H_4 - 4Me)$ (4)

A solution of 0.25 g of $Ta(OAr)_3(CH_2C_6H_4Me)_2$ dissolved in toluene (5 cm^3) was heated at 120°C for 6 h in a sealed tube. The solvent was evaporated *in vacuo* to yield the crude product as a yellow solid. ^{1}H NMR (C_6D_6, 30°C): δ 0.71 (d), 2.39 (d, Ta—*CH*$_2$), 5.51 (d), 6.38 (d), 6.5–8.4 (m, aromatics). ^{13}C NMR (C_6D_6, 30°C): δ 200.7 (Ta—*C*), 86.6 (Ta—*C*H$_2$), 2.16 (4*Me*). Found: C, 72.0; H, 4.7. Calc. for $TaC_{62}H_{47}O_3$: C; 72.9; H, 4.6%.

$Nb(OC_6H_3Ph-C_6H_4)(OAr-2,6Ph_2)_2(Cl)$ (5)

To a solution of $Nb(OAr-2,6Ph_2)_3Cl_2$ (1.50 g) in benzene (15 cm^3) was added $Mg(CH_2C_6H_4-4Me)_2$ (0.14 g) in small portions. The resulting mixture was stirred for 1 h, filtered and the deep red filtrate concentrated, whereupon deep-red crystals of the product were obtained. Yield = 1.1 g (78%). Found: C, 74.1; H, 4.6; Cl, 4.8. Calc. for $NbClO_3C_{54}H_{38}$: C, 75.1; H, 4.4; Cl, 4.1%. ^{1}H NMR (C_6D_6, 30°C): δ 6.6–7.8 (m, aromatics). ^{13}C NMR (C_6D_6, 30°C): δ 192.1 (Nb—*C*).

$Nb(OC_6H_3Ph - C_6H_4)(OAr - 2,6Ph_2)_2(CH_2C_6H_4 - 4Me)$ (6)

To a solution of **5** (0.30 g) in benzene (15 cm^3) was added $Mg(CH_2C_6H_4-4Me)_2$ (0.05 g). The solution was stirred for 4 h, filtered and concentrated to yield

Table 4. Crystal data and data collection parameters

Compound	2	3	4
Formula	$TaC_{64}H_{50}O_3$	$TaO_3C_{64}H_{53}$	$NbClO_3C_{54}H_{38}$
*f*w	1048.05	1051.08	863.26
Space group	$P\bar{1}$	$P2_1c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	13.497(3)	18.202(5)	18.830(4)
b (Å)	17.033(6)	17.930(3)	11.2856(9)
c (Å)	10.744(2)	15.282(3)	20.725(5)
β (°)	96.34(1)	96.05(2)	102.81(1)
V (Å^3)	2411.01	4959(3)	4294(2)
Z	2	4	4
d_{calc} (g cm^{-3})	1.444	1.408	1.335
Crystal size (mm)	0.15 × 0.15 × 0.18	0.60 × 0.45 × 0.28	0.49 × 0.45 × 0.44
Temperature (°C)	−155	−130	20
Radiation	Mo-K_α	Mo-K_α 22.35	Mo-K_α
Linear absorption coefficient (cm^{-1})	22.979	22.35	3.72
Monochromator	Graphite	Graphite	Graphite
Scan method	ω–2θ	ω–2θ	ω–2θ
h, *k*, *l* limits:	0 to 14, −17 to 18, −11 to 10	0 to 16, 0 to 19, −19 to 19	−20 to 19, 0 to 12, 0 to 22
2θ range (°)	6.00–45.00	4.00–45.00	4.00–45.00
Scan width (°)	2.0	0.42 + 0.35 tan (θ)	0.50 + 0.35 tan (θ)
Take-off angle (°)	2.0	1.90	2.30
Data collected	7429	6711	5958
Unique data	6354	6711	5958
Data with $I > 3.0\sigma(I)$	5659	5391	3502
Largest shift/ESD in final	0.05	0.00	0.00
R	0.0355	0.027	0.038
R_w	0.0356	0.038	0.045
Goodness-of-fit	0.840	1.232	1.246

the product as a fine yellow powder. ^{1}H NMR (C_6D_6, 30°C): δ 1.21 (d), 2.65 (d, Nb—CH_2); 5.62 (d), 6.35 (d), 6.6–8.0 (m, aromatics), 1.84 (s, 4-*Me*). ^{13}C NMR (C_6D_6, 30°C): δ 193.9 (Nb—*C*); 84.3 (Nb—CH_2).

X-ray crystallography

The X-ray diffraction analysis of **2** was carried out at the Indiana University Molecular Structure Center while those of **3** and **5** were obtained through the Purdue University Chemistry Department Facility. Crystal data and data collection parameters are gathered in Table 4. A more detailed account of the data collection and refinement is collected in the supplementary material.

Acknowledgements—We thank the National Science Foundation (Grant CHE 8612063) for support of this research. NSF support for the Chemistry Crystallographic Unit at Purdue is also gratefully acknowledged.

REFERENCES

1. I. P. Rothwell, in *Activation and Functionalization of Alkanes* (Edited by L. Hill), Ch. V. John Wiley, New York (1989).
2. M. E. Thompson, S. M. Baster, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. R. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.* 1987, **108**, 203.
3. P. L. Watson and G. W. Parshall, *Accts Chem. Res.* 1985, **18**, 51 and refs therein.
4. J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.* 1986, **108**, 40 and refs therein.
5. A. R. Bulls, W. P. Schaefer, M. Serfas and J. E. Bercaw, *Organometallics* 1987, **6**, 1219.
6. W. J. Evans, L. R. Chamberlain, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.* 1988, **110**, 6423.
7. I. P. Rothwell, *Accts Chem. Res.* 1988, **27**, 153.
8. L. R. Chamberlain, I. P. Rothwell and J. C. Huffman, *J. Am. Chem. Soc.* 1986, **108**, 1502.
9. L. R. Chamberlain, J. L. Kerschner, A. P. Rothwell, I. P. Rothwell and J. C. Huffman, *J. Am. Chem. Soc.* 1987, **109**, 6471.
10. R. W. Chesnut, B. D. Steffey, I. P. Rothwell and J. C. Huffman, *Polyhedron* 1988, **7**, 753.
11. G. D. Smith, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.* 1989, **111**, 750.
12. R. W. Chesnut, L. D. Durfee, P. E. Fanwick, I. P. Rothwell, K. Folting and J. C. Huffman, *Polyhedron* 1987, **6**, 2019.
13. (a) L. R. Chamberlain, I. P. Rothwell, K. Folting and J. C. Huffman, *J. Chem. Soc., Dalton Trans.* 1987, 155; (b) J. S. Yu, R. W. Chesnut and I. P. Rothwell, *Organometallics*, submitted.
14. R. R. Schrock, in *Reactions of Coordinated Ligands* (Edited by P. S. Bratermann). Plenum Press, New York (1968).
15. R. R. Schrock, *Accts Chem. Res.* 1979, **12**, 98.
16. M. R. Churchill, J. W. Ziller, J. H. Freudenberger and R. R. Schrock, *Organometallics* 1984, **3**, 1554.
17. C. McDade, J. C. Green and J. E. Bercaw, *Organometallics* 1982, **1**, 1629.
18. S. L. Latesky, A. K. McMullen, I. P. Rothwell and J. C. Huffman, *J. Am. Chem. Soc.* 1985, **107**, 5981.
19. J. Halpern, *Accts Chem. Res.* 1982, **15**, 238 and refs therein.