Intramolecular activation of aromatic C–H bonds by tantalum alkylidene groups: evaluating 'cyclometallation resistant' aryloxide ligation

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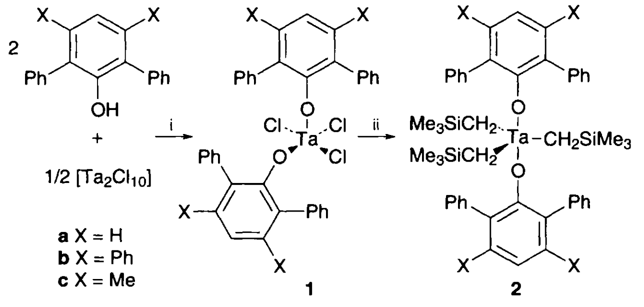
The ligands 2,3,5,6-tetraphenylphenoxide and 3,5-dimethyl-2,6-diphenylphenoxide undergo intramolecular aromatic C–H bond activation by tantalum alkylidene groups at rates 20 and 100 times slower than simple 2,6-diphenylphenoxide.

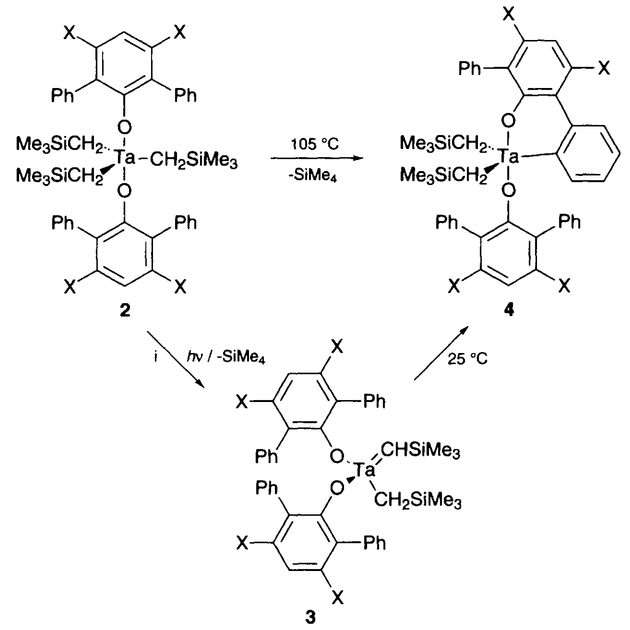
The early transition-metal chemistry supported by sterically demanding aryloxide ligation continues to grow. One continuing difficulty in the development of the organometallic chemistry of these ligands is the sometimes facile intramolecular activation (cyclometallation) of C–H bonds that are a part of the aryloxide ligand.[1] In this context we are presently examining the chemistry of 3,5-disubstituted-2,6-diphenylphenoxides[†] in the expectation that the *meta*-substituents will sterically hinder cyclometallation of the *ortho*-phenyl rings.[2] This communication details a study aimed at quantifying the metallation resistance of these new ligands.

The new tantalum tris(trimethylsilylmethyl) compounds $[Ta(OC_6HX_2\text{-}3,5\text{-}Ph_2\text{-}2,6)_2(CH_2SiMe_3)_3]$ (X = H **2a**, Ph **2b**, Me **2c**)[‡] can be obtained in almost quantitative yield as white crystalline solids by alkylation of the corresponding trichlorides **1** (Scheme 1). Solutions of **2** in C_6D_6 solvent undergo efficient and high-yield conversion to the alkyl, alkylidene compounds **3** along with 1 equiv. of $SiMe_4$ upon photolysis (Scheme 2).[3] The alkylidene group in these molecules is spectroscopically characterized by the Ta=C*H*SiMe$_3$ singlet in the ^{1}H NMR spectrum as well as the Ta=*C*HSiMe$_3$ resonance at δ 237.0 (**3a**), 234.4 (**3b**) and 229.2 (**3c**) in the ^{13}C NMR spectrum. The magnitude of the $^1J(^{13}C\text{–}^1H)$ coupling constant between these nuclei (116.4, 113.5 and 113.6 Hz respectively) implies there is minimal *agostic* interaction between the metal and the α-CH bond of the alkylidene ligand.[4]

The stability of alkylidene **3** is strongly dependent upon the nature of the *meta*-substituents on the aryloxide ligation. In the case of the 2,6-diphenylphenoxide derivative **3a** (X = H) the first-order formation of the mono-cyclometallated compound **4a** occurs at 25 °C with a half-life (monitored by ^{1}H NMR) of 11(1) h in C_6D_6 solvent. In contrast the 3,5-diphenyl derivative **3b** forms **4b** approximately twenty times slower under identical conditions (Fig. 1, Table 1) while formation of **4c** from **3c** is even more retarded. At 105 °C the half-lives are reduced to 15(3) and 75(8) min for **3b** and **3c** respectively, with the rate for **3a** being too fast to measure under these conditions.



Scheme 1 *Reagents and conditions*: i, C_6H_6 solvent, 25 °C; ii, 3 equiv. $LiCH_2SiMe_3$, C_6H_6 solvent, 25 °C



Scheme 2 *Reagents and conditions*: i, 450 W Ace Hanovia Hg lamp, C_6D_6 solvent

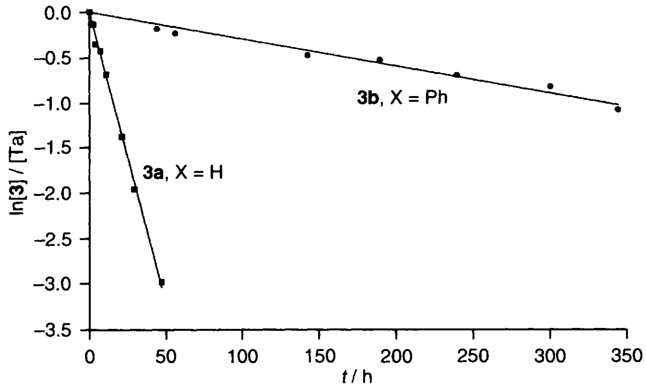


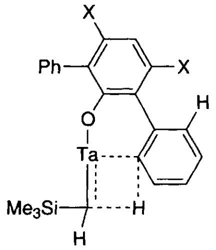
Fig. 1 First-order plots of the decay of alkylidene **3** into cyclometallated **4** at 25 °C

Table 1 First-order half-lives for the formation of **4** in C_6D_6 solvent

X	3 → 4 at 25 °C/h	3 → 4 at 105 °C/min	2 → 4 at 105 °C/h
H	11(1)	[a]	22(3)
Ph	240(20)	15(3)	[b]
Me	[c]	75(8)	[d]

[a] Too fast to measure. [b] 40% conversion in 100 h. [c] 10% conversion in 200 h. [d] 9% conversion in 100 h.

The formation of **4** from **3** involves the overall intramolecular addition of an aromatic C–H bond across the tantalum–carbon double bond.[5] This reaction is the microscopic reverse of thermal α-hydrogen abstraction and is believed to proceed *via* the transition state shown.



Although the exact geometry of this entity is unknown, it clearly requires a low value for the dihedral angle between the *ortho*-phenyl and phenoxy rings in order for the C–H bond to approach the metal–alkylidene functionality. It is highly doubtful that the substituents in the *meta*-position will have a significant electronic effect upon this reactivity. They will, however, sterically destabilize conformations in which the *ortho*-phenyl rings approach planarity with the central phenoxy ring. The spectroscopic properties of *meta*-substituted *ortho*-phenylphenols indicate that they adopt larger dihedral angles than unsubstituted *ortho*-phenylphenols.[6]

This reactivity trend is also apparent in the direct thermal conversion of **2** into **4** (Table 1, Scheme 2). Although it will require further mechanistic study to conclusively show that this reaction proceeds *via* direct σ-bond metathesis (*i.e.* without the intermediacy of **3**) it is highly unlikely that the *meta*-substituents would have such a dramatic effect on α-hydrogen elimination of $\mathrm{SiMe_4}$ from **2**. At higher temperatures the conversion of **2** into **4** is complicated by secondary reactions which are under study.

It can, therefore, be concluded from this study that *meta*-substituted 2,6-diarylphenoxide ligands are indeed more metallation resistant than their unsubstituted counterparts and can help stabilize reactive organometallic derivatives of early transition metals.

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Footnotes

† 2,6-Diphenylphenol is commercially available; 2,3,5,6-tetraphenylphenol was synthesized by literature methods (ref. 2); 3,5-dimethyl-2,6-diphenylphenol was obtained by condensing pent-3-ene-2-one with 1,3-diphenylpropanone and dehydrogenating the resulting 3,5-dimethyl-2,6-diphenylcyclohexenone (ref. 7). *Spectroscopic data*: 3,5-dimethyl-2,6-diphenylcyclohexenone: ^{1}H NMR ($\mathrm{CDCl_3}$, 30 °C), δ 1.01 (d, 3 H), 1.93 (s, 3 H), 2.4–2.8 (m, 3 H), 3.39 (d, 1 H), 7.1–7.5 (m, 10 H); ^{13}C NMR ($\mathrm{CDCl_3}$, 30 °C), δ 20.2, 22.5, 35.0, 40.4, 60.8, 126.4, 126.7, 127.6, 128.0, 128.9, 128.95, 135.7, 137.3, 138.7, 155.1, 197.6. HRMS: calc. for $\mathrm{C_{20}H_{20}O}$, *m/z* 276.1514; found, *m/z* 276.1516. 3,5-Dimethyl-2,6-diphenylphenol: ^{1}H NMR ($\mathrm{CDCl_3}$, 30 °C), δ 2.16 (s, 6 H), 4.78 (s, 1 H), 6.88 (s, 1 H), 7.3–7.6 (m, 10 H); ^{13}C NMR ($\mathrm{CDCl_3}$, 30 °C), δ 20.2, 123.3, 125.8, 127.5, 128.3, 128.8, 130.2, 136.2, 149.9. HRMS: calc. for $\mathrm{C_{20}H_{18}O}$, *m/z* 274.1358; found, *m/z* 274.1359.

‡ *Selected spectroscopic data*: ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): **2a**, δ 6.78–7.58 (m, 26 H, aromatics), 0.04 (s, 27 H, $\mathrm{CH_2Si}\mathit{Me}_3$), −0.05 (s, 6 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **2b**, δ 6.89–7.41 (m, 42 H, aromatics), 0.15 (s, 27 H, $\mathrm{CH_2Si}\mathit{Me}_3$), −0.24 (br s, 6 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **2c**, δ 7.00–7.35 (m, 20 H, aromatics), 6.74 (s, 2 H, *para-H*), 1.87 (s, 12 H, *meta*-Me), 0.10 (s, 27 H, $\mathrm{CH_2Si}\mathit{Me}_3$), −0.43 (s, 6 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **3a** δ 8.56 (s, 1 H, Ta=CH), 6.86–7.45 (m, 26 H, aromatics), 0.07 (s, 9 H, $\mathrm{SiMe_3}$), 0.06 (s, 9 H, $\mathrm{SiMe_3}$), −0.05 (s, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **3b**, δ 7.85 (s, 1 H, Ta=CH), 6.91–7.36 (m, 42 H, aromatics), 0.12 (s, 9 H, $\mathrm{SiMe_3}$), 0.07 (s, 9 H, $\mathrm{SiMe_3}$), −0.49 (s, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **3c**, δ 6.90–7.45 (m, 21 H, Ta=CH plus aromatics), 6.66 (s, 2 H, *para*-H), 2.01 (s, 12 H, *meta*-Me), 0.10 (s, 9 H, $\mathrm{SiMe_3}$), 0.02 (s, 9 H, $\mathrm{SiMe_3}$), −0.83 (s, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$); **4a**, δ 8.25 (d, 1 H), 7.99 (d, 1H), 7.89 (d 1 H), 7.69–6.83 (m, 19 H, aromatics), 0.90 (d, 2 H), −0.31 (d, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), [$^2J(^1\mathrm{H}^1\mathrm{H})$ 11.8 Hz], −0.14 (s, 18 H, $\mathrm{SiMe_3}$); **4b**, δ 8.18 (d, 1 H); 6.7–7.6 (m, 40 H, aromatics), 0.77 (d, 2 H), −0.58 (d, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), [$^2J(^1\mathrm{H}^1\mathrm{H})$ 11.9 Hz]; −0.14 (s, 18 H, $\mathrm{SiMe_3}$); **4c**, δ 8.03 (d, 1 H), 7.67 (d, 1 H), 6.6–7.4 (m, 20 H, aromatics), 2.57 (s, 3 H), 1.90 (s, 6 H), 2.07 (s, 3 H, *meta*-Me), 0.54 (d, 2 H), −0.81 (d, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), [$^2J(^1\mathrm{H}^1\mathrm{H})$ 11.9 Hz], −0.18 (s, 18 H, $\mathrm{SiMe_3}$), ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): **2a**, δ 157.7 (Ta–O–C), 72.2 (Ta–C), 3.8 ($\mathrm{SiMe_3}$); **2b**, δ 158.3 (Ta–O–*C*), 72.3 (br, Ta–C), 3.9 ($\mathrm{SiMe_3}$); **2c**, δ 158.1 (Ta–O–*C*), 70.5 (br, Ta–*C*), 21.3 (*meta*-Me), 4.0 ($\mathrm{SiMe_3}$); **3a**, δ 237.0 (Ta=*C*), 157.3 (Ta–O–C), 52.6 (Ta–C), 2.06 ($\mathrm{SiMe_3}$), 2.00 ($\mathrm{SiMe_3}$); **3b**, δ 234.4 (Ta=C), 158.7 (Ta–O–C), 51.7 (Ta–C), 3.68 ($\mathrm{SiMe_3}$), 2.52 ($\mathrm{SiMe_3}$); **3c**, δ 229.2 (Ta=C), 158.1 (Ta–O–C); 48.3 (Ta–C), 22.5 (*meta*-Me), 3.36 ($\mathrm{SiMe_3}$), 2.63 ($\mathrm{SiMe_3}$); **4a**, δ 203.8 (Ta–C *ipso*), 76.5 ($\mathrm{Ta{-}CH_2}$), 2.0 ($\mathrm{SiMe_3}$); **4b**, δ 207.2 (Ta–C *ipso*), 76.0 ($\mathrm{Ta{-}CH_2}$), 2.1 ($\mathrm{SiMe_3}$); **4c**, δ 205.5 (Ta–C *ipso*), 75.0 ($\mathrm{Ta{-}CH_2}$), 21.3, 20.8, 20.7 (*meta*-Me), 2.1 ($\mathrm{SiMe_3}$).

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