750 *J. Am. Chem. Soc.* **1989**, *111*, 750–751

Facile Activation of Arene CH Bonds Contained in Aryloxide Ligation by Tin(IV) Metal Centers

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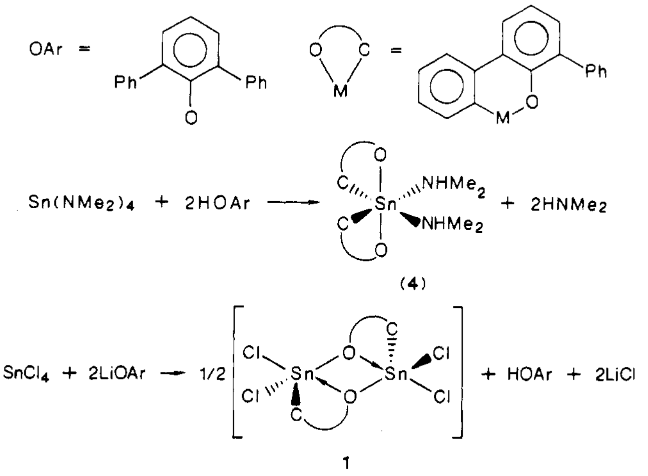
Received July 21, 1988

Despite the enormous body of research literature dealing with the intramolecular activation of carbon–hydrogen bonds by the d-block, lanthanide, and actinide metals,[2-5] there is a surprising lack of studies dealing with related reactivity at p-block element centers.[6,7] This is despite the early, pioneering work of Wade et al.[7] as well as the great importance that alkyl and aryl derivatives of these elements play in chemistry today.[8] During our synthetic and mechanistic studies of the cyclometalation chemistry associated with aryloxide ligation at high valent, early d-block metal centers (Ti^{4+}, Zr^{4+}, Ta^{5+}),[5] we have sought to discover related reactivity involving the main group metals for direct mechanistic comparison. We wish to communicate here our initial observations on the facile cyclometalation of 2,6-diphenylphenoxide ligands by Sn(IV) derivatives and comment on the importance of the leaving group in these particular systems.

The simple treatment of $SnCl_4$ with 2 equiv of $LiOAr\text{-}2,6Ph_2$ ($OAr\text{-}2,6Ph$ = 2,6-diphenylphenoxide) in toluene solution leads to the formation of the cyclometalated dimer **1** in moderate yield over a few hours at room temperature (Scheme I).[9] Refluxing the mixture for 1 h increases the yield of **1** significantly from 30% to 75%. The presence of the new six-membered metallacycle ring in **1** is readily detected spectroscopically (^1H, ^{13}C NMR)[9] and was confirmed by a single-crystal X-ray diffraction analysis (Figure 1).[10] It can be seen that a dimeric structure is found for **1** with two pentacoordinate tin atoms being bridged by the two aryloxide oxygen atoms. All of the chlorine atoms are terminal, and the fifth coordination site at the metal consists of the new tin–aryl σ-bond.

Scheme I



An interesting structural feature of **1** concerns the definite asymmetry in the phenoxide bridging. For example O(10) is strongly bound to Sn(2) with a distance of 2.035 (2) Å but only weakly bound to Sn(1), 2.326 (2) Å, despite the fact that it is chelated to Sn(1) via the metalated ring. The alternating covalent/dative bonds shown for for **1** in Scheme I, therefore, have strong structural support.

The facile metalation observed using $SnCl_4$ contrasts with the extreme thermal stabilities observed for the alkyl derivatives $SnMe_3(OAr\text{-}2,6Ph_2)$ (**2**) and $SnMe_2(OAr\text{-}2,6Ph_2)_2$ (**3**).[11] Extended thermolysis of these complexes at temperatures up to 250 °C failed to show any evidence of cyclometalation occurring with loss of either methane or 2,6-diphenylphenol. However, metalation of two 2,6-diphenylphenoxide ligands is observed to occur on treating $Sn(NMe_2)_4$ with 2 equiv of $HOAr\text{-}2,6Ph_2$ at 50 °C in hydrocarbon solvents. The monomeric product, $[Sn(OC_6H_3Ph\text{-}C_6H_4)_2(HNMe_2)_2]$ (**4**), containing two coordinated dimethylamine ligands, can be envisaged as being generated by initial formation of a mixed aryloxide, amido intermediate followed by aromatic CH bond activation involving transfer of the generated protons to the remaining dimethylamido ligands.[12] The solid-state structure of **4**[13] shows the six-coordinate tin atom chelated by the two six-membered metalacycle rings (Figure 2). A crystallographically imposed 2-fold axis is present in the molecule, with the two aryloxide oxygen atoms approximately trans to each other. The two dimethylamine ligands which are bound to the metal by a long distance of 2.32 (1) Å are considerably compressed together, with an N–Sn–N angle of only 63.3 (5)°. An interesting structural feature of **4** involves the Sn–O–C angle of only 122.8 (7)°. This contrasts with the much larger (140–150°) angle common for similar metalacycles bound to high valent d-block metals where oxygen-p to metal-d π-bonding is an important aspect of the structural chemistry.[14]

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[9] Recrystallization of sparingly soluble **1** from hot benzene (used in the diffraction study) or toluene yielded crystals containing one hydrocarbon per Sn_2 unit. Anal. Calcd for $Sn_2Cl_4O_2C_{42}H_{30}$, **1**·C_6H_6: C, 53.33; H, 3.20; Cl, 14.99. Found: C, 52.85; H, 3.53; Cl, 13.09. Calcd for $Sn_2Cl_4O_2C_{43}H_{30}$, **1**·C_7H_8: C, 53.80; H, 3.36, Cl, 14.77. Found: C, 54.50; H, 3.40; Cl, 14.41. The ^1H NMR of **1** (C_6D_6, 30 °C, 470 MHz) showed the presence of a series of multiplets between δ 6.3 and δ 8.0 ppm. Although a conclusive assignment is difficult, the pattern is consistent with a metalated 2,6-diphenylphenoxide group (see Supplementary Material). Again the $[^1H]^{13}C$ NMR of **1** shows too many resonances for a simple, unmetalated $OAr\text{-}2,6Ph_2$ ligand.

[10] Crystal data for $Sn_2Cl_4O_2C_{42}H_{30}$, **1**·C_6H_6 at 20 °C: space group $P2_1/n$, $a = 11.680$ (1) Å, $b = 26.909$ (3) Å, $c = 12.884$ (1) Å, $\beta = 110.720$ (8)°, $Z = 4$, $d_{calcd} = 1.659$ g cm^{-3}. A total of 5050 unique data were collected with Mo Kα radiation, $4° \leq 2\theta \leq 45°$ of which 4132 with $I > 3\sigma(I)$ were used in the final refinement to yield $R = 0.026$, $R_w = 0.038$.

[11] **$Me_3Sn(OAr\text{-}2,6Ph_2)$ (2)**: Refluxing a mixture of Me_3SnCl with $LiOAr\text{-}2,6Ph_2$ (1 equiv) in toluene yielded $Me_3Sn(OAr\text{-}2,6Ph)$ (**2**) as white microcrystalline needles following filtration and concentration of the filtrate. Anal. Calcd for $SnC_{21}H_{22}O$: C, 61.65; N, 5.42. Found: C, 61.14; H, 5.47. ^1H NMR (C_6D_6, 30 °C) δ –0.31 (Sn-CH_3; $^2J(^{117}Sn{-}^1H) = 58$ Hz); ^{13}C NMR (C_6D_6, 30 °C) δ –4.2 (Sn-CH$_3$; $^1J(^{119}Sn{-}^1H) = 373$ Hz). The aromatic region of **2** showed a pattern characteristic of a nonmetalated $OAr\text{-}2,6Ph_2$ ligand (Supplementary Material). **$Me_2Sn(OAr\text{-}2,6Ph_2)_2$ (3)**: Obtained in a similar manner to **2** only by using Me_2SnCl_2. Anal. Calcd for $SnC_{38}H_{32}O_2$: C, 71.39; H, 5.04. Found: C, 71.17; H, 5.24. ^1H NMR (C_6D_6, 30 °C) δ –0.73 (Sn-CH_3; $^2J(^{119}Sn{-}^1H) = 66$ Hz).

[12] Anal. Calcd for $SnC_{40}H_{38}O_2N_2$ (**4**): C, 68.89; H, 5.49; N, 4.02. Found: C, 67.14; H, 5.53; N, 3.96. ^1H NMR (C_6D_6, 30 °C) δ 1.49 (s, Sn-NHMe_2), 1.88 (br, Sn-NHMe$_2$); aromatic region see Supplementary Material; ^{13}C NMR ($CDCl_3$, 30 °C) δ 38.1 (HNMe_2).

[13] Crystal data for $SnC_{40}H_{38}H_2O_2$ (**4**) at 22 °C: space group $c2$ (no. 5), $a = 18.223$ (1) Å, $b = 7.644$ (2) Å, $c = 13.709$ (1) Å, $\beta = 121.440$ (7)°, $Z = 2$, $d_{calcd} = 1.422$ g cm^{-3}. A total of 1156 unique data were collected with Mo Kα radiation, $4° \leq 2\theta \leq 45°$ of which 1131 with $I > 3p\sigma(I)$ were used in the final refinement to yield $R = 0.049$, $R_w = 0.070$.

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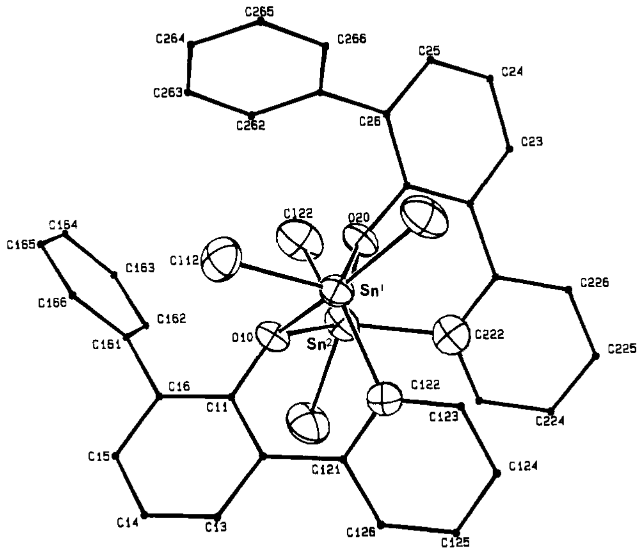

Figure 1. ORTEP view of **1** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: Sn(1)–Sn(2) = 3.4192 (4), –O(10) = 2.326 (2), –O(20) = 2.045 (2), –Cl(11) = 2.354 (1), –Cl(12) = 2.290 (1), –C(122) = 2.113 (4), Sn(2)–O(10) = 2.035(2), –O(20) = 2.259 (2), –Cl(21) = 2.363 (1), –Cl(22) = 2.297 (1), –C(222) = 2.103 (5), Sn(1)–O(10)–Sn(2) = 103.1 (1), Sn(1)–O-(20)–Sn(2) = 105.1 (1).

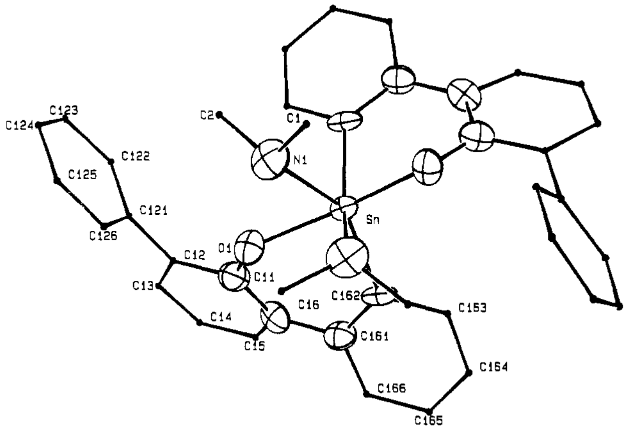

Figure 2. ORTEP view of **4** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: Sn–O(1) = 2.091 (8), –N(1) = 2.32 (1), –C(162) = 2.12 (1), O(1)–Sn–O(1) = 157.0 (4), –N(1) = 71.2 (3), –N(1) = 89.0 (3), –C(162) = 86.5 (3), –C(102) = 105.3 (4), N(1)–Sn–N(1) = 63.3 (5), C(162)–Sn–C(162) = 118.7 (5), Sn–O(1)–C(11) = 122.8 (7).

Although an electrophilic mechanism for these aromatic CH bond activation processes seems reasonable, careful mechanistic studies are planned comparable to those both reported[5] and underway on related d-block metal systems.[15]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063) for support of the research. NSF support for the Crystallographic Unit at Purdue (Grant CHE-8615556) is also gratefully acknowledged.

Supplementary Material Available: Expansions of the aromatic region of the ^{1}H NMR spectra of **1**, **2**, and **4** and tables of positional parameters, general temperature factors, and bond distances and angles (26 pages); tables of observed and calculated structure factors for **1** and **4** (37 pages). Ordering information is given on any current masthead page.

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[15] A very minor component from the reaction of $SnCl_4$ with LiOAr-2,6Ph_2 was identified as the cage material [Li(μ-OAr-2,6Ph_2)$_3$Sn]. Hence redox chemistry is a possible mechanistic complication: Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.*, in press.

UV Laser Photochemistry of Azoalkanes: Surprising Effects of Phenyl Substitution on the Lifetimes of 1,3-Cyclopentanediyl and 1,4-Cyclohexanediyl Triplet Diradicals

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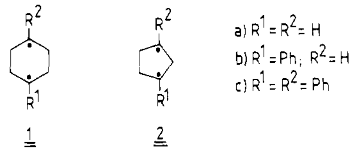
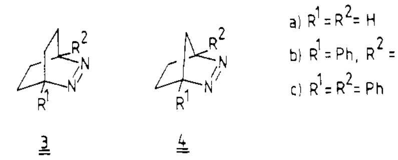
Received August 17, 1988

One might intuitively expect that the lifetimes of hydrocarbon diradical intermediates tend to increase upon phenyl substitution at the radical site. Indeed, 1,4-cyclohexanediyl (**1a**), $^3\tau \leq 0.1$ ns,[2] is over 3000-fold shorter lived than its phenyl derivative **1b**, $^3\tau = 275$ ns.[3] The effect of a second phenyl group, e.g. as in **1c**, on the triplet lifetime is difficult to anticipate because diradicals are not simply "double radicals".[4] In fact, no systematic studies of the degree of phenyl substitution in simple hydrocarbon diradicals appear to have been reported at this time.[5] However, an increase in lifetime has been observed with increasing chain length in phenyl-substituted polymethylene diradicals.[5c-e] In this work we show that the effect of phenyl substitution on the lifetime of triplet 1,4-cyclohexanediyl differs dramatically from that of 1,3-cyclopentanediyl.



The azoalkanes **3**[6] and **4** were chosen as precursors for the diradicals **1** and **2** in this first systematic study on the effect of phenyl substituents on triplet lifetimes. The unknown azoalkanes **4b,c** were prepared by the usual triazolinedione route[7] via the appropriate phenyl-substituted cyclopenta-1,3-dienes.[8] The



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