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Communications to the Editor

Arylamine C−N Bond Oxidative Addition to (silox)$_3$Ta (silox = ^{t}Bu$_3$SiO)

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Oxidative additions of carbon−nitrogen and −oxygen single bonds may be critical in the hydrodenitrogenation (HDN)[1,2] and hydrodeoxygenation (HDO)[3] of crude oil,[4] yet few clear examples are evident.[5−11] In support of such pathways, extensive investigations of transition metal-mediated C−N[12−15] and C−O[16−18] bond formations—the microscopic reverse—have recently been undertaken. While studying substituent effects on 1,2-H$_2$-elimination from (silox)$_3$HTaN(H)(C$_6$H$_4$X) (silox = ^{t}Bu$_3$SiO), oxidative addition of H$_2$NC$_6$H$_4$X to (silox)$_3$Ta (**1**) deviated from the expected N−H cleavage.[19] Oxidative additions of aryl C−N and related C−O bonds to **1** are reported herein.

As Figure 1 illustrates, treatment of (silox)$_3$Ta (**1**) with H$_2$NC$_6$H$_4$X afforded N−H addition to provide (silox)$_3$HTaNH(C$_6$H$_4$X) (**2**-X) and/or C−N activation to give (silox)$_3$(H$_2$N)Ta(C$_6$H$_4$-X) (**3**-X) depending on the substituent. For example, the ^{1}H NMR spectrum of **3**-*p*-CF$_3$ exhibited a broad singlet at δ 5.27 attributed to the NH$_2$, and its IR spectrum revealed telltale 3375- and 3460-cm^{-1} NH stretching vibrations.[20] Related thermally stable **3**-X derivatives were similarly discerned, while prototypical downfield TaH chemical shifts clearly distinguished the **2**-X species,[21] which subsequently eliminated H$_2$ to give (silox)$_3$Ta=N(C$_6$H$_4$X), as previously reported.[19]

A single-crystal X-ray structural study of (silox)$_3$(H$_2$N)Ta(C$_6$H$_4$-*p*-CF$_3$) (**3**-*p*-CF$_3$) revealed a slightly distorted square-pyramidal geometry (Figure 1). Angles between the apical (O2) and basal silox oxygens are 104.7(3)° ($\angle$O2−Ta−O1) and 102.9(2)° ($\angle$O2−Ta−O3), while related O2−Ta−N and O2−Ta−C angles are 112.8(3)° and 108.1(3)°, respectively. The geometry attenuates strong *trans*-influences of the C$_6$H$_4$-*p*-CF$_3$, NH$_2$ ($\angle$N−Ta−C = 139.1(4)°), and apical silox (d(Ta−O$_{ap}$) = 1.865(6) Å) groups, yet accommodates the steric demands of the slightly flexed ($\angle$Ta−O−Si(ave) = 168(5)°) silox linkages ($\angle$O1−Ta−O3 = 152.4(3)°). Remaining bond distances in **3**-*p*-CF$_3$ are normal, with d(Ta−C) = 2.233(8) Å and d(Ta−O$_{eq}$)$_{ave}$ = 1.914(18) Å, but the amide bond length (d(Ta−N) = 1.998(8) Å) is somewhat long,[22] probably because silox O(pπ) → Ta(dπ) interactions are competitive with N(pπ) → Ta(dπ) donation.

The propensity for C−N vs N−H activation may be correlated with substituent Hammett σ-parameters,[23] as indicated in Table 1. Since (silox)$_3$Ta (**1**) reacts with various functionalities and steric factors are critical, the substrate survey is limited, but contrasting effects are revealed. Although the correlation is moderate ($\rho = -0.69$, $R = 0.93$), substituents that increase the basicity of aniline increase the relative rate of NH activation, suggesting that nucleophilic attack by the amine at an empty d$_{xz}$/d$_{yz}$ orbital of **1** precedes oxidative addition. Use of separate parameters indicates a slightly greater resonance ($\rho_R = -0.95$) than inductive ($\rho_I = -0.65$) contribution ($\rho = -1.6$, $R = 0.95$),[23,24] reminiscent of a recent correlation involving arylthiolate reductive elimination.[25] Substituent effects on CN

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[20] **3**-*p*-CF$_3$: ^{1}H NMR (THF-d_8) δ 1.18 (s, ^{t}Bu), 5.27 (s, NH$_2$), 7.51 (d, J = 8 Hz, 2 H, Ar), 8.20 (d, J = 8 Hz, 2 H, Ar); ^{13}C{^{1}H} NMR δ 24.60 (Si*C*), 31.05 (C(*C*H$_3$)$_3$), 124.53 (q, Ar, $^3J_{CF}$ = 4 Hz), 125.65 (q, CF$_3$, J_{CF} = 272 Hz), 129.23 (q, Ar, $^2J_{CF}$ = 32 Hz), 137.93 (Ar), 201.99 (Ta*C*);^{19}F NMR δ −62.55. Anal. Calcd for TaSi$_3$NF$_3$O$_3$C$_{43}$H$_{87}$: C, 52.26; H, 8.87; N, 1.42. Found: C, 52.40; H, 8.81; N, 0.98. Crystal data: monoclinic, $P2_1/n$, a = 14.236(9) Å, b = 26.209(8) Å, and c = 15.068(4) Å, β = 111.09(8)°, V = 5246(4) Å^3, Z = 4, D_{calcd} = 1.252 g/cm^3, T = 293(2) K, 6790 independent reflections, full matrix refinement on F^2 (Syntex P4, SHELX93), $R_1(F)$ = 7.58%, $R_2(wF^2)$ = 14.25%, GOF(F^2) = 0.943.

[21] **2**-X, ^{1}H NMR (C$_6$D$_6$) δ(Ta*H*): X = *m*-CF$_3$, 21.63; *m*-F, 21.63; *p*-F, 21.42; H, 21.47; *p*-Ph, 21.54; *p*-Me, 21.38; *p*-OMe, 21.26; *p*-NMe$_2$, 21.13.

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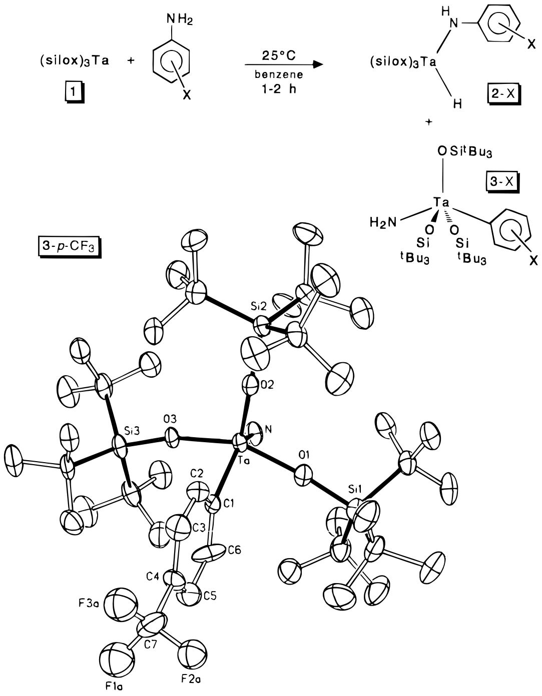


Figure 1. Selected bond distances (Å) and angles (deg) for $(silox)_3(H_2N)Ta(C_6H_4$-*p*-$CF_3)$ (**3**-*p*-CF_3): see text and Ta−O1 = 1.901(6), Ta−O3 = 1.927(5), Si−O(ave) = 1.688(13); O1−Ta−N = 83.6(3), O1−Ta−C1 = 87.1(3), O3−Ta−N = 85.5(3), O3−Ta−C1 = 84.8(3); Ta−O1−Si1 = 168.9(4), Ta−O2−Si2 = 172.2(4), Ta−O3−Si3 = 162.6(4).

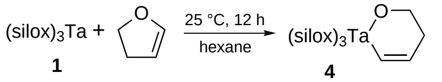
Table 1. Relative Rates of NH- and CN-Bond Oxidative Addition of Substituted Anilines to $(silox)_3Ta$ (**1**)[a]

X	$\sigma_{m,p}(X)^b$	$k_{NH}(rel)^c$	$k_{CN}(rel)^d$	$\Delta\Delta G^{\ddagger}$ (kcal/mol)[a]
3,5-$(CF_3)_2$	0.86[e]		48(9)	−2.3(1)
4-CF_3	0.54		21(4)	−1.8(1)
3-CF_3	0.43		3.0(7)	−0.65(12)
		0.30(7)		0.71(12)
3-F	0.34		0.74(14)	0.18(11)
		0.63(12)		0.28(11)
4-F	0.06	0.89(17)		0.07(11)
aniline	0.00	1		0.0
4-Ph	−0.01		1.3(2)	−0.16(10)
		0.93(17)		0.04(12)
4-Me	−0.17	1.2(2)		−0.11(10)
4-OMe	−0.27	1.9(2)		−0.38(6)
4-NMe_2	−0.83	2.5(2)		−0.54(4)

[a] Relative to NH addition of aniline at 25 °C; oxidative additions were irreversible and determined via competition experiments under pseudo-first-order conditions. [b] Use of σ^+ (k_{NH}) and σ^- (k_{CN}) did not improve the correlations. [c] For NH oxidative addition: $\rho = -0.69$, *R* (corr coeff) = 0.93. [d] For CN oxidative addition: $\rho = 2.1$, $R = 0.84$. [e] Assuming $\sigma_m(CF_3)$ is additive.

activation, while severely limited in scope, are opposite ($\rho = 2.1$, $R = 0.84$) and approach those of electrophilic aromatic substitution ($\rho \sim 3-9$).[26,27] Nucleophilic attack by the filled d_{z^2} orbital of **1**[28] is expected to occur at the arylamine ipso carbon (LUMO+1) preceding C−N oxidative addition,[29] hence electron withdrawing substituents increase k_{CN}(rel) while decreasing the relative rate of NH activation.

The premise that an adjacent electrophilic site enables a pathway for severing carbon−heteroatom bonds was probed through additional substrates. Comparable oxidative additions were not observed for *p*-$CF_3C_6H_4$-CH_3 (no reaction), *p*-$CF_3C_6H_4$-OH (O-H addition), and *p*-CF_3-$C_6H_4OCH_3$ (no reaction), but 1,2-dihydrofuran cleanly added to $(silox)_3Ta$ (**1**) to afford $(silox)_3TaOCH_2CH_2CH{=}CH$ (**4**, 52%),[30] indicative of nucleophilic attack at the LUMO of the vinyl ether, rather than the saturated O−CH_2 linkage (eq 1). Epoxides were cleanly deoxygenated to give $(silox)_3Ta{=}O$ (**5**)[31] and the corresponding olefin in a process judged as concerted[7] on the basis of stereospecific (>95%) O-atom removal from *cis*- and *trans*-decene oxide, but no intermediates were detected, even at −78 °C. In contrast, treatment of **1** with 3,3-dimethyloxetane cleanly yielded $(silox)_3TaOCH_2CMe_2CH_2$ (**6**, 55%, eq 2),[32] which was thermally stable for weeks at 100 °C.



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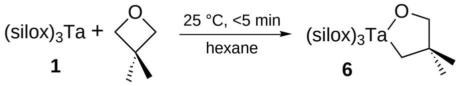

(2)

The carbon−heteroatom cleavages can be accommodated by mechanisms using both electrophilic and nucleophilic sites on the metal center. Arylamine N−H vs C−N activation is a consequence of energetically similar pathways; electrophilic attack on the nitrogen lone pair is dominant in N−H scission, and nucleophilic attack on the arene ring is most important to C−N cleavage, yet the filled d_{z^2} and empty d_{xz}/d_{yz} orbitals are necessary for both reactions. O-atom donation and electrophilic attack by the α-positions of the oxygenated substrates are integral features of oxidative additions leading to oxymetallacycle formation and epoxide deoxygenation.[7]

Lastly, in the the Satterfield mechanism[1,33] regarding quinoline hydrodenitrogenation, sp^3 C−N bond cleavage is implicated as the most significant. This study suggests that low-energy arylamine C−N bond cleavage pathways are available to heterogeneous surfaces of suitable nucleophilicity, such as the relatively electron rich catalyts involved in hydrotreating, lending credence to modification of the conventional mechanism as proposed by Gioia and Lee.[34]

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Supporting Information Available: NMR data and procedures pertaining to Table 1 and X-ray structural data for $(silox)_3(H_2N)Ta(C_6H_4$-*p*-$CF_3)$ (**3**-*p*-CF_3): a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (13 pages); structure factor tables (16 pages). Ordering information is given on any current masthead page.

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[27] $\rho = 3.6$, $\rho_R = 1.5$, $\rho_I = 2.1$, using specific $\sigma_{m,p}$ inductive and resonance values in: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323−400. Interpretations based on this limited set of data are extremely tentative, and use of other data sets (i.e., refs 22 and 23) gave unrealistic fits.

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[29] For a related orbital argument relevant to C−S bond activation, see: Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704−11709.

[30] **4**: ^1H NMR (C_6D_6) δ 1.32 (s, ^tBu), 2.17 ("q", $J = 6$ Hz, CH_2), 4.30 (t, $J = 6$ Hz, OCH_2), 7.32 (dt, $J = 13$, 4 Hz, =CH−), 8.42 (d, $J = 13$ Hz, TaCH=); $^{13}C\{^1H\}$ NMR δ 23.83 (Si*C*), 31.05 ($C(CH_3)_3$), 35.83 (CH_2), 67.23 (OCH_2), 144.17 (=CH−), 186.29 (TaCH=). Anal. Calcd for $TaSi_3O_4C_{40}H_{87}$: C, 53.54; H, 9.77. Found: C, 53.74; H, 10.21.

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[32] **6**: ^1H NMR (C_6D_6) δ 1.20 (s, Me_2), 1.32 (s, ^tBu), 2.21 (s, $TaCH_2$), 4.50 (s, OCH_2); $^{13}C\{^1H\}$ NMR δ 24.00 (Si*C*), 30.73 (Me_2), 31.15 ($C(CH_3)_3$), 47.81 (CMe_2), 85.81 (OCH_2), 86.50 ($TaCH_2$). Anal. Calcd for $TaSi_3O_4C_{41}H_{89}$: C, 54.03; H, 9.84. Found: C, 54.24; H, 9.90.

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