primary intermediate in ANU alkylation of DNA.

The tetrahedral precursor lesion **2** is an attractive alternative to carbocation-like intermediates, and the sequence in Scheme I provides a self-consistent, regioselective mechanism for the mutagenic and oncogenic DNA alkylation reactions of ANUs. Environmental mutagens and carcinogens such as alkylnitrosamines, or their in situ metabolites, may have a similar mechanism of action.

Metal–Metal Bonds Involving Actinides. Functionalization of Activated C–H Bonds and Unusual Oligomerization Chemistry Mediated by a Thorium–Ruthenium Complex

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Actinide-to-transition metal bonds[1-3] represent a new type of heterobimetallic[4,5] linkage, the chemistry of which remains largely unexplored. Such functionalities offer the potential of cooperative chemistry involving strong metallonucleophiles and metalloelectrophiles. We report here two unusual $Cp'_2Th(Cl)Ru(Cp)(CO)_2$ (**1**, $Cp' = \eta^5$-$(CH_3)_5C_5$; $Cp = \eta^5$-C_5H_5)-mediated transformations involving both facile heterobimetallic C–H functionalization and actinide-centered substrate insertion/oligomerization. In the case of acetonitrile, the result is a novel diazathoracyclobutene (amidinate).

Complex **1** undergoes rapid, quantitative reaction (by NMR) with acetonitrile (no detectable intermediates) to yield **2** (eq 1)


2, colorless microcrystals
44% isolated yield
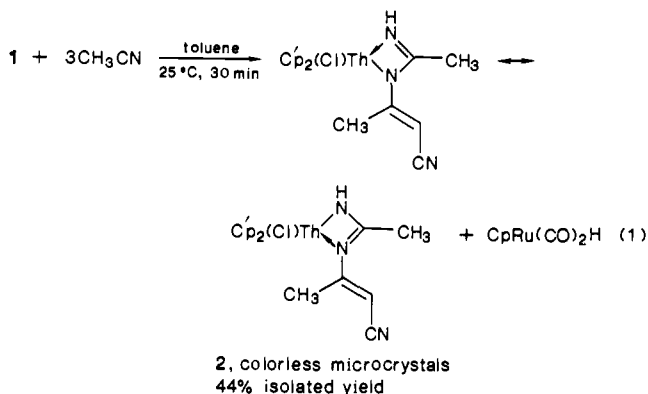
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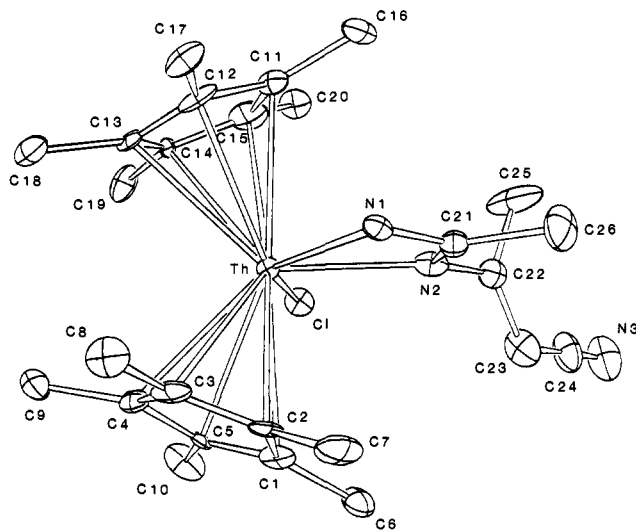
Figure 1. Perspective drawing of the molecular structure of Cp'_2Th-$(Cl)(C_6H_8N_3)$ (**1**). The shapes of the ellipsoids correspond to 30% probability contours of atomic displacement. Individual bond lengths (Å) and angles (deg) of interest: Th–N1, 2.46 (1); Th–N2, 2.46 (1); N1–C21, 1.29 (2); N2–C21, 1.32 (2); C21–C26, 1.50 (2); N2–C22, 1.43 (2); C22–C23, 1.36 (3); C23–C24, 1.39 (3); C24–N3, 1.17 (3); N1–Th–N2, 52.2 (5); Th–N1–C21, 98 (1); Th–N2–C21, 97 (1); N1–C21–N2, 112 (2); Th–N2–C22, 140 (1).

and $CpRu(CO)_2H$ (by NMR[6]). The structural assignment follows from $^1H/^{13}C$ NMR,[7] IR[7,8] ($\nu_{NH} = 3345$, $\nu_{C\equiv N} = 2203$ cm^{-1}), MS,[7] elemental analysis,[7] and X-ray diffraction.[9] The latter data (Figure 1) reveal an unexceptional[10] Cp'_2ThCl fragment ($\angle Cp'$ centroid–Th–Cp' centroid = 135.5°; Th–Cl = 2.697 (4) Å; Th–C(ring) = 2.80 (2, 1, 4, 10)[11] Å) and a bidentate amidinate[12] ligand. The observed equality of Th–N1, Th–N2, the near equality of N1–C21, N2–C21, and the coplanarity (to within

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(7) ^1H NMR (C_6D_6, 22 °C) δ 5.10 (br s, 1 H, NH), 4.13 (s, 1 H, CH), 2.23 (s, 3 H, CH$_3$), 1.87 (s, 30 H, Cp'_2Th), 1.25 (s, 3 H, CH$_3$); ^{13}C NMR (C_6D_6, 20 °C) δ 172.2 (s, C-CH$_3$), 166.5 (s, C-CH$_3$), 124.6 (s, Cp' ring), 118.1 (s, C≡N), 86.54 (d, $J_{CH} = 169$ Hz, CH), 23.76 (q, $J_{CH} = 126$ Hz, C-CH$_3$), 21.89 (q, $J_{CH} = 126$ Hz, C-CH$_3$), 11.46 (q, $J_{CH} = 127$ Hz, Cp'-CH$_3$); IR (Nujol, cm^{-1}) 3345 s, 2203 m, 1608 sh, 1594 m, 1310 s, 1255 s, 1141 m, 1020 m, 820 m, 565 w; MS, 15 eV [m/e (rel abundance), assignment] 659 (2), $Cp'_2Th(Cl)(C_6H_8N_3)^+$; 624 (1), $Cp'_2Th(C_6H_8N_3)^+$; 537 (1), Cp'_2ThCl^+; 524 (100), $Cp'Th(Cl)(C_6H_8N_3)^+$. Anal. Calcd for $C_{26}H_{38}N_3ClTh$: C, 47.31; H, 5.80; N, 6.37. Found: C, 47.19; H, 5.86; N, 6.70.

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(9) Crystal data: $C_{26}H_{38}N_3ClTh$; $M = 660.1$; orthorhombic, space group $P2_12_12_1$ (No. 19) $a = 15.139$ (5) Å, $b = 15.766$ (4) Å, $c = 10.930$ (3) Å at –120 °C; $V = 2609$ (2) Å^3; $Z = 4$; $d_{calcd} = 1.68$ g/cm^3. The structure was solved by Patterson and Fourier techniques and refined to $R(F)$ and $R_w(F)$ of 0.044 and 0.047, respectively, with use of 2181 absorption-corrected reflections with $I > 3\sigma(I)$ measured on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å, $2\theta_{max} = 55°$). A full description of the structure determination is included in the Supplementary Material.

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(11) The first number in parentheses following an averaged value of a bond length or angle is the estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

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0.04 (2) Å) of Th, N1, N2, C21, C22, C26 argue that the metallacycle is highly delocalized. Correcting the Th–N contacts for differences in Th(IV)/U(IV) ionic radii[13] (−0.06 Å) yields a U–N distance near those in $Cp'_2U(\eta^2\text{-pyrazolate})_2$ (2.405 (5)–2.360 (5) Å),[14] $Cp'_2U(Cl)(\eta^2\text{-pyrazolate})$ (2.351 (5), 2.349 (5) Å),[14] longer than in Cp_3UNPh_2 (2.29 (1) Å) and other amido complexes,[15] and shorter than in $Cp'_2UCl_2(\eta^1\text{-pyrazole})$ (2.607 (8) Å)[14] and other dative-bonded U–N complexes.[15] The cyanopropenyl fragment is twisted 85.4° from coplanarity with the metallacycle (Figure 1) and exhibits metrical parameters consistent with valence bond expectations.[16]

A possible scenario for eq 1 (Scheme I) would involve "heterolytic" C–H scission (A)[17,18] and insertion[18a,b,19] of —C≡N into the Th–C bond (B). Tautomerization[20] of the resulting imido complex, followed by insertion[18a,b] of —C≡N(C) and a 1,3-hydrogen shift yields **2**.

In a similar process, **1** undergoes rapid, quantitative reaction (by NMR) with excess acetone to yield aldol-like complex **3** (eq 2) and $CpRu(CO)_2H$ with no detectable intermediates. The

3, colorless microcrystals
70% isolated yield
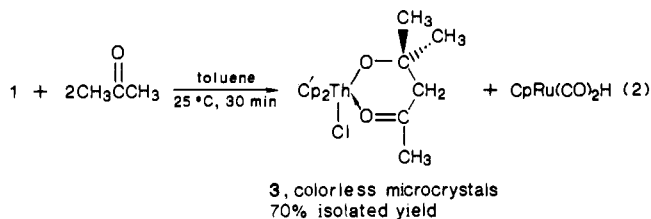
structural formulation follows from spectroscopic and analytical data.[21] Again, a plausible mechanism involves heterolytic C–H cleavage to produce a Th–C σ bond $(Cp'_2Th(Cl)CH_2COCH_3)$, followed by C=O insertion[22] into the Th–C bond.

Scheme I. Acetonitrile Functionalization

From a thermochemical perspective, it is likely that the initial C–H activation process is endothermic for most substrates (eq 3 and 4). Taking $D(\text{Th–Ru}) \approx 60$ kcal/mol,[23] $D(\text{R–H}) = 98$

$$\text{Th–Ru} + \text{R–H} \rightleftharpoons \text{Th–R} + \text{Ru–H} \qquad (3)$$

$$\Delta H = D(\text{Th–Ru}) + D(\text{R–H}) - D(\text{Th–R}) - D(\text{Ru–H}) \qquad (4)$$

$(\text{R} = CH_2COCH_3)$, 93 $(\text{R} = CH_2CN)$ kcal/mol,[24] $D(\text{Th–R}) \approx$ 75 kcal/mol,[23,25] and $D(\text{Ru–H}) \approx 60$ kcal/mol,[26] it can be seen that $\Delta H \approx +23$ and $\approx +18$ kcal/mol for functionalization of acetone[27] and acetonitrile, respectively. Hence, these reactions must be driven by the subsequent insertion/Th–N, Th–O bond formation processes, which are likely rather exothermic.[28] Efforts to elaborate upon and to mechanistically/thermochemically characterize such sequential heterobimetallic functionalization processes are in progress.

Supplementary Material Available: X-ray experimental details, including tables of positional and anisotropic displacement parameters, and tables of bond lengths and angles (7 pages); listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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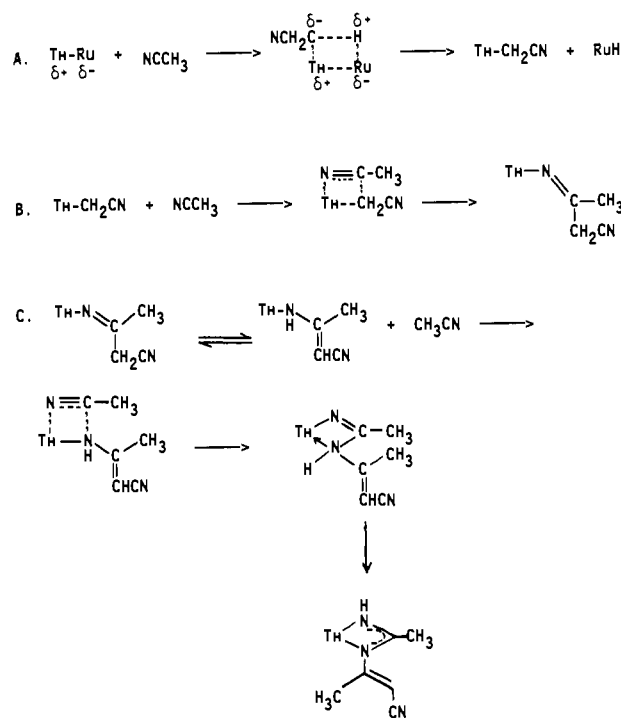
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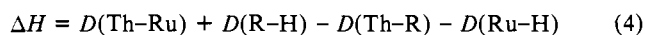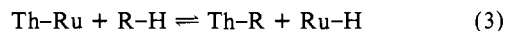(20) Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev.* **1979** 48(2), 107–117.

(21) **13:** ^1H NMR $(C_6D_6, 22 \, °C)$ δ 2.13 (s, 30 H, Cp'_2Th), 2.07 (s, 2 H, CH_2), 1.79 (s, 3 H, $-H_2C$-C(O)-CH_3), 0.96 (s, 6 H, $C(CH_3)_2$); ^{13}C NMR $(C_6D_6, 22 \, °C)$ δ 220.6 (s, $H_3CC(O)CH_2$), 124.1 (s, Cp' ring), 76.39 (s, C-O-Th), 53.48 (t, $J_{CH} = 126$ Hz, CH_2), 34.65 (q, $J_{CH} = 128$ Hz, $-H_2C$-C-(O)-CH_3), 33.16 (q, $J_{CH} = 126$ Hz, $C(CH_3)_2$), 12.22 (q, $J_{CH} = 126$ Hz, Cp'-CH_3); IR (Nujol, cm^{-1}) 1664 s, 1252 w, 1179 m, 1159 m, 1000 s, 945 w. Anal. Calcd for $C_{26}H_{41}O_2ClTh$: C, 47.82; H, 6.32. Found: C, 47.69; H, 6.34.

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(23) Sonnenberger, D. A.; Marks, T. J., unpublished results from the thermochemical titration of **1** with *t*-BuOH.[1a] This result assumes D-$(CpRu(CO)_2$-H$) \approx 60$ kcal/mol.[26] Thorium–ligand bond enthalpies are relative to $D(\text{Th–OR}) = 124$ kcal/mol.[25]

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(27) Assuming the acetonyl oxygen does not interact with Th.

(28) By using published organoactinide[25] and organic molecule[24] bond enthalpy data, we estimate $\Delta H \approx -42$ and -34 kcal/mol for Th–CH_3 addition to acetone and acetonitrile, respectively.