$\label{eq:combined} Room-temperature Activation of Aliphatic C-H Bonds in Cyclohexane and Pentane by the System [Os_3(CO)_{11}(NCMe)]-Te(CF_3)_2: X-Ray Crystal Structure of [Os_3(CO)_{11} \{Te(C_6H_{11})_2\}]$

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The reaction of $[Os_3(CO)_{11}(NCMe)]$ with bis(trifluoromethyl)telluride, $Te(CF_3)_2$, in cyclohexane yields the cluster $[Os_3(CO)_{11}\{Te(C_6H_{11})_2\}]$ in which the CF₃ substituents at the tellurium are replaced by two cyclohexyl substituents; the isolation of the intermediate $[Os_3(CO)_{11}\{Te(CF_3)(C_6H_{11})\}]$ in the dark reveals that the first C–H activation of the cyclohexane is a thermal process, whereas the second C–H activation requires sunlight.

In recent years the activation of aliphatic C–H bonds has received much attention.¹ In particular the functionalization of unmodified alkanes by transition metals is a topical challenge in coordination chemistry. Classical examples are the photochemical syntheses of $[(C_5Me_5)Ir(H)(PMe_3)-(CH_2CMe_3)]$ from $[(C_5Me_5)Ir(H)_2(PMe_3)]$ and neopentane,² $[(C_5Me_5)Rh(H)(PMe_3)(Pr^n)]$ from $[(C_5Me_5)Rh(H)_2(PMe_3)]^3$ and propane, and $[(C_5Me_5)Ir(H)(CO)(C_6H_{11})]$ from $[(C_5Me_5)Ir(CO)_2]$ and cyclohexane.⁴ Apart from these reactions, which proceed only under UV irradiation, some thermal C–H activations have also been reported, *e.g.* the oxidative addition of methane and cyclohexane to the thermally generated fragment bis(dicyclohexylphosphino)ethane-platinum.⁵

We report here the C–H activation of cyclohexane and n-pentane by a reactive intermediate generated from $[Os_3(CO)_{11}(NCMe)]^6$ and $Te(CF_3)_2$.⁷ the first alkane molecule is functionalized thermally at room temperature; the activation of the second alkane molecule by the cluster formed requires sunlight (Scheme 1).

The reaction of $[Os_3(CO)_{11}(NCMe)]$ and $Te(CF_3)_2$ in cyclohexane yields after 36 h at room temperature and in



sunlight the cluster $[Os_3(CO)_{11}{Te(C_6H_{11})_2}]$ 2 which is obtained by chromatographic methods in a high yield.† If carried out in the dark, the intermediate $[Os_3(CO)_{11}]$ ${Te(CF_3)(C_6H_{11})}$ 1 can be trapped and isolated.[‡] On exposure to sunlight, 1 in cyclohexane is converted to 2.

The postulated intermediate $[Os_3(CO)_{11}{Te(CF_3)_2}]$ is presumably susceptible to the activation of aliphatic C-H bonds at room temperature and in the dark because of a high electron deficiency at the tellurium atom, caused by the electron-withdrawing effect of the two CF₃ groups and the electron donation to the osmium atom. This is in line with the ¹²⁵Te NMR spectra, which show the resonances of 1 at δ 886.3 and of 2 at δ 436.9 as compared to that of the uncomplexed Te(CF₃)₂ at δ 1368.7

A single crystal X-ray structure analysis of 2 revealed the molecular structure depicted in Fig. 1.§ Unlike the acetonitrile ligand of the starting complex $[Os_3(CO)_{11}(NCMe)]^8$ the bulky tellurium ligand occupies an equatorial position on the Os₃ skeleton, which consequently is considerably distorted. The Os(1)-Os(2) edge is longer than the other two metal-metal distances, probably owing to the steric interaction of the cyclohexyl substituents with the cis-equatorial carbonyl ligand at Os(1). The deviation of the C(1a)–Te–C(1b) angle (95.4°) from the sp³ tetrahedral angle may be explained by a high p character of the bonding orbitals as well as by steric effects due to cyclohexyl groups.

The analogous C-H activation reaction works also with n-pentane giving the complex $[Os_3(CO)_{11}{Te(C_5H_{11})_2}]$ 3 which is, however, a mixture of isomers differing in the position of the carbon atom in the pentyl substitutents bonded to tellurium. This finding demonstrates the low selectivity of the C-H activation steps.

 \dagger Reagents and conditions: $[Os_3(CO)_{11}(NCMe)]$ (0.22 mmol), cyclohexane (30 ml) Te(CF₃)₂ (0.1 ml), argon, 22 °C, sunlight, 36 h; TLC (silica, pentane-CH₂Cl₂, 5:1), extraction with CH₂Cl₂; yield 90%; IR (cyclohexane) v(CO)/cm⁻¹ 2106m, 2054vs, 2028vs, 2019vs, 2000m, 1989s, 1974s, 1954m and 1948m; ¹H NMR (CD₂Cl₂) δ 3.48-3.24 (m, 2H) and 2.30-1.20 (m, 20H).

 \ddagger Reagents and conditions: $[Os_3(CO)_{11}(NCMe)]$ (0.49 mmol), cyclohexane (40 ml), Te(CF₃)₂ (0.2 ml), argon, 22 °C, in complete darkness, 72 h; TLC (silica, pentane-CH₂Cl₂, 5:1, dark); yield 92%; IR (cyclohexane) v(CO)/cm⁻¹2112m, 2059vs, 2039vs, 2025vs, 2007m, 1994s, 1979m and 1960w; ¹H NMR (CDCl₃) δ 4.10–3.80 (m, 1H) and 2.25-1.20 (m, 10H); ¹⁹F NMR (CDCl₃) & 93.4 [q, J(125Te-19F) 366 Hz].

§ Crystal data for 2: monoclinic, space group A2/n, a = 17.901(2), b =17.958(4), c = 19.577(2) Å, $\beta = 108.21(1)^{\circ}$, U = 5978.16 Å³, Z = 8, D_{c} = 2.606 g cm⁻³, μ = 13.75 mm⁻¹, 2 θ_{max} 45°; 3908 unique reflections, 2891 with $I > 2.5\sigma(I)$. Data measured with Mo-K α radiation (Stoe-Siemens AED 2 four-circle diffractometer, graphite monochromator, $\lambda = 0.71073$ Å, room temperature). Empirical correction of absorption,10 transmission factors 0.226(max) and 0.095(min). Structure solved using SHELXS-86,11 refined with NRCVAX.12 H atoms were included in calculated positions $U_{iso} = U_{eq}(C) + 0.01$, C-H 1.08 Å) and renormalised after every second round of least-squares refinement; weighted anisotropic full-matrix least-squares refinement gave R = 0.033 and $R_w = 0.039$ with $w^{-1} = \sigma^2(F_0) + 0.000140(F_0^2)$. Residual density in final difference map: +1.03(max), -1.18(min) e $Å^{-3}$. Atomic coordinates, and bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Reagents and conditions: [Os₃(CO)₁₁(NCMe)] (0.49 mmol), n-pentane (40 ml), Te(CF₃)₂ (0.1 mol), argon, 22 °C, sunlight, 96 h; TLC (silica, cyclohexane–CH₂Cl₂, 1:2); yield 78%; IR (cyclohexane) v(CO)/cm⁻¹ 2107m, 2069s, 2055vs, 2029vs, 2020vs, 2002m, 1991s, 1976m, 1956m and 1950w; ¹H NMR (CDCl₃) & 2.00-0.70 (m, 22H).



Fig. 1 Molecular structure of 2 (PLUTO plot 9); selected bond distances (Å) and bond angles (°): Os(1)-Os(2) 2.8985(8), Os(2)-Os(3) 2.8785(9), Os(1)-Os(3) 2.8495(8), Te(1)-C(1a) 2.174(13), Os(1)-Te(1) 2.6704(11), Te(1)-C(1b) 2.165(13), Os(2)-Os(1)-Os(3)60.10(2), Os(1)-Os(3)-Os(2) 60.80(2), Os(2)-Os(1)-Te(1) 96.83(3),Os(1)-Te(1)-C(1a) 108.2(4), Os(3)-Os(1)-Te(1) 156.67(3), Os(1)-C(1)Te(1)-C(1b) 105.8(4), Os(1)-Os(2)-Os(3) 59.11(2), C(1a)-Te(1)-C(1b)C(1b) 95.4(5)

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