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 $[Os_3(CO)_{11}\{Te(C_6H_{11})_2\}]$

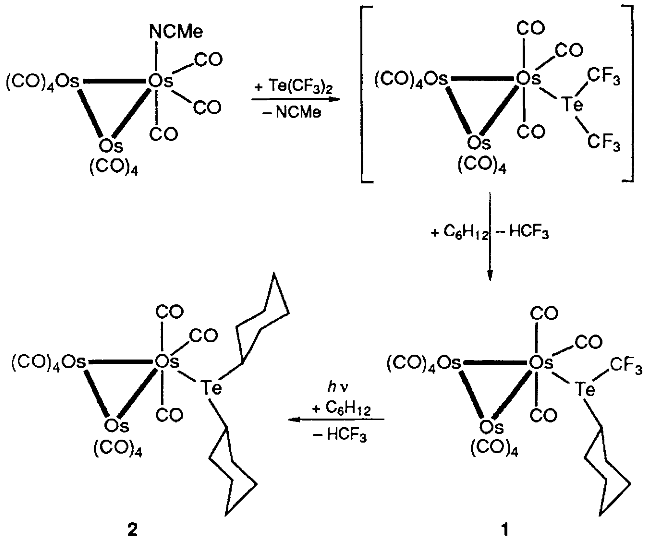
Georg Süss-Fink,*[a] Meinhard Langenbahn,[a] Helen Stoeckli-Evans[a] and Dieter Naumann[b]

[a] *Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*
[b] *Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-5000 Köln 41, Germany*

The reaction of $[Os_3(CO)_{11}(NCMe)]$ with bis(trifluoromethyl)telluride, $Te(CF_3)_2$, in cyclohexane yields the cluster $[Os_3(CO)_{11}\{Te(C_6H_{11})_2\}]$ **2** in which the CF_3 substituents at the tellurium are replaced by two cyclohexyl substituents; the isolation of the intermediate $[Os_3(CO)_{11}\{Te(CF_3)(C_6H_{11})\}]$ **1** 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)ethaneplatinum.[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).



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 CF_3 groups and the electron donation to the osmium atom. This is in line with the ^{125}Te 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 $Te(CF_3)_2$ 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 Os_3 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 sp^3 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.

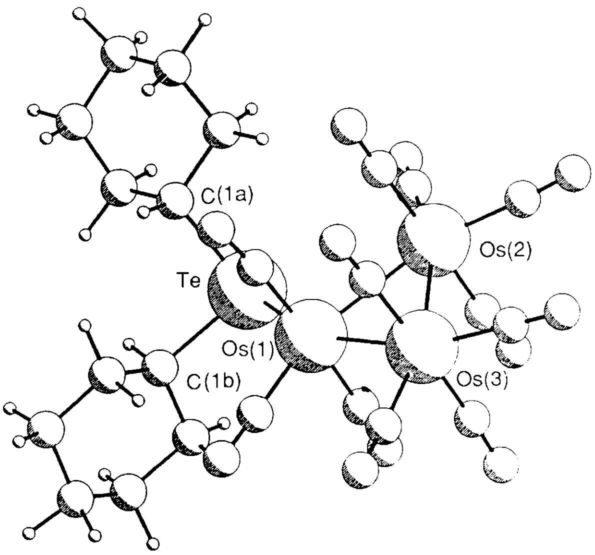


Fig. 1 Molecular structure of **2** (PLUTO plot [9]); selected bond distances (Å) and bond angles (°): Os(1)–Os(2) 2.8985(8), Os(2)–Os(3) 2.8785(9), Os(1)–Os(3) 2.8495(8), Te(1)–C(1a) 2.174(13), Os(1)–Te(1) 2.6704(11), Te(1)–C(1b) 2.165(13), Os(2)–Os(1)–Os(3) 60.10(2), Os(1)–Os(3)–Os(2) 60.80(2), Os(2)–Os(1)–Te(1)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

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† *Reagents and conditions*: $[Os_3(CO)_{11}(NCMe)]$ (0.22 mmol), cyclohexane (30 ml) $Te(CF_3)_2$ (0.1 ml), argon, 22 °C, sunlight, 36 h; TLC (silica, pentane–CH_2Cl_2, 5:1), extraction with CH_2Cl_2; yield 90%; IR (cyclohexane) $\nu(CO)/cm^{-1}$ 2106m, 2054vs, 2028vs, 2019vs, 2000m, 1989s, 1974s, 1954m and 1948m; ^1H NMR (CD_2Cl_2) δ 3.48–3.24 (m, 2H) and 2.30–1.20 (m, 20H).

‡ *Reagents and conditions*: $[Os_3(CO)_{11}(NCMe)]$ (0.49 mmol), cyclohexane (40 ml), $Te(CF_3)_2$ (0.2 ml), argon, 22 °C, in complete darkness, 72 h; TLC (silica, pentane–CH_2Cl_2, 5:1, dark); yield 92%; IR (cyclohexane) $\nu(CO)/cm^{-1}$ 2112m, 2059vs, 2039vs, 2025vs, 2007m, 1994s, 1979m and 1960w; ^1H NMR ($CDCl_3$) δ 4.10–3.80 (m, 1H) and 2.25–1.20 (m, 10H); ^{19}F NMR ($CDCl_3$) δ 93.4 [q, $J(^{125}Te-^{19}F)$ 366 Hz].

§ *Crystal data* for **2**: monoclinic, space group $A2/n$, a = 17.901(2), b = 17.958(4), c = 19.577(2) Å, β = 108.21(1)°, U = 5978.16 Å^3, Z = 8, D_c = 2.606 g cm^{-3}, μ = 13.75 mm^{-1}, $2\theta_{max}$ 45°; 3908 unique reflections, 2891 with $I > 2.5\sigma(I)$. Data measured with Mo-Kα radiation (Stoe–Siemens AED 2 four-circle diffractometer, graphite monochromator, λ = 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 $w^{-1} = \sigma^2(F_o) + 0.000140(F_o^2)$. 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*: $[Os_3(CO)_{11}(NCMe)]$ (0.49 mmol), n-pentane (40 ml), $Te(CF_3)_2$ (0.1 mol), argon, 22 °C, sunlight, 96 h; TLC (silica, cyclohexane–CH_2Cl_2, 1:2); yield 78%; IR (cyclohexane) $\nu(CO)/cm^{-1}$ 2107m, 2069s, 2055vs, 2029vs, 2020vs, 2002m, 1991s, 1976m, 1956m and 1950w; ^1H NMR ($CDCl_3$) δ 2.00–0.70 (m, 22H).

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