Carbon–Hydrogen Cleavage *versus* Ring Opening in the Oxidative Addition Reactions of Furan, Thiophene, Selenophene and Tellurophene with $[Os_3(CO)_{10}(MeCN)_2]$

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Reactions of the cluster $[Os_3(CO)_{10}(MeCN)_2]$ with furan, thiophene, selenophene or tellurophene lead to compounds of corresponding stoichiometry, $[Os_3(CO)_{10}(C_4H_4E)]$ (E = O, S, Se or Te), but, whereas for E = O or S these are furyl or thienyl hydrido compounds formed by C–H cleavage, the Se and Te clusters are formed by E–C cleavage (X-ray structure for the E = Se cluster).

Furan adds oxidatively to $[Os_3(CO)_{10}(MeCN)_2]$ to give the hydrido furyl cluster $[Os_3(\mu\text{-H})(\mu\text{-}C_4H_3O)(CO)_{10}]$ **1** with metallation at the 2-position.[1] The crystal structure shows furyl bridging as a three-electron donating μ,η^1,η^2-vinyl ligand and the O-atom is *exo* to the $Os(CO)_4$ group.[1] We have now examined related reactions for all the heavier analogues through to tellurophene with particular interest in thiophene because of the importance of the hydrodesulphurization (HDS) process which requires C–S bond cleavage. Thiophene is known to bind to single metal atoms in an η^1, η^4 or η^5 manner,[2] but few studies have been made with transition-metal clusters.[3,4]

The reactive compound $[Os_3(CO)_{10}(MeCN)_2]$ has previously been used to incorporate pyrrole, furan and thiophene rings into clusters *via* oxidative addition of their 2-formyl derivatives and subsequent decarbonylation of the acyl complexes formed.[5,6] We have now shown that direct reactions of the parent heterocycles are also possible. The bis-acetonitrile complex reacts with thiophene in refluxing cyclohexane (20 min) to give the oxidative addition hydrido product $[Os_3(\mu\text{-H})(\mu\text{-}C_4H_3S)(CO)_{10}]$ **2** (57%), isolated as orange-red crystals after TLC on silica. Small amounts of the known decarbonylation product $[Os_3(\mu\text{-H})_2(\mu_3\text{-}C_4H_2S)(CO)_9]$ are also formed since decarbonylation occurs easily; the structure of this compound has been described.[6] Based on ^1H NMR and IR data[†] and the X-ray structure of the analogous species derived from 2-methylthiophene,[7] we have identified **2** as having a structure related to that established for the furyl compound, with the S atom *exo*. Although a single set of coalesced NMR signals was observed at room temperature and above, the spectrum showed separate resonances for two isomers at −55 °C. The similarity of the spectra for the two

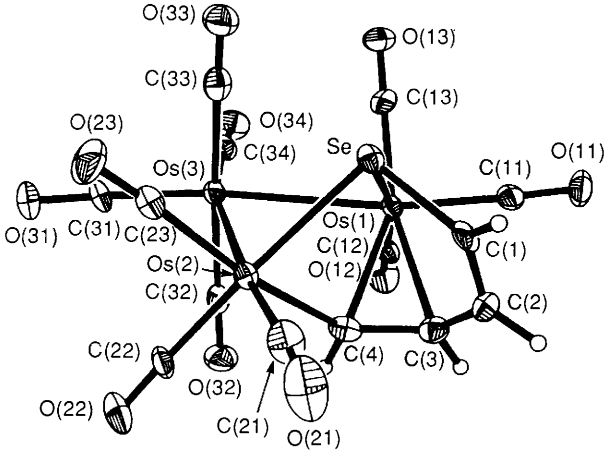
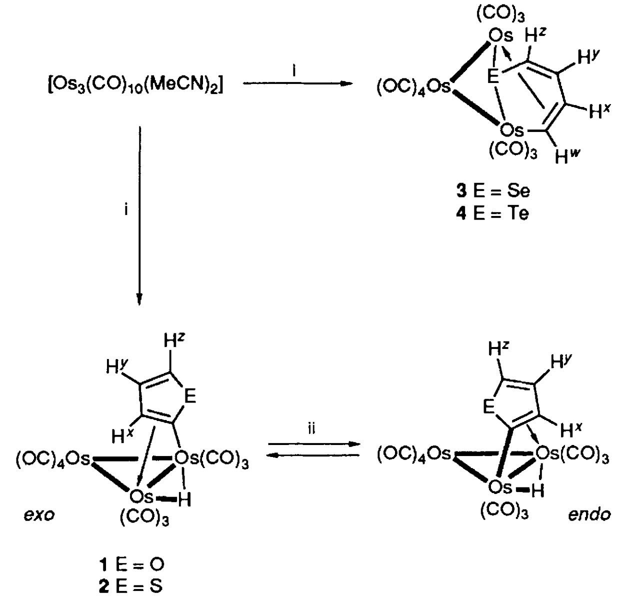


Fig. 1 Molecular structure of the cluster $[Os_3(\mu\text{-}C_4H_4Se)(CO)_{10}]$ **3**; selected bond lengths (Å) and angles (°): Os(1)–Os(3), 2.957(1); Os(2)–Os(3), 2.909(1); Os(1)···Os(2), 3.378(1); Os(1)–Se, 2.560(2); Os(2)–Se, 2.592(2); Se–C(1), 1.94(2); C(1)–C(2), 1.31(3); C(2)–C(3), 1.49(3); C(3)–C(4), 1.40(2); Os(2)–C(4), 2.13(2); Os(1)–C(4), 2.34(2); Os(1)–C(3), 2.38(2); Os(3)–Os(1)–Se, 84.6(1); Os(3)–Os(2)–Se, 85.0(1); Os(1)–Se–Os(2), 82.0(1); Os(2)–Se–C(1), 97.0(5); Se–C(1)–C(2), 120(2); C(1)–C(2)–C(3), 122(2); C(2)–C(3)–C(4), 125(2)



Scheme 1 i, C_4H_4E, refluxing cyclohexane, 20 min; ii, rapid for E = S, slow for E = O

[†] *Selected spectroscopic data* for clusters **1–4**. IR data (ν/cm^{-1}) for cyclohexane solutions; ^1H NMR data (300 MHz; *J* values in Hz). Cluster **1**: IR data in ref. 1; ^1H NMR ($CDCl_3$, 20 °C): *endo* isomer (10%), δ 8.10 (d, H^x), 7.93 (d, H^z), 5.54 (m, H^y) and −14.7 (s, OsH) (J_{xy} 3.6, J_{yz} 1.5); *exo* isomer (90%), δ 7.84 (d, H^x), 7.40 (d, H^z), 5.33 (dd, H^y) and −15.5 (s, OsH) (J_{xy} 3.3, J_{yz} 1.8). Cluster **2**: ν(CO), 2104w, 2066vs, 2053s, 2020vs, 2009s, 1993m and 1983w; ^1H NMR ($CDCl_3$, 56 °C): δ 8.69 (d, H^x), 8.07 (br. s, H^z), 7.00 (br. dd, H^y) and −14.88 (s, OsH) (J_{xy} 4.6, J_{yz} 3.6); (CD_2Cl_2, −55 °C): *endo* isomer (20%), δ 9.26 (d, H^x), 8.69 (d, H^z), 7.35 (m, H^y) and −14.41 (s, OsH) (J_{xy} 4.3, J_{yz} 3.6); *exo* isomer (80%), δ 8.36 (d, H^x), 7.46 (d, H^z), 6.86 (dd, H^y) and −15.21 (s, OsH) (J_{xy} 5.2, J_{yz} 3.2). Cluster **3**: ν(CO) 2100w, 2063vs, 2051m, 2014vs, 2009s, 1996w, 1988w and 1976w; ^1H NMR ($CDCl_3$, 23 °C) δ 7.10 (dd, H^y), 6.54 (d, H^w), 6.30 (dd, H^z) and 5.55 (ddd, H^x) (J_{yz} 7.3, J_{xy} 4.4, J_{wx} 10.2, J_{xz} 0.6). Cluster **4**: ν(CO) 2098w, 2059vs, 2049m, 2014s, 2005s, 1995m, 1988m, 1983(sh) and 1976w; ^1H NMR ($CDCl_3$, 23 °C): δ 7.28 (dd, H^y), 6.43 (d, H^w), 6.34 (dd, H^z) and 5.62 (ddd, H^x) (J_{yz} 8.1, J_{xy} 4.6, J_{wx} 11.2, J_{xz} 0.5). For **3** and **4** the assignment of signals to *w*, *x*, *y* and *z* could be in the reverse order.

isomers indicates that these are the *endo* and *exo* forms which are in rapid equilibrium at room temperature. We have re-examined the published furyl system and have found the presence of a minor concentration of the *endo* isomer in the presence of the major *exo* isomer reported previously,[1] although there is no coalescence behaviour in this case. Rapid *exo–endo* interconversion when E = S but not when E = O supports the intermediacy of an *S*-bonded thienyl complex. There is no evidence for any products resulting from S–C bond cleavage.

In complete contrast the cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with selenophene[8] and tellurophene,[9] likewise in cyclohexane (20 min), to give the non-hydridic species $[Os_3(CO)_{10}(C_4H_4E)]$ **3** (E = Se) (20%) and **4** (E = Te) (35%) respectively as yellow crystalline solids. Spectroscopic data indicate that these complexes are similar but quite different from **1** or **2**; in particular the four H atoms remain bonded to carbon. Other products are formed in these reactions, none of which corresponds with **1** or **2**, and their characterisation will be reported later. The single-crystal X-ray structure of **3** (Fig. 1)[‡] shows that a Se–C bond has been cleaved and that the selenophene is donating six electrons. There are only two Os–Os bonds as expected and the ligand bridges the non-bonded pair of metal atoms with a closely symmetrical Se bridge and a μ-vinyl group. The σ-vinyl to Os bond [Os(2)–C(4) 2.13(2) Å] is shorter than the distances in the η^2-bond [Os(1)–C(4) 2.34(2) and Os(1)–C(3) 2.38(2) Å].

Preliminary coordination of the heteroatom to osmium may be necessary for E–C cleavage and, in the case of phospholes such as 1-phenyl-3,4-dimethylphosphole (L), isolated complexes such as $[Os_3(CO)_{12-x}L_x]$ (x = 1 or 2) thermally decarbonylate with P–C bond cleavage.[7] Transients of this kind could be formed when E = Se or Te but we have not detected them. Heteroatoms are not required or C–H activation to give μ-vinyl complexes.

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[‡] *Crystal structure determination* for **3**: yellow crystal of $C_{14}H_4O_{10}Os_3Se$, $M = 981.74$, triclinic, space group $P\bar{1}$, $a = 9.155(2)$, $b = 9.270(3)$, $c = 13.409(4)$ Å, $\alpha = 97.92(3)$, $\beta = 98.36(2)$, $\gamma = 118.21(2)°$, $U = 936.9(4)$ Å^3, $Z = 2$, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 215.1 cm^{-1}, $F(000) = 860$. Direct methods (SHELX-86), 2897 unique absorption-corrected data for $5 \leqslant 2\theta \leqslant 50°$ and with $F_o \geqslant 3\sigma(F_o)$ used in the refinement, 253 parameters in the model (all non-H atoms anisotropic), final $R = 0.0502$ and $R_w = 0.0545$, with minimisation of $[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.004F_o^2]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.