Formation of a novel Re_3(μ-ethyne) cluster and the possible involvement of Re=Re electrons in the bonding

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The homoleptic neopentoxide cluster $[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6]$ reacts with ethyne to give a novel adduct having ethyne bridged perpendicular to one edge of a Re_3 triangle and with substituted alkynes to yield alkenyl clusters and pivaldehyde.

The chemistry of $[Re_3(\mu\text{-}X)_3X_6]$ clusters, which have a robust triangular Re_3 core with three Re–Re double bonds, is characterized primarily by reactions involving X substitution or transformation, ligand adduct formation and, in a few cases, cluster breakdown.[1] Herein we report the formation of a novel ethyne adduct derived from a $[Re_3(\mu\text{-}X)_3X_6]$ cluster, $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$, which may be best described as a dimetallatetrahedrane.

The homoleptic neopentoxide cluster $[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6]$, synthesized by the same method used to prepare $[Re_3(\mu\text{-}OPr^i)_3(OPr^i)_6]$,[2] reacts in hot hexane with 10 equiv. of ethyne (closed flask heating at 50 °C for 12 h) to give $[Re_3(OCH_2Bu^t)_9(HCCH)]$. The product was isolated in 61% yield as green crystals from a cold saturated hexane solution. A single-crystal X-ray crystallographic analysis shows that ethyne bridges perpendicularly to one edge of a Re_3 triangle (Fig. 1).† The ethyne-bridged Re–Re bond is slightly longer (0.021 Å) than the neopentoxide-bridged bond, and both distances are significantly longer than the Re–Re distances in $[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6]$ [av. 2.368 (1) Å][3] and other Re_3 alkoxide clusters.[2,4,5] The C–C bond distance [1.414(33) Å] is between those of a single and double bond but the large e.s.d. indicates the distance should be interpreted with caution. The Re–C distances are close to those found, for example, in $[Re_3Me_9(PPhEt_2)_2]$,[6] and the Re–O_t distances are normal. The bridging neopentoxide is 0.2 Å closer to Re(1) than Re(2).

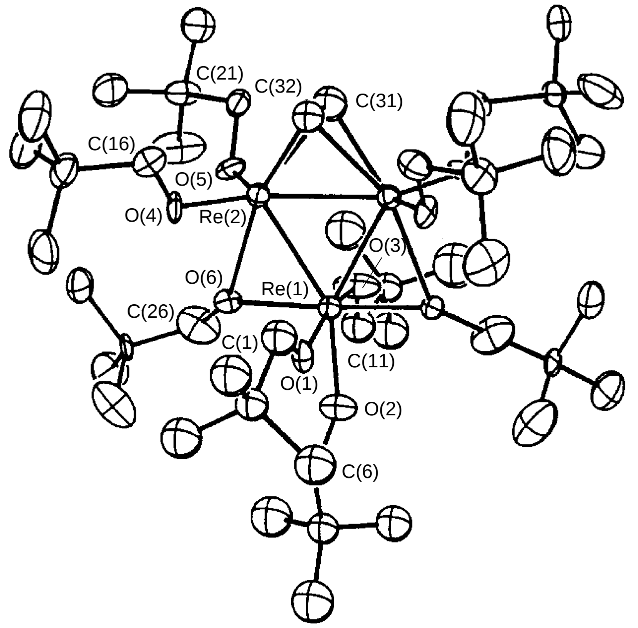

Fig. 1 View of the $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$ molecule showing the atom numbering scheme. Only one orientation of each disordered group is shown. Bond lengths (Å) and angles (°): Re(1)–Re(2) 2.496(1), Re(1)–O(1) 1.895(13), Re(1)–O(2) 2.025(16), Re(1)–O(3) 1.912(14), Re(1)–O(6) 1.990(11), Re(2)–Re(2′) 2.517(2), Re(2)–O(4) 1.910(10), Re(2)–O(5) 1.902(10), Re(2)–O(6) 2.203(10), Re(2)–C(31) 2.143(22), Re(2)–C(32) 2.155(18), C(31)–C(32) 1.414(33); O(1)–Re–O(2) 84.1(6), O(1)–Re–O(3) 165.6(6), O(6)–Re–O(6′) 175.1(6), O(4)–Re(2)–O(5) 111.6(5), O(6)–Re(2)–O(4) 82.5(4), O(6)–Re(2)–O(5) 83.7(4).

The room-temperature ^1H NMR spectrum of $[Re_3(OCH_2Bu^t)_9(HCCH)]$ is fully consistent with the solid-state structure. The coupling constants associated with the ethyne ligand were obtained for $[Re_3(OCH_2Bu^t)_9(H^{13}C^{13}CH)]$ from proton and carbon-13 spectra, which each consisted of one-half of an expected AA′XX′ pattern in the ethyne region. Two of the four constants, $^1J_{CH}$ = 210 Hz and $^2J_{CH}$ = 4.5 Hz, were determined analytically from the spectrum,[7] and the other two, $^1J_{CC}$ = 23–26 Hz and $^3J_{HH}$ = 0–3 Hz, were obtained by a combination of analytical methods and spectrum simulations. The small one-bond ^{13}C–^{13}C coupling constant (*cf.* $^1J_{CC}$ = 172 Hz for ethyne)[8] suggests there is substantial electron transfer from the Re=Re bonds to the coordinated ethyne. The observed $^1J_{CC}$ is comparable, in fact, to those for $[M_2(OR)_6(py)_n(\mu\text{-}C_2H_2)]$ complexes (M = Mo, 23–28 Hz; M = W, 10–19 Hz), which have been described as closely approaching the dimetallatetrahedrane description on the basis of structural, theoretical, spectroscopic and reactivity studies.[9] The lengthening of the Re–Re bonds in the adduct compared to the parent cluster is also consistent with the dimetallatetrahedrane model.

Steric factors are important in the formation of the ethyne adduct. The reactions of $[Re_3(OCH_2Bu^t)_9]$ with MeCCMe, Me_3CCH and PhCCPh, for example, all give alkenyl products and pivaldehyde [eqn. (1)]. Analogous products were observed previously in reactions between $[Re_3(\mu\text{-}OPr^i)_3(OPr^i)_6]$ and alkynes, including ethyne.[4] The proposed mechanism for formation of the alkenyl products in these systems is alkoxide β-hydrogen elimination from $[Re_3(\mu\text{-}OR)_3(OR)_6]$ to give the terminal hydride cluster $[Re_3H(\mu\text{-}OR)_3(OR)_5]$, and subsequent trapping of the hydride by alkyne.

$$[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6] + RCCR' \xrightarrow[50\ ^\circ C]{C_6D_6} [Re_3(\mu\text{-}OCH_2Bu^t)_3\{\eta^1\text{-}CR{=}C(H)R'\}(OCH_2Bu^t)_5] + Bu^tC(O)H \quad (1)$$

(R = R′ = Me, Et or Ph; R = H, R′ = Bu^t)

To summarize, $[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6]$ and ethyne react to give $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$, a triangular cluster in which ethyne bridges perpendicularly to a Re–Re edge. There are a few low-valent transition-metal alkyne clusters having cores resembling that in $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$,[10,11] but there appear to be no other mid- or high-valent examples. The ethyne in $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$ is substantially reduced as judged by the long C–C bond and small ^{13}C–^{13}C coupling constant, suggesting there is electron transfer from the Re=Re bonds to the ethyne. Although this appears to be the first example of this type of internal electron-transfer behaviour in the $[Re_3(\mu\text{-}X)_3X_6]$ system, it is a common feature in the chemistry of midvalent early transition-metal multiply bonded compounds. Two prototypical examples are the reactions of triply bonded $[M_2(OR)_6]$ (M = Mo, W) compounds with CO and alkynes to form, respectively, alkylidene- and dimetallatetrahedrane-like $[M_2(OR_6)(\mu\text{-CO})]$ and $[M_2(OR)_6(\mu\text{-alkyne})]$ complexes. In contrast to the reaction between ethyne and $[Re_3(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6]$, reactions involving substituted alkynes give pivaldehyde and alkenyl clusters *via* a proposed hydride intermediate.

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Footnote

† *Crystal data* for $[Re_3(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_7(\mu\text{-}HCCH)]$ at −50 °C, $C_{47}H_{101}O_9Re_3 \cdot 2CH_2Cl_2$, dark olive green plate, 0.12 × 0.40 × 0.45 mm, M = 1538.94, monoclinic, space group $P2_1/m$, a = 11.879(2), b = 22.847(5), c = 12.004(2) Å, β = 95.46(1)°, U = 3243 Å^3, Z = 2, D_c = 1.58 g cm^{-3}, μ(Mo-Kα) = 58.7 cm^{-1}. Data were collected on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) in the ω scan mode. Lorentz and polarization corrections as well as an empirical absorption correction based on ten reflections having χ values between 70 and 90° were applied to the data. A total of 5023 reflections were collected in the range $4 < 2\theta < 48°$; 3452 unique reflections with $I > 3\sigma(I)$ were used in the structure solution. Three of the neopentoxide groups [C(1), C(6), C(11)] were treated as independently rotating rigid bodies because of disorder. Two significant areas of residual electron density were noted on the mirror plane which were indicative of a severe positional disorder of the entire molecule, and these were refined as partial Re atoms having a total of 3% occupancy. $R(F)$ = 0.061; $R_w(F)$ = 0.054 where $w = [\sigma(F)]^{-2}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/338.

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