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Preliminary communication

A BENZAMIDO BRIDGED RHENIUM CARBONYL CLUSTER PRODUCED BY ATTACK OF OH^- ON COORDINATED PhCN. X-RAY CHARACTERIZATION OF THE ANION $[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$

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Summary

The novel anion $[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$, obtained by reaction of $Re_3(\mu\text{-}H)_3(CO)_{10}(NCPh)_2$ with $(NBu_4)OH$, has been characterized by X-ray analysis. It contains a triangle of rhenium atoms, with the three Re—Re edges bridged by the hydrides, bearing a benzamido ligand diaxially bridging the shortest Re—Re bond. ^1H NMR spectroscopy has revealed dynamic behaviour of the ligand. Treatment of the anion with H^+ in PhCN solution results in regeneration of the parent compound and liberation of one molecule of benzamide.

We recently reported the synthesis and structure of the reactive species $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2$, obtained by oxidation of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with CF_3SO_3H [1] or $C_7H_7^+$ [2] in the presence of MeCN. Other nitriles give analogous $Re_3(\mu\text{-}H)_3(CO)_{10}(NCR)_2$ compounds. The two nitrile molecules are rather labile and can be easily replaced by a variety of nucleophiles, such as I^-, RCO_2^-, MeO^-, py, PPh_3 [1]. This type of reactivity, however, is not unique for these species, as shown by their behaviour toward OH^-. In fact, after treating $Re_3(\mu\text{-}H)_3(CO)_{10}(NCPh)_2$ with $(NBu_4)OH$ in anhydrous CH_2Cl_2 at room temperature, we isolated (by crystallization from CH_2Cl_2/Et_2O) pale-yellow crystals of the novel species $(NBu_4)[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]$ (yield ca. 30%)*, which contains a bridging benzamido group. This ligand is apparently

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*The main product (yield ca. 60%) was the substitution derivative $[Re_3(\mu\text{-}H)_3(\mu\text{-}OH)(CO)_{10}]^-$, as judged from the IR data and, mainly, from the ^1H NMR spectrum, which shows two hydridic signals at δ −9.5 and −13.8, in 1/2 ratio, very close to the values of the hydridic resonances of the analogous (μ-OMe) compound (δ −9.65 and −13.84). The same species is also the dominant product of the reaction of $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2$ with OH^-, which, however, gives more complex mixtures.

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formed, in accord with the well established mechanism of hydrolysis of coordinated nitriles [3], by attack of OH^- on the C atom of one PhCN ligand followed by rearrangement of the imino (N=C(Ph)OH) to the amido (N(H)C(Ph)O) group, which is able to bridge displacing the second PhCN molecule.

The novel anion shows ν(CO) bands in the IR spectrum in CH_2Cl_2 solution at 2095w, 2020ms, 2000s, 1995sh, 1940m, 1906ms and 1890sh cm^{-1}. The ^1H NMR spectrum, in CD_2Cl_2, at −70°C, exhibits, besides the $(NBu_4)^+$ signals, the following resonances: δ 7.23 (m, 5H, phenyl), 6.13 (s, 1H, N-H), −9.58 (s, 1H), −12.66 (s, 1H) and −14.22 (s, 1H) ppm, the last three being due to three non-equivalent hydrides.

The structure of the anion* is shown in Fig. 1 and bond distances and angles

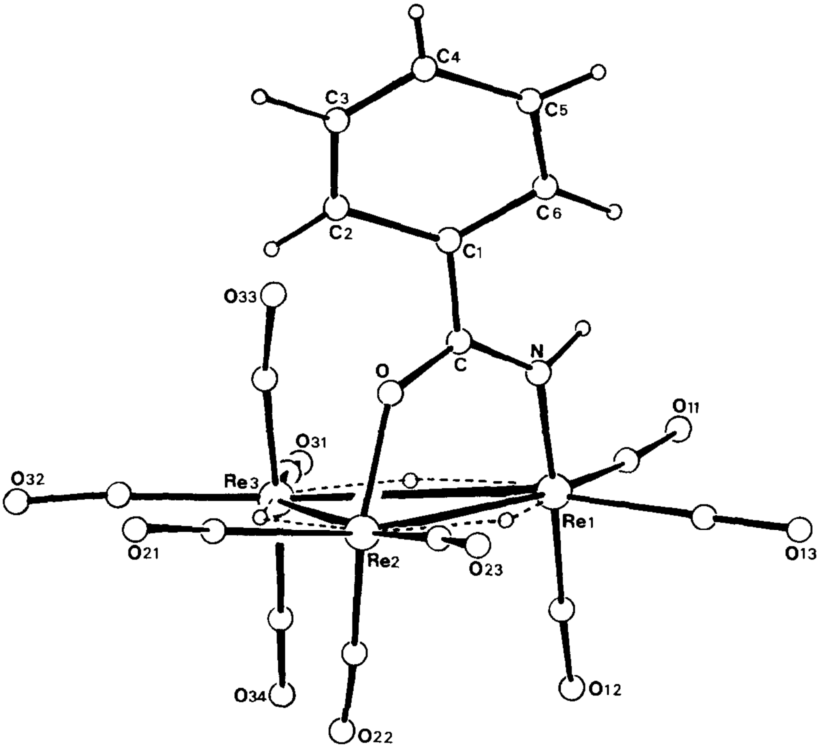

Fig. 1. A view of the anion $[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$. The hydride atoms, not directly located, are in postulated positions. All the hydrogens of the benzamido ligand have been placed in their ideal calculated positions. The carbonyls are indicated by their oxygen atoms.

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*Crystal data. $C_{33}H_{45}N_2O_{11}Re_3$, $M = 1204.3$, monoclinic, space group Cc (No. 9), with a 16.979(3), b 16.496(4), c 15.124(4) Å, $\beta = 108.30(2)°$, V 4021.8 Å^3, D_c 1.99 g cm^{-3} for $Z = 4$. Mo-K_α radiation (λ 0.71073 Å); μ(Mo-K_α) 91.84 cm^{-1}. The intensities were collected on an Enraf—Nonius CAD4 diffractometer within the limits $3 < \theta < 25°$. The structure was solved by Patterson methods and refined by least-squares, on the basis of 2366 significant ($I > 3\sigma(I)$) independent reflections up to a current conventional R and R' values of 0.033 and 0.049, respectively. The assignment of the N and O atoms of the benzamido ligand was based on thermal parameters and bond distances, but some disorder cannot be ruled out. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication. Tables of temperature factors and calculated and observed structure amplitudes are available from the authors.

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (deg.) WITHIN THE ANION $[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}\eta^2\text{-}OC(Ph)NH)]^-$

Distances		Angles	
Re(1)—Re(2)	3.153(2)	Re(3)—Re(1)—C(11)	102(1)
Re(1)—Re(3)	3.289(2)	Re(3)—Re(1)—C(12)	87(1)
Re(2)—Re(3)	3.274(1)	Re(3)—Re(1)—C(13)	168(1)
Re(1)—C(11)	1.93(5)	Re(3)—Re(1)—N	87.8(5)
Re(1)—C(12)	1.92(3)	Re(3)—Re(2)—C(21)	100(1)
Re(1)—C(13)	1.83(3)	Re(3)—Re(2)—C(22)	90(1)
Re(2)—C(21)	1.96(3)	Re(3)—Re(2)—C(23)	169(1)
Re(2)—C(22)	1.98(2)	Re(3)—Re(2)—O	85.1(4)
Re(2)—C(23)	1.95(4)	Re(2)—Re(1)—C(11)	161(1)
Re(3)—C(31)	1.90(3)	Re(2)—Re(1)—C(12)	98(1)
Re(3)—C(32)	1.85(3)	Re(2)—Re(1)—C(13)	111(1)
Re(3)—C(33)	1.84(5)	Re(2)—Re(1)—N	78.8(5)
Re(3)—C(34)	1.98(2)	Re(1)—Re(2)—C(21)	161(1)
Re(1)—N	2.14(2)	Re(1)—Re(2)—C(22)	92(1)
Re(2)—O	2.13(2)	Re(1)—Re(2)—C(23)	108(1)
N—C	1.34(2)	Re(1)—Re(2)—O	78.5(5)
C—O	1.29(2)	Re(1)—Re(3)—C(31)	104(1)
C—C(1)	1.50(2)	Re(1)—Re(3)—C(32)	166(1)
C(1)—C(2)	1.41(2)	Re(1)—Re(3)—C(33)	94(1)
C(1)—C(6)	1.35(2)	Re(1)—Re(3)—C(34)	89(1)
C(2)—C(3)	1.45(3)	Re(2)—Re(3)—C(31)	161(1)
C(3)—C(4)	1.30(3)	Re(2)—Re(3)—C(32)	109(1)
C(4)—C(5)	1.34(3)	Re(2)—Re(3)—C(33)	97(1)
C(5)—C(6)	1.42(3)	Re(2)—Re(3)—C(34)	86(1)
C(11)—O(11)	1.22(5)	C(11)—Re(1)—N	94(2)
C(12)—O(12)	1.19(3)	C(12)—Re(1)—N	175(1)
C(13)—O(13)	1.18(3)	C(13)—Re(1)—N	99(1)
C(21)—O(21)	1.12(3)	C(21)—Re(2)—O	94(1)
C(22)—O(22)	1.14(3)	C(22)—Re(2)—O	171(1)
C(23)—O(23)	1.11(4)	C(23)—Re(2)—O	89(1)
C(31)—O(31)	1.20(3)	N—C—O	124(2)
C(32)—O(32)	1.19(3)	N—C—C(1)	119(2)
C(33)—O(33)	1.27(5)	O—C—C(1)	117(2)
C(34)—O(34)	1.19(3)	Re(1)—N—C	128(1)
		Re(2)—O—C	130(1)

are reported in Table 1. It contains an isosceles triangle of Re atoms, with two longer hydrogen-bridged edges (mean Re—Re 3.281 Å) and one shorter edge doubly bridged by a hydride ligand and by the diaxial chelate benzamide ligand (Re—Re 3.153(2) Å). The ligand stereochemistry is similar to that previously observed in the carboxylate cluster species $[Re_3(\mu\text{-}H)_3(CO)_{10}(\mu\text{-}O_2CR)]^-$ [4]. The three bridging hydrides are assumed to be almost coplanar with the Re_3 plane, on the basis of the disposition of the other ligands. The mean Re—N,O bond length (2.13 Å) is similar to the corresponding Re—O interactions in the (μ-O_2CR) species (R = H 2.17 Å, R = CF_3 2.18 Å). The bond parameters within the benzamido ligand are as expected [5]: the mean C—O,N interaction, 1.31 Å, is slightly longer than the mean C—O interaction in the carboxylato-bridged species (1.25 Å), and the N—C—O angle (124(2)°) is slightly smaller than the O—C—O ones (mean 129°). In order to minimize the non-bonding interactions between the hydrogen atom bound to N and the α-phenyl-hydrogen (computed N—H···H—C(6) distance 2.07 Å) the plane of the phenyl group is rotated with respect to the N—C—O plane, the dihedral angle between the best planes (N,C,O,C(1)) and (C(1) to C(6)) being 30.6°.

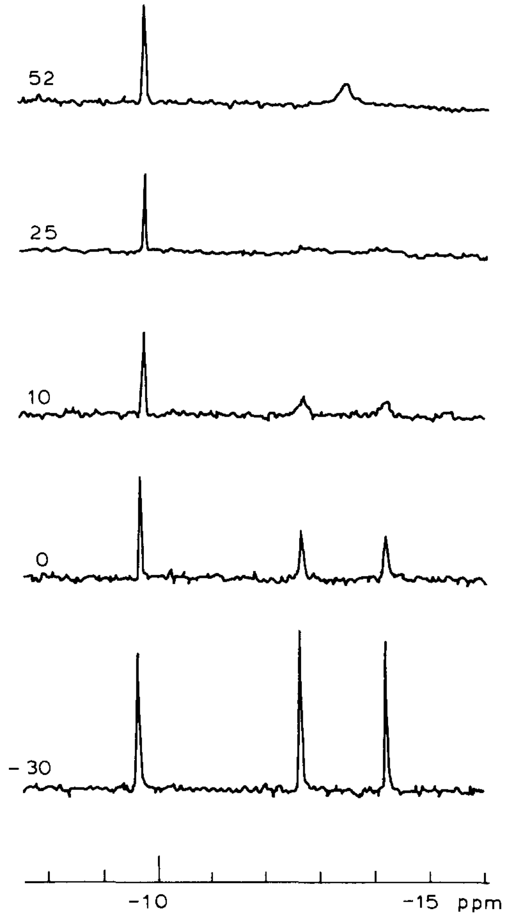
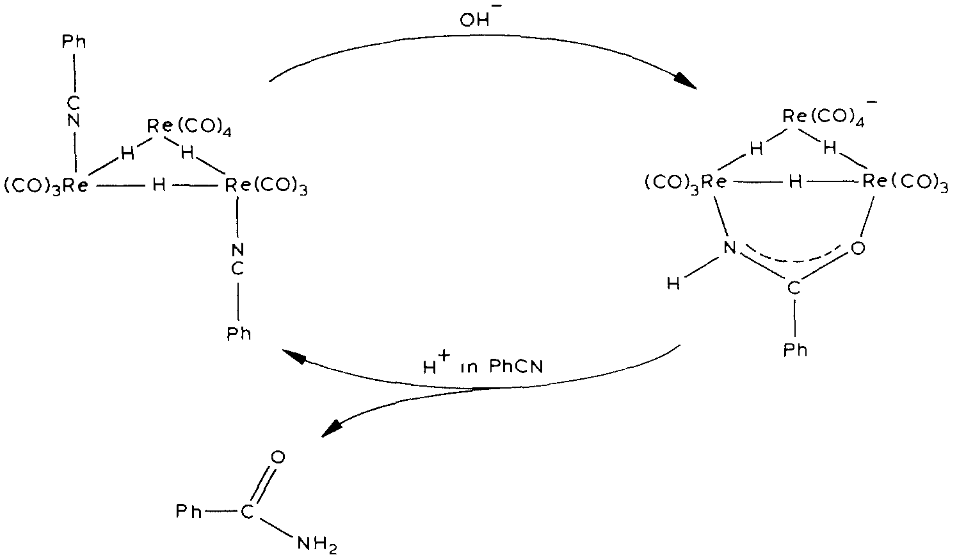


Fig. 2. ^{1}H NMR spectra of the compound, in the hydridic region, at different temperatures. The solvent was CD_2Cl_2 in the range −30/+25°C and $CDCl_3$ at 50°C. The obtainment of spectra at higher temperatures was prevented by decomposition of the sample.

The anion shows dynamic behaviour in solution, as shown by ^{1}H NMR spectra at different temperatures (Fig. 2). The low temperature spectrum, in accord with the solid state structure, exhibits three hydridic signals, that at lowest field being attributable to the hydride bridging the Re(1)—Re(2) edge by reference to the observed trend for resonances in similar $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ species ($X = O_2CR$ [4], OMe [1], Cl, Br, I [6]). On increase of temperature the two higher field signals broaden, then collapse at room temperature, and at about 50°C give rise to one broad signal at an intermediate chemical shift. The most simple rationalization of these variations is that there is fluxional behaviour of the benzamido ligand, which interchanges its donor atoms N and O on the Re(1) and Re(2) atoms, probably via η^1-intermediates bridging through either the N or O atoms ($\Delta G^{\ddagger}$ of about 14.5 kcal/mol).

Upon reaction with strong acids as CF_3SO_3H (with non-coordinating anion) in PhCN, benzamide is formed (identified by GLC) and the parent $Re_3(\mu\text{-}H)_3(CO)_{10}(NCPh)_2$ is recovered. Thus the cycle shown in Scheme 1 can be written.



SCHEME 1

The results suggest the possibility of realizing a catalytic cycle for the hydrolysis of nitriles to amides and further investigation along these lines is in progress.

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