

Preliminary communication

Insertion reactions of diazoalkanes into an Re–H–Re bridge of  
 $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$   
Synthesis and characterization of  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^1\text{-N(H)NCPH}_2)]$   
and of  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^2\text{-CH}_2\text{CO}_2\text{Et})]$

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Abstract

Diphenyldiazomethane reacts in good yields with the unsaturated hydrido-carbonyl compound  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$  (**1**) to give insertion into an Re–H–Re bridge; the derivative,  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^1\text{-N(H)NCPH}_2)]$  (**2**), has been characterised by a single crystal X-ray analysis. On the contrary, the reaction of ethyldiazoacetate with **1** occurs with loss of  $\text{N}_2$  to give  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^2\text{-CH}_2\text{CO}_2\text{Et})]$  (**3**).

Keywords: Rhenium; Carbonyl; Hydride; Diazoalkane; Crystal structure

Unsaturated hydrido-carbonyl cluster compounds are particularly attractive starting materials for the study of the reactions of hydride transfer to organic substrates containing polarised multiple bonds, because they may potentially react with electron donor ligands without CO-dissociation or metal–metal bond cleavage and display the ability of bonding to the same metallic frame both the organic molecule and the hydrogen to be transferred. In this concern we are currently investigating the reactivity of  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$  (**1**) [1,2], which contains an unsaturated  $\text{M}(\mu\text{-H})_2\text{M}$  unit, similar to that present in  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ , whose chemistry has been extensively studied (see for instance Ref. [3]). By contrast, the reactivity of **1** is rather poorly known, due to its ready fragmentation upon interaction with donor molecules [4]. Compound **1**, however, is able to transfer

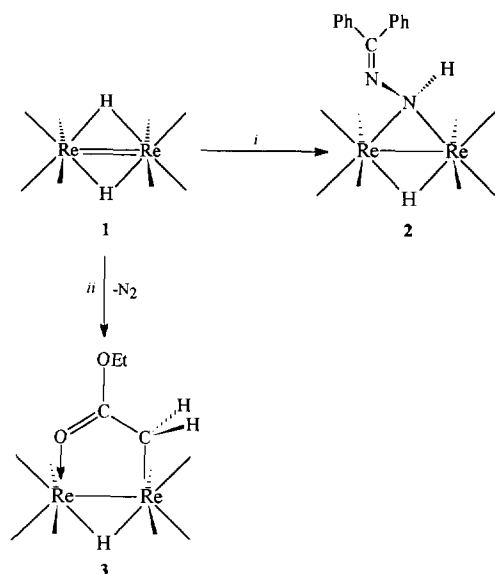
hydrogen to a  $\text{CS}_2$  molecule, in a reaction analogous to that of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  [5], affording an  $\text{H}_2\text{CS}_2^{2-}$  methanedithiolate fragment, co-ordinated to four metal atoms [6].

We have now found that **1** is able to transfer H also to diazoalkanes  $\text{N}_2\text{CRR}'$ , with reaction processes which are completely different on varying the nature of the R groups (see Scheme 1).

The reaction of **1** with an excess of diphenyldiazomethane at room temperature for about 1 h<sup>1</sup> gave the complex  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^1\text{-N(H)NCPH}_2)]$  (**2**),

<sup>1</sup> Compound **1** (0.0422 g, 0.071 mmol) has been treated with an excess of diphenyldiazomethane (0.0405 g, 0.209 mmol) in  $\text{CH}_2\text{Cl}_2$  at RT for about 1 h. Precipitation with *n*-hexane gave spectroscopically pure **2** (0.0020 g, isolated yields ca. 40%). Colourless crystals, suitable for X-ray analysis, have been grown from dichloromethane–*n*-hexane at  $-20^\circ\text{C}$ . Spectroscopic data for **2**: IR [ $\nu(\text{CO})$ ,  $\text{CH}_2\text{Cl}_2$ ] 2115w, 2092m, 2017vs, 1995s, 1954s  $\text{cm}^{-1}$ , [ $\nu(\text{NH})$ , nujol] 3222m  $\text{cm}^{-1}$ ; NMR  $\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ )  $-12.18$  [1H, s,  $\mu\text{-H}$ ]; 6.48 [1H, s,  $\text{N(H)NC(C}_6\text{H}_5)_2$ ]; 7.59–7.27 [10H, m,  $2\text{C}_6\text{H}_5$ ].

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Scheme 1. (i)  $\text{N}_2\text{CPh}_2$ ,  $\text{CH}_2\text{Cl}_2$ , RT; (ii)  $\text{N}_2\text{C(H)CO}_2\text{Et}$ ,  $\text{CH}_2\text{Cl}_2$ , RT.

shown by X-ray single crystal analysis<sup>2</sup> to contain one hydrazonate ligand, originated by 1,1-insertion [7] of the diazo group into an Re–H–Re bond. The spectroscopic data<sup>3</sup> are in line with the solid state structure, depicted in Fig. 1. As the parent compound, it contains a binuclear rhenium unit, which is bridged by one hydride and one  $[\text{N(H)NCPH}_2]^-$  ligand. Since this ligand is a three-electron donor, the derivative is saturated, as shown by the lengthening of the Re–Re interaction, of 3.018(6) Å vs. 2.876(1) Å in compound 1 [2]. The coordination around each Re atom is distorted octahedral. The nitrogen donor ligand forms a symmetric bridge, with Re–N(1) bond distances of 2.173(4) and 2.165(4) Å. Due to the hydride transfer to N(1) this atom displays a distorted  $\text{sp}^3$ -type environment [Re–N(1)–Re 88.2(2)°, the other five angles ranging from 110 to 118°] and an almost single bond length with N(2), 1.422(6) Å. The N(2)–C(9) interaction is much shorter [1.276(6) Å] and indicative of the presence of a double bond. The carbon atom C(9) is  $\text{sp}^2$ -hybridised and bears two phenyl rings mutually almost perpendicu-

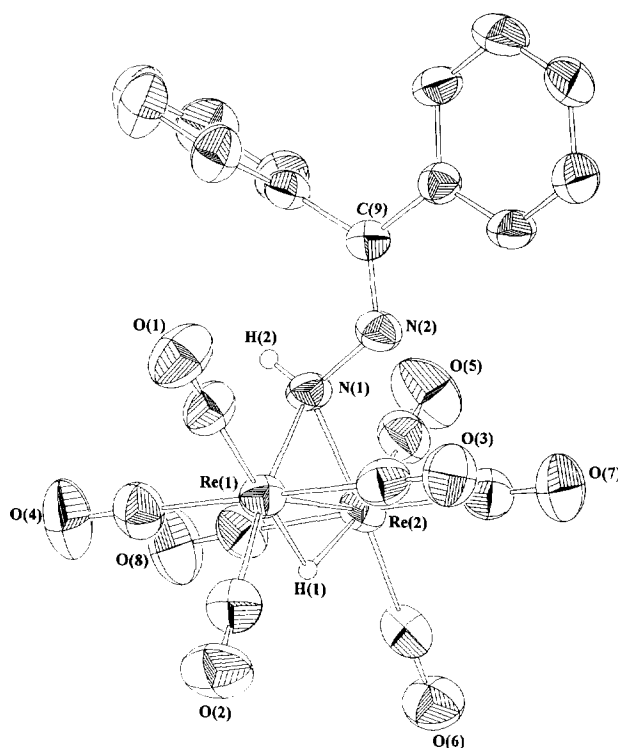


Fig. 1. X-ray structure of 2.

lar. The Re–C(carbonyl) bond lengths belong to two classes: those *trans* to other CO groups are, as expected, longer (four, mean 1.999 Å) than those *trans* to an N or H atom (four, mean 1.938 Å).

The triosmium cluster  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$  shows the same reactivity towards diphenyldiazomethane [8] and the derivative  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^1\text{-N(H)NCPH}_2)]$  exhibits bond parameters and coordination mode quite similar to those observed in 2.

Differently from that found in the previous reaction, ethyldiazoacetate reacts with 1 with  $\text{N}_2$  evolution<sup>4</sup> to give the derivative  $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu\text{-}\eta^2\text{-CH}_2\text{CO}_2\text{Et})]$  (3), in which the hydride transfer has occurred to the  $\alpha$  carbon of the diazoalkane (see Scheme 1). The nature of 3 has been established on the basis of its analytical and spectroscopic data.<sup>5</sup> Particularly diagnostic are the molecular ion in the mass spectrum at 684  $e/m$ , the

<sup>2</sup> Crystal data for 2.  $\text{C}_{21}\text{H}_{12}\text{N}_2\text{O}_8\text{Re}_2$ ,  $M = 792.7$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 9.632(2)$ ,  $b = 15.461(5)$ ,  $c = 16.139(3)$  Å,  $\beta = 103.56(2)^\circ$ ,  $U = 2336.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.254$  g cm<sup>-3</sup>, Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The data collection was performed at 293 K on an Enraf–Nonius CAD4 diffractometer, by the  $\omega$ -scan method, within the limits  $3 < \theta < 25^\circ$ . The structure was solved by direct methods (STR92) and the refinements (SHELX-93), by full-matrix least squares against  $F^2$ , gave a final agreement index  $R$  of 0.0226 for 3081 significant [ $F_o > \sigma(F_o)$ ] absorption corrected data, out of the 3872 unique collected reflections. All the hydrogen atoms were directly located in the final difference Fourier map and refined. Anisotropic thermal factors were assigned to all the non-hydrogen atoms.

<sup>3</sup> See footnote 1.

<sup>4</sup> In a typical synthesis a sample of 1 (0.0721 g, 0.120 mmol) was treated with an excess of  $\text{N}_2\text{C(H)CO}_2\text{Et}$  (0.0631 ml, 0.6 mmol) in  $\text{CH}_2\text{Cl}_2$  at RT and the reaction was monitored by IR spectroscopy up to complete disappearance of the signals of 1. Flash chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ –*n*-hexane 1:2 allowed the isolation of 3 as a yellow oil (0.0201 g, isolated yields ca. 30%). Anal. Found: C, 21.74; H, 1.37%;  $\text{C}_{12}\text{H}_8\text{O}_{10}\text{Re}_2$  requires C, 21.05; H, 1.18%. Spectroscopic data for 3: IR [ $\nu(\text{CO})$ , *n*-hexane] 2116w, 2091m, 2017vs, 1998s, 1978s, 1968s, 1962sh, [ $\nu(\text{CO}_2\text{Et})$ ] 1550m cm<sup>-1</sup>; NMR  $\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ ) –14.71 [1H, s,  $\mu\text{-H}$ ], 4.05 [2H, q,  $\text{CH}_2\text{CH}_3$ ], 1.20 [3H, t,  $\text{CH}_2\text{CH}_3$ ], 1.76 [2H, s,  $\text{CH}_2\text{CO}_2\text{Et}$ ]; e.i. mass spectrum:  $m/z$  684 ( $M^+$ ).

<sup>5</sup> See footnote 4.

low value of the  $\nu(\text{C}=\text{O})$  band of the ester carbonyl ( $1550\text{cm}^{-1}$  in the IR spectrum), indicative of a bridging  $\eta^2$ -coordination, and the  $^1\text{H}$  NMR resonance at  $\delta$  1.76 ppm, of intensity 2 with respect to the hydridic signal. Moreover, the IR and NMR data are quite similar to those observed for the corresponding osmium compound  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CH}_2\text{CO}_2\text{Et})]$  [9]. Also, this bridging ligand is a three-electron donor, so that **3**, like **2**, is a saturated derivative.

Low-temperature NMR monitoring did not show any evidence of the intermediate formation of addition derivatives, either in this case or in the previous reaction leading to **2**. The lack of detectable addition intermediates is reminiscent of the reactions of the unsaturated triangular rhenium complex  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  with two-electron donors (see Ref. [10]), and is probably attributable to the ready transformation of the ligands in the intermediate adducts.

The results reported here establish a strict parallelism between the reactivity of the unsaturated  $\text{M}(\mu\text{-H})_2\text{M}$  moieties of **1** and that of  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ , since the latter reacts with the two diazo compounds investigated here in exactly the same way as **1** does. The main difference between the two unsaturated complexes is related to the presence in the Os triangular cluster of a 'bridging'  $\text{Os}(\text{CO})_4$  unit which stabilises the compound in the addition of two-electron donors, while in **1** these reactions easily lead to decomposition, as mentioned above. A substantial stabilisation of the  $\text{Re}_2$  system in

addition reactions was indeed achieved by replacing two axial CO ligands of **1** with a bridging diphosphine [11]. However, when bridging groups are formed, as in the cases of **2**, **3** and  $[\{\text{Re}_2(\mu\text{-H})(\text{CO})_8\}_2(\mu_4\text{-S}_2\text{CH}_2)]$  [6], they are able to stabilise the  $\text{Re}_2$  moiety and the reactivity of **1** becomes identical to that of the triosmium species.

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