

Preliminary communication

REACTIONS OF THE UNSATURATED ANION $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ WITH PHOSPHINES. SYNTHESIS OF THE ANIONS $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]^-$, AND CRYSTAL STRUCTURE OF $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$

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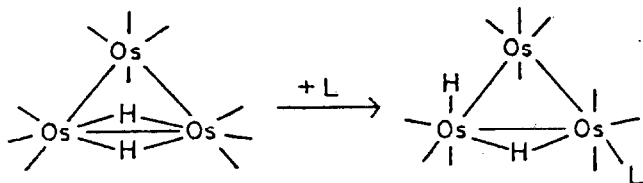
Summary

The reaction of the unsaturated cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ with tertiary phosphines at room temperature results in the substitution of two hydride ligands (eliminated as H_2) by two PR_3 ligands, leading to saturated $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]^-$ compounds. A single crystal X-ray diffraction study of the PPh_3 derivative revealed that the two phosphines occupy non-equivalent equatorial coordination sites on the triangular cluster. The rate of the reaction greatly increases with increase of the basicity of the phosphine.

Carbonyl complexes containing a $\text{M}(\mu\text{-H})_2\text{M}$ moiety [1] have two electrons less than required by the noble gas rule and their chemical behavior is thus expected to be dominated by a tendency to attain the closed-shell configuration through addition reactions. This is the case for many of them; in particular, the most widely studied member of this family, the triangular osmium cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ [2] readily adds donor species L (such as CO, phosphines, isocyanides, etc) to give saturated 1/1 adducts (see Scheme 1).

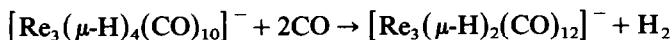
In contrast, this type of reactions has never been observed for the triangular cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (compound 1) [3], though this species is structurally and electronically (46 valence electrons) closely related to the triosmium cluster mentioned above. The rhenium anion is quite reactive, but most of its reactions involve interaction of electrophilic reagents with one of the H ligands of the $\text{Re}(\mu\text{-H})_2\text{Re}$ moiety, leading to its substitution by one X^- or two L donor groups [4].

The recently reported [5] synthesis of a series of unsaturated derivatives $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$, by substitution of a carbonyl ligand of the $\text{Re}(\text{CO})_4$ unit in compound 1 by a donor L (nitrile, phosphine, pyridine) confirms the small tendency of



SCHEME 1.

1 to undergo addition reactions. It has also been observed that compound **1** reacts with CO (under high pressure, and very slowly), again not by an addition but with substitution of two hydrides by two carbonyl ligands [3]:



We have now found that a similar reaction can be observed with phosphines. On treating the NEt_4^+ salt of compound **1** with a large excess (70 equiv.) of PPh_3 , at room temperature in tetrahydrofuran, slow evolution of H_2 identified by gas-chromatography was observed. The solution progressively darkened in color, from yellow to yellow-orange. After about 24 h, IR monitoring showed the complete disappearance of compound **1**. Addition of an excess of a n-heptane/diethyl ether mixture produced a precipitate, which was analyzed by ^1H NMR spectroscopy. The hydridic region showed two multiplets (a doublet and a doublet of doublets) whose integrals compared with those for the signals from the hydrogen of the phenyl groups and of the cation suggested the formation (in nearly quantitative yield) of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ (compound **2**), and this formulation was supported by the elemental analysis. Reactions of compound **1** with other phosphines (PPh_2Me , PPhMe_2) proceeded in the same way, as judged from the spectroscopic data (Table 1), to give the corresponding $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]^-$ anions.

In order to confirm the formulation of these products and to establish their stereochemistry many attempts were made to obtain crystals suitable for X-ray

TABLE 1

SPECTROSCOPIC DATA FOR THE ANIONS $[\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)_2]^-$

R	IR ($\nu(\text{CO})$, acetone) (cm^{-1})	NMR ($\delta(\text{ppm})$, deuteroacetone, 200 MHz)
PPh_3	2046w, 2017m, 1963sh, 1952s, 1927m, 1910sh, 1897sh, 1884ms	7.5 (m, 30H, PPh), -16.15 (d, 1H, ReH, $J(\text{PH})$ 24 Hz) -16.83 (dd, 1H, ReH, $J(\text{PH})$ 14.5 Hz, $J(\text{P}'\text{H})$ 4.5 Hz)
PMePh_2	2037w, 2014m, 1953s, 1940sh, 1925m, 1908sh, 1892m, 1887ms.	7.4 (m, 20H, PPh) 2.50 (d, 3H, PMe, $J(\text{PH})$ 7.5 Hz) 2.47 (d, 3H, PMe, $J(\text{PH})$ 7.5 Hz) -16.46 (d, 1H, ReH, $J(\text{PH})$ 24 Hz) -16.83 (dd, 1H, ReH, $J(\text{PH})$ 14.5 Hz, $J(\text{P}'\text{H})$ 2.5 Hz)
PMe_2Ph	2035w, 2011m, 1951s, 1939sh, 1921m, 1905sh, 1888sh, 1873ms.	7.4 (m, 10H, PPh) 2.14 (d, 6H, PMe, $J(\text{PH})$ 9 Hz) 2.12 (d, 6H, PMe, $J(\text{PH})$ 9 Hz) -16.74 (d, 1H, ReH, $J(\text{PH})$ 24 Hz) -16.93 (d, 1H, ReH, $J(\text{PH})$ 17 Hz)

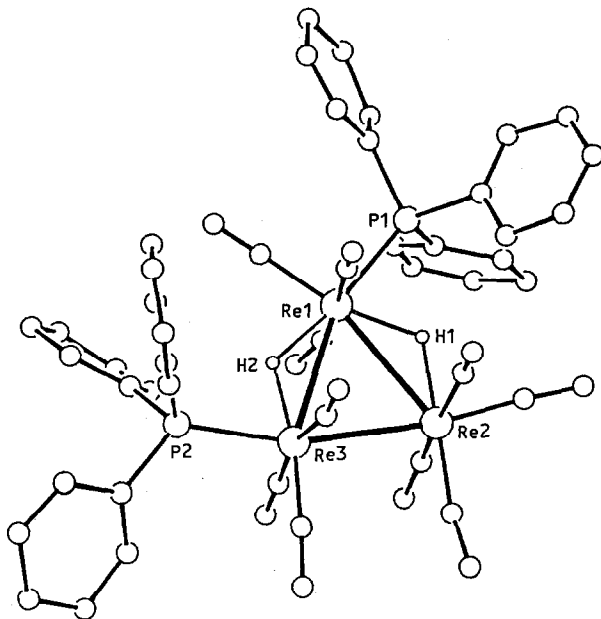


Fig. 1. A schematic view of the anion in $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ with the hydridic hydrogen atoms shown in postulated positions. Bond distances (Å) are: Re(1)–Re(2) 3.190(4), Re(1)–Re(3) 3.203(4), Re(2)–Re(3) 3.009(3), Re(1)–P(1) 2.388(17), Re(3)–P(2) 2.369(14).

investigation, but only for compound **2** was this possible; in this case needle-shaped crystals were obtained by slow diffusion of diethyl ether vapor into a concentrated methylene chloride solution at about 0°C. Though the crystals gave poor diffractions (broad reflections, limited number of significant data) a structural analysis was undertaken*, with the aim of ascertaining at least the main structural features.

A schematic view of the anion in **2** is shown in Fig. 1. It contains an isosceles Re_3 triangle bearing ten terminal carbonyls, two equatorially bonded phosphines, and two hydrides, very probably in bridging position on the two longer triangular edges. On this basis, the higher field hydridic multiplet (showing coupling with both the phosphorus atoms) is attributable to the ligand H(2). The equatorial coordination of the PPh_3 ligands is reminiscent of the situation present in $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{PPh}_3)$ [6], but differs from that assumed to be present in $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{PPh}_3)_2$, (which is assumed to involve *trans*-diaxial coordination) [4]**.

* *Crystal data.* $\text{C}_{54}\text{H}_{52}\text{NP}_2\text{O}_{10}\text{Re}_3$, $M = 1495.6$, orthorhombic, space group $Pc2_1n$ (non-standard of No. 33), with a 14.776(5), b 14.227(5), c 26.283(9) Å, $Z = 4$. The current values of R and R_w , for 1180 significant ($I > 2\sigma(I)$) independent counter data, are 0.060 and 0.063, respectively. The bond parameters involving the light atoms are subject to large uncertainties.

** This species, obtained by substitution of the labile *trans*-diaxial nitriles of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{NCMe})_2$, exhibits, in the hydridic region of its NMR spectrum, two signals, a doublet and a triplet, in 2/1 ratio. In contrast, protonation of compound **2** with $\text{CF}_3\text{SO}_3\text{H}$ gives an isomer of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{PPh}_3)_2$ containing three non equivalent hydridic ligands ($\delta - 15.67$ d, $J(\text{PH})$ 19 Hz, -16.10 d, $J(\text{PH})$ 17.5 Hz, -16.97 ppm)

The high difference in the reaction rates on varying the R groups in the PR_3 reagent is noteworthy. While the reaction with PPh_3 goes to completion in about 24 h when a large excess of the reagent is used (as described above), the reaction with PPh_2Me takes about the same time when only the stoichiometric amount of reagent is used, and that with a stoichiometric amount of PPhMe_2 is practically instantaneous. Both steric and electronic factors could be responsible for this very large kinetic effect, since in the series PPh_3 , PPh_2Me , PPhMe_2 there is a progressive decrease in bulk (cone angle 145, 136 and 122°, respectively [7]) and increase in the basicity. However, we think that the electronic factor is dominant, since the related reagent P(OPh)_3 , with intermediate cone angle (128°) but with poor basicity, did not react under similar conditions.

It is reasonable to assume that the reaction involves as first step the addition of PR_3 , to give a saturated $[\text{Re}_3\text{H}(\mu\text{-H})_3(\text{CO})_{10}(\text{PR}_3)]^-$ species, comparable with those isolated from the analogous reactions of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (see Scheme 1). However, we have not yet been able to obtain evidences for this intermediate (even on monitoring the progress of the reaction by NMR at low temperature), and we assume that as soon as it is formed it quickly loses H_2 and adds a second PR_3 molecule. On this hypothesis, the lack of observable addition reactions for compound **1** would be due to the instability of the addition products (likely in view of the presence of H ligands of opposite polarization). Work to test this hypothesis, involving various bi-electron donor reagents, is in progress.

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