

### Preliminary communication

## $^{13}\text{C}$ - $\{^{103}\text{Rh}\}$ NMR OF $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$

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### Summary

$^{13}\text{C}$ - $\{^{103}\text{Rh}\}$  NMR measurements on  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  at  $-72^\circ\text{C}$  show that the structure in solution is consistent with that found in the crystalline state.

Direct  $^{103}\text{Rh}$  NMR measurements on  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  and “ $[\text{Rh}_{12}(\text{CO})_{34}]^{2-}$ ” have recently been reported and, in both cases, only two resonances were found even at very low temperatures [1]. These observations are consistent with the recent reformulation of “ $[\text{Rh}_{12}(\text{CO})_{34}]^{2-}$ ” as  $[\text{Rh}_5(\text{CO})_{15}]^-$ , which

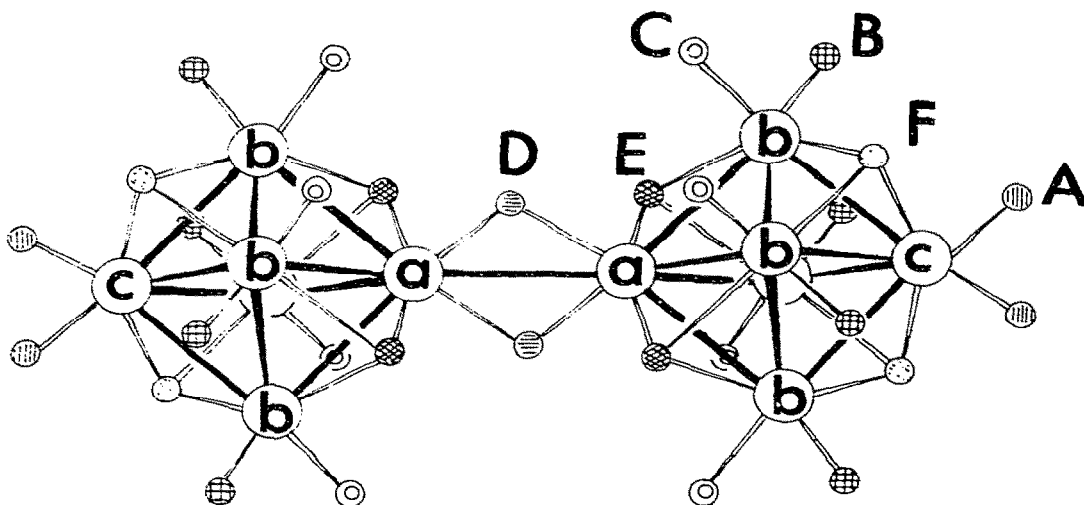


Fig. 1. X-ray structure of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  [3].

contains a trigonal bipyramidal metal skeleton, and thus gives two rhodium resonances due to the equatorial and apical metal atoms [2]. However, the puzzling observation of only two rhodium resonances for  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  is inconsistent with both the solid state structure [3] (see Fig. 1) and previous  $^{13}\text{C}$  NMR measurements on this cluster in solution [4]; this prompts us to report our  $^{103}\text{Rh}$  NMR data on  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  which was obtained via  $^{13}\text{C}\{-^{103}\text{Rh}\}$  NMR measurements using the method described previously [5,6].

The undecoupled  $^{13}\text{C}$  NMR spectrum of  $\text{PPN}_2[\text{Rh}_{12}(\text{CO})_{30}]$  (PPN = bis(tri-phenylphosphino)iminium; ca. 30%  $^{13}\text{CO}$ ) in acetone- $d_6$  at  $-72^\circ\text{C}$  is shown in Fig. 2(d) with chemical shifts and spin-spin coupling constants essentially the same as those reported previously [4]. Irradiation at 3.160500 MHz collapses the triplet due to the edge-bridging carbonyls, D, leaving the terminal carbonyls unchanged and thus allows this resonance to be assigned to  $\text{Rh}_a$  (Fig. 2(a)). Similarly, the resonance at 3.158950 MHz can be assigned to  $\text{Rh}_b$

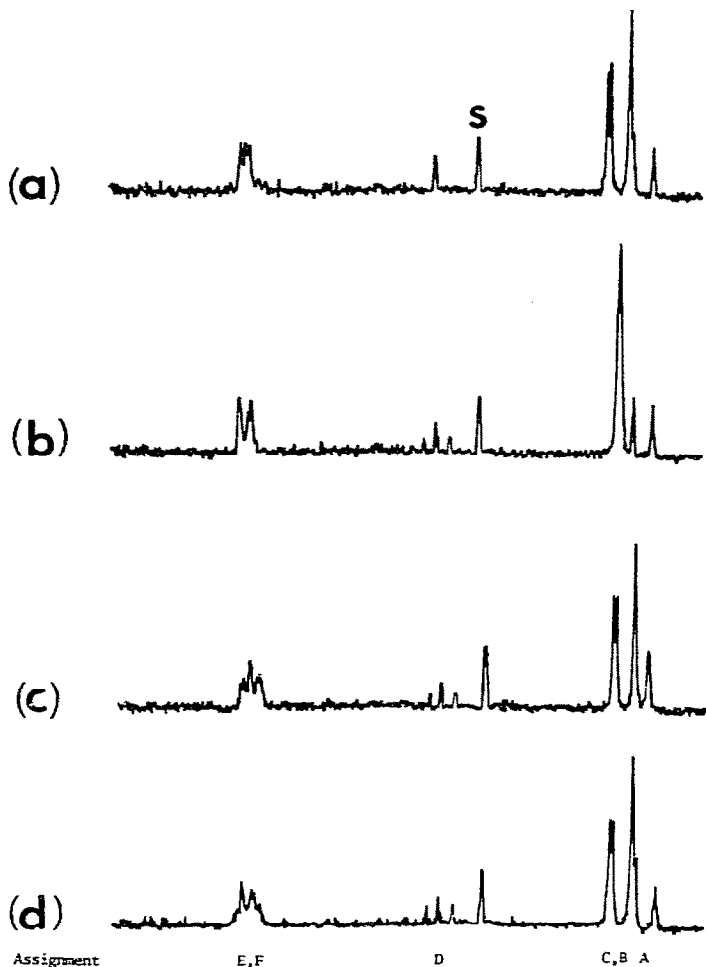


Fig. 2.  $^{13}\text{C}\{-^{103}\text{Rh}\}$  NMR spectra of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  at  $-72^\circ\text{C}$ . Decoupling at: (a) 3.160500 MHz;  $\delta(\text{Rh}_a) = +168$  ppm, (b) 3.158950 MHz;  $\delta(\text{Rh}_b) = -322$  ppm, (c) 3.158200 MHz;  $\delta(\text{Rh}_c) = -560$  ppm, (d) undecoupled (S = solvent, acetone- $d_6$ ).

since both doublets due to the terminal carbonyls, B and C, collapse to singlets, which are almost coincident, while at the same time the face-bridging resonances due to E and F are considerably simplified (Fig. 2(b)). Finally, irradiation at 3.158200 MHz causes the doublet due to the terminal carbonyls, A, to collapse to a singlet and thus allows this frequency to be assigned to Rh<sub>c</sub> (Fig. 2(c)). Thus, there are clearly three rhodium resonances,  $\delta(\text{Rh}_a) = +168$ ,  $\delta(\text{Rh}_b) = -322$  and  $\delta(\text{Rh}_c) = -560$  ppm\* which is consistent with both the solid state structure [3] and earlier <sup>13</sup>C NMR measurements [4]. It remains unclear why direct <sup>103</sup>Rh measurements apparently only give two resonances;

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\*3.16 MHz = 0 ppm at a magnetic field such that the protons in TMS resonate at exactly 100 MHz; high frequency (low field) shifts are positive.