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A Comment on the Structures of some Bridged Carboxylato, Triazenido and Methylenediphosphine Complexes: the Reformulation of '$Ru_3H_6(Ph_2PCH_2PPh_2)_6$'

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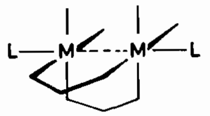
Bidentate V- or Y-form ligands, prominent examples of which include carboxylate (O_2CR^-) anions, triazenide ($RN{\underline{\cdots}}N{\underline{\cdots}}NR^-$) anions and methylene diphosphines ($R_2PCH_2PR_2$) (R = alkyl or aryl) can coordinate in chelate or bridging mode. When bound in the latter manner they generate a range of well-established binuclear structures including (**I–IV**) in which the axial ligands, L, are optional and the maximum coordination number exerted by the metal centre, M, is five (excluding the M–M interactions) [1, 2]. In each case the close approach of the two metal atoms, dictated by the geometry of the bridging groups, precludes the coordination of a sixth donor atom at either metal centre. However, several authors [3–5] have recently postulated structures involving carboxylate, triazenide or methylene diphosphine bridges between *six coordinate* octahedral metal centres (**V**) and (**VI**) which, though plausible at first sight, can be seen on closer examination to involve unacceptable steric interactions within the bridge system. Structure (**V**) results in serious steric conflict between the *internal* ligands X while structure (**VI**), which imposes unrealistic bond angles at the donor atoms, is prevented from folding (see **II**) to relieve steric strain by the presence of the axial ligands Y. Given that alternative, less strained arrangements are possible, structures (**V**) and (**VI**) are rather improbable even for methylene diphosphine complexes in which the saturated nature of the $P{-}CH_2{-}P$ linkage offers a greater degree of stereochemical freedom, and it is significant that no examples of either have been established by X-ray diffraction methods.


I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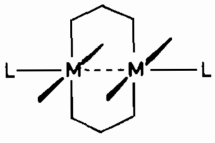
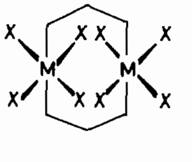

III


IV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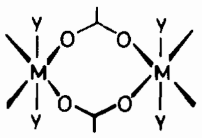
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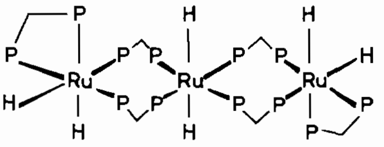
VII

A recently postulated example, the ruthenium poly hydrido species '$Ru_3H_6(Ph_2PCH_2PPh_2)_6$', formulated, apparently without the benefit of MWt data, as a trinuclear complex (**VII**) with octahedral ruthenium(II) centres linked by $Ph_2PCH_2PPh_2$ bridges, [5] has now been reinvestigated and found to be a mixture of *cis*- and *trans*-$RuH_2(Ph_2PCH_2PPh_2)_2$. The product was originally prepared by treatment of $Ru(C_8H_{12})(C_8H_8)$ with $Ph_2PCH_2PPh_2$ under hydrogen and isolated as yellow crystals. The chief evidence offered in support of the trinuclear structure was provided by the ^1H and $^{31}P\{^1H\}$ NMR spectra [^1H, δ −4.7 ppm (quintet, J_{PH} 19.7 Hz), δ −7.4 ppm (doublet of quartets, J_{PH} 72.8 and 18.7 Hz) signal intensity ratio 1:2; $^{31}P\{^1H\}$, δ 12.9 and 0.3 ppm (triplets, J_{PP} 30 Hz) and 8.6 ppm (singlet) signal ratio 1:1:1] which remained constant throughout recrystallisation. However, these spectra do not show the number of inter- and intra-ligand couplings expected for a single complex containing phosphorus nuclei in six different chemical environments and hydride ligands in three non-identical sites.

We now find that borohydride 'reduction' of the ruthenium carboxylates *trans*-$Ru(O_2CR)_2(Ph_2PCH_2PPh_2)_2$ in benzene/ethanol affords a product with physical properties similar to those reported for '$Ru_3H_6(Ph_2PCH_2PPh_2)_6$' and essentially identical NMR spectra. However, we observe one important difference, in our hands the intensity ratios in the ^1H and $^{31}P\{^1H\}$ NMR spectra change substantially

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from sample to sample thus clearly establishing that we have a binary mixture of variable composition – under favourable conditions pure isomers can be isolated. The ^1H, $^{31}P\{^1H\}$ and $^{31}P\{organic\ ^1H\}$ NMR spectra are all consistent with the conclusion that the product is in fact a mixture of *cis*- and *trans*-$RuH_2(Ph_2PCH_2PPh_2)_2$, a possibility which was considered by the earlier authors but discarded in favour of the trinuclear formulation [5]. The failure of the original authors to achieve any detectable separation of the two isomers on recrystallisation is perhaps not surprising since the small size of the hydride ligands is likely to result in highly distorted structures, dominated by the bulky $Ph_2PCH_2PPh_2$ ligands, in which structural differences between *cis* and *trans* isomers are minimised [6].

References

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