Inorganica Chimica Acta, 54 (1981) L265–L266
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New Binuclear Bis(diphenylphosphino)methane Complexes of Rhodium(I) incorporating 2-Methylallyl Ligands

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Received July 1, 1981

The use of 1,1-bis(diphenylphosphino)methane (dppm) as a bridging ligand to generate binuclear transition metal complexes is well known [1–4]. With one exception [3], bimetallic complexes in either square-planar or A-frame geometries with *two* bridging dppm ligands have *trans* [4] disposed phosphine donors, a consequence of using monodentate donor ligands (*cf.* CO, RNC, Cl, H, and SO_2) in the remaining coordination sites. As part of a general study on the catalytic potential of allylrhodium(I) diphosphine complexes, we report here the synthesis and characterization of the η^3-2-methylallylrhodium(I) dppm complex; this new derivative is mononuclear in the solid state but in solution is binuclear with *two* bridging dppm ligands constrained in a *cis* disposition at each rhodium center.

The reaction of dppm with 1,5-cyclooctadiene-2-methylallylrhodium(I), $[\eta^3\text{-}(2\text{-Me-}C_3H_4)Rh(COD)]$ [5], *1*, results in the smooth displacement of the COD ligand [6] to generate a deep red-orange solutions from which yellow or orange air-sensitive crystals of the formula $[\eta^3\text{-}(2\text{-Me-}C_3H_4)Rhdppm]\cdot 0.5CH_2Cl_2$ (*2*) can be isolated after recrystallization (CH_2Cl_2/hexane). The mass spectrum of *2* contains a peak at m/e 542 due to the unsolvated, *mononuclear* parent ion; no peaks above m/e 542 are observable. Dissolution of the yellow–orange crystals of *2* in aromatic solvents or dichloromethane regenerates the deep red-orange solutions which exhibit ambient temperature $^{31}P\{^1H\}$ and ^1H NMR spectra consistent with the isomeric binuclear complexes *3a*, *3b*, and *3c* (Fig. 1). The $^{31}P\{^1H\}$ spectrum consists of a complicated, but symmetrical pattern which can be analyzed as an AA′A″A‴XX′ spin system. Consideration of the possible isomers of this binuclear structure indicates that only *3a* or *3c* can accommodate this analysis; *3b* would be a more complicated AA′BB′-XY spin system. The rhodium-phosphorus coupling constant, $^1J_{Rh-P}$, is 200 Hz typical of other allylrhodium(I) phosphine complexes [5], the small two bond phosphorus–phosphorus coupling constant ($^2J_{P-Rh-P}$) of 22.7 Hz is indicative of *cis* disposed phosphorus donors.

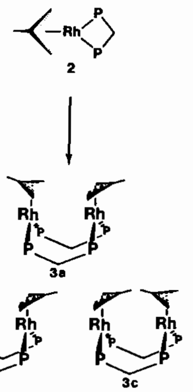

Fig. 1. Proposed dimerization of mononuclear *2* to the isomeric binuclear derivatives *3a, 3b,* and *3c* by dissolution in organic solvents (phenyl substituents on phosphorus donors omitted for clarity).

The ^1H NMR spectrum (Fig. 2) indicates the presence of a major isomer and two minor isomers in the approximate percentage ratio of 85:10:5*; we assign structure *3a* to the major isomer (P–CH_2–P, 3.63 (br, s); syn-*H*, 2.79 (s); anti-*H*, 2.49 (br, s); 2-CH_3, 1.44 (d, $^3J_{Rh}$ = 2.4 Hz)) as it engenders a minimum of steric repulsions between adjacent 2-methylallyl ligands analogous to that previously reported for the related allylpalladium carboxylate dimers [7]. That *3b* and *3c* are the corresponding structures of the minor isomers is tentatively inferred only from the ^1H NMR spectrum which indicates the presence of two minor products, both of which contain 2-methylallyl groups bonded to rhodium (Fig. 2 inset: two methyl doublets at 1.95 and 1.90 ppm with $^3J_{Rh}$ = 1.9 and 2.4 Hz respectively). The sharp resonance at 3.09 ppm (Fig. 2) is assigned to the syn protons of the more abundant minor isomer since it integrates in the ratio 2:3 *versus* the doublet at 1.95 ppm; we believe the remaining resonances for the minor isomers are obscured by those of the major isomer. It is tempting to assign structure *3b* to the more abundant minor isomer and structure *3c* to the least abundant isomer, again by virtue of the different steric interactions of adjacent 2-methylallyl groups; however, the inherent symmetry of structure *3b* requires two different allyl environments [7], which could theoretically give

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*Based solely on integration without regard to the identity of the isomers.

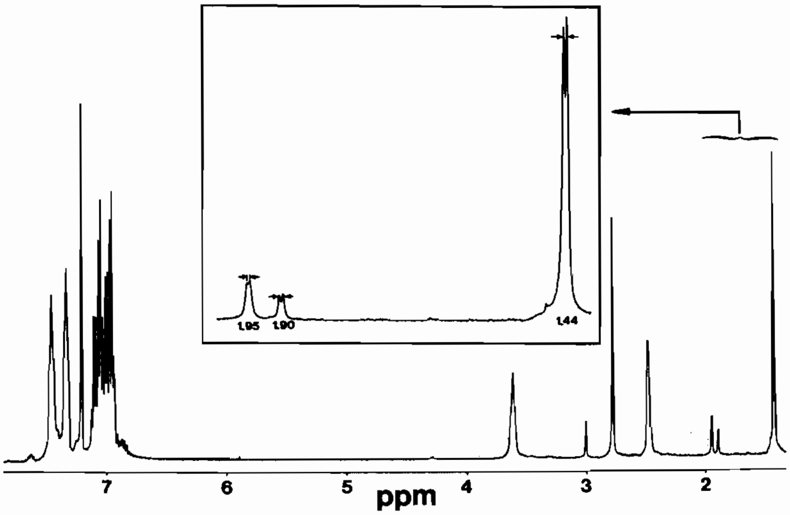

Fig. 2. 400 MHz ^{1}H NMR spectrum of *2* dissolved in d_6-benzene. Expanded portion shows the methyl doublets of the major and minor isomers.

rise to six resonances, three for each allyl ligand. The fact that so few resonances are observed makes unambiguous assignment of the isomers impossible at this point.

We are at present investigating both the dynamic solution behaviour and the reactivity of this and related complexes. Preliminary spin saturation transfer experiments indicate that at ambient temperatures the major isomer is in slow equilibrium with the more abundant minor isomer but not measurably with the least abundant isomer.

Acknowledgements

Support by the Natural Sciences and Engineering Research Council of Canada, by Research Corporation and by the Department of Chemistry is gratefully acknowledged. The generous loan of hydrated rhodium chloride from Johnson Matthey is also appreciated.

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