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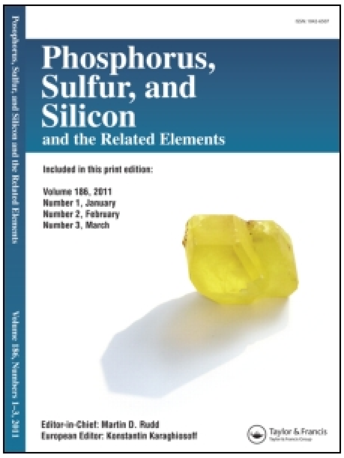

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The Coordination Chemistry of Two Chelating Diphosphines

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THE COORDINATION CHEMISTRY OF TWO CHELATING DIPHOSPHINES

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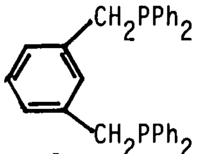
Abstract The coordination chemistry of the ligands 1,2- and 1,3-$(Ph_2CH_2)_2C_6H_3$, 1 and 2, with Ni(II), Pd(II), Pt(II), Rh(I), Cu(I) and Ag(I) is described.

The coordination chemistry of chelating diphosphines is much influenced by ring-size and ring-conformation.[1] It has also been shown that seven-membered chelate rings can be useful in inducing selective reaction.[1] Two chelating diphosphines, 1 and 2, which appear to have been little investigated are shown below. Some preliminary studies of their coordinating properties are reported below.[2]



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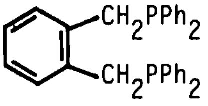

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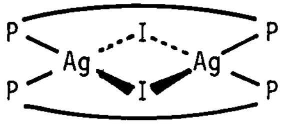

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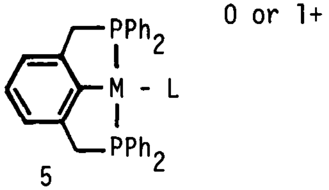
The *m*-substituted ligand, 1, shows a pronounced tendency to form polynuclear complexes. While the state of aggregation of those of the type $[MX_2(1)]$, 3, (M = Ni, Pd and Pt; X = halide) could not be determined, the complexes of the composition $\{MX(1)\}$, (M = Cu(I) and Ag(I); X = halide) are likely to be dinuclear as found by X-ray diffraction of $[Ag_2I_2(1)]$, 4,: here the two tetrahedrally coordinated silver ions are bridged both by iodide anions and by the chelating phosphines.

Complexes 3 undergo cyclometallation rections with great ease to give conpounds of type 5.[3]



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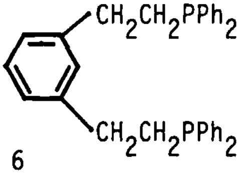
M = Ni(II), Pd(II) and Pt(II)

L = *anionic or uncharged* ligand

X-Ray crystallographic studies of these complexes show that the chelate rings are strained and that the P-M-P angles are in the range 161-165°.[4]

It is found that the ease with which cyclometallation occurs is related to the ability of ligand 1 to react with [MX$_2$L$_2$] used as starting material forming an intermediate in which 1 coordinates to M spanning *trans*-positions so as to place the central C-H bond above the metal centre. Thus complexes of ligand 6 such as [PdCl$_2$(6)], 7, in which there is a larger chelate ring, do not undergo cyclometallation. [2]

It was also found that complexes of ligands 8 (R = Me and Et) such as [PtCl$_2$(8)] easily cyclometallate giving complexes analogous to 4.[2] Thus, it appears that bulky phosphine substituents are not required to induce cyclometallation as previously postulated.[5]



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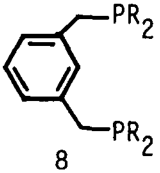

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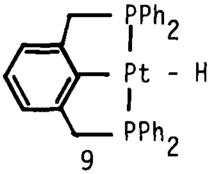
The stable hydrido-complex 9 can be easily obtained by reacting the corresponding chloro-complex with BH$_4^-$.[3] Complex 9 undergoes a normal insertion reaction with CH$_2$=CHCO$_2$Me giving exclusively the branched alkyl derivative "Pt-CH(CH$_3$)CO$_2$Me".[2] However, 9 reacts with C$_2$H$_4$ giving the hydrido-bridged binuclear complex, 10.[2,6]



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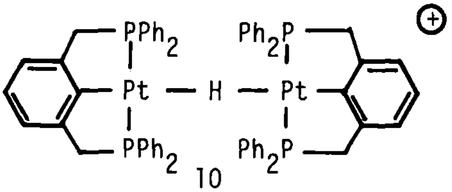

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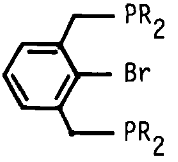
The corresponding palladium complex has also been obtained. The latter is the first reported complex containing the Pd-H-Pd unit which is very stable as it is not split by ligands such as CO or alkenes.[6]

Other ligands related to 1, i.e., those of type 10 (M = Me and Et) and 11 have been prepared.[2] The former, 10, allows the



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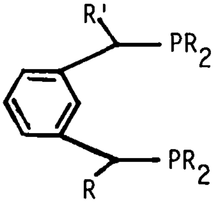
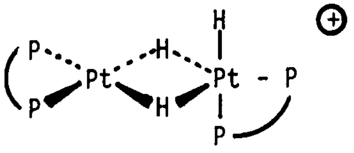


11

preparation of cyclometallated complexes from oxidative addition reactions,[2] while ligands of the latter type, 11, should allow the preparation of chiral complexes analogous to 5.

The coordination chemistry of ligand 2 differs significantly from that of ligand 1 in that the latter forms mononuclear complexes with Ni(II), Pd(II) and Pt(II) of the type [MX$_2$(2)], 12, containing seven-membered chelate rings.[2] The presence of this chelate ring in the case of platinum leads to the easy formation of platinum(0) three-coordinate complexes, e.g., [PtCl$_2$(2)], C_2H_4 and $NaBH_4$ give [Pt(C_2H_4)(2)], 13. This complex reacts with H_2 in the presence of CH_3SO_3H giving [PtH$_2$(2)], 14, and a second complex, [(2)Pt(μ-H)$_2$PtH(2)]$^+$, 15, which can be more easily obtained by reacting [PtBr$_2$(2)] with H_2 and $NaBH_4$.[2]



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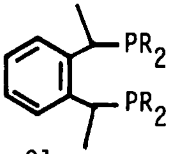

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Ligand 2 reacts with $[Rh(COD)_2]BF_4$, 16, (COD = 1,5-*cyclo*-octadiene) to give complexes which differ depending on the solvent used. Thus in CH_2Cl_2 one obtains $[Rh(COD)(2)]^+$, 17, while in acetone one obtains $[Rh(acetone)_2(2)]^+$, 18. When 2 and 16 are reacted in the ratio 2:1 the complex $[Rh(2)_2]^+$, 19, is obtained.[3] The latter reacts with H_2 to give *cis*-$[RhH_2(2)_2]^+$, 20.[2]

Finally, ligand 2 reacts easily with copper(I) and silver(I) halides to give complexes of composition {MX(2)}.[2] These are binuclear but it is as yet unknown whether the diphosphine is present as a chelating or bridging ligand.

In conclusion, easily synthesized ligands such as 1 and 2 have a rich coordination chemistry which, in all likelyhood, can be extended to ligands of types 11 and 21 which are chiral and suitable for a study of asymmetric induction.

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