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Dinuclear Palladium Complexes of 2-diphenylphosphinopyridine

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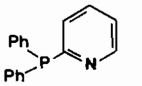
We have recently described the utility of 2-diphenylphosphinopyridine, 1, (Ph_2Ppy) in the stepwise construction of binuclear metal complexes. Now we report on the preparation of the Pd(I) dimer, $Pd_2(Ph_2Ppy)_2Cl_2$, using this ligand and compare the reactivity of this dimer with that of $Pd_2(dpm)_2Cl_2$ (dpm = $PPh_2CH_2PPh_2$). The latter complex has been shown to readily form molecular A frames by the insertion of a number of small molecules, including carbon monoxide, sulfur dioxide and methyl isocyanide into the Pd–Pd bond [3–6].



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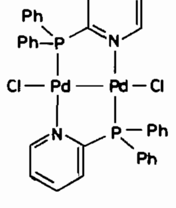
The reaction chemistry to be described is summarized in Fig. 1. Treatment of $(PhCN)_2PdCl_2$ with two moles of 1 in dichloromethane solution, followed by precipitation with ethyl ether yields the yellow complex $Pd(Ph_2Ppy)_2Cl_2$. In solution this compound is a non-electrolyte. Its $^{31}P\{^1H\}$-NMR spectrum in CD_2Cl_2 consists of two resonances at 23.79 and 29.29 ppm with relative intensities 1:1.9 respectively. Thus in solution it exists as a mixture of *cis* and *trans* isomers. The pyridine nitrogens are presumed to be uncoordinated. Reaction of $Pd(Ph_2Ppy)_2Cl_2$ with the zero-valent palladium complex, $Pd_2(dba)_3 \cdot CHCl_3$, (dba = dibenzylideneacetone) [7] at 25 °C in dichloromethane produces a red solution from which deep red crystals of $Pd_2(Ph_2Ppy)_2Cl_2$ may be obtained by the slow addition of ethyl ether. The $^{31}P\{^1H\}$ nmr spectrum of this complex consists of a single line at 4.47 ppm. In dichloromethane, it is a non-electrolyte. While these data are consistent with either structure 2A or 2B for this compound, structural data on other binuclear complexes of 1 [1, 2] indicate that the head-to-tail arrangement of phosphinopyridine ligands is more likely. Moreover the mixed palladium/platinum dimer $PdPt(Ph_2Ppy)_2Cl_2$ possess the head-to-tail orientation of phosphinopyridine ligands (*vide infra*).



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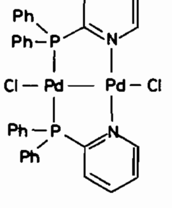

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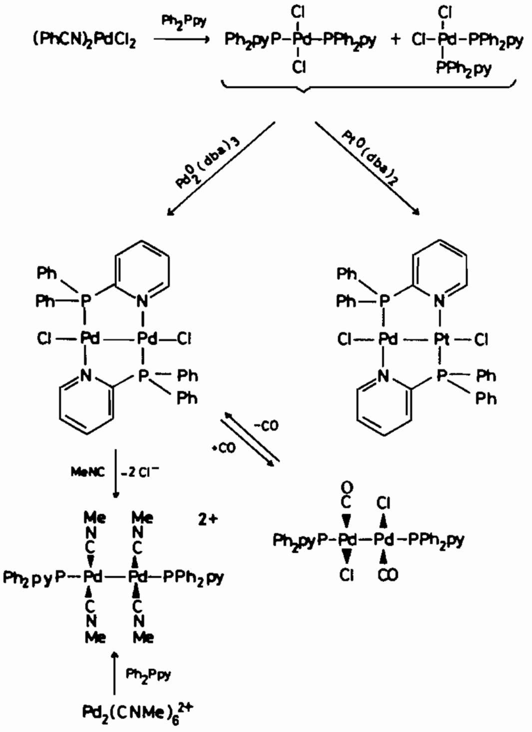

Fig. 1. Reaction chemistry of palladium complexes.

The Pd–Pd bond in $Pd_2(Ph_2Ppy)_2Cl_2$ lacks the reactivity of the Pd–Pd bond in $Pd_2(dpm)_2Cl_2$. Exposure of a dichloromethane solution of $Pd_2(Ph_2Ppy)_2Cl_2$ to one atmosphere of carbon monoxide results in the addition of terminal carbonyl groups as indicated by the growth of new absorption bands at 2019 and 1994 cm^{-1}. No new bands appear in the region between 1994 and 1500 cm^{-1}, so no bridging carbonyl group is present. The addition of carbon monoxide is reversible. Heating a dichloromethane solution of the carbonylated product to reflux for 1 min. results in regeneration of $Pd_2(Ph_2Ppy)_2Cl_2$ which is fully capable of being recarbonylated. Attempts to isolate the carbonylated product from solution results only in the isolation of $Pd_2(Ph_2Ppy)_2Cl_2$. Since carbonylation does not cause any increase in the negligible electrical conductivity of a dichloromethane solution of $Pd_2(Ph_2Ppy)_2Cl_2$,

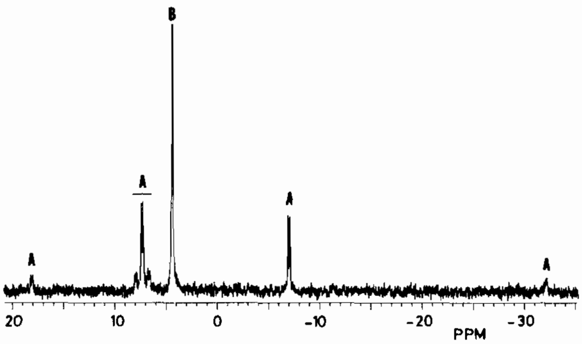

Fig. 2. $^{31}P\{^1H\}$-NMR spectrum of a dichloromethane solution of A, $PtPd(Ph_2Ppy)_2Cl_2$ and B, $Pd_2(Ph_2Ppy)_2Cl_2$, resulting from the reaction of $Pd(Ph_2Ppy)_2Cl_2$ with $Pt^{\circ}(dba)_2$.

we believe that the uptake of carbon monoxide is accompanied by the displacement of the pyridine nitrogens from palladium. While the spectroscopic data do not identify the geometry of the product, it is likely for steric reasons that the phosphine ligands occupy the axial coordination sites in $Pd_2(PPh_2py)_2(CO)_2Cl_2$. $Pd_2(Ph_2Ppy)_2Cl_2$ may be recovered unchanged after saturating a dichloromethane solution of this complex with sulfur dioxide at 25 °C. $Pd_2(Ph_2Ppy)_2Cl_2$ reacts with methyl isocyanide. But, again, there is no evidence of insertion of the isocyanide into the Pd–Pd bond. The reaction yields the cation $Pd_2(CNCH_3)_4(PPh_2py)_2^{2+}$ which has been isolated as the hexafluorophosphate salt. The yellow crystalline solid has only terminal isocyanide ligands as shown by the infrared absorption due to ν(CN) at 2223 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of the complex shows a single line at 11.82 ppm due to the cation as well as the anticipated hexafluorophosphate septet. The ^1H-NMR spectrum shows a single methyl resonance at 3.23 ppm. This complex may also be obtained through the reaction of 1 with $[Pd_2(CNCH_3)_6][PF_6]_2$. We have previously reported that triphenylphosphine substitution in $M_2(CNCH_3)_6^{2+}$ (M = Pd or Pt) occurs exclusively at the axial position [8]. Thus the spectral properties and similarily to the triphenylphosphine complexes suggests that $[Pd_2(CNCH_3)_4(Ph_2Ppy)_2]^{2+}$ contains Ph_2Ppy ligands bound in the axial positions with the pyridine nitrogen uncoordinated.

The redox condensation used to prepare $Pd_2(Ph_2Ppy)_2Cl_2$ and other palladium(I) and platinum(I) [4, 9] complexes may be modified to form the mixed metal complex $PdPt(Ph_2Ppy)_2Cl_2$. Treatment of $Pd(Ph_2Ppy)_2Cl_2$ with the zero valent platinum complex, $Pt(dba)_2$, produces both $Pd_2(Ph_2Ppy)_2Cl_2$ and $PdPt(Ph_2Ppy)_2Cl_2$. The latter complex may be readily identified from the $^{31}P\{^1H\}$-NMR spectrum shown in Fig. 2. Two chemically distinct phosphorus atoms are evident from the spectrum. They exhibit a coupling constant of 14.3 Hz, a value which is entirely consistent with previously observed P–P coupling in similar molecules [1, 2]. The platinum bound phosphorus at –6.96 ppm exhibits satalites due to coupling to the 34% natural abundance of ^{195}Pt with $^1J(P, Pt) = 2040$ Hz. The palladium bound phosphorus at 7.41 ppm exhibits much smaller coupling to ^{195}Pt, $^2J(Pt, P) = 51.76$ Hz.

We attribute the unreactivity of the metal–metal bond in these complexes to two features. One is the ease with which the pyridine nitrogen is displaced from the palladium coordination plane. The other is the limited flexibility of the ligand 1. This ligand lacks the articulation available to dpm which can allow the metal–metal distance in its bridged complexes to vary from 2.2 to 3.5 Å [6, 10]. 2-Diphenylphosphinopyridine, because of the planar nature of the pyridine ring and the short N–C distance, does not appear able to span the long end of metal–metal separations spaned by dpm. Consequently the Pd–Pd bond in $Pd_2(Ph_2Ppy)_2Cl_2$ is not able to open up to form a A-frame structure.

Acknowledgements

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