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Head-to-Head and Head-to-Tail Isomers of Compounds with Bridging (Diphenylarsino)(diphenylphosphino)methane Ligands

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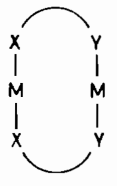
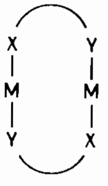
Binuclear complexes formed with two unsymmetrical bidentate ligands can exist as head-to-head (**HH**) *1* or head-to-tail (**HT**) *2* isomers. The isolation of several pairs of such isomers has been reported for complexes with bridging 2-(diphenylphosphino)pyridine (Ph_2Ppy) [1–3]. (Diphenylarsino)(diphenylphosphino)methane (dapm) [4], which should form complexes similar to the extensive group [5] formed from bis-(diphenylphosphino)methane (dpm), also has the potential for forming **HH** and **HT** isomers. The similarity of phosphorus and arsenic as donors makes it difficult to predict which isomer will be favored. It was somewhat surprising to read a recent report [6] that a group of dinuclear dapm complexes of rhodium were formed exclusively as the **HT** isomers. Here, we report results which establish the existence of both **HH** and **HT** isomers for dimeric dapm-bridged complexes.



1 HH



2 HT

cis-$Pt(dapm)_2Cl_2$ (from 1,5-cyclooctadiene)$PtCl_2$ and two moles of dapm in dichloromethane followed by precipitation with ether, $^{31}P\{^1H\}$ NMR: δ, 6.1 ppm; $^1J(P,Pt)$, 3675 Hz), with its uncoordinated arsenic atoms, reacts with Pt(dibenzylideneacetone)$_2$ [7] in boiling dichloromethane solution over a 24-hour period to yield tan crystals of $Pt_2(\mu\text{-dapm})_2Cl_2$ (30% yield) after precipitation with ethyl ether. The $^{31}P\{^1H\}$ NMR spectrum of the product is shown in Fig. 1. The presence of **HH** and **HT** isomers is clear. Peaks labeled T arise from the **HT** isomer. $\mathbf{T_a}$ is the resonance of the unlabeled (Pt) isotopomer, and $\mathbf{T_b}$ indicates the resonances for the isotopomer with one ^{195}Pt atom (33.4% natural abundance, S = ½). Peaks labeled H arise from the **HH** isomer. H_a is the resonance of the unlabeled isotopomer, H_b indicates the resonances of the singly ^{195}Pt labeled isotopomer *3* and H_b' designates the resonances of the other singly labeled isotopomer *4*.

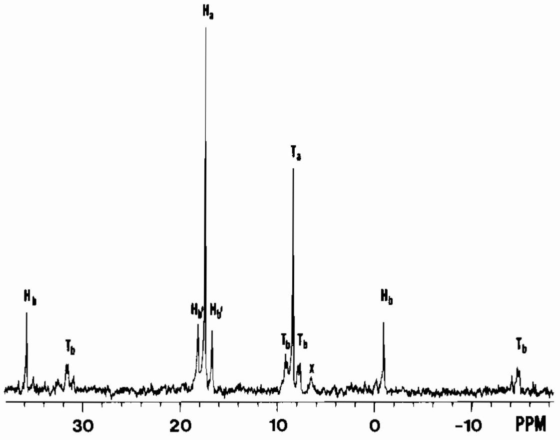
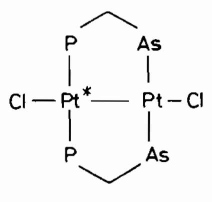


Fig. 1. The 81 MHz $^{31}P\{^1H\}$ NMR spectrum of a mixture of HH and HT isomers of $Pt_2(\mu\text{-dapm})_2Cl_2$ in chloroform-*d* solution. Resonance assignments are given in the text, X indicates an impurity. Resonances of the doubly ^{195}Pt-labeled isotopomers which occur in low natural abundance are not labeled.



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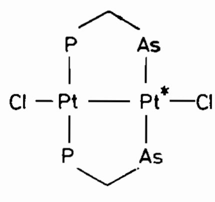

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The presence of P–P coupling in the spectrum of the **HT** isomer, and its absence in the spectrum of the **HH** isomer establishes the structural identification and is fully in accord with detailed studies on the isomers of $Pt_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ [3].

We find evidence also for the formation of **HH** and **HT** isomers of binuclear rhodium (I) compounds. The compounds $Rh_2(\mu\text{-dapm})_2(\mu\text{-S})(CO)_2$ [8] $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$ [9], $[Rh_2(\mu\text{-dapm})_2(\mu\text{-Cl})(CO)_2]$-$[Rh(CO)_2Cl_2]$ [10], and $[Rh_2(\mu\text{-dapm})_2(CNC_6H_{11})_4]$-$[BPh_4]_2$ [11] have been prepared using procedures (indicated by the references) analogous to those developed for their dpm analogs. In each case the $^{31}P\{^1H\}$ NMR spectra consist of two doublets. The

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TABLE I. $^{31}P\{^1H\}$ NMR Spectral Parameters for Binuclear Complexes.

Compound	δ, ppm[a] $^1J(M,P)$, Hz HH Isomer		δ, ppm $^1J(M,P)$, Hz HT Isomer	
$Pt_2(\mu\text{-dapm})_2Cl_2$	17.2	2977[b]	8.1	3754[c]
$Rh_2(\mu\text{-dapm})_2(\mu\text{-S})(CO)_2$	18.5	130	23.0	154
$Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$	23.3	127	28.1	149
$[Rh_2(\mu\text{-dapm})_2(\mu\text{-Cl})(CO)_2][Rh(CO)_2Cl_2]$	20.7	114	24.8	134
$[Rh_2(\mu\text{-dapm})_2(CNC_6H_{11})_4][BPh_4]_2$	23.4	122	26.6	143
$Rh(CO)Cl(PPh_3)_2$	29.6	127		
$Rh(CO)Cl(AsPh_3)(PPh_3)$			32.1	150

[a] Recorded in dichloromethane solution at 25° and 81 MHz. [b] $^2J(Pt,P)$ = 118 Hz. [c] $^2J(Pt,P)$ = 106 Hz, $J(P,P)$ = 17 Hz.

data are collected in Table I.* In the absence of long range coupling, the resonances have been assigned to **HH** and **HT** isomers based on comparison with *trans*-$Rh(CO)Cl(PPh_3)_2$ and *trans*-$Rh(CO)Cl(PPh_3)(AsPh_3)$ which have phosphorus environments corresponding to those of the **HH** and **HT** isomers respectively. As can be seen from the Table, P *trans* to P leads to $^1J(Rh,P)$ in the range 114–130 Hz (which is consistent with other observations [12] while P trans to As gives larger coupling constants. Additionally, resonances assigned to P trans to P environments all have the smaller chemical shifts. For each pair of these rhodium isomers the relative abundances of the two isomers range from 4:1 **HT**:**HH** for $Rh_2(\mu\text{-dapm})_2(\mu\text{-S})(CO)_2$ and $[Rh_2(\mu\text{-dapm})_2(\mu\text{-Cl})(CO)_2]$-$[Rh(CO)_2Cl_2]$ to 7:1 for $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$. These ratios vary somewhat from preparation to preparation so that an equilibrium population has not been obtained. Separation of these isomers has not been achieved. The similarity of physical and chemical properties of arsenic and phosphorus will not lead to great differences in polarity or shape of these molecules and consequently separation may be expected to be difficult.

Acknowledgements

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*Other spectral observations on the last three entries in the Table are in reasonable agreement with previously reported data [6]. The inability of these investigators to observe the two isomers may have resulted from poor signal-to-noise ratios in their ^{31}P NMR spectra and/or differences in the preparative procedures which gave lower amounts of the less abundant isomer. They appear to have detected only the more abundant isomer.