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Evidence for Metal-Phosphorus d_{π} - d_{π} Bonding from ν (C==C) Raman Shifts in Complexes of Bis(diphenylphosphino)acetylene

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THERE has been considerable recent interest in the question of σ - vs. π - bonding in transition-metal phosphine complexes.¹ Although correlations of ν (CO) and ν (M–C) frequencies with metal–carbon π -bonding have been extensively utilized in carbonyl chemistry, direct evidence for metal–phosphorus (M–P) π -bonding from vibrational spectroscopy is lacking. Few studies of ν (M–P) frequencies have been reported² and no attempts have been made to relate frequency changes within a phosphine ligand on complexing to M–P

bond character. We report here preliminary results of a new approach to M-P bonding in which changes in the stretching frequency of a detector group C = C attached to phosphorus are correlated

$$Ph_2PC \equiv CPPh_2(I)$$

with $d\pi - d\pi$ interaction in complexes of bis(diphenylphosphino)acetylene (I) (DPPA).

 $v(C \equiv C)$ of (I) appears at 2097 cm.⁻¹ in the Raman spectra, a value considerably lower than the

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Raman	$v(C \equiv C)$	frequencies	and Δv	$(cm.^{-1})$	for	bis(diphenvl	bhosbh	ino)acetvlene	complexes
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Compound		v(C≡C)	Δν	Compound		v(C≡C)	Δν	
$Ph_2PC \equiv CPPh_2(DPPA)$		2097		$[Pt(NCS)_2]_2(DPPA)_2$		2143	46	
(CuCl) ₂ (DPPA) ₃	•••		2124	27	(PdCl ₂) ₂ (DPPA) ₂	••	2135	38
(CuI) ₂ (DPPA) ₃ .			2123	26	$(HgBr_2)_2(DPPA)_2$		2118	21
(CuNO ₃) ₂ (DPPA) ₃			2125	28	(HgI,), (DPPA),		2115	18
(CuNCS) (DPPA)			2121	24	$\tilde{R}h(\tilde{C}\tilde{O})Cl(DP\tilde{P}A]n$		2128	31
(AuCl) (DPPA)			2136	39	[Ni(CO),],(DPPA)		2113	16
(AuBr), (DPPA)			2131	34	ĨNi(CO),Ĩ,(DPPA),		2117	20
(AuI) (DPPA),			2117	20	Ni(CO)1,(DPPA),		2120	23
(AuNĈS), (DPPA),			2120	23	$Ph_{P}P(:O)C \equiv CP(:O)Ph_{Ph_{P}}$		2143	46
(AuBF ₄), (DPPA)			2113	16	2 () () 2			
(PtCl.), (DPPA),			2136	39	$Ph_{\bullet}P(:S)C \equiv CP(:S)Ph_{\bullet}$		2150	53
(2)2(72					+			
$(PtBr_2)_2(DPPA)_2$	••	••	2139	41	$Ph_2P(Me)C \equiv CPPh_2I^-$	••	2109	12

* $\Delta v = v_{complex} - v_{ligand}$

normal range for disubstituted acetylenes (2190—2260 cm.⁻¹)³ even when highly electronegative substituents such as CF₃ are present.⁴ It is probable that this low frequency is caused, at least in part, by a drift of bonding π -electron density from the triple bond to empty $d\pi$ -orbitals on phosphorus. $p\pi$ - $d\pi$ (\rightarrow P) bonding of this type will be facilitated by the linear P-C-C-P skeleton and the strongly electron-withdrawing character of the Ph₂P groups.⁵ The Figure illustrates C($p\pi$)-P($d\pi$) interaction within the P-C-C-P system.



FIGURE. $p\pi$ - $d\pi$ (C-P) overlap in linear skeleton of DPPA.

We have recently prepared numerous binuclear complexes of (I) and shown, from infrared and Raman measurements, that (I) behaves as a bidentate bridging ligand in which the C=C bond is unco-ordinated. A remarkable feature of this work is a shift of $\nu(C=C)$ to higher frequency on complexing, the magnitude $\Delta\nu$ of the shift being dependent both on complex type and metal involved. $\nu(C=C)$ frequencies for a representative series of complexes are collected in the Table.[†] $\Delta\nu$ in some cases is only of the order of 16 cm.⁻¹ but the accuracy of the measurements and the variation with metal clearly indicate that the results are meaningful. We believe the results

are interpretable in terms of M-P π -bonding. Thus back-donation $M(d\pi) \rightarrow P(d\pi)$ will necessarily decrease the extent of $C(p\pi)-P(d\pi)$ interaction, raise the C-C bond order and hence increase the $\nu(C \equiv C)$ frequency. If this hypothesis is correct, $\Delta \nu$ should be large for the dioxide and disulphide of (I) where physical evidence suggests appreciable P-O and P-S double bonding due to $O(p\pi)-P(d\pi)$ and $S(p\pi)-P(d\pi)$ overlap.⁷ Conversely, the dimethiodide of (I) should exhibit a small or negligible $\Delta \nu$. Attempts to prepare this compound by us and previous workers⁸ were unsuccessful but the data for the dioxide, disulphide, and monomethiodide confirm the proposed mechanism.

Several inferences can be drawn from the data in the Table. Qualitatively the order of π -bonding ability of the metals with phosphorus in halide complexes appears to be $Pt^{\mathbf{II}} > |Pd^{\mathbf{II}}| \gg |$ Hg^{II}; Au^I ~ Cu^I. Δv is also affected by the number of ligands bridging the two metal atoms. In the series (AuCl)₂DPPA, (AuNCS)₂(DPPA)₃, and $(AuBF_4)_2(DPPA)_4$, $\Delta \nu$ decreases $39 \rightarrow 23 \rightarrow 16$ cm.-1 as the number of phosphorus atoms per gold atom increases from one to three to four. Mercury(II) has the smallest tendency to π -bond with phosphorus; nevertheless, Δv for these tetrahedral complexes suggests some π -bonding in agreement with the well known stability of mercury-phosphine complexes.9 The polymeric rhodium(I) complex $[Rh(CO)Cl(DPPA)]_n$ has Δv 31 cm.⁻¹ indicating appreciable Rh–P $d\pi$ - $d\pi$ interaction even though the strong π -acceptor carbon monoxide is present. ν (CO) is at 1998 cm.-1, a value 40 cm.-1 higher than the normal range for [Rh(CO)Cl(PR₃)₂]¹⁰ and consistent with the strong π -acceptor properties of DPPA compared with phosphines of the type PR_3 (R = alkyl, arvl).

DPPA successively replaces carbonyl groups

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 $[\]dagger$ Measured as solids using a helium-neon laser Raman spectrometer; values accurate to ± 2 cm.⁻¹.

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from Ni(CO)₄ under mild conditions to give [Ni(CO)₃]₂DPPA, [Ni(CO)₂]₂(DPPA)₂, and [Ni- $(CO)]_2(DPPA)_3$. $\nu(C \equiv C)$ increases from 2113 to 2117 to 2120 cm.⁻¹ and the highest frequency v(CO)absorption decreases from 2078 to 2005 to 1945 cm.⁻¹ as the number of carbonyl groups per nickel atom changes from three to one and the relative amount of π -back-donation Ni \rightarrow P increases.

 $PhP(C \equiv CR)_2$ and $P(C \equiv CR)_3$ (R = Me, Ph) is in progress to obtain more information on M-P π -bonding in these systems.

We acknowledge the financial support of the National Research Council of Canada, and thank Dr. R. J. Gillespie, McMaster University, for providing Raman facilities.

Received, October 4th, 1968; Com. 1360.)

Further work along these lines with the ligands

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