Zerovalent and Divalent Palladium and Platinum
Complexes with Phosphinoacetylenes

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Complexes of zerovalent and divalent palladium and platinum have been prepared using bis(diphenylphosphino)acetylene and diphenylphosphino-methylacetylene as ligands. Spectroscopic evidence indicates phosphorus coordination with no bonding participation of the acetylenic moiety in both oxidation states. The ultraviolet spectra indicate that the zerovalent complexes ML_4 ($M = Pd$, Pt; $L = Ph_2PC \equiv CCH_3$) undergo an oxidative addition reaction with dichloromethane.

Introduction

Phosphine,[3,4] acetylene[5-10] and olefin[5-10] complexes of the nickel triad in both the zero and plus two oxidation states have been known for several years. Only recently, however, have any attempts been made to study the possibilities of coordinative competition in ligands which contain both an unsaturated organic moiety and a donor atom such as nitrogen, arsenic, phosphorus or sulfur.[11-20] With one exception[19] these ligands have all been olefins.

In the complexes formed by these ligands coordination was found to occur through (1) both the olefin and the nitrogen atom,[11-13] (2) through both the olefin and the phosphorus or arsenic atoms,[14-18] (3) through both the olefin and the sulfur atom[20] or (4) through the phosphorus atom only.[15,19] The nature of the bonding[11-20] has been controlled by the steric requirements of the ligands.

This paper describes studies of bis(diphenylphosphino)acetylene (DPPA) and diphenylphosphinomethylacetylene (DPPMA) with zerovalent palladium and platinum as well as the complexes formed by these two metals in the +2 oxidation state with the monophosphinoacetylene. The study was performed to determine if a change in oxidation state influences the coordinative competition.

Experimental Section

Physical Measurements. Infrared spectra in the region 4000-625 cm^{-1} were obtained as KBr disks, nujol mulls, or chloroform solutions using a Beckman IR—8 infrared recording spectrophotometer and were calibrated with known frequency bands of polystyrene. Ultraviolet absorption spectra in the region 200-350 mµ were obtained as dichloromethane solutions using a Cary 14 recording spectrophotometer. The 60 MHz pmr spectra were obtained for deuteriochloroform solutions with tetramethyl-silane as an internal standard using a Varian Associates model A—60 nmr spectrometer. The ^{31}P nmr spectra could not be obtained due to the low solubility of all the compounds and only the phosphoric acid reference signal was observed for saturated solutions. The melting points were determined on a Fischer-Johns melting point stage open to the atmosphere (except where noted) and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of the Ligands. Both bis(diphenylphosphino)acetylene[21] and diphenylphosphinomethylacetylene[22] were prepared by literature methods using chlorodiphenylphosphine (Aldrich) and lithium propynilide (Foote Mineral Co.) as obtained without further purification.

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Preparation of the Complexes: Tetrakis(triphenyl-phosphine) - μ - di[bis(diphenylphosphino)acetylene]di-platinum(0). Tetrakis(triphenylphosphine)platinum(0) prepared according to Malatesta[23] using 80.4 mg sodium tetrachloroplatinate(II) (K and K) was washed twice with 20 ml portions of absolute ethanol and dissolved in 20 ml diethyl ether (nitrogen degassed). To this solution was added a solution containing 100 mg bisdiphenylphosphinoacetylene in 20 ml of diethyl ether (nitrogen degassed). The color changed from an intense yellow to a pale yellow. Absolute ethanol (10-ml nitrogen degassed) was added to the solution and the solvent removed by aspiration. The product which began to precipitate after ~5 min. was filtered and re-crystallized from ethanol-dichloromethane yielding 48.0 mg of yellow microcrystals (20.5% based on starting sodium tetrachloroplatinate(II)) d.p. 226-227° (*in vacuo*). *Anal.* Calcd. for $C_{124}H_{100}P_8Pt_2$: C, 66.86; H, 4.49; P, 11.14. Found: C, 65.32; H, 4.43; P, 11.47.

Tetrakis(triphenylphosphine)-μ-di[bis(diphenylpho-sphino)acetylene]dipalladium(0). The compounds was prepared in the same manner as the platinum analog starting with 66.9 mg sodium tetrachloropalladate(II) (Research Inorganic). Attempts at recrystallization always led to decomposition. The preparation gave 33.6 mg of yellow microcrystals (14.4% based on starting sodium tetrachloropalladate(II) d.p. 267-268° (*in vacuo*). *Anal.* Calcd. for $C_{124}H_{100}P_8Pd_2$: C, 72.63; H, 4.88; Pd, 10.41. Found: C, 73.23; H, 4.88; Pd, 10.87.

Tetrakis(diphenylphosphinomethylacetylene)plati-num(0). A solution containing 399.5 mg diphenyl-phosphinomethylacetylene in 20 ml of dichloromethane was added to a filtered solution of 71.3 mg sodium tetrachloroplatinate(II) in 50 ml absolute methanol. To this solution was added 3 ml of 97% aqueous hydrazine slowly since vigorous effervescence occurred. After cooling on ice for 5 min. the fine yellow needles, which began to appear, were filtered, washed twice with 10 ml portions of absolute methanol and recrystallized from dichloromethane-methanol to yield 210.9 mg (52.1%) m.p. 173-177°. *Anal.* Calcd. for $C_{60}H_{52}P_4Pt$: C, 65.99; H, 4.81; P, 11.37. Found: C, 65.60; H, 4.77; P, 11.66.

Tetrakis(diphenylphosphinomethylacetylene)palla-dium(0). This compound was prepared in the same manner as the platinum analog starting with 56.3 mg sodium tetrachloropallate(II). The compound was recrystallized from dichloromethane-methanol yielding 99.0 mg of yellow-orange needles (51.7%) d.p. 151-153°. *Anal.* Calcd. for $C_{60}H_{52}P_4Pd$: C, 71.78; H, 5.18; Pd, 10.16. Found: C, 71.43; H, 5.13; Pd, 10.51.

Cis-dichlorobis(diphenylphosphinometylacetylene)-platinum(II). The compound was synthesized using the method of Wymore and Bailar,[24] starting with 116.1 mg sodium tetrachloroplatinate(II) and 185.7 mg diphenylphosphinometylacetylene. The compound

precipitated from the reaction mixture as fine white microcrystals and was recrystallized from dichloro-methane-n-hexane yielding 85.1 mg of white microcrystals (40.2%) d.p. 272-274°. *Anal.* Calcd. for $C_{30}H_{26}P_2PtCl_2$: C, 50.42; H, 3.64; P, 8.68; Cl, 9.94. Found: C, 50.47; H, 3.64; P, 8.51; Cl, 10.12.

Trans-dichlorobis(diphenylphosphinomethylacetyl-ene)palladium(II). The compound was prepared in the same manner as the platinum analog starting with 137.3 mg PdCl₂ (D. F. Goldsmith Chemical and Metal Co.) and 269.3 mg diphenylphosphinomethylace-tylene. The preparation gave a cream-colored precipitate which was recrystallized from dichlorome-thane-ethanol yielding 276.9 mg of yellow needles (57.4%) d.p. 245-248°. *Anal.* Calcd. for $C_{30}H_{26}P_2$-PdCl₂: C, 57.63; H, 4.16; Cl, 11.34; Pd, 17.08. Found: C, 57.41; H, 4.05; Cl, 11.51; Pd, 16.89.

Results and Discussion

Infrared Spectra. (a) Complexes of DPPA. Complexation of the acetylenic triple bond to a zero-valent metal results in dramatic shifts of the $C \equiv C$ stretching frequency $\nu_{C\equiv C}$ of the order of 400-500 cm⁻¹ to the region 1600-1800 cm⁻¹, the region where $\nu_{C=C}$ is normally found.[25-27] This indicates a decrease in the bond order of the acetylenic moiety to essentially a carbon-carbon double bond which has been attributed[28] to extensive population of π-antibonding levels in the acetylene; it therefore is a measure of the π-bonding in the complex.

The DPPA complexes do not exhibit any absorption in the infrared attributable to $\nu_{C\equiv C}$ when measured in KBr. However, in chloroform solution $\nu_{C\equiv C}$ appears at a slightly higher frequency than that observed in the Raman for the free ligand. Carty and Efraty[19] have found that this ligand forms dimeric complexes with platinum(II) and palladium(II) halides and they suggested that the complexes possessed the structure(I).

(I)
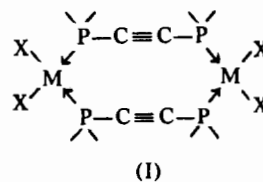
The small shifts in $\nu_{C\equiv C}$ to higher energy (Table I) for chloroform solutions, the absence of $\nu_{C\equiv C}$ or a band attributable to $\nu_{C\equiv C}$ in the region 2100-1600 cm⁻¹ in the solid state indicates that coordination occurs through the phosphorus only with no bonding participation of the acetylene triple bond.[29-31]

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Table I. Infrared Stretching Frequencies for Palladium and Platinum Phosphino-acetylene Complexes

Compound	$\nu_{C\equiv C}$ (cm^{-1})	$\Delta\nu_{C\equiv C}$ (cm^{-1})
Ph$_2$PC $\equiv$ CPPh$_2$*	2097	—
[Pd(PPh$_3$)$_2$(Ph$_2$PC $\equiv$ CPPh$_2$)]$_2$	2114 ^{a}	+17
[Pt(PPh$_3$)$_2$(Ph$_2$PC $\equiv$ CPPh$_2$)]$_2$	2105 ^{a}	+8
Ph$_2$PC $\equiv$ CCH$_3$	2208	—
t—PdCl$_2$(Ph$_2$PC $\equiv$ CCH$_3$)$_2$	2212	+4
c—PdCl$_2$(Ph$_2$PC $\equiv$ CCH$_3$)$_2$	2212	+4
Pd(Ph$_2$PC $\equiv$ CCH$_3$)$_4$	2222	+14
Pt(Ph$_2$PC $\equiv$ CCH$_3$)$_4$	2217	+9

^{a} CHCl$_3$ solution. * In the Raman, data from Ref. 19.

These data are consistent with structures such as (II) in the solid state and (III) in solution. Complete dissociation and/or decomposition of these complexes producing free
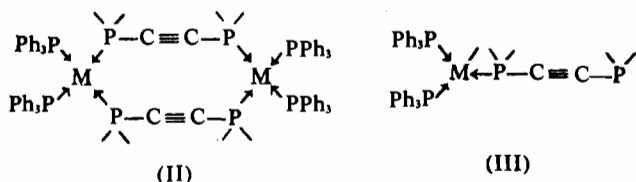
DPPA can be ruled out since $\nu_{C\equiv C}$ is infrared inactive for symmetrical acetylenes such as DPPA. Thus in solution DPPA must remain coordinated and in an unsymmetrical fashion. . Osmometric molecular weight determinations to substantiate this were not successful owing to (1) limited solubility (2) facile oxidative decomposition and (3) oxidative addition reactions involving the halocarbon solvents. Tetrakis(phosphine)platinum(0) and palladium(0) complexes have been previously reported to undergo both dissociation[33] in and oxidative addition reactions[25] with halocarbon solvents. The predominant species in solution being the tris(phosphine) complex[33] which has a trigonal planar structure.[32] Thus the species in solution exhibiting an infrared active $\nu_{C\equiv C}$ stretch is probably (III).

Similar shifts to higher energy have been observed for the complexes [(MCl$_2$)$_2$(DPPA)$_2$] with $\Delta\nu_{C\equiv C}$ = +39 cm^{-1} and +38 cm^{-1}, M = Pt and Pd respectively.[19] These authors argue that the shift to higher energy of $\nu_{C\equiv C}$ in complexes of DPPA is a result of metal-phosphorus dπ–pπ back bonding[29-31] and that the magnitude of the shift reflects the amount of π-bonding. The magnitude of $\nu_{C\equiv C}$ is less for the zerovalent complexes of platinum and palladium (8 and 17 cm^{-1} respectively) than for the divalent complexes indicating less π–bonding in the zerovalent complexes. This is due to competition for π-bonding with the other ligands. Similar effects have been observed previously for nickel carbonyl complexes of DPPA.[29]

b) *Complexes of DPPMA.* For both the zerovalent and divalent complexes of DPPMA the triple bond stretching frequency $\nu_{C\equiv C}$ also increases indicating

coordination of the phosphorus atom only. If the magnitude of $\Delta\nu_{C\equiv C}$ reflects the amount of metal-phosphorus dπ–pπ bonding for this ligand similar to DPPA, then more π-bonding is present in the zerovalent than in the divalent complexes. Furthermore, more π-bonding with zerovalent palladium than platinum is indicated.

The interpretation of these shifts in terms of π-bonding, however, neglects such factors as force constants, mass differences, and coupling effects and the differences in $\Delta\nu_{C\equiv C}$ are near the experimental uncertainty. As suggested by one of the referees, the fact that the $\Delta\nu_{C\equiv C}$'s for DPPMA complexes are smaller than those observed for DPPA complexes does suggest that coupling effects are not negligible for DPPMA complexes.

c) *Ultraviolet Spectra.* The ultraviolet spectra are presented in Table II. The bands at energies higher than 33,300 cm^{-1} are assigned to the B (40,000-34,000 cm^{-1}) and the K (45,500-41,500 cm^{-1}) bands of the phenyl group, with both bands exhibiting vibrational fine structure. The electronic spectra of the palladium complexes reveal more vibrational fine structure than those of the platinum complexes.

The following dissociations (eq. 1 and 2) have been previously measured for these type complexes:[33]

$$Pt(PPh_3)_4 \rightleftharpoons Pt(PPh_3)_3 + PPh_3; \quad K \text{ large} \quad (1)$$

$$Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3; \quad K = 1.6 \pm 1 \times 10^{-4} \quad (2)$$

Even though the isolation of Pt(PPh$_3$)$_2$ has been claimed,[34] it has been isolated as either a cluster compound with a ring of three platinum atoms or as the solvate from halocarbon solvents. However, in halocarbon solvents the oxidative addition (Eq. 3) is known to occur for platinum acetylene complexes.[25,35]

$$L_2Pt(Ac) + XY \longrightarrow L_2XPtY + Ac \quad (3)$$

Ac = an acetylene; L = tertiary phosphine; X = halogen; Y = hydrocarbon or halocarbon fragment. Reactions are indeed indicated by the presence of low energy transitions (29,600 cm^{-1} for Pd(Ph$_2$PC $\equiv$ C—CH$_3$)$_4$ and 31,200 cm^{-1} for Pt(Ph$_2$P—C $\equiv$ C—CH$_3$)$_4$) in dichloromethane solutions as zerovalent palladium complexes of the type [M(PhP(OR)$_2$]$_4$ do not possess any transitions at energies lower than 32,000 cm^{-1}.[36] Furthermore these bands are not present in solutions containing 1:1 mole ratio of complex and ligand, indicating that the excess ligand suppresses the dissociation (eqs 1 and 2). It then seems reasonable to postulate that the species giving rise to the 29,600 cm^{-1} band in the palladium complex and the 31,200 cm^{-1} band in the platinum complex are due to the oxidative addition product of M(DPPMA)$_2$ with CH$_2$Cl$_2$(M = Pd, Pt). Table II shows that *trans*—Cl$_2$Pd(DPPMA)$_2$ has an absorption band at 29,400 cm^{-1}. The remarkable agreement of this band with the 29,600 cm^{-1} band for dichloromethane solutions of

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Table II. Ultraviolet Spectra of Platinum and Palladium Phosphino-acetylene Complexes (in CH_2Cl_2)

Compound	$\bar{v}$ (cm^{-1})	$\leftarrow(\ell m^{-1}\ cm^{-1})$	Tentative Assignment
$Ph_2PC \equiv CPPh_2$	45,300	56,400	K
	39,600	35,800	B
$[Pd(PPh_3)_2(Ph_2PC \equiv CPPh_2)]_2$	44,300	141,000	K
	43,400	138,000	K
	37,500	55,700	B
	36,400	47,300	B
$[Pt(PPh_3)_2(Ph_2PC \equiv CPPh_2)]_2$	44,300	127,000	K
	43,400	124,000	K
Ph_3P	44,600	2,310	K
	43,500	1,990	K
	38,300	1,170	B
	37,500	1,180	B
	36,600	1,090	B
$Ph_2PC \equiv CCH_3$	43,800	5,940	K
	43,100	5,630	K
	38,500	929	B
	37,600	2,170	B
t—$(Ph_2PC \equiv CCH_3)_2PdCl_2$	44,300	29,100	K
	43,500	28,100	K
	35,600	25,100	B
	29,400	6,100	C.T.
c—$(Ph_2PC \equiv CCH_3)_2PtCl_2$	43,100	47,100	K
	37,400	14,900	B
	36,500	12,700	B
$Pd(Ph_2PC \equiv CCH_3)_4$	43,800	54,600	K
	43,400	52,100	K
	38,500	21,300	B
	37,500	21,000	B
	36,600	19,200	B
	29,600*	5,460	C.T.
$Pt(Ph_2PC \equiv CCH_3)_4$	43,800	51,400	K
	43,100	50,800	K
	37,600	15,600	B
	36,500	12,600	B
	31,200*	1,130	C.T.

* Not present in equimolar solutions of ligand and complex.

Table III. Proton Magnetic Resonance Spectra of Palladium and Platinum Phosphino-acetylene Complexes [a]

Compound	τ		Assignment
$Ph_2PC \equiv CPPh_2$	2.54	complex multiplet	PhH
$[Pd(PPh_3)_2(Ph_2PC \equiv CPPh_2)]_2$	2.79	complex multiplet	PhH
$[Pt(PPh_3)_2(Ph_2PC \equiv CPPh_2)]_2$	2.81	complex multiplet	PhH
$Ph_2PC \equiv CCH_3$	2.54	complex multiplet	PhH
	8.09		CH_3
	8.13		
t—$Pd(Ph_2PC \equiv CCH_3)_2Cl_2$	2.34	complex multiplet	PhH
	8.30		
	8.37		CH_3
	8.40		
c—$Pd(Ph_2PC \equiv CCH_3)_2Cl_2$	2.37	complex multiplet	PhH
	8.32		CH_3
	8.37		
$Pd(Ph_2PC \equiv CCH_3)_4$	2.43	complex multiplet	PhH
	7.66		
	7.84		CH_3
	7.89		
$Pt(Ph_2PC \equiv CCH_3)_4$	2.76	complex multiplet	PhH
	8.05	unresolved	CH_3

[a] Deuteriochloroform solution, τ values relative to internal TMS.

Pd(DPPMA)₄ seems to suggest strongly that the 29,600 cm^{-1} band is due to the product of oxidative addition, *trans*—Pd(DPPMA)₂Cl₂. It is difficult to assign the bands to either charge transfer or d—d transitions because of the presence of the phenyl groups and the uncertainty of the d-electron configuration.

For th DPPMA complexes, the dissociation pro-ceeds to both ML₃ and ML₂, with the ML₃ species predominating. The absence of a band in the ultra-violet at ~30,000 cm^{-1} and the presence of $v_{C \equiv C}$ in the infrared for solutions of the DPPA complexes seems to indicate that the dissociation proceeds pre-dominantly to compound (III) and that the solvent oxidative addition reaction is much slower.

d) *NMR Spectra.* The 60 MH$_z$ proton spectra (Table III) are largely uninformative due to the limited solubility of the complexes. The resonances indicate phenyl groups or phenyl groups and methyl groups with the integrated intensities supporting the elemental analyses. The formulation of the bridged complexes as [(Ph$_3$P)$_2$M(DPPA)]$_2$ was substantiated by relative integration with hexamethylbenzene as an internal calibration.[37]

Conclusion

In line with previous structural determinations[3,4] for the zerovalent palladium and platinum compounds, these data seem to support the assignment of tetrahedral structures for both the monophosphine and the diphosphine complexes in the zerovalent state.

Previous structure determinations, absorption characteristics and other properties of the complexes in the plus two oxidation state seem to support the assignment of *trans*-planar and *cis*-planar structures for the palladium(II) and platinum(II) complexes respectively.

It has been shown that a change in oxidation state of the metal does not bring about participation of the acetylene group in bonding. This is probably a consequence of the steric requirements of these ligands.

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