

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia, U.S.A.

Complexes of Trivalent Phosphorus Derivatives. XIV. Metal Complexes of Diphenylphosphinophenylacetylene¹

R. B. King² and A. Efraty³

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The following metal complexes of diphenylphosphinophenylacetylene $((C_6H_5)_2PC \equiv CC_6H_5)$ were prepared by conventional methods: $[(C_6H_5)_2PC \equiv CC_6H_5]_3CuCl$, $[(C_6H_5)_2PC \equiv CC_6H_5]AuCl$, $[(C_6H_5)_2PC \equiv CC_6H_5]_2MCl_2$ ($M = Pd$ or Pt), $[(C_6H_5)_2PC \equiv CC_6H_5]_3NiCO$, $[(C_6H_5)_2PC \equiv CC_6H_5]RhCOCl_2$, trans- $[(C_6H_5)_2PC \equiv CC_6H_5]_2Fe(CO)_3$, trans- $[(C_6H_5)_2PC \equiv CC_6H_5]_2Cr(CO)_4$, cis- and trans- $[(C_6H_5)_2PC \equiv CC_6H_5]_3Cr(CO)_3$, cis- $[(C_6H_5)_2PC \equiv CC_6H_5]_3M(CO)_3$, ($M = Mo$ and W), $C_5H_5CoI_2[(C_6H_5)_2PC \equiv CC_6H_5]$, $C_5H_5FeCOBr[(C_6H_5)_2PC \equiv CC_6H_5]$, and $C_5H_5Mo(CO)_2(COR)[(C_6H_5)_2PC \equiv CC_6H_5]$ ($R = CH_3$ or $C_6H_5CH_2$). The reaction of cycloheptatrienetricarbonylchromium with $(C_6H_5)_2PC \equiv CC_6H_5$ at room temperature yielded the expected cis- $[(C_6H_5)_2PC \equiv CC_6H_5]_3Cr(CO)_3$ but this reaction when carried out at 80° gave some of the corresponding trans-isomer as well as the cis-isomer thereby indicating a thermal rearrangement. Similarly, the reaction of norbornadienetetracarbonylchromium with $(C_6H_5)_2PC \equiv CC_6H_5$ gave trans- $[(C_6H_5)_2PC \equiv CC_6H_5]_2Cr(CO)_4$ rather than the corresponding cis isomer. The infrared-active $\nu(C \equiv C)$ frequencies in the various metal complexes of diphenylphosphinophenylacetylene can be used as indicators of the relative amounts of retrodative π -bonding from filled metal d orbitals to the empty phosphorus d orbitals of the phosphine ligand. Using this frequency as an indicator, retrodative π -bonding is shown to be weaker in tetrahedral complexes than in octahedral, trigonal bipyramidal, or square planar complexes.

The Raman-active $\nu(C \equiv C)$ frequencies of these complexes were shown to be a measure of metal-phosphorus retrodative π -bonding with higher values indicating increased metal-phosphorus retrodative bonding. This paper examines the preparation and infrared spectra of metal complexes of the related acetylenic tertiary phosphine $(C_6H_5)_2PC \equiv CC_6H_5$. Since the triple bond in this acetylene is unsymmetrically substituted, the $\nu(C \equiv C)$ frequency is infrared active and hence more readily measured in a wide range of complexes.

Experimental Section

Diphenylchlorophosphine was purchased from Eastern Chemical Corporation, Pequannock, New Jersey, and converted to diphenylphosphinophenylacetylene, $(C_6H_5)_2PC \equiv CC_6H_5$, by reaction with lithium phenylacetylide prepared from butyllithium and phenylacetylene.⁹ Transition metal derivatives were either commercial materials or samples prepared by well-established procedures.¹⁰ Melting and decomposition points were determined in capillaries and are uncorrected. Reactions with organometallic compounds were performed in a nitrogen atmosphere.

Preparation of Complexes of $(C_6H_5)_2PC \equiv CC_6H_5$ (Table I). The preparation of most of the complexes described in this paper followed techniques already

Introduction

Recently a variety of metal complexes of the acetylenic ditertiary phosphine bis(diphenylphosphino)acetylene, $(C_6H_5)_2PC \equiv CP(C_6H_5)_2$, have been prepared^{4,5,6,7,8}

- (1) For Part XIII of this series see R. B. King and A. Efraty, *Inorg. Chim. Acta*, 4, 123 (1970).
- (2) Fellow of the Alfred P. Sloan Foundation, 1967-1969.
- (3) Post-doctoral research associate, 1968-1971.
- (4) A. J. Carty and A. Efraty, *Chem. Comm.*, 1559 (1968).
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- (9) W. Chodkiewicz, P. Cadot, and A. Willemart, *Compt. Rend.*, 250, 866 (1960).
- (10) The preparations of the indicated starting materials are given in the following references: (a) $[Rh(CO)_2Cl]_2$: J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8, 211 (1966). (b) $C_7H_7W(CO)_5$: R. B. King and A. Fronzaglia, *Inorg. Chem.*, 5, 1837 (1966). (c) $C_5H_5Fe(CO)_2Br$: B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956). (d) $C_5H_5Co(CO)_2$: R. B. King, *Inorg. Chem.*, 5, 82 (1966). (e) $C_5H_5CH_2-Mo(CO)_3C_5H_5$: R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, 88, 709 (1966). (f) $[C_5H_5NiCO]_2$, $C_6H_5Fe(CO)_3$, nor- $C_7H_7Cr(CO)_4$, $C_7H_7Rr(RO)_3$, $C_7H_7Mo(CO)_3$, and $CH_3Mo(CO)_3C_5H_5$: R. B. King, «Organometallic Syntheses», Vol. 1, Academic Press, New York, 1965.

Table I. New Metal Complexes of (Phenylethynyl)diphenylphosphine Prepared in this Work.

Compound ^a	Properties		Reactant ^a	Preparation		Yield, %	Analyses ^c				Other
	Color	m.p.		Solvent	Temp ^b		C	H	O		
L ₂ CuCl	white	168-169°	CuCl ₂ (H ₂ O) ₂	EtOH	25°(2)	54 ^d	Calcd.	75.4	4.7	—	
LAuCl	white	190-191°	HAuCl ₄	EtOH	85°(0.25)	18	Found	74.2	4.7	—	
L ₂ PdCl ₂	yellow	183-184°	(MeCN) ₂ PdCl ₂	C ₆ H ₆ /CH ₂ Cl ₂	25°(20)	76 ^{dd}	Calcd.	46.3	2.9	—	7.0(Cl)
L ₂ PtCl ₂	white	159-161°	H ₂ PtCl ₆ (40% Pt)	EtOH	25°(24)	93 ^e	Found	46.5	3.0	—	7.0(Cl)
L ₃ NiCO	pale green	124-125°	[CpNiCO] ₂	C ₆ H ₆	25°(72)	14 ^{eee}	Calcd.	64.1	4.0	—	
[LRhCOC]l ₂	orange-brown	104-105°	[Rh(CO) ₂ Cl] ₂	CH ₂ Cl ₂ / hexane	25°(12)	17 ^f	Found	64.1	4.1	—	
<i>t</i> -L ₂ Fe(CO) ₃	yellow	217-218°	C ₆ H ₅ Fe(CO) ₃	cyclo- hexane	25°(40)	25 ^h	Calcd.	57.3	3.6	—	
<i>t</i> -L ₂ Cr(CO) ₃	pale yellow	196-198°	C ₆ H ₅ Cr(CO) ₃	hexane	85°(14)	70 ^g	Found	57.4	3.8	—	
<i>c</i> -L ₂ Cr(CO) ₃	yellow	166-168°	C ₆ H ₅ Cr(CO) ₃	C ₆ H ₆	25°(80)	23 ^{ig}	Calcd.	77.5	4.8	1.7	9.8(P)
<i>t</i> -L ₂ Cr(CO) ₃	orange	128-129°	C ₆ H ₅ Cr(CO) ₃	C ₆ H ₆	85°(14)	24 ^{ig}	Found	77.3	4.7	2.2	10.0(P)
<i>c</i> -L ₂ Mo(CO) ₃	yellow	185-187°	C ₆ H ₅ Mo(CO) ₃	C ₆ H ₆	25°(78)	44 ^g	Calcd.	56.1	3.3	3.5	
<i>c</i> -L ₂ W(CO) ₃	pale yellow	200-202°	C ₆ H ₅ W(CO) ₃	MCH ^d	100°(14)	38 ^{ig}	Found	57.1	3.8	4.0	
CpCoI ₂ L	dark blue	185-187°	CpCo(CO)I ₂	benzene	25°(40)	74 ^g	Calcd.	72.6	4.3	6.6	
CpFe(CO)BrL	green	127-128°	CpFe(CO) ₂ Br	benzene	80°(1)	31 ^g	Found	72.2	4.2	6.7	
CpMo(CO) ₂ - (COMe)L	yellow	114-115°	CpMo(CO) ₂ Me	MeCN	25°(72)	14 ^{ig}	Calcd.	71.6	4.1	8.7	
CpMo(CO) ₂ - (COCH ₂ Ph)L	yellow	123-124°	CpMo(CO) ₂ CH ₂ Ph	MeCN	25°(80)	15 ^{ig}	Found	71.0	4.2	8.7	
							Calcd.	76.2	4.6	4.8	
							Found	76.0	4.5	4.6	
							Calcd.	75.7	4.8	4.8	
							Found	72.8	4.4	4.6	8.8(P)
							Calcd.	67.2	4.0	4.3	8.9(P)
							Found	67.3	4.2	4.1	
							Calcd.	45.2	3.0	38.1 (I)	8.9(Co)
							Found	45.6	3.1	39.8 (I)	8.6(Co)
							Calcd.	60.1	3.9	3.1	15.5(Br)
							Found	60.7	3.8	3.3	15.9(Br)
							Calcd.	63.8	4.2	8.8	5.7(P)
							Found	63.9	4.3	8.9	5.8(P)
							Calcd.	68.4	4.4	7.8	5.0(P)
							Found	67.5	4.4	7.8	4.8(P)

^a The following abbreviations are used: L = (C₆H₅)₂PC≡CC₆H₅; Cp = π -cyclopentadienyl; Me = methyl; Ph = phenyl; *c* = *cis*; *t* = *trans*; MCH = methylcyclohexane. ^b The reaction time in hours at the indicated temperature is given in parentheses. ^c These microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. ^d This compound was recrystallized from a mixture of dichloromethane and ethanol. ^e The excess ligand was washed out with boiling cyclohexane. ^f The reaction mixture was chromatographed on an alumina column. The bands were eluted with mixtures of benzene and hexane. ^g This compound was recrystallized from a mixture of dichloromethane and hexane. ^h This compound was recrystallized from a mixture of benzene and hexane. ⁱ The reaction mixture was chromatographed on an alumina column. The bands were eluted with mixtures of dichloromethane and hexane.

well-established^{11,12} for similar transition metal complexes of closely related tertiary phosphines. Details of these reactions including reactant, solvent, temperature, time, and purification procedures are listed in Table I; individual reactions will not be described. In all cases the transition metal derivative and diphenylphosphinophenylacetylene were stirred in the indicated solvent under the indicated reaction conditions. In the cases of the reactions carried out in ethanol, hexane, or cyclohexane, the product precipitated from the reaction mixture at least upon cooling to room temperature and was purified further by the procedure indicated in Table I. In the cases of the other reactions, where the product did not precipitate, either the solvent was removed from the reaction mixture or the reaction mixture was chromatographed on a 2 × 40 cm alumina column as indicated in Table I.

Reaction of Cycloheptatrienetricarbonylchromium with Diphenylphosphinophenylacetylene. A mixture of 0.75 g (3.3 mmoles) of cycloheptatrienetricarbonylchromium,^{10f} 2.5 g (8.8 mmoles) of diphenylphosphinophenylacetylene, and 75 ml of C. P. benzene was boiled under reflux for 14 hours. Solvent was then removed at 25°/35 mm. A concentrated solution of the residue in 1:1 dichloromethane-hexane was chro-

matographed on a 2 × 60 cm alumina column. An orange band of *trans*-[(C₆H₅)₂PC≡CC₆H₅]₃Cr(CO)₃ appeared followed by a much more slowly moving yellow band of the corresponding *cis*-isomer. Both bands were eluted with 1:1 dichloromethane-hexane mixtures and the eluates evaporated at 25°/35 mm. Both compounds were purified by several recrystallizations from mixtures of dichloromethane and hexane.

When the reaction between cycloheptatrienetricarbonylchromium and diphenylphosphinophenylacetylene was carried out at room temperature rather than in boiling benzene, the product was exclusively *cis*-[(C₆H₅)₂PC≡CC₆H₅]₃Cr(CO)₃ with none of the corresponding *trans*-isomer being isolated.

Infrared Spectra (Table II). All infrared spectral data reported in Table II were taken in dichloromethane solution and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Because of the small differences involved, the $\nu(\text{C}\equiv\text{C})$ frequencies were measured on a tenfold expanded abscissa scale with each spectrum being calibrated with the spectrum of free (C₆H₅)₂PC≡CC₆H₅. The reproducibility of these measurements was better than $\pm 0.5 \text{ cm}^{-1}$.

Proton N.M.R. Spectra. Proton n.m.r. spectra of the new compounds were taken in chloroform-d solution on a Perkin-Elmer Hitachi R-20 spectrometer at 60 Mc or a Varian HA-100 spectrometer at 100 Mc.

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Table II. Infrared and Raman Spectra of Metal Complex of Acetylenic Phosphines, cm^{-1} .

Compound	$\nu(\text{C}\equiv\text{C})^a$	Ph ₂ PC≡CPh Derivative		$\nu(\text{CO})^c$	Ph ₂ PC≡CPPh ₂ Derivative ^e	
		$\Delta\nu^b$			$\nu(\text{C}\equiv\text{C})^a$	$\Delta\nu^b$
L	2165	0.0			2097	0
L ₃ CuCl	2173.5	8.5			2124	27
LAuCl	2181	16.0			2136	39
L ₂ PdCl ₂	2179	14.0			2135	38
L ₂ PtCl ₂	2180.5	15.5			2136	39
L ₃ NiCO	2170.5	5.5	1925(s)		2113	16
[LRh(CO)Cl] ₂	2179	14.0	1994(s)		2128	31
<i>t</i> -L ₂ Fe(CO) ₃	2177	12.0	1898(s), 1886(s)			
<i>t</i> -L ₂ Cr(CO) ₄	2175	10.0	1898(s)			
<i>c</i> -L ₂ Cr(CO) ₃	2176.5	11.5	1938(s), 1846(s)			
<i>t</i> -L ₂ Cr(CO) ₃	2176	11.0	1957(w), 1855(s) ^f			
<i>c</i> -L ₂ Mo(CO) ₃	2176.5	11.5	1950(s), 1853(s)		2128	31
<i>c</i> -L ₂ W(CO) ₃	2177	12.0	1945(s), 1848(s)			
CpCoI ₂ L	2178	13.0				
CpFe(CO)BrL	2176	11.0	1965(s)			
[CpMn(CO)(NO)L][PF ₆]	2175	10.0	2035(s), 1798(s) ^g			
CpMo(CO) ₂ (COMe)L	2174.5	9.5	1943(s), 1856(vs), 1606(m) ^h			
CpMo(CO) ₂ (COCH ₂ Ph)L	2174.5	9.5	1944(s), 1859(vs), 1614(m) ^h			
LO	2180	15.0			2143	46
LS	2180	15.0			2150	53

^a Infrared frequencies measured as described in the Experimental Section. ^b Shift of the $\nu(\text{C}\equiv\text{C})$ frequency relative to the free ligand. ^c Dichloromethane solutions. ^d Helium-neon laser Raman data of A. J. Carty and A. Efraty, *Chem. Comm.*, 1559 (1968).

^e In all cases the derivative with both phosphorus atoms of the ligand bonded to metal atoms is considered. ^f $\nu(\text{CO})$ frequencies in the Nujol mull spectrum: 1962(m), 1878(s), 1846(s) cm^{-1} . ^g $\nu(\text{NO})$ frequency. ^h Acyl $\nu(\text{CO})$ frequency.

All compounds exhibited two distinct envelopes of phenyl resonances at τ 1.8 to 2.5 and at τ 2.4 to 3.5 of approximate relative intensities 1:2 corresponding to the five phenylethynyl and the ten diphenylphosphino protons of the diphenylphosphinophenylacetylene ligand, respectively. For compounds with other hydrogen-containing ligands, the following additional n.m.r. resonances were observed.

A. $\text{C}_6\text{H}_5\text{CoI}_2[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]$. τ 4.69 (singlet) from the five π -cyclopentadienyl protons.

B. $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{Br}[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]$. τ 5.32 (broad singlet, width at half-height 8 c.p.s.) from the five π -cyclopentadienyl protons.

C. $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{COCH}_3)[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]$. τ 4.81 (doublet, $J = 2$ c.p.s.) from the five π -cyclopentadienyl protons and τ 7.41 (singlet) from the three methyl protons of the acetyl group.

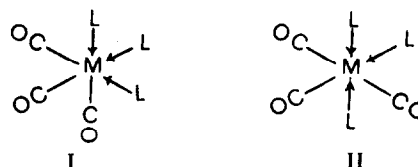
D. $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{COCH}_2\text{C}_6\text{H}_5)[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]$. τ 4.91 (doublet, $J = 2$ c.p.s.) from the five π -cyclopentadienyl protons and τ 2.8 (complex: three apparent peaks) and τ 5.72 (singlet) from the five phenyl protons and the two methylene protons of the phenylacetyl group.

Discussion

The following two features of the metal complexes of diphenylphosphinophenylacetylene were of greatest interest: (1) Isomerism in the chromium carbonyl derivatives; (2) Variation of $\nu(\text{C}\equiv\text{C})$ with changes in the structure of the complex.

Reactions of diphenylphosphinophenylacetylene with norbornadiene and cycloheptatriene complexes of chromium carbonyl indicate that two acetylenic phosphine ligands preferentially occupy *trans*-positions

in relatively small octahedral metal atoms. Thus the single strong $\nu(\text{CO})$ frequency in the $[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]_2\text{Cr}(\text{CO})_4$ obtained from norbornadienetetracarbonylchromium and the ligand in boiling benzene clearly indicates it to be the *trans* isomer¹³ rather than the *cis*-isomer which would be formed by simple replacement of the norbornadiene system with two ligand molecules. Reactions of the cycloheptatriene complexes $\text{C}_7\text{H}_8\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}$, and W) with diphenylphosphinophenylacetylene at room temperature gave $[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]_3\text{M}(\text{CO})_3$ products exhibiting the two infrared $\nu(\text{CO})$ frequencies with positions and relative intensities corresponding to those expected for the *cis*-isomer¹⁴ (I: $\text{L} = (\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}$, and W) formed by simple replacement of the cycloheptatriene ring with three ligand molecules as in a variety of known¹⁵ reactions of cycloheptatriene-metal tricarbonyls with tricovalent phosphorus and other Lewis base ligands. However, if the reaction between the chromium complex $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3$ and diphenylphosphinophenylacetylene is carried out at 85°, two isomeric $[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]_3\text{M}(\text{CO})_3$ derivatives were obtained which could be separated readily by chromatography on alumina. The more strongly adsorbed yellow isomer was identical to the *cis*- $[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]_3\text{Cr}(\text{CO})_3$ obtained in the room temperature reaction. The less strongly adsorbed orange isomer also exhibited two $\nu(\text{CO})$ frequencies in solution, but with a relative intensity pattern consistent with that of known *trans*- $\text{L}_3\text{M}(\text{CO})_3$ complexes II; the orange isomer, therefore, is formulated as *trans*- $[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CC}_6\text{H}_5]_3\text{Cr}(\text{CO})_3$.



(II: $L = (C_6H_5)_2PC \equiv CC_6H_5$; $M = Cr$). The occurrence of only two rather than the predicted¹⁴ three $\nu(CO)$ frequencies in *trans*-(R_3P)₃ $M(CO)_3$ derivatives has been a matter of some controversy^{16,17} but appears to arise from accidentally superposed A_1 and B_1 bands. In this connection, the observation of three distinct $\nu(CO)$ frequencies in the solid state spectrum of *trans*-[(C_6H_5)₂ $PC \equiv CC_6H_5$]₃ $Cr(CO)_3$ is of interest since it is quite possible that unequal shifts of the two bands presumed to be superposed in the solution spectrum could result in the appearance of the third $\nu(CO)$ frequency in the solid state spectrum. However, the possibility of this additional $\nu(CO)$ frequency in the solid state spectrum arising from other more usual solid state effects cannot be excluded at the present time.

The infrared $\nu(C \equiv C)$ frequencies could be readily observed for all of the diphenylphosphinophenylacetylene complexes. In general, the measured shifts parallel those previously⁴ found for the Raman $\nu(C \equiv C)$ frequencies of analogous metal complexes of the bridging acetylenic ditertiary phosphine (C_6H_5)₂ $PC \equiv CP(C_6H_5)_2$ but are only 0.29 ± 0.07 times as great owing to the presence of only one diphenylphosphino substituent on the carbon-carbon triple bond in (C_6H_5)₂ $PC \equiv CC_6H_5$ as contrasted with the presence of two diphenylphosphino substituents on the carbon-carbon triple bond in (C_6H_5)₂ $PC \equiv CP(C_6H_5)_2$. Nevertheless, the shifts in the infrared $\nu(C \equiv C)$ frequencies of the complexes of (C_6H_5)₂ $PC \equiv CC_6H_5$ are still greater than the shifts in the Raman $\nu(C \equiv C)$ frequencies in the relatively limited number of (C_6H_5)₂ $PCH_2C \equiv CCH_2P(C_6H_5)_2$ complexes which have been measured;¹ the insulating methylene groups between the diphenylphosphino groups and the carbon-carbon triple bond in (C_6H_5)₂ $PCH_2C \equiv CCH_2P(C_6H_5)_2$ appear to make the $\nu(C \equiv C)$ frequency essentially independent of changes at the phosphorus atoms.

The $\nu(C \equiv C)$ frequencies in disubstituted acetylenes of the type $RC \equiv CR$ occur in the range 2260–2190 cm^{-1} . Successive substitution of carbon substituents on the carbon-carbon triple bond with phosphorus substituents result in the lowering of the $\nu(C \equiv C)$ frequency. Thus the $\nu(C \equiv C)$ frequency in the monosubstituted (C_6H_5)₂ $PC \equiv CC_6H_5$ is 2165 cm^{-1} and that in the disubstituted (C_6H_5)₂ $PC \equiv CP(C_6H_5)_2$ is 2097 cm^{-1} . That this is an effect of the empty d orbitals rather than the lone electron pair of the phosphorus atom is demonstrated by the occurrence of a similar lowering of the $\nu(C \equiv C)$ frequency upon replacing carbon substituents on a carbon-carbon triple bond with organosilicon or organotin substituents;^{19,20} silicon and tin also have empty d orbitals but do not have lone electron pairs. Thus, the infrared $\nu(C \equiv C)$ frequency²⁰ in $(CH_3)_3SiC \equiv CSn(CH_3)_3$ occurs at 2079 cm^{-1} which

is close to that in (C_6H_5)₂ $PC \equiv CP(C_6H_5)_2$ and far below the $\nu(C \equiv C)$ frequencies in disubstituted acetylenes with only carbon substituents on the carbon-carbon triple bond.

The lowering of the $\nu(C \equiv C)$ frequency in acetylenic phosphines such as (C_6H_5)₂ $PC \equiv CC_6H_5$ is thus a result of the drift of electron density from the filled bonding π orbitals of the carbon-carbon triple bond to the empty d orbitals of the phosphorus atom.⁴ Any retrodative $d\pi-d\pi^*$ bonding from filled d orbitals of a transition metal atom into the empty d orbitals of the phosphorus atom will reduce the ability of these phosphorus d orbitals to pull electron density from the filled bonding π orbitals of the carbon-carbon triple bond and hence will raise the $\nu(C \equiv C)$ frequency. Thus the magnitude of the increase in the $\nu(C \equiv C)$ frequency in going from the free (C_6H_5)₂ $PC \equiv CC_6H_5$ ligand to various complexes ($\Delta\nu$) can be taken as a measure of the retrodative bonding from the transition metal atom to the phosphorus atom. Unfortunately, this effect of retrodative bonding on the $\nu(C \equiv C)$ frequencies of acetylenic phosphines is a very small one. Thus in the series of bis(diphenylphosphino)acetylene complexes of nickel carbonyl of the type $[Ni(CO)_n]_2[(C_6H_5)_2PC \equiv CP(C_6H_5)_2]_{4-n}$ the variation in $\nu(C \equiv C)$ upon successive replacement of carbonyl groups with tertiary phosphines is only 3 cm^{-1} per carbonyl group which is far less than the change in $\nu(CO)$ of 35–50 cm^{-1} per carbonyl group. The variation in $\nu(C \equiv C)$ frequencies in (C_6H_5)₂ $PC \equiv CC_6H_5$ complexes parallels that in (C_6H_5)₂ $PC \equiv CP(C_6H_5)_2$ complexes (Table II) but is only about one-third as much as discussed above.

The increase in the $\nu(C \equiv C)$ frequency ($\Delta\nu$) in going from (C_6H_5)₂ $PC \equiv CC_6H_5$ to its metal complexes is thus an indicator of the back donation of electrons into the empty phosphorus d orbitals albeit a rather insensitive one. An indication of the magnitude of this effect is given by the $\Delta\nu$ values of 15 cm^{-1} for the oxide and sulfide (C_6H_5)₂ $P(E)C \equiv CC_6H_5$ ($E = O$ and S) owing to $p\pi-d\pi^*$ donation of the lone electron pairs of the chalcogen atom into the empty phosphorus d orbitals. Similar $\Delta\nu$ values in the range 14 to 16 cm^{-1} are found for the square planar complexes $[(C_6H_5)_2PC \equiv CC_6H_5]_2MCl_2$ ($M = Pd$ or Pt) which have four electron pairs on the metal atom available for back-donation into empty phosphorus d orbitals of the two diphenylphosphinophenylacetylene ligands and for the linear gold(I) complex $[(C_6H_5)_2PC \equiv CC_6H_5]AuCl$ which has five electron pairs on the metal atom available for back-donation into the empty phosphorus d orbitals of the ligand.

The remaining metal complexes of diphenylphosphinophenylacetylene exhibit appreciably lower $\Delta\nu$ values for the $\nu(C \equiv C)$ frequency. The octahedral metal carbonyl derivatives of the type $[(C_6H_5)_2PC \equiv CC_6H_5]_nM(CO)_{6-n}$ ($M = Cr, Mo, \text{ and } W$) have $\Delta\nu$ values in the range 10 to 12 cm^{-1} ; here there are only three electron pairs on the metal atom for back donation to six ligands including some strongly π -accepting carbonyl groups. The $\Delta\nu$ for the trigonal bipyramidal iron carbonyl complex $[(C_6H_5)_2PC \equiv CC_6H_5]_2Fe(CO)_3$ of 12 cm^{-1} with four electron pairs on the metal atom for back donation to five ligands is higher than that of the octahedral metal carbonyl complexes ex-

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cept for the tungsten derivative $[(C_6H_5)_2PC \equiv CC_6H_5]_3W(CO)_3$. This is consistent both with the availability of more electron pairs on the metal atom for back donation in the case of the five-coordinate complexes relative to the six-coordinate complexes and with the recently demonstrated²¹ greater availability of the electron pairs on tungsten than of the electron pairs on molybdenum and chromium for back donation into appropriate empty ligand orbitals in analogous compounds.

The tetrahedral complexes studied in this work are found to have relatively low $\Delta\nu$ values indicative of smaller retrodative π -bonding in tetrahedral systems than in octahedral, square planar, or linear systems. Thus the tetrahedral copper(I) derivative $[(C_6H_5)_2PC \equiv CC_6H_5]_3CuCl$ has a $\Delta\nu$ value of only 8.5 cm^{-1} . Furthermore, the tetrahedral nickel(0) $[(C_6H_5)_2PC \equiv CC_6H_5]_3NiCO$ with a very strongly π -accepting carbonyl group competing with the three diphenylphosphinophenylacetylene ligands for the electron pairs of the metal atom has a still lower $\Delta\nu$ value of only 5.5 cm^{-1} . This work thus demonstrates the low tendency for electron pairs on tetrahedral metal atoms to participate in retrodative bonding as compared with electron pairs on trigonal bipyramidal and octahedral metal atoms. This is consistent with numerous previous observations such as the facile decomposition of tetrahedral $Ni(CO)_4$ to metallic nickel and carbon monoxide only slightly above room temperature as contrasted with the much greater thermal stability of trigonal bipyramidal $Fe(CO)_5$ and octahedral $Cr(CO)_6$,²² as well as the higher $\nu(CO)$ frequencies and the higher Cotton-Kraihanzel approximate carbon-oxygen stretching force constants in tetrahedral metal carbonyl

derivatives²³ as compared with analogous frequencies and force constants in comparably substituted octahedral metal carbonyl derivatives.^{13,14} The small retrodative π -bonding in tetrahedral derivatives relative to octahedral derivatives is particularly striking since tetrahedral derivatives like $Ni(CO)_4$ have five electron pairs to share between four ligands whereas octahedral derivatives such as $Cr(CO)_6$ have only three electron pairs to share between six ligands.

The $\Delta\nu$ values for the π -cyclopentadienyl derivatives studied in this work are also consistent with the expected availability of metal electron pairs for back donation into the phosphorus d orbitals. In this connection the π -cyclopentadienyl ligand is conveniently regarded as tridentate.²⁴ The increases in $\Delta\nu$ in the series of six-coordinate derivatives $[C_5H_5Mn(CO)(NO)-(C_6H_5)_2PC \equiv CC_6H_5][PF_6]$, $C_5H_5Fe(CO)Br[(C_6H_5)_2PC \equiv CC_6H_5]$, and $C_5H_5CoI_2[(C_6H_5)_2PC \equiv CC_6H_5]$ is consistent with the increased availability of the metal electron pairs for back donation into the phosphorus d orbitals upon replacement of the strongly π -accepting carbonyl and nitrosyl groups with more weakly π -accepting ligands. The $\Delta\nu$ values for the seven-coordinate derivatives of the type $C_5H_5Mo(CO)_2(COR)-[(C_6H_5)_2PC \equiv CC_6H_5]$ ($R = CH_3$ or $C_6H_5CH_2$) are similar within experimental error to those of six-coordinate π -cyclopentadienyl derivatives with similar numbers of strongly π -accepting ligands.

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