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Complexes of Trivalent Phosphorus Derivatives. XIV.
Metal Complexes of Diphenylphosphinophenylacetylene[1]

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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*), $[(C_6H_5)_2PC{\equiv}CC_6H_5]_3NiCO$, $[(C_6H_5)_2PC{\equiv}CC_6H_5RhCOCl]_2$, 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.*

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] 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

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[1] For Part XIII of this series see R. B. King and A. Efraty, *Inorg. Chim. Acta*, *4*, 123 (1970).

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[4] A. J. Carty and A. Efraty, *Chem. Comm.*, 1559 (1968).

[5] A. J. Carty and A. Efraty, *Canad. J. Chem.*, *47*, 1429 (1969).

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[7] A. J. Carty and A. Efraty, *Inorg. Nucl. Chem. Letters*, *4*, 427 (1968).

[8] A. J. Carty and A. Efraty, *Inorg. Chem.*, *8*, 543 (1969).

[9] W. Chodkiewicz, P. Cadiot, 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) $C_7H_8W(CO)_3$: 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) $C_5H_5Co(CO)I_2$: R. B. King, *Inorg. Chem.*, *5*, 82 (1966). (e) $C_6H_5CH_2$-$Mo(CO)_3C_5H_5$: R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, *88*, 709 (1966). (f) $[C_5H_5NiCO]_2$, $C_8H_8Fe(CO)_3$, nor-$C_7H_8Cr(CO)_4$, $C_7H_8Rr(RO)_3$, $C_7H_8Mo(CO)_3$, 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.

	Properties			Preparation				Analyses [c]			
Compound [a]	Color	m.p.	Reactant [a]	Solvent	Temp [b]	Yield, %		C	H	O	Other
L_3CuCl	white	168-169°	$CuCl_2(H_2O)_2$	EtOH	25°(2)	54 [d]	Calcd.	75.4	4.7	—	
							Found	74.2	4.7	—	
$LAuCl$	white	190-191°	$HAuCl_4$	EtOH	85°(0.25)	18	Calcd.	46.3	2.9	—	7.0(Cl)
							Found	46.5	3.0	—	7.0(Cl)
L_2PdCl_2	yellow	183-184°	$(MeCN)_2PdCl_2$	C_6H_6/CH_2Cl_2	25°(20)	76 [dd]	Calcd.	64.1	4.0	—	
							Found	64.1	4.1	—	
L_2PtCl_2	white	159-161°	H_2PtCl_6 (40% Pt)	EtOH	25°(24)	93 [e]	Calcd.	57.3	3.6	—	
							Found	57.4	3.8	—	
L_3NiCO	pale green	124-125°	$[CpNiCO]_2$	C_6H_6	25°(72)	14 [fggg]	Calcd.	77.5	4.8	1.7	9.8(P)
							Found	77.3	4.7	2.2	10.0(P)
$[LRhCOCl]_2$	orange-brown	104-105°	$[Rh(CO)_2Cl]_2$	CH_2Cl_2/hexane	25°(12)	17 [g]	Calcd.	56.1	3.3	3.5	
							Found	57.1	3.8	4.0	
t—$L_2Fe(CO)_3$	yellow	217-218°	$C_8H_8Fe(CO)_3$	cyclohexane	25°(40)	25 [h]	Calcd.	72.6	4.3	6.6	
							Found	72.2	4.2	6.7	
t—$L_2Cr(CO)_4$	pale yellow	196-198°	$C_7H_8Cr(CO)_4$	hexane	85°(14)	70 [g]	Calcd.	71.6	4.1	8.7	
							Found	71.0	4.2	8.7	
c—$L_3Cr(CO)_3$	yellow	166-168°	$C_7H_8Cr(CO)_3$	C_6H_6	25°(80)	23 [ig]	Calcd.	76.2	4.6	4.8	
							Found	76.0	4.5	4.6	
t—$L_3Cr(CO)_3$	orange	128-129°	$C_7H_8Cr(CO)_3$	C_6H_6	85°(14)	24 [ig]	Found	75.7	4.8	4.8	
c—$L_3Mo(CO)_3$	yellow	185-187°	$C_7H_8Mo(CO)_3$	C_6H_6	25°(78)	44 [g]	Calcd.	73.0	4.5	4.6	8.8(P)
							Found	72.8	4.4	4.6	8.9(P)
c—$L_3W(CO)_3$	pale yellow	200-202°	$C_7H_8W(CO)_3$	MCH [d]	100°(14)	38 [ig]	Calcd.	67.2	4.0	4.3	
							Found	67.3	4.2	4.1	
$CpCoI_2L$	dark blue	185-187°	$CpCo(CO)I_2$	benzene	25°(40)	74 [g]	Calcd.	45.2	3.0	38.1 (I)	8.9(Co)
							Found	45.6	3.1	39.8 (I)	8.6(Co)
$CpFe(CO)BrL$	green	127-128°	$CpFe(CO)_2Br$	benzene	80°(1)	31 [g]	Calcd.	60.1	3.9	3.1	15.5(Br)
							Found	60.7	3.8	3.3	15.9(Br)
$CpMo(CO)_2$-(COMe)L	yellow	114-115°	$CpMo(CO_3Me$	MeCN	25°(72)	14 [ig]	Calcd.	63.8	4.2	8.8	5.7(P)
							Found	63.9	4.3	8.9	5.8(P)
$CpMo(CO)_2$-$(COCH_2Ph)L$	yellow	123-124°	$CpMo(CO)_3CH_2Ph$	MeCN	25°(80)	15 [ig]	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=$(C_6H_5)_2PC\equiv CC_6H_5$; 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 dichromethane 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[1,11,12] 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 stirerd 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 chromatographed on a 2×60 cm alumina column. An orange band of *trans*—$[(C_6H_5)_2PC\equiv CC_6H_5]_3Cr(CO)_3$ appeard 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*—$[(C_6H_5)_2PC\equiv CC_6H_5]_3Cr(CO)_3$ 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 $\nu(C\equiv C)$ frequencies were measured on a tenfold expanded abscissa scale with each spectrum being calibrated with the spectrum of free $(C_6H_5)_2PC\equiv CC_6H_5$. The reproducibility of these measurements was better than ±0.5 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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(11) G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).
(12) T. A. Manuel, *Advan. Inorg. Chem. Radiochem.*, 3, 181 (1965).

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

Compound	$Ph_2PC{\equiv}CPh$ Derivative			$Ph_2PC{\equiv}CPPh_2$ Derivative[e]	
	$\nu(C{\equiv}C)$[a]	$\Delta\nu$[b]	$\nu(CO)$[c]	$\nu(C{\equiv})$[a]	$\Delta\nu$[b]
L	2165	0.0		2097	0
L_3CuCl	2173.5	8.5		2124	27
$LAuCl$	2181	16.0		2136	39
L_2PdCl_2	2179	14.0		2135	38
L_2PtCl_2	2180.5	15.5		2136	39
L_3NiCO	2170.5	5.5	1925(s)	2113	16
$[LRh(CO)Cl]_2$	2179	14.0	1994(s)	2128	31
t—$L_2Fe(CO)_3$	2177	12.0	1898(s), 1886(s)		
t—$L_2Cr(CO)_4$	2175	10.0	1898(s)		
c—$L_3Cr(CO)_3$	2176.5	11.5	1938(s), 1846(s)		
t—$L_3Cr(CO)_3$	2176	11.0	1957(w), 1855(s)[f]		
c—$L_3Mo(CO)_3$	2176.5	11.5	1950(s), 1853(s)	2128	31
c—$L_3W(CO)_3$	2177	12.0	1945(s), 1848(s)		
$CpCoI_2L$	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]		
$CpMo(CO)_2(COCH_2Ph)L$	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 $\nu(C{\equiv}C)$ 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] $\nu(CO)$ frequencies in the Nujol mull spectrum: 1962(m), 1878(s), 1846(s) cm^{-1}. [g] $\nu(NO)$ frequency. [h] Acyl $\nu(CO)$ 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. $C_5H_5CoI_2[(C_6H_5)_2PC{\equiv}CC_6H_5]$. τ 4.69 (singlet) from the five π-cyclopentadienyl protons.

B. $C_5H_5Fe(CO)Br[(C_6H_5)_2PC{\equiv}CC_6H_5]$. τ 5.32 (broad singlet, width at half-height 8 c.p.s.) from the five π-cyclopentadienyl protons.

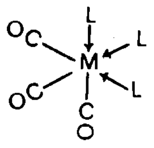
C. $C_5H_5Mo(CO)_2(COCH_3)[(C_6H_5)_2PC{\equiv}CC_6H_5]$. τ 4.81 (doublet, $J = 2$ c.p.s.) from the five π-cyclopentadienyl protons and τ 7.41 (singlet) from the three methyl protons of the acetyl group.

D. $C_5H_5Mo(CO)_2(COCH_2C_6H_5)[(C_6H_5)_2PC{\equiv}CC_6H_5]$. 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 $\nu(C{\equiv}C)$ 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 $\nu(CO)$ frequency in the $[(C_6H_5)_2PC{\equiv}CC_6H_5]_2Cr(CO)_4$ obtained from norbornadienetetracarbonylchromium and the ligand in boiling benzene clearly indicates it to be the *trans* isomer[13] 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 $C_7H_8M(CO)_3$ (M = Cr, Mo, and W) with diphenylphosphinophenylacetylene at room temperature gave $[(C_6H_5)_2PC{\equiv}CC_6H_5]_3M(CO)_3$ products exhibiting the two infrared $\nu(CO)$ frequencies with positions and relative intensities corresponding to those expected for the *cis*-isomer[14] (I: $L = (C_6H_5)_2PC{\equiv}CC_6H_5$; M = Cr, Mo, and W) formed by simple replacement of the cycloheptatriene ring with three ligand molecules as in a variety of known[15] reactions of cycloheptatriene-metal tricarbonyls with tricovalent phosphorus and other Lewis base ligands. However, if the reaction between the chromium complex $C_7H_8Cr(CO)_3$ and diphenylphosphinophenylacetylene is carried out at 85°, two isomeric $[(C_6H_5)_2PC{\equiv}CC_6H_5]_3M(CO)_3$ derivatives were obtained which could be separated readily by chromatography on alumina. The more strongly adsorbed yellow isomer was identical to the *cis*—$[(C_6H_5)_2PC{\equiv}CC_6H_5]_3Cr(CO)_3$ obtained in the room temperature reaction. The less strongly adsorbed orange isomer also exhibited two $\nu(CO)$ frequencies in solution, but with a relative intensity pattern consistent with that of known *trans*—$L_3M(CO)_3$ complexes II; the orange isomer, therefore, is formulated as *trans*—$[(C_6H_5)_2PC{\equiv}CC_6H_5]_3Cr(CO)_3$



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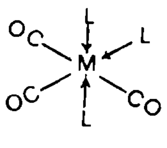

II

(II: $L = (C_6H_5)_2PC{\equiv}CC_6H_5$; $M = Cr$). The occurrence of only two rather than the predicted[14] three $\nu(CO)$ frequencies in *trans*–$(R_3P)_3M(CO)_3$ 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*–$[(C_6H_5)_2PC{\equiv}CC_6H_5]_3Cr(CO)_3$ 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 previously[4] found for the Raman $\nu(C{\equiv}C)$ frequencies of analogous metal complexes of the bridging acetylenic ditertiary phosphine $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ as contrasted with the presence of two diphenylphosphino substituents on the carbon-carbon triple bond in $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$. Nevertheless, the shifts in the infrared $\nu(C{\equiv}C)$ frequencies of the complexes of $(C_6H_5)_2PC{\equiv}CC_6H_5$ are still greater than the shifts in the Raman $\nu(C{\equiv}C)$ frequencies in the relatively limited number of $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ complexes which have been measured;[1] the insulating methylene groups between the diphenylphosphino groups and the carbon-carbon triple bond in $(C_6H_5)_2PCH_2C{\equiv}CCH_2P(C_6H_5)_2$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ is 2165 cm^{-1} and that in the disubstituted $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ is 2097 cm^{-1}. That this is an effect of the empty d orbitals rather 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 $\nu(C{\equiv}C)$ frequency[20] in $(CH_3)_3SiC{\equiv}CSn(CH_3)_3$ occurs at 2079 cm^{-1} which is close to that in $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ complexes parallels that in $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ 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 $(C_6H_5)_2PC{\equiv}CC_6H_5$ 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 $(C_6H_5)_2P(E)C{\equiv}CC_6H_5$ ($E = O$ 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 $[(C_6H_5)_2PC{\equiv}CC_6H_5]_nM(CO)_{3-n}$ ($M = Cr$, Mo, 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 demonstrated[21] 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 ν(CO) frequencies and the higher Cotton-Kraihanzel approximate carbon-oxygen stretching force constants in tetrahedral metal carbonyl derivatives[23] 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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