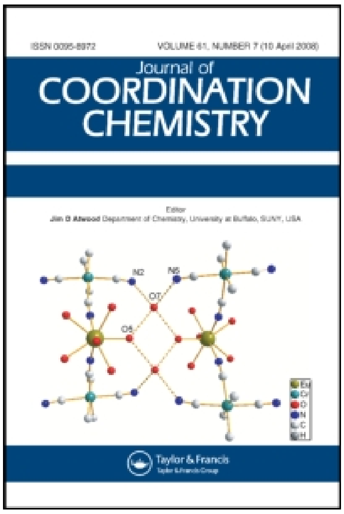

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A PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE STUDY OF TERTIARY PHOSPHINE DERIVATIVES OF GROUP VI METAL CARBONYLS. IV. SUBSTITUTED TRIARYLPHOSPHINES

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A PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE STUDY OF TERTIARY PHOSPHINE DERIVATIVES OF GROUP VI METAL CARBONYLS. IV. SUBSTITUTED TRIARYLPHOSPHINES

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Thirty compounds of the type $(ZC_6H_4)_3PM(CO)_5$ where Z is $3\text{-}CH_3$, $4\text{-}CH_3$, $3\text{-}CH_3O$, $4\text{-}CH_3O$, $3\text{-}CF_3$, $4\text{-}CF_3$, 4-Cl, 4-F, $4\text{-}CH_3S$, or $4\text{-}(CH_3)C$ and M is Cr, Mo, or W are reported, in addition to $[4\text{-}(CH_3)_3SiC_6H_4]_3PW(CO)_5$ and $[(2\text{-}CH_3C_6H_4)_n(C_6H_5)_{3-n}P]M(CO)_5$ where n is 1 or 2 and M is Cr, Mo, or W. Phosphorus-31 NMR and infrared data are presented. In general, the compounds containing the more effective electron withdrawing substituents on the tertiary arylphosphines exhibit the larger ^{31}P coordination chemical shifts, the higher carbonyl stretching frequencies, and the larger phosphorus-31-tungsten-183 coupling constants.

INTRODUCTION

Very early in the study of phosphorus coordination compounds by ^{31}P NMR spectroscopy, we observed that the magnitude of phosphorus-31-heavy metal (e.g., W[2], Pt[3], and Rh[4]) coupling constants varies inversely with the basicity of the phosphorus ligand. This observation has been repeatedly substantiated over the ensuing years, particularly for tungsten compounds[5–7]. However, the reasons for the experimental observations have been the subject of different interpretations[8–10]. We proposed that the less basic phosphorus ligands are better π-acceptors, thereby strengthening the metal-phosphorus total bonding and concomitantly increasing the coupling constant. However, since the π-acceptor theory for phosphorus has been much maligned[9–13], alternative explanations have been advanced[5, 6, 9, 10,] to explain the experimental trend. For example, when Z is very electronegative in PZ_3, the ZPZ angles are smaller (containing more p-character) than when Z is less electronegative. As a consequence, the donor lone pair of phosphorus contains more s-character so that in a coordination compound involving donation of this lone pair, the resulting coordinate bond contains more s-character and the coupling constant is larger, since the Fermi constant mechanism is mainly responsible for the coupling. It should be pointed out that this simplified "s-character" theory and the π-bonding theory are not incompatible, but, indeed are complementary. Usually, with large changes in electronegativity of the phosphorus substituent (i.e. in the series F, O, N, C), a corresponding ZPZ angle change occurs[8]. To investigate this problem further we have prepared numerous complexes of substituted arylphosphines with the Group 6 metal carbonyls. The strategy is that the steric aspects, especially bond angles around phosphorus, in the meta- and para-substituted compounds are essentially like the parent triphenylphosphine, but that the electronic aspects are sufficiently different to detect differences in the properties of the compounds. In this way, if the steric properties are identical, then differences in physical properties, *e.g.*, tungsten-phosphorus coupling, could be attributed to electronic aspects.

RESULTS AND DISCUSSION

Coordination compounds of the type $(Ar_3P)M(CO)_5$ where M is Cr, Mo, or W have been synthesized for each of twelve substituted arylphosphines[14], viz., (4-$CH_3C_6H_4)_3P$, (4-$CH_3OC_6H_4)_3P$, (4-$CH_3SC_6H_4)_3P$, (4-$CF_3C_6H_4)_3P$, [4-$(CH_3)_3CC_6H_4]_3P$, (4-$ClC_6H_4)_3P$, (4-$FC_6H_4)_3P$, (3-$CH_3C_6H_4)_3P$, (3-$CH_3OC_6H_4)_3P$, (3-$CF_3C_6H_4)_3P$, (2-$CH_3C_6H_4)(C_6H_5)_2P$, and (2-$CH_3C_6H_4)_2(C_6H_5)P$. The synthetic and analytical data for these compounds, most of which are previously unreported, are given in Table I. The ligands with ortho-substituents have considerable steric effects so that, for example, the tri-o-tolylphosphine did not form isolatable complexes. Indeed, the phenyldi-o-tolylphosphine formed only an impure complex with the small chromium moiety, but did form stable complexes with the larger molybdenum and tungsten pentacarbonyl groups.

The qualitative basicities of these arylphosphines have been measured[15] by their behavior in dichloromethane or diethyl ether solution with anhydrous hydrogen bromide and fall into four categories:

A. No hydrobromide precipitate forms in diethyl ether: (3-$CF_3C_6H_4)_3P$ and (4-$CF_3C_6H_4)_3P$;

TABLE I

Analytical and Preparative Data for $(ZC_6H_4)_3PM(CO)_5$

Z	M	Yield (%)	Color	Melting point (°C)	% C Calcd	% C Found	% H Calcd	% H Found
4-CH_3	Cr	24	yellow	136 d	62.91	62.23	4.26	4.37
3-CH_3	Cr	79	yellow	128–129	62.91	61.44	4.26	4.18
4-CH_3O	Cr	53	yellow	114–116	57.35	58.10	3.89	4.21
3-CH_3O	Cr	56	yellow	74–75	57.35	57.65	3.89	3.69
4-Cl	Cr	68	yellow	155 d[a]	49.54	49.24	2.17	2.28
4-F	Cr	73	yellow	131–132[b]	54.33	54.81	2.38	2.53
4-CF_3	Cr	21	yellow	175 d	47.43	47.27	1.84	1.94
3-CF_3	Cr	63	yellow	121 d	47.43	46.88	1.84	1.90
4-CH_3S	Cr	66	yellow	145 d	52.70	53.01	3.57	3.71
4-$(CH_3)_3C$	Cr	84	yellow	160 d	67.52	67.10	6.31	6.35
4-CH_3	Mo	–	colorless	125 d	57.80	56.96	3.92	3.95
3-CH_3	Mo	75	colorless	128 d	57.80	58.31	3.92	4.45
4-CH_3O	Mo	14	colorless	119–122	53.08	51.95	3.60	3.69
3-CH_3O	Mo	20	colorless	79–81	53.08	52.65	3.60	3.69
4-Cl	Mo	5	colorless	135 d	45.92	45.88	2.01	2.20
4-F	Mo	31	colorless	130–132	50.03	52.20	2.19	2.59
4-CF_3	Mo	16	colorless	150 d	44.47	44.15	1.72	2.01
3-CF_3	Mo	14	colorless	120 d	44.47	44.02	1.72	2.15
4-CH_3S	Mo	20	colorless	115 d	49.06	50.31	3.33	3.69
4-$(CH_3)_3C$	Mo	28	colorless	185 d	63.07	62.75	5.90	6.24
4-CH_3	W	–	colorless	150–152	49.71	49.47	3.37	3.37
3-CH_3	W	88	colorless	141–143	49.71	49.57	3.37	3.35
4-CH_3O	W	45	yellow	123–125	46.18	46.99	3.13	3.37
3-CH_3O	W	17	colorless	90–92	46.18	45.55	3.13	3.37
4-Cl	W	67	colorless	160–161	40.07	39.14	1.75	2.00
4-F	W	–	colorless	136–138	43.16	43.40	1.89	2.13
4-CF_3	W	59	colorless	196–199	39.52	39.30	1.53	1.80
3-CF_3	W	61	colorless	138–139	39.52	39.30	1.53	1.72
4-CH_3S	W	51	colorless	150–152	43.11	42.14	2.92	3.12
4-$(CH_3)_3C$	W	9	colorless	220 d	55.72	53.49	5.21	5.54
Other Compounds, $Ar_3PM(CO)_5$								
Ar_3P	M							
(2-$CH_3C_6H_4)(C_6H_5)_2P$	Cr	55	yellow	150 d	61.55	61.82	3.66	3.72
(2-$CH_3C_6H_4)_2(C_6H_5)P$	Cr	–	yellow	–	–	–	–	–
(2-$CH_3C_6H_4)(C_6H_5)_2P$	Mo	40	colorless	115 d	56.27	56.72	3.34	3.52
(2-$CH_3C_6H_4)(C_6H_5)P$	Mo	41	colorless	125 d	57.05	56.52	3.64	3.73
(2-$CH_3C_6H_4)(C_6H_5)_2P$	W	20	colorless	171–173	48.03	46.90	2.85	3.16
(2-$CH_3C_6H_4)_2(C_6H_5)P$	W	–	colorless	175 d	48.89	47.50	3.12	3.83

[a] 158–160°, ref. 21.

[b] 125–129°, ref. 21.

B. A hydrobromide precipitate forms in ether, but no PH doublet is observable in the ^{31}P NMR spectrum in CH_2Cl_2 solution at room temperature: $(3\text{-}ClC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, and $(3\text{-}CH_3OC_6H_4)_3P$;

C. A PH doublet is observable in the NMR spectrum only after extended treatment with HBr: $(C_6H_5)_3P$ and $[4\text{-}(CH_3)_3SiC_6H_4]_3P$;

D. A PH doublet is observable after routine HBr treatment in CH_2Cl_2: $(4\text{-}CH_3OC_6H_4)_3P$, $(4\text{-}CH_3C_6H_4)_3P$, $(3\text{-}CH_3C_6H_4)_3P$, $[4\text{-}(CH_3)_3CC_6H_4]_3P$ and $(4\text{-}CH_3SC_6H_4)_3P$.

Category D phosphines are the most basic of these tertiary arylphosphines since the proton is coordinated without rapid exchange on the NMR time scale. Category A phosphines with the electronegative trifluoromethyl substituents are the least basic of the group, since there is no evidence of hydrobromide formation under the conditions employed. The relative basicities found in this way generally agree with the order of phosphorus lone pair ionization energies determined by ultraviolet photoelectron spectroscopy[16].

The phosphorus-31 NMR results are given in Table II. The change (coordination shift) in ^{31}P chemical shift of the meta and para substituted phosphines averages 62.7, 44.4 and 27.2 ppm, respectively, for the Cr, Mo, and W complexes. These values are in agreement with previous studies[2a, 17]. On the other hand, the ortho-substituted arylphosphine ligands, $(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$ and $(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$, have coordination shifts which are considerably greater, viz., 72.8 and 67.7 (Cr), 53.3 and 49.1 (Mo), and 37.8 and 32.4 ppm (W), respectively. These unusually large coordination shifts are not due to unusually stronger metal-phosphorus bonding in these complexes, since the other properties such as carbonyl stretching frequencies are normal (vide infra), but are probably due to the loss of the special interaction of the phosphorus lone pair with the ortho substituent (commonly called the γ-effect)[18, 19] in the free ligand. The ortho-substituted arylphosphines have abnormally large upfield chemical shifts which are lost upon quaternization[15] or coordination, so that the chemical shifts of the resulting quaternary phosphonium salts or coordination compounds are essentially normal and the corresponding coordination or quaternization shifts are large.

In a closely related series of compounds where the ligand bond angles are essentially constant and the metal moiety is the same, it might be expected that the better coordinating ligand would have the larger coordination shift. This premise has not been proven but seems a reasonable expectation if the variables are restricted as they have been in this study. Table III lists the coordination shifts for these compounds. In order to smooth out the small differences between some of the compounds, the Cr, Mo, and W coordination shifts are summed for each ligand. It is clear that the ligands with the largest total coordination shifts are those with the lowest basicities. The groupings by coordination shifts seem to fall into three categories. Those with larger than average coordination shifts: $(3\text{-}CF_3C_6H_4)_3P$ and $(4\text{-}CF_3C_6H_4)_3P$; those with moderately large coordination shifts: $(4\text{-}ClC_6H_4)_3P$ and $(4\text{-}FC_6H_4)_3P$; and the remainder with smaller coordination shifts. Thus the ligands seem to behave in roughly the same order as they did in the protonation basicity studies,

TABLE II

Phosphorus-31 Chemical Shifts[a] in $Ar_3PM(CO)_5$

Ar_3P	δ_{ligand}	$\delta_{Cr\ complex}$	$\delta_{Mo\ complex}$	$\delta_{W\ complex}$	Δ^b_{Cr}	Δ^b_{Mo}	Δ^b_W
$(4\text{-}CH_3C_6H_4)_3P$	−8.0	52.8	34.5	17.7	60.8	42.5	25.7
$(3\text{-}CH_3C_6H_4)_3P$	−5.3	54.6	36.7	20.4	59.9	42.0	25.7
$(4\text{-}CH_3OC_6H_4)_3P$	−10.2	50.9	33.0	15.4	61.1	43.2	25.7
$(3\text{-}CH_3OC_6H_4)_3P$	−2.1	58.5	40.5	23.5	60.6	42.6	25.6
$(4\text{-}ClC_6H_4)_3P$	−8.5	56.9	38.3	20.4	65.4	46.8	28.9
$(4\text{-}FC_6H_4)_3P$	−9.0	55.2	36.5	18.8	64.2	45.5	27.8
$(4\text{-}CF_3C_6H_4)_3P$	−6.0	60.6	42.5	24.2	66.6	48.5	30.5
$(3\text{-}CF_3C_6H_4)_3P$	−5.0	62.4	43.2	25.1	67.4	48.2	30.1
$(4\text{-}CH_3SC_6H_4)_3P$	−8.3	53.6	35.3	18.3	61.9	43.6	26.6
$[4\text{-}(CH_3)_3CC_6H_4]_3P$	−9.1	51.3	33.4	16.6	60.4	42.5	25.7
$(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$	−13.4	54.3	35.7	19.0	67.7	49.1	32.4
$(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$	−21.4	51.4	31.9	16.4	72.8	53.3	37.8

[a] δ (ppm) is positive if downfield from 85% H_3PO_4.

[b] Δ (ppm) = $\delta_{complex} - \delta_{ligand}$; coordination shift.

TABLE III
Coordination Shifts in $(ZC_6H_4)_3PM(CO)_5$

Z	Δ^a_{Cr}	Δ^a_{Mo}	Δ^a_W	Δ_{sum}
3-CF_3	67.4	48.2	30.1	145.7
4-CF_3	66.6	48.5	30.5	145.6
4-Cl	65.4	46.8	28.9	141.1
4-F	64.2	45.5	27.8	137.6
4-CH_3S	61.9	43.6	26.6	132.1
H^c	61.3	43.5	26.6	131.4
4-CH_3O	61.1	43.2	25.7	130.0
4-CH_3	60.8	42.5	25.7	129.0
3-CH_3O	60.6	42.6	25.6	128.8
4-$(CH_3)_3C$	60.4	42.5	25.7	128.6
4-CH_3	59.9	42.0	25.7	127.6

[a] Δ (ppm) = $\delta_{complex} - \delta_{ligand}$.
[b] $\Delta_{sum} = \Delta_{Cr} + \Delta_{Mo} + \Delta_W$.
[c] Ref. 2a.

TABLE IV
$^1J_{W-P}$ for $(ZC_6H_4)_3PW(CO)_5$

Z	J_{W-P}(Hz)	Z	J_{W-P}(Hz)
4-CH_3O	266	H	243
3-CF_3	266	4-$(CH_3)_3Si$	243
4-CF_3	258	3-CH_3O	242
4-F	258	4-CH_3S	240
4-Cl	254	4-$(CH_3)_3C$	236
4-CH_3	250	4-CH_3	234

with the obvious exception that the order is now inverse, i.e., the less basic arylphosphines have the largest coordination shifts.

The phosphorus-31-tungsten-183 coupling constants in the $(ZC_6H_4)_3PW(CO)_5$ compounds are listed in Table IV. Again, with the exception of the

TABLE V
Infrared Spectra of the Carbonyl Region for $Ar_3PM(CO)_5$

Ar_3P	M	$\nu_{CO}(cm^{-1})^a$				
$(4\text{-}CH_3C_6H_4)_3P$	Cr	2061.0 m	1980.0 w		1940.0 vs	
$(3\text{-}CH_3C_6H_4)_3P$	Cr	2061.5 m	1980.5 w		1941.0 vs	1914.0 w
$(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$	Cr	2064.5 m	1982.6 w	1946.6 vs	1941.6 vs	
$(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$	Cr	2060.5 m	1979.6 w		1940.0 vs	
$(4\text{-}CH_3OC_6H_4)_3P$	Cr	2060.6 m	1979.6 w		1939.6 vs	
$(3\text{-}CH_3OC_6H_4)_3P$	Cr	2062.0 m	1982.0 w		1940.6 vs	
$(4\text{-}ClC_6H_4)_3P$	Cr	2064.5 m	1983.6 w	1954.0 vs	1945.0 vs	1913.5 w
$(4\text{-}FC_6H_4)_3P$	Cr	2061.0 m	1984.0 w	1953.0 vs	1942.0 vs	
$(4\text{-}CF_3C_6H_4)_3P$	Cr	2060.5 m			1957.0 vs	
$(3\text{-}CF_3C_6H_4)_3P$	Cr	2068.0 m	1991.0 w	1961.0 s	1949.6 vs	
$(4\text{-}CH_3SC_6H_4)_3P$	Cr	2065.5 m	1984.6 w		1940.6 vs	
$(4\text{-}tBuC_6H_4)_3P$	Cr	2070.0 m	1992.0 w		1942.0 vs	
$(4\text{-}CH_3C_6H_4)_3P$	Mo	2071.0 m		1948.6 s	1941.0 vs	
$(3\text{-}CH_3C_6H_4)_3P$	Mo	2071.0 m	1986.0 w		1948.6 vs	
$(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$	Mo	2072.0 m	1984.6 w		1949.6 vs	
$(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$	Mo	2073.5 m	1987.6 w	1948.6 vs	1941.6 vs	
$(4\text{-}CH_3OC_6H_4)_3P$	Mo	2070.5 m	1984.0 w		1947.0 vs	
$(3\text{-}CH_3OC_6H_4)_3P$	Mo	2072.0 m	1986.6 w		1949.0 vs	
$(4\text{-}ClC_6H_4)_3P$	Mo	2073.0 m	1993.0 w	1951.6 vs	1945.0 s	
$(4\text{-}FC_6H_4)_3P$	Mo	2075.0 m			1953.0 vs	1923.0 w
$(4\text{-}CF_3C_6H_4)_3P$	Mo	2074.0 m		1953.6 vs	1944.6 vs	
$(3\text{-}CF_3C_6H_4)_3P$	Mo	2079.5 m			1956.6 vs	
$(4\text{-}CH_3SC_6H_4)_3P$	Mo	2071.0 m			1940.6 vs	
$(4\text{-}tBuC_6H_4)_3P$	Mo	2061.5 m		1940.6 s	1938.6 s	
$(4\text{-}CH_3C_6H_4)_3P$	W	2071.0 m		1948.6 s	1941.0 vs	
$(3\text{-}CH_3C_6H_4)_3P$	W	2070.5 m	1978.6 w		1940.0 vs	1911.0 w
$(2\text{-}CH_3C_6H_4)(C_6H_5)_2P$	W	2076.0 m	1981.0 w	1944.6 vs	1939.6 vs	
$(2\text{-}CH_3C_6H_4)_2(C_6H_5)P$	W	2074.6 m	1978.6 w	1945.0 vs	1939.6 vs	
$(4\text{-}CH_3OC_6H_4)_3P$	W	2069.5 m	1978.0 w		1938.6 vs	
$(3\text{-}CH_3OC_6H_4)_3P$	W	2071.0 m	1979.0 w		1942.0 vs	
$(4\text{-}ClC_6H_4)_3P$	W	2073.0 m	1983.6 w	1952.5 s	1944.0 vs	1912.0 w
$(4\text{-}FC_4H_4)_3P$	W	2069.5 m		1950.0 s	1942.0 vs	
$(4\text{-}CF_3C_6H_4)_3P$	W	2074.0 m		1959.0 s	1947.5 vs	
$(3\text{-}CF_3C_6H_4)_3P$	W	2074.5 m		1959.6 s	1948.6 vs	
$(4\text{-}CH_3SC_6H_4)_3P$	W	2073.0 m	1980.5 w		1940.0 vs	
$(4\text{-}tBuC_6H_4)_3P$	W	2069.5 m	1978.6 w		1939.6 vs	

[a] m, medium; w, weak; s, strong; vs, very strong

TABLE VI
CO Force Constants[a] in $(ZC_6H_4)_3PM(CO)_5$

Z	Cr			Mo			W		
	k_1	k_2	k_i	k_1	k_2	k_i	k_1	k_2	k_i
4-CH_3	15.38	15.79	0.30	15.54	15.85	0.32	15.54	15.85	0.32
3-CH_3	15.40	15.80	0.29	15.52	15.93	0.31	15.40	15.84	0.32
4-CH_3O	15.37	15.78	0.30	15.50	15.91	0.30	15.38	15.82	0.32
3-CH_3O	15.39	15.80	0.30	15.53	15.94	0.30	15.43	15.86	0.32
4-Cl	15.61	15.86	0.29	15.59	15.90	0.31	15.60	15.89	0.31
4-F	15.60	15.81	0.29	15.59	16.00	0.30	15.56	15.85	0.31
4-CF_3	15.62	15.98	0.25	15.62	15.90	0.32	15.71	15.93	0.31
3-CF_3	15.73	15.92	0.29	15.65	16.07	0.30	15.72	15.95	0.31
4-CH_3S	15.40	15.82	0.31	15.41	15.85	0.32	15.40	15.85	0.33
4-$(CH_3)_3C$	15.42	15.86	0.31	15.40	15.78	0.30	15.39	15.83	0.32

[a] Force constants (mdynes/angstrom) calculated according to Cotton and Kraihanzel[20].

p-methoxy compound which has a relatively large coupling constant (266 Hz), the largest coupling constants occur in those compounds which have the most electronegative substituents on the phenyl ring, i.e., those compounds in basicity categories A and B. The two compounds which have substituents whose mesomeric effect is nil and whose inductive effect is electron donating, viz. $(3\text{-}CH_3C_6H_4)_3P$ and $[4\text{-}(CH_3)_3CC_6H_4]_3P$, have the smallest W-P coupling constants of 234 and 236 Hz, respectively. The other tertiary phosphines have intermediate W-P coupling constants. $[4\text{-}(CH_3)_3SiC_6H_4]_3P$ behaves like triphenylphosphine in this respect, with the inductive electron releasing and mesomeric electron attracting properties of the para-trimethylsilyl group apparently balancing each other. It should be noted however that the uncertainty (±5 Hz) of the W-P coupling constant measurements is about the same magnitude as the differences between compounds, so that these comparisons must be used with caution.

Infrared data in the carbonyl stretching frequency region are given in Table V and the CO force constants calculated according to the Cotton-Kraihanzel method[20] are given in Table VI. Qualitatively these data are in agreement with the chemical shift and coupling constant data, i.e., the less basic phosphines have the higher CO stretching frequencies and stronger CO stretching force constants which is expected for better π-acceptor ligands. This trend can easily be seen if the data are reduced by separately averaging the individual k_1 (CO trans to the phosphine) and the individual k_2 (CO's cis to the phosphine) force constants over the three compounds (Cr, Mo, and W) for each ligand. These average force constants appear in Table VII, along with the known phosphorus lone pair ionization energies (IE). A rather good, and perhaps fortuitous, correlation (correlation coefficient = 0.95) exists between the average k_1 CO force constant and the phosphorus ionization energies for the eight compounds for which the I.E.'s are known.

A previous infrared study of several $(ZC_6H_4)_3PCi(CO)_5$ compounds where Z is H, 3-F, 3-Cl, 4-F, and 4-Cl has been reported[21]. The results are in substantial agreement with our results for the ligands in common, $(4\text{-}FC_6H_4)_3P$ and $(4\text{-}ClC_6H_4)_3P$.

In conclusion, there is reasonable qualitative agreement in the order of basicities of substituted aryl tertiary phospines as measured by NMR protonation studies and by ultraviolet photoelectron spectroscopy with the order of ^{31}P coordination shifts in

TABLE VII
Average CO Force constants in $(ZC_6H_4)_3PM(CO)_5$

Z	k_1^a	k_2^a	IE(ev)[b]
3-CF_3	15.70	15.98	–
4-CF_3	15.65	15.94	8.65
4-Cl	15.60	15.88	8.18
4-F	15.58	15.89	8.12
4-CH_3	15.49	15.83	7.6
3-CH_3O	15.45	15.87	7.72
3-CH_3	15.44	15.86	7.68
4-CH_3O	15.42	15.84	7.48
4-CH_3S	15.40	15.84	–
4-$(CH_3)_3C$	15.40	15.82	7.52

[a] Force constants (mdynes/angstrom) obtained by averaging k for the Cr, Mo, and W compounds.
[b] From ref. 16.

$Ar_3PM(CO)_5$, with the carbonyl stretching frequencies and CO force constants in $(Ar_3P)M(CO)_5$, and with the phosphorus-31-tungsten-183 coupling constants in $(Ar_3P)W(CO)_5$. These trends are expected and simply explained by the π-bonding theory, whereby the more electron deficient phosphorus donor ligand is a better π-acceptor and the M–P bond is thus synergically strengthened by increased σ-bonding.

EXPERIMENTAL

Phosphorus-31 NMR measurements were made on concentrated CH_2Cl_2 solutions with a Varian Associates DP-60 spectrometer operating at 24.3 MHz with 85% H_3PO_4 as the external standard. Chemical shifts are reported as positive when downfield from H_3PO_4. Infrared spectra were recorded on cyclohexane solutions of the metal carbonyl derivatives in sodium chloride cells of 0.1 mm sample thickness with a Perkin-Elmer Model 621 or 421 double beam spectrometer and were calibrated using either the polystyrene absorption at 1601 cm^{-1} or saturated water vapor lines at 2016.0, 1942.6, 1919.0, and 1889.6 cm^{-1}. Microanalyses were performed by Dr. Franz Kasler of the University of Maryland and by Galbraith Laboratories, Knoxville, TN.

Arylphosphines were prepared as described previously[14]. The $(Ar_3P)Cr(CO)_5$ and $(Ar_3P)W(CO)_5$ compounds were made by heating the metal carbonyl (about 5 g) with the ligand in a 3:1 (metal carbonyl:ligand) molar ratio in 40 ml of refluxing diethylene glycol dimethyl ether under N_2 for 15–30 min. $(Ar_3P)Mo(CO)_5$ compounds were prepared in the same manner in methylcyclohexane solution. After cooling, the mixture was filtered to remove some of the unreacted metal carbonyl and the filtrate was evaporated under reduced pressure. The residue was crystallized by chilling a CH_2Cl_2/CH_3OH solution at $-78°C$. The crude product was heated at 40–50°C and 1 mm of Hg in order to remove any excess metal hexacarbonyl by sublimation, after which the remaining product was chromatographed on alumina (12 cm x 4 cm diameter) with benzene:pentane (1:3) as the eluent. The chromatographed product was recrystallized from CH_2Cl_2/CH_3OH solution. Analytical and preparative data for these compounds are given in Table I.

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