complexes[37] as well as in pure triphenylphosphine,[30] the C–P–C angle averages 103°. On the other hand, in all of these complexes the M–P–C angles are correspondingly larger than the value expected for sp^3 hybridization of phosphorus. This may indicate that in the pure ligand and in its complexes the P–C bonds have a p character more than sp^3.

Some of the $P_i-C_{ij1}-C_{ij4}$ angles seem to indicate significant bending of the rings when compared with the ideal angle of 180°, although none is less than 173°.

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Tungsten-183–Phosphorus-31 Spin–Spin Coupling Interactions in Pentacarbonyltungsten Complexes

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The magnitudes of $^{183}W-^{31}P$ nuclear spin–spin coupling constants have been determined in a series of $LW(CO)_5$ complexes and are found to increase linearly with a correlation coefficient of greater than 0.95 as the electronegativity of the substituents on the phosphorus ligand L increases: $P(CH_2O)_3CC_4H_9 < P(SCH_2)_3CC_5H_{11} < P(N(CH_3)CH_2)_3CC_5H_{11} < P(OCH_2)_3CCH_3 < PF_3$. This trend can be interpreted in terms of the increasing s character of the $^{183}W-^{31}P$ bond and the rise in positive charge on phosphorus as more electronegative substituents are bound to phosphorus. Carbonyl stretching frequencies for these complexes have been assigned to A_1^1, B_1, A_1^2, and E modes and to the ^{13}CO satellites of the E band. The approximate method of Cotton and Kraihanzel was used to obtain the force constants k_1, k_2, and k_i. The stretching frequencies of the E mode were found to increase in the series: $P(N(CH_3)CH_2)_3CC_5H_{11} < P(CH_2O)_3CC_4H_9 < P(OCH_2)_3CC_5H_{11} < P(SCH_2)_3CC_5H_{11} < PF_3$. Attempts to correlate the $^{183}W-^{31}P$ coupling constants with the A_1^1 or E mode frequencies and k_1 produced correlation coefficients of 0.70, 0.79 and 0.51, respectively. Evaluation of the ligands in terms of σ- and π-donating capacities after the method of Graham resulted in correlation coefficients of 0.55 and 0.35, respectively.

Introduction

The magnitudes of nuclear spin–spin coupling constants for ^{31}P coupled to various heavy-metal nuclei have been measured[2–10] in hopes of gaining further information on the nature of phosphorus–metal bonding. It is generally agreed that spin–spin coupling is transmitted through σ bonds and is a function of the s character of the bonding atoms. Whether or not the s-electron density may be increased by a synergic mechanism which depends upon the π-bonding capacity of the trivalent phosphorus ligand is still under discussion.[11] Theoretical calculations by Schneider and Buckingham[12] suggest that the effect of π bonding on metal–phosphorus coupling constants is extremely small. Pidcock, *et al.*,[2] and Allen and Pidcock[3] have provided further evidence suggesting that a π-bonding coupling mechanism is negligible.

On the other hand, the increase in $^{195}Pt-^{31}P$ coupling values observed in *cis* and *trans* complexes of the type L_2PtCl_2 has been attributed by Grim and coworkers[5] to an increasing π-acceptor capacity in the series: $R_3P < R_2C_6H_5P < R(C_6H_5)_2P$. Moreover, in complexes of the type $LW(CO)_5$ it has been shown[4] that a linear correlation exists between the increasing $^{183}W-^{31}P$ coupling constants and the increasing frequency of the carbonyl E mode in the series: $L = R_3P < R_2C_6H_5P < R(C_6H_5)_2P < (C_6H_5)_3P$. More recently Grim, McAllister, and Singer[13] found a similar correlation having a different slope among the phosphites: $(i\text{-}C_3H_7O)_3P < (n\text{-}C_4H_9O)_3P < (C_2H_5O)_3P < (CH_3O)_3P < (C_6H_5O)_3P$.

The purpose of the present study was to determine the extent to which the $^{183}W-^{31}P$ coupling constant depends upon various parameters which have been used as a measure of the σ- and/or π-bonding characteristics of the phosphorus ligand. In this work are reported $^{183}W-^{31}P$ constants and carbonyl stretching frequency assignments for complexes of the type LW-

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$(CO)_5$ where L = PF_3, $P(OCH_2)_3CC_5H_{11}$, $P(CH_2O)_3CC_4H_9$, $P(N(CH_3)CH_2)_3CC_5H_{11}$, and $P(SCH_2)_3CC_5H_{11}$. For all but the first ligand, the structures of these donors are constrained so that configurational changes on coordination are minimal and steric requirements are relatively constant. The observed $^{183}W-^{31}P$ coupling constants for the complexes are compared to the electronegativity of the phosphorus substituent, the $A_1{}^1$ and E mode carbonyl stretching frequencies, the Cotton–Kraihanzel[14] force constant k_1, and the $\Delta\pi$ and $\Delta\sigma$ parameters derived by Graham.[15]

Experimental Section

Infrared spectra of the carbonyl region from cyclohexane solutions of the compounds were obtained on a Beckman Model 12 grating spectrometer using potassium bromide optics. The spectrometer was calibrated with water vapor in the region below 2000 cm^{-1} and with carbon monoxide in the region above 2000 cm^{-1} just prior to the measurements. Proton nmr spectra were recorded using neat samples or approximately 15% deuteriochloroform solutions with a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard.

The ^{31}P nmr measurements of saturated solutions in 15-mm tubes were recorded with a Varian Associates HR-60 spectrometer using phosphoric acid as an external standard. Dichloromethane was used as a solvent for all of the ligands and complexes except $C_5H_{11}C(CH_2S)_3PW(CO)_5$ which required carbon disulfide to overcome solubility problems. The $^{183}W-^{31}P$ coupling constant of $PF_3W(CO)_5$ in Freon was obtained from the ^{19}F spectrum by using indor techniques. Thus $^{31}P-^{19}F$ decoupling was observed in the ^{19}F spectrum while irradiation in the ^{31}P region was carried out.

Melting points are reported uncorrected. Analyses were done by Gaibraith Laboratories, Knoxville, Tenn. Molecular weights were determined from mass spectra recorded on an Atlas CH4 single-focusing spectrometer at an energy of 70 eV.

Tungsten hexacarbonyl was purchased from Pressure Chemical Co. Hexamethylphosphoramide and trimethyl orthovalerate were purchased from Eastman Organic Chemicals.

The triol $(HOCH_2)_3CC_5H_{11}$[16] was prepared as previously described as were $P(CH_2OH)_3$,[17] $P(SCH_3)_3$,[18] $C_6H_5NH_2W(CO)_5$,[19] $(C_6H_5O)_3PW(CO)_5$,[13] and $(C_2H_5)_3PW(CO)_5$.[13] The complexes $(C_6H_5)_3PW(CO)_5$, $(C_4H_9)_3PW(CO)_5$, and $C_6H_{11}NH_2W(CO)_5$ were kindly provided by R. J. Angelici.

$(BrCH_2)_3CC_5H_{11}$.—The tribromide was prepared from the reaction of PBr_3 and $(HOCH_2)_3CC_5H_{11}$ in a manner previously described but in yields of no greater than 13%.[20] A greatly improved synthesis resulted from the application of a modified Michaelis–Arbuzov reaction.[21] A solution of 279 g (0.9 mol) of triphenyl phosphite, 157 g (1.0 mol) of benzyl bromide, and 53 g (0.3 mol) of $(HOCH_2)_3CC_5H_{11}$ was heated at 160° for 32 hr. The solution was distilled under a pressure of 0.1 mm and a mixture of phenol and $(BrCH_2)_3CC_5H_{11}$ was collected within a temperature range of 55–115°. The distillate was dissolved in 200 ml of ether and extracted with 0.1 *N* KOH. The ether layer was dried with magnesium sulfate and stripped of solvent, and the product was redistilled at 115° (0.1 mm) to give 87 g (78.2%) of product. The methylene resonance was observed at 3.89 ppm in deuteriochloroform and at 3.36 ppm in a neat sample. The proton resonances of the pentyl group were observed between 0.7 and 1.7 ppm as a broad second-order spectrum of peaks.

$(HSCH_2)_3CC_5H_{11}$.—The reduction of the tribromide to the trimercaptan was effected by previously described methods.[22] The new mercaptan was distilled at 110–115° (1.5 mm) in 40% yield. The nmr spectrum obtained from a deuteriochloroform solution showed a doublet ($J_{HSCH_2} = 8.45$ Hz) at 2.52 ppm. The expected sulfhydryl proton triplet was lost in the pentyl proton region which ranged from 0.65 to 1.8 ppm.

$(CH_3HNCH_2)_3CC_5H_{11}$.—The tribromide was converted to the triamine by methods previously described.[23] The new amine was distilled at 70° (0.5 mm) in 57% yield. The proton spectrum of a neat sample showed a singlet methyl signal at 2.32 ppm, a methylene signal at 2.42 ppm, an NH signal at 1.5 ppm, and pentyl proton resonances from 0.7 to 1.4 ppm.

$P(SCH_2)_3CC_5H_{11}$.—The thiophosphite ligand was prepared by a procedure previously described but with some modification.[22] To 17 g (0.08 mol) of trimercaptan stirred at 70° under nitrogen was added dropwise over a period of 30 min 13 g (0.08 mol) of $P(N(CH_3)_2)_3$. The temperature was raised to 120° and held at that point for 16 hr. A viscous light yellow oil formed which was not distillable at 170° (0.1 mm). Purification was afforded chromatographically by eluting the oil with Skelly B on a silica gel column. The light yellow oil was obtained in 50% yield (10 g). The proton nmr spectrum, in addition to the broad pentyl region ranging from 0.8 to 1.5 ppm, consisted of a doublet ($J_{PSCH_2} = 2.12$ Hz) at 2.85 ppm. The ligand (mol wt 252) exhibited a parent peak in the mass spectrum at 252.

$P(N(CH_3)CH_2)_3CC_5H_{11}$.—The triamine was converted to the bicyclic aminophosphine by methods previously described.[23] The new ligand was found to distil at 80° (0.5 mm) and was prepared in 86% yield. The proton nmr spectrum of a deuteriochloroform solution showed two doublets ($J_{PNCH_3} = 16.45$ Hz and $J_{PNCH_2} = 3.30$ Hz) at 2.55 and 2.58 ppm, respectively. The pentyl proton resonances ranged from 0.8 to 1.5 ppm. The parent peak of the mass spectrum of the ligand (mol wt 243) was at 243.

$P(N(CH_3)CH_2)_3CC_3H_7$.—The ligand was prepared in a way identical with that of the pentyl analog described above. The product, which distilled at 60° (0.5 mm), was obtained in 84.6% yield. The proton nmr spectrum was identical with that of the pentyl analog except for the propyl proton region (0.7–1.4 ppm).

$P(CH_2O)_3CC_4H_9$.—This ligand was synthesized from $C_4H_9C(OCH_3)_3$ and $P(CH_2OH)_3$ by using previously described methods.[24] The sweet-smelling liquid distilled at 63° (0.75 mm) and was prepared in 29% yield. The proton nmr spectrum, in addition to the broad butyl region (0.8–1.8 ppm), showed a doublet ($J_{PCH_2} = 7.84$ Hz) at 4.37 ppm. The expected parent peak at 190 was not observed in the mass spectrum. The peak of highest mass at 160 probably resulted from the relatively facile loss of CH_2O from the ring system.

$PF_3W(CO)_5$.—This compound was generously donated by R. Clark of Florida State University.

$C_5H_{11}C(CH_2O)_3PW(CO)_5$.—The complex was prepared by the method of Magee and coworkers.[25] The white crystals were obtained in 22% yield, melted at 147–148°, and had a parent peak in the mass spectrum at 527 as expected. The ^1H nmr spectrum showed a methylene proton doublet at 4.22 ppm ($J_{POCH_2} = 4.50$ Hz) and pentyl proton resonances from 0.8 to 1.6 ppm. *Anal.* Calcd for $WPC_{14}H_{17}O_8$: C, 31.82; H, 3.24; P, 5.87. Found: C, 32.08; H, 3.27; P, 6.26.

$C_4H_9C(OCH_2)_3PW(CO)_5$.—To anhydrous benzene under nitrogen were added 4.2 g (0.01 mol) of $C_6H_5NH_2W(CO)_5$ and 2.0 g (0.01 mol) of $P(CH_2O)_3CC_4H_9$. The reaction was carried out at room temperature for 24 hr. The solution was filtered, evaporated to an oil, and eluted on a silica gel column with benzene. The white crystals (1.5 g) were obtained in 29% yield, melted at

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114–115°, and had a parent peak in the mass spectrum at 513 as expected. The ^1H nmr spectrum revealed a methylene proton doublet at 4.47 ppm ($J_{PCH_2} = 1.35$ Hz) and butyl proton resonances from 0.7 to 1.7 ppm. *Anal.* Calcd for $WPC_{13}H_{15}O_8$: C, 30.33; H, 2.84; P, 6.02. Found: C, 30.52; H, 3.01; P, 5.99.

$C_5H_{11}C(CH_2S)_3PW(CO)_5$.—This complex was prepared by displacing aniline in the manner described above. A yield of 65.2% of the off-white complex was obtained. The compound had a melting range of 158–160° and a parent peak at 575 in the mass spectrum as expected. The ^1H nmr spectrum showed a methylene proton doublet at 3.10 ppm ($J_{PSCH_2} = 4.00$ Hz) and pentyl proton resonances from 0.7 to 1.6 ppm. *Anal.* Calcd for $WPC_{14}H_{17}S_3O_5$: C, 29.17; H, 2.97; P, 5.37; S, 16.69. Found: C, 29.41; H, 3.09; P, 5.25; S, 16.89.

$C_5H_{11}C(CH_2(CH_3)N)_3PW(CO)_5$.—This white complex was prepared as described above in a 61.2% yield. The compound melted at 83–84° and its mass spectrum showed a parent peak at 566 as expected. The ^1H nmr spectrum showed doublets for the NCH_3 and NCH_2 protons at 2.77 ppm ($J_{PNCH_3} = 15.60$ Hz) and 2.92 ppm ($J_{PNCH_2} = 4.80$ Hz), respectively, and pentyl proton resonances from 0.75 to 1.55 ppm. *Anal.* Calcd for $WPC_{17}H_{27}N_3O_5$: C, 36.00; H, 4.11; N, 7.99; P, 5.75. Found: C, 33.62; H, 4.39; N, 7.60; P, 6.03.

$((CH_3)_2N)_3PW(CO)_5$.—The aniline-displacement reaction was used to prepare the white complex. The compound was purified by eluting the crude reaction mixture with petroleum ether (bp 60–80°) on a silica gel column. The desired complex was found in the first fraction collected. A mass spectrum exhibited the expected parent peak at 486. The ^1H nmr spectrum showed a methylene proton doublet at 1.90 ppm ($J_{PNCH_3} = 10.8$ Hz).

$(CH_3S)_3PW(CO)_5$.—Irradiation of 50 ml of a tetrahydrofuran solution containing 1.72 g (0.01 mol) of $(CH_3S)_3P$ and 3.5 g (0.01 mol) of $W(CO)_6$ with a uv lamp (200-W Hanovia Model 645A) for 14 hr produced a dark blue solution. The solution was filtered through charcoal to remove decomposition product and the filtrate evaporated to 10 ml at which time it was eluted with a 25% ethyl acetate in Skelly B solution through a silica gel column. The light yellow solid (0.2 g) in the first fraction gave a mass spectrum containing the expected parent peak at 495. The ^1H nmr spectrum in benzene consisted of one doublet ($J_{PSCH_3} = 12.95$ Hz) at 2.00 ppm.

Results

The phosphorus-31 nmr spectra of the $LW(CO)_5$ complexes consist of a 1:11.5:1 system of equally spaced peaks which results from the coupling of 14.83% abundant ^{183}W with 100% abundant ^{31}P. The magnitude of the $^{183}W-^{31}P$ coupling constants reported in this research and some of those reported previously are listed in Table I. The relative signs have not been determined.

The infrared spectra of the carbonyl stretching region were characterized by the A_1^2, A_1^1, E, and the ^{13}CO satellite of the E band. In addition to these four absorptions, the forbidden B_1 of very weak intensity was observed in several of the complexes. The assignments shown in Table II are based on previous work with similar complexes.[14,26] In amine complexes the A_1^1 band is observed at a lower frequency than the E mode[17] but for phosphines the A_1^1 band is often obscured or occurs as a shoulder of the E band.[4] In the complexes reported here the A_1^1 band was found to be at a higher frequency than the E band in each case. In the complex $((CH_3)_2N)_3PW(CO)_5$, the E mode was observed to be split into two peaks of nearly equal intensity. This type of splitting has been observed in some amine complexes[14,19] but was not observed previously for $((CH_3)_2N)_3PMo(CO)_5$.[27] The average of the two E mode components observed for the latter complex in our expanded spectrum (1942.5 and 1934.5 cm^{-1}) agrees well with the value of 1938.0 cm^{-1} reported earlier for this band.[27]

TABLE I

PHOSPHORUS-31 NMR DATA FOR PENTACARBONYLTUNGSTEN COMPLEXES[a]

Compound	Chemical shift,[b] ppm Free ligand	Chemical shift,[b] ppm Complex	$J_{^{183}W-^{31}P}$,[c] Hz
$C_4H_9C(OCH_2)_3PW(CO)_5$	+81.0	+40.7	234
$C_5H_{11}C(CH_2O)_3PW(CO)_5$	−92.8	−115.0	393
$C_5H_{11}(CH_2S)_3PW(CO)_5$[d]	−32.8	−31.1	276
$C_5H_{11}C(CH_2N(CH_3))_3PW(CO)_5$	−86.6	−112.0	318
$(C_6H_5)_3PW(CO)_5$[e]	+6.0	−20.6	280
$(C_4H_9)_2(C_6H_5)PW(CO)_5$[e]	+26.2	+0.8	235
$C_4H_9(C_6H_5)_2PW(CO)_5$[e]	+17.1	−7.9	250
$(C_4H_9)_3PW(CO)_5$[e]	+32.3	+6.4	200
$PF_3W(CO)_5$[f]	−97.8		485

[a] Phosphorus-31 chemical shifts relative to external 85% phosphoric acid in dichloromethane unless otherwise indicated. [b] These values are precise to ±0.5 ppm. [c] These values are precise to ±5 Hz. [d] Measured in carbon disulfide. [e] These values are taken from ref 4. [f] This coupling constant was obtained from the ^{19}F spectrum by the indor method. The chemical shift of the free ligand was taken from H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954). The indor experiment does not directly afford a ^{31}P chemical shift relative to 85% phosphoric acid.

The method of Cotton and Kraihanzel[14] was used to calculate force constants from the A_1^2, A_1^1, and E mode frequencies given in Table II. The values of k_2, k_1, and k_i refer to the C–O stretching force constants of the four equivalent C–O groups, the CO *trans* to L, and the interaction constant between the CO groups, respectively. The A_1^1 bands of the bicyclic phosphite and bicyclic aminophosphine complexes appeared as well-defined shoulders of the E mode in expanded spectra. The assignment of the A_1^1 band of the bicyclic thiophosphite complex was somewhat more difficult as it falls so close to the E band that the shoulder is not defined even at maximum expansion. For this reason force constant calculations were made by assuming that the A_1^1 mode occurs 5.5 cm^{-1} higher than the E mode as was experimentally observed for the $P(OCH_2)_3CC_5H_{11}$ complex. The small changes in force constants arising from a 2-cm^{-1} error in the A_1^1 frequency assignments do not reverse any trends or in fact alter any of the arguments which follow in the discussion.

The force constants listed in Table II have been used to calculate σ- and π-bonding capacities after the method of Graham.[15,28] The two equations $\Delta k_1 = \Delta\sigma + 2\Delta\pi$ and $\Delta k_2 = \Delta\sigma + \Delta\pi$ as derived by Graham are solved to give $\Delta\pi = \Delta k_1 - \Delta k_2$ and $\Delta\sigma = \Delta k_2 - \Delta\pi$. By choosing a reference compound such as an amine complex in which the π bonding may be assumed to be zero, relative scales of σ-bonding and π-bonding

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Table II

C–O Stretching Frequencies (cm^{-1}) Force Constants (mdyn/Å), and σ- and π-Bonding Parameters for LW(CO)$_5$ Complexes in Cyclohexane

L	A_1^2	B_1[a]	A_1^1	E	E(^{13}C)	k_1	k_2	k_i	Δk_1	Δk_2	$\Delta\sigma$[b]	$\Delta\pi$[b]
$C_6H_{11}NH_2$	2071.0	*c*	1916.5	1929.0	*c*	15.04	15.72	0.35	0	0	0.00	0.00
PF_3	2103.0	*c*	2007.0	1983.0	1952.0	16.59	16.45	0.29	1.47	0.73	−0.01	0.74
$P(OCH_2)_3CC_5H_{11}$	2085.5	1989.0	1963.5	1958.0	1928.0	15.79	16.10	0.31	0.75	0.38	+0.01	0.37
$P(SCH_2)_3CC_5H_{11}$	2081.0	1990.5	1965.0[d]	1959.5	1930.5	15.80	16.09	0.30	0.76	0.37	−0.02	0.39
$P(N(CH_3)CH_2)_3CC_5H_{11}$	2071.5	*c*	1949.0	1943.0	1914.0	15.56	15.87	0.31	0.52	0.15	−0.22	0.37
$P(C_6H_5)_3$	2072.0	*c*	1947.5[e]	1942.0		15.54	15.86	0.31	0.50	0.14	−0.22	0.36
$P(CH_2O)_3CC_4H_9$	2079.0	1983.0	1965.5	1951.5	1921.5	15.83	15.99	0.31	0.79	0.27	−0.25	0.52
$P(C_4H_9)_3$	2067.5	*c*	1941.0[f]	1934.0	*c*	15.44	15.75	0.32	0.40	0.03	−0.34	0.37
$P(N(CH_3)_2)_3$	2070.0	1971.0		1940.5[g] 1931.5	1902.6							
$P(OC_2H_5)_3$	2078.0	*c*	1959.0	1944.5	*c*	15.74	15.91	0.31	0.70	0.19	−0.31	0.51
$P(OC_6H_5)_3$	2083.0	*c*	1965.0	1957.5	*c*	15.35	15.79	0.29	0.29	0.07	−0.15	0.22
$P(SCH_3)_3$[f]	2062.0	*c*	1946.0	1939.5	*c*	15.50	15.78	0.30	0.46	0.06	−0.34	0.40

[a] Precision lowered by weak intensity and poor definition of these peaks. [b] Uncertainties in $\Delta\sigma$ and $\Delta\pi$ estimated in ref 15 to be ±0.12 and 0.08, respectively. [c] Not observed. [d] Value obtained by assuming A_1^1 was 5.5 cm^{-1} greater than the E mode as in the $P(OCH_2)_3CC_5H_{11}$ analog. The A_1^1 mode was not resolved although the breadth of the band was virtually equal to that of the $P(OCH_2)_3CC_5H_{11}$ complex. [e] Value obtained by assuming A_1^1 was 4.5 cm^{-1} greater than the E mode as has been previously discussed in ref 19. [f] The A_1^1 value was approximated from a poorly defined shoulder. [g] E mode split into two approximately intense peaks.

capacities emerge. In this study, $C_6H_{11}NH_2W(CO)_5$ was selected as the reference compound.

Plots were constructed of the ^{183}W–^{31}P coupling constants *vs.* the A_1^1 and E mode frequencies and the k_1, $\Delta\sigma$, and $\Delta\pi$ parameters for the complexes. The mathematical description of the results is given in Table III. Plots were also made of the ^{183}W–^{31}P couplings *vs.* the Pauling, Allred–Rochow, and Sanderson electronegativity scales for the atoms directly bound to phosphorus in the ligand. The complexes used in determining the least-squares lines in the electronegativity plots involved the ligands $P(C_4H_9)_3$, $P(SCH_2)_3CC_5H_{11}$, $P(N(CH_3)CH_2)_3CC_5H_{11}$, $P(OCH_2)_3CC_5H_{11}$, and PF_3. Thus $P(C_6H_5)_3$, $PC_6H_5(C_4H_9)_2$, $P(C_6H_5)_2C_4H_9$, and $P(CH_2O)_3CC_4H_9$ were not included since they involved groups such as unsaturated phenyl rings in the case of the butyl derivatives and oxygens bonded to the phosphorus carbon atoms in the last compound. Apparently the alterations in the effective electronegativity on phosphorus compared to that determined by the butyl groups in $P(C_4H_9)_3$ is small since all of these compounds lie on or very near the least-squares lines. The equations for all of the least-squares lines, the standard deviations from this line, and the correlation coefficients are given in Table IV.

Table III

Statistical Data of Plots[a] of E Mode, k_1, A_1^1 Mode, $\Delta\sigma$, and $\Delta\pi$ *vs.* $J_{^{183}W-^{31}P}$ Coupling Constants

Parameter *vs.* $J_{^{183}W-^{31}P}$	Equation	Std dev, y	Correln coeff
E mode	$y = 0.124x + 1910$	9.761 cm^{-1}	0.79
k_1	$y = 18.65 \times 10^{-3}x + 15.11$	0.311 mdyn/cm	0.51
A_1^1 mode	$y = 0.1458x + 1914$	14.11 cm^{-1}	0.70
$\Delta\sigma$	$y = -7.718 \times 10^{-4}x + 0.524$	0.119 mdyn/cm	0.55
$\Delta\pi$	$y = 539.5 \times 10^{-3}x + 0.2487$	0.1472 cm^{-1}	0.35

[a] These plots include all complexes for which both $J_{^{183}W-^{31}P}$ and carbonyl data are recorded in Tables I and II.

Table IV

Statistical Data of Plots of Electronegativities *vs.* $J_{^{183}W-^{31}P}$ Coupling Constants

Electronegativity scale *vs.* $J_{^{183}W-^{31}P}$	Equation	Std dev, y	Correln coeff
Sanderson[a]	$y = 5.386 \times 10^{-3}x + 1.287$	0.1042	0.99
Pauling[b]	$y = 5.039 \times 10^{-3}x + 1.445$	0.1663	0.97
Allred–Rochow[b]	$y = 6.137 \times 10^{-3}x + 1.070$	0.2247	0.96

[a] R. T. Sanderson, "Inorganic Chemistry," Reinhold Publishing Co., New York, N. Y., 1967, p 78. [b] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 103.

Discussion

Observation of the low-intensity ^{31}P resonance satellites due to ^{183}W in spectra of the LW(CO)$_5$ complexes requires an extremely high solubility of approximately 40%. Polycyclic ligands form complexes which are generally less soluble than ligands of the open-chain variety. This is especially true for the phosphite and thiophosphite ligands in the case of LW(CO)$_5$. An ethyl group in the "tail" position of the polycyclic phosphite gave a complex with enough solubility to obtain a ^{31}P chemical shift (identical with that of the complex in which an *n*-pentyl group was in the "tail" position) but the ^{183}W–^{31}P satellites were still unobservable above the noise. Thus it was necessary to synthesize ligands in which the bridgehead-carbon group was *n*-butyl or *n*-pentyl. No ^{31}P resonance satellites could be observed for $(CH_3S)_3PW(CO)_5$ in view of the relatively small yields in which it was obtained and its general instability.

The ^{183}W–^{31}P coupling constants increase in the series: $(C_4H_9)_3P < (C_4H_9)_2C_6H_5P < P(CH_2O)_3CC_4H_9 < C_4H_9(C_6H_5)_2P < P(SCH_2)_3CC_5H_{11} < (C_6H_5)_3P < ((CH_3)_2N)_3P < P(N(CH_3)CH_2)_3CC_5H_{11} < P(OC_2H_5)_3 \cong P(OCH_2)_3CC_5H_{11} < (C_6H_5O)_3P < PF_3$.

The upward trend in ^{183}W–^{31}P coupling appears to parallel rather well the increase in electronegativity of the substituents on phosphorus. This is demonstrated by the correlation coefficients of 0.96, 0.97, and 0.99 for the plots of the couplings against the Allred–Rochow, Pauling, and Sanderson electronegativity scales, respectively (pertinent data in Table IV).

Insofar as $^{183}W-^{31}P$ coupling is generally agreed to occur through bonding orbitals having s character,[2,3,12] the correlation with electronegativity can be explained without invoking π bonding. Walsh[29] has argued that the replacement of a group X attached to a carbon by a more electronegative group Y results in less s character in the C–Y bond than in the C–X bond. This has been discussed further by Bent,[30] who pointed out that atomic s character concentrates in orbitals which are directed toward the most electropositive substituents. Furthermore, the magnitudes of phosphorus–phosphorus coupling constants in directly bonded phosphorus nuclei with appropriate sign considerations can be explained in terms of higher s character in the P–P bond as more electronegative substituents use less of the phosphorus 3s electrons.[31] For our $LW(CO)_5$ complexes, the above arguments appear to be applicable since the $W(CO)_5$ moiety serves as the most electropositive substituent on phosphorus in each of the complexes and as the remaining substituent groups on phosphorus are replaced by more electronegative ones, the s character should increase in the tungsten–phosphorus bond. It is also expected that the positive nuclear charge on phosphorus will increase with more electronegative substituents and this effect has been shown to be even more important than the s-character term in the coupling equation on theoretical grounds.[32] The few structural data available on phosphorus ligands and their derivatives seem to be consistent with the idea that the substituent–phosphorus–substituent angles on the ligand very likely decrease with increasing electronegativity of the substituent in coordination complexes.[33]

Although the π-bonding capacity of ligands is generally believed to be a factor which partially controls carbonyl stretching frequencies in $LM(CO)_5$ molecules ($M = Mo, W$),[14,15,28] it has been postulated that basicity arguments alone adequately explain certain trends in carbonyl stretching frequencies.[19] Moreover, intensity studies suggest that substituting L for a CO group in an $M(CO)_6$ molecule decreases C–O bonding by weakening the M–C σ bonds without appreciably altering the M–C π bonding.[34] The extent to which the CO stretching frequencies of the carbonyl groups decrease upon substitution by L will depend upon the extent to which the energy of the π orbitals on the metal are lowered which in turn depends upon both the σ-donating and the π-accepting capacities of the ligand. Employing the assumption that metal–carbonyl π bonding is influenced by other ligands present in the complex, the carbonyl stretching frequencies have been used in a variety of ways to infer the π-bonding capacity of the ligand. The values of raw frequency data have been used to compare π-bonding character, especially from values of the A_1^1 mode which stem from the CO group *trans* to L. As A_1^1 stretching frequency values increase for a given series of ligands, the C–O bond order should increase as a result of increased π-bonding in the metal–phosphorus link. Grim, *et al.*,[4] have plotted the E mode stretching frequencies of a number of $LW(CO)_5$ complexes *vs.* the $^{183}W-^{31}P$ coupling constants and have observed a straight-line correlation between these two parameters. As they were unable to assign the A_1^1 mode for all of the complexes because of overlap with the E mode, the E mode was used as a reasonable approximation since the A_1^1 and the E modes have very similar stretching frequencies. Although there is a general increase in the E mode carbonyl stretching frequency with the value of $J_{^{183}W-^{31}P}$, the linear correlation data in Table III are rough in view of the low correlation coefficient of 0.79 and the relatively small errors in the two parameters. It should be noted, however, that the range in these parameters defined by the $(C_4H_9)_3P$ and $(C_6H_5)_3P$ complexes was much smaller for the much better linear correlation observed by Grim and coworkers.[4] The A_1^1 mode could be observed for all but three of the complexes and reasonable estimates could be made for two of these unobserved peaks (Table II). The correlation coefficient of 0.70 for the plot of the A_1^1 mode against $^{183}W-^{31}P$ did not represent a significant improvement. Although force constants are more reliable than raw frequency data for bonding interpretations, values of k_1 (CO stretching force constant *trans* to L) plotted *vs.* $^{183}W-^{31}P$ coupling constants revealed a large decrease in the correlation coefficient (0.51). This result tends to suggest that the increase of $^{183}W-^{31}P$ coupling at best only roughly parallels the rising of the π-acceptor properties of the phosphorus ligand.

The σ-bonding and π-bonding capacities of the ligands calculated in the manner of Graham[15] are shown in Table II. A positive value of the σ or π parameter implies that the ligand is a σ or π acceptor whereas a negative value implies that the ligand is a σ or π donor compared to the reference compound $C_6H_{11}NH_2(CO)_5$. The order of increasing π-acceptor character ($\Delta\pi$) of the ligands in the complex is: $P(OC_6H_5)_3 < P(C_6H_5)_3 < P(C_4H_9)_3 \cong P(N(CH_3)CH_2)_3CC_5H_{11} \cong P(OCH_2)_3CC_5H_{11} < P(SCH_2)_3CC_5H_{11} < P(SCH_3)_3 < P(OC_2H_5)_3 < P(CH_2O)_3CC_4H_9 < PF_3$. On electronegativity grounds it seems strange that the first three members of this group are not reversed in order and that $P(CH_2O)_3CC_4H_9$ appears so late in the series. In any case the correlation coefficient of the $^{183}W-^{31}P$ coupling values with $\Delta\pi$ (0.35) clearly implies a negligible correlation. Moreover the standard deviation of 0.16 is twice as large as the error in $\Delta\pi$. These results would be expected if indeed $^{183}W-^{31}P$ coupling were not dependent upon π bonding in the W–P link.

The order of decreasing σ-donating capacity ($\Delta\sigma$) of the complexed phosphorus compounds is: $P(C_4H_9)_3 > P(SCH_3)_3 > P(OC_2H_5)_3 > P(CH_2O)_3CC_4H_9 > P(C_6H_5)_3 > P(N(CH_3)CH_2)_3CC_5H_{11} > P(OC_6H_5)_3 > P(SCH_2)_3CC_5H_{11} > PF_3 > P(OCH_2)_3CC_5H_{11}$. Again some of

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[29] A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

[30] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[31] E. G. Finer and R. K. Harris, *Chem. Commun.*, 111 (1968).

[32] D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).

[33] F. Ogilvie, R. J. Clark, and J. G. Verkade, *Inorg. Chem.*, **8**, 1904 (1969).

[34] D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

the orders are somewhat unexpected on electronegativity grounds, particularly the result that PF_3 is comparable to $P(OCH_2)_3CC_5H_{11}$ in σ-donor capacity. It is possible, however, that "normal" basicity orders are not necessarily operative when the ligand is complexed to a transition metal.[15] If indeed $^{183}W-^{31}P$ coupling occurs through orbitals having s character, a better correlation with $\Delta\sigma$ than with $\Delta\pi$ might have been expected since increasing s character of the phosphorus lone pair in the complex should parallel its decreasing σ-donating character. The poor correlation of $^{183}W-^{31}P$ coupling with $\Delta\sigma$ could arise from the small range in $\Delta\sigma$ values for these phosphorus ligands (+0.01 to −0.34) and the large standard deviation (0.12) in the correlation compared to the acknowledged error[15] (0.12) in the $\Delta\sigma$ evaluation.

We tentatively draw the following conclusions from these studies. (a) Increases in the electronegativity of the phosphorus ligand account very well for the rise in $^{183}W-^{31}P$ coupling constants in $W(CO)_5L$ complexes. (b) Although greater ligand electronegativity is expected to raise the π-acceptor capacity of the ligand, the rise in $^{183}W-^{31}P$ coupling can be explained quite well without invoking π bonding as a coupling mechanism. (c) No significant correlation was found between tungsten–phosphorus coupling and the carbonyl stretching frequencies, force constants, and the $\Delta\sigma$ and $\Delta\pi$ quantities in the series of complexes studied.

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Axial Ligand Exchange Reactions of Ferrous Phthalocyanine. Exchange of Imidazole for Dimethyl Sulfoxide

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Ferrous phthalocyanine dissolves in dimethyl sulfoxide to give a diamagnetic blue solution. The rate of exchange of imidazole (Imid) for dimethyl sulfoxide at the axial sites to give green $FePc(Imid)_2$ obeys the rate law

$$\frac{d[FePc(Imid)_2]}{dt} = 4.17 \times 10^{13}e^{-17,900/RT}[FePc][Imid] \ M^{-1}\,sec^{-1}$$

At 25° $\Delta H^{\ddagger} = 17.3$ kcal/mole and $\Delta S^{\ddagger} = 1.8$ eu. Replacement of coordinated dimethyl sulfoxide by the first imidazole molecule is rate determining and exerts a powerful *trans* effect on the exchange of the second dimethyl sulfoxide ligand.

Introduction

One family of inorganic reactions convenient to follow experimentally involves ligand exchanges at a low-spin d^6 octahedral center. The majority of studies have been on Co(III) complexes, with a number on Rh(III) and Pt(IV) systems.[1] Ferrous complexes have biological importance, but far fewer are low-spin than is the case with Co(III), and easy oxidation to Fe(III) is an experimental complication. Work to date has been restricted to tris-diimine complexes, *e.g.*, tris(*o*-phenanthroline)iron(II) perchlorate.[2]

It has been known for 30 years that derivatives of ferrous phthalocyanine (FePc) (Figure 1) of the formula $FePc(base)_2$[3a] are low-spin[3b] d^6 complexes, and it seemed that a study of axial ligand replacement rates would be of interest. The system has a fixed geometry, with the ligands undergoing replacement *trans* to each other. The advent of a variety of dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMA), or trimethyl phosphate has removed the serious experimental disadvantage of ferrous phthalocyanine—its insolubility in common solvents. This paper describes the exchange of axially bound dimethyl sulfoxide by imidazole at a ferrous phthalocyanine center in dimethyl sulfoxide as solvent. Some preliminary results at 25° have been presented in ref 4.

Experimental Section

Purification of Materials.—(a) British Drug Houses reagent grade DMSO was purified by two methods, each of which gave samples of the same refractive index, producing the same kinetic results.

(i) The solvent was dried over solid potassium hydroxide, decanted, and then distilled at ~1.5 mm at 40°. Distillation was through a 2-ft vacuum-jacketed column packed with stainless steel gauze helices, with a nitrogen gas bleed. The middle three-fifths of the distillate was retained, treated with calcium

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