from the aqueous basic solution were washed with water and brine and were dried over Na_2SO_4. Removal of the benzene under reduced pressure yielded crude plazH (**10**), an amber oil (5.5 g).

Purification of plazH (10). Crude plazH (**10**) (5.5 g) was dissolved in degassed EtOH (200 mL) under nitrogen, and solid $Zn(OAc)_2{\cdot}2H_2O$ (3.59 g, 0.016 mol) was added. The solution was heated to 60–70 °C and $LiClO_4{\cdot}3H_2O$ (5.23 g, 0.033 mol) in degassed EtOH (60 mL) was added dropwise over 0.5 h. The stirred mixture was slowly cooled to room temperature. After 1 h at room temperature, the mixture was filtered under nitrogen and the precipitate was washed with degassed EtOH and then with degassed hexane. Drying under high vacuum yielded [Zn(plaz)]ClO_4 (6.3 g, 74%) as an off-white solid. Anal. Calcd for $C_{16}H_{24}N_5S_2O_5ClZn$: C, 36.2; H, 4.6; N, 13.2; S, 12.1; Cl, 6.7. Found: C, 36.3; H, 4.8; N, 13.0; S, 12.2; Cl, 6.6.

[Zn(plaz)]ClO_4 (6.3 g, 0.012 mol) and Na_2EDTA (8.33 g, 0.012 mol) were suspended in degassed water (150 mL) under nitrogen. After the mixture was stirred for 0.5 h, the resulting clear light yellow solution was made basic with solid $NaHCO_3$ (2.99 g, 0.036 mol) and was thoroughly extracted under nitrogen with degassed EtOAc. The combined organic layers were dried over Na_2SO_4, and then the solvent was removed under reduced pressure, yielding **10** (4.2 g, 97%), a viscous yellow-green oil. ^1H NMR (CD_3CN): δ 1.50 (3 H, s), 1.60 (3 H, s), 2.95 (3 H, s), 3.47 (2 H, s), 3.54 (3 H, s), 3.67 (3 H, s), 3.82 (2 H, s), 5.96 (1 H, s), 6.8–6.9 (4 H, m).

Preparation of Metal Complexes. All metal complexes were made in degassed solvents under argon.

[Co(plaz)]ClO₄. A solution of plazH (**10**) (0.97 g, 2.6 mmol) in MeOH (20 mL) was added dropwise to $Co(OAc)_2{\cdot}4H_2O$ (0.66 g, 2.6 mmol) in MeOH (35 mL). $LiClO_4{\cdot}3H_2O$ (1.7 g, 10.4 mmol) in MeOH (20 mL) was added dropwise over 0.5 h to the resulting dark blue solution. The mixture as then heated to 70 °C, and the fluffy blue solid was dissolved by the addition of CH_3CN (30 mL). At this temperature the volume was reduced to 25–30 mL, and the reaction was slowly cooled to room temperature. The mixture was filtered, and the precipitate was washed with MeOH containing a little CH_3CN and was dried under reduced pressure, yielding [Co(plaz)]ClO_4, a light blue solid (0.90 g, 66%). Anal. Calcd for $C_{16}H_{24}N_5O_5S_2ClCo$: C, 36.6; H, 4.6; N, 13.3; S, 12.2; Cl, 6.8. Found: C, 36.9; H, 4.6; N, 13.2; S, 11.8; Cl, 6.7.

[Co(plaz)]BPh₄. The tetraphenyl borate salt was made in a similar manner by using $NaBPh_4$, but in this case no CH_3CN was added and the mixture was filtered directly from MeOH, yielding [Co(plaz)]BPh_4, a light blue powder (70%). Anal. Calcd for $C_{40}H_{44}N_5OS_2BCo$: C, 64.5; H, 6.0; N, 9.4; S, 8.6. Found: C, 64.3; H, 6.0; N, 9.6; S, 8.6.

"[Cu(plaz)]BPh₄". A solution of plazH (**10**) (0.90 g, 2.4 mmol) in MeOH (100 mL) was added dropwise to $Cu(OAc)_2{\cdot}H_2O$ (0.48 g, 2.4 mmol) in MeOH (50 mL) at −50 °C. $NaBPh_4$ (0.92 g, 2.7 mmol) in MeOH (50 mL) was added dropwise over 1 h to the dark blue-green solution at −50 °C. The mixture was stirred a further 0.5 h at −50 °C and filtered cold, and the precipitate was washed with cold MeOH and dried under high vacuum, yielding "[Cu(plaz)]BPh_4", a light blue-green powder (1.2 g, 67%). Anal. Calcd for $C_{40}H_{44}N_5OS_2BCu$: C, 64.1; H, 5.9; N, 9.3; S, 8.6. Found: C, 64.0; H, 5.9; N, 9.3; S, 8.4.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1**, 40446-60-4; **2**, 103817-34-1; **3**, 103817-35-2; **4**, 103817-36-3; **5**, 103817-37-4; **7**, 78667-04-6; **8**, 103817-38-5; **9**, 103817-39-6; **10**, 103817-40-9; [Zn(plaz)]ClO_4, 103817-42-1; [Co(plaz)]ClO_4, 103817-44-3; [Co(plaz)]BPh_4, 103817-45-4; [Cu(plaz)]BPh_4, 103817-47-6; $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1; $ClCH_2CN$, 107-14-2; 3,4-dihydro-2*H*-pyran, 110-87-2; thioacetic acid, 507-09-5; 1-methylimidazole, 616-47-7; mercaptoacetic acid, 68-11-1.

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Spectroscopic Study of the Effect of Methyl and Phenyl Substituents on the Basicity of Phosphine Ligands in Tungsten Carbonyl Derivatives

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The He I photoelectron spectra of diphosphine ligands (LL = $Me_2PCH_2PMe_2$, dmpm; $Me_2PCH_2CH_2PMe_2$, dmpe; $Ph_2PCH_2PPh_2$, dppm; $Ph_2PCH_2CH_2PPh_2$, dppe; $Et_2PCH_2PEt_2$, depm; $Et_2PCH_2CH_2PEt_2$, depe) and of the complexes $[W(CO)_4(LL)]$ and $[W(CO)_5(PMe_{3-n}Ph_n)]$ have been measured. In all cases the first ionization energies are lower both for the free phosphine ligands (lone pair on P) and for the complexes (tungsten 5d) when the phosphine has phenyl, rather than methyl or ethyl, substituents. These results are interpreted to indicate that the phenyl groups increase the donor ability of the phosphine ligands compared to the methyl or ethyl groups. The IR and ^{13}C NMR spectra have also been measured, but the Cotton–Kraihanzel force constants and the trends in the coupling constant $^1J(^{183}W-^{13}C)$ for the carbonyls trans to phosphine indicate that the basicity differences between the methyl- or phenyl-substituted phosphines are too small to be detected by these methods.

Introduction

The basicity of tertiary phosphine ligands has been studied by various spectroscopic methods. Infrared spectroscopy of phosphine-substituted metal carbonyls has enabled the study of carbonyl stretching frequencies and force constants, and on the basis of their trends, the donor strengths of various ligands have been compared.[1-5] From ^{13}C NMR studies it has been found that the replacement of one or more carbonyl ligands with tertiary phosphines in $M(CO)_n$ complexes leads to a deshielding of CO resonances for the remaining CO.[6] This implies that $\delta(^{13}CO)$ depends on the occupation of the antibonding orbital in CO, and the observation of a linear correlation between $\nu(CO)$ and $\delta(^{13}CO)$ has extended this idea.[7] More recently, the study of the coupling constants $[^1J(^{183}W-^{13}C)_{trans}]$ for the tungsten–carbonyl group trans to phosphorus in the complexes $[W(CO)_5L]$, where L = a tertiary phosphine ligand, had led to the formulation of a trans-influence series.[8] ^{31}P NMR spectroscopy studies the M–P bond more directly than IR and ^{13}C NMR studies, but it has been demonstrated that bond angle variations, or the differences in the hybridization of the unshared electrons of the phosphorus, is important in determining ^{31}P chemical shifts and coupling constant.[9-12] This leads to a greater difficulty in interpretion of these parameters.

Gas-phase ultraviolet photoelectron spectroscopy (UPS) is in principle the most direct method of investigating the electronic

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Table I. Vertical Ionization Energies (eV) from the He I Photoelectron Spectra of [W(CO)$_4$(LL)]

[W(CO)$_4$(LL)] LL	W(5d)^a	Ph(π)	σ(W–P)^b	n(P)^d	Δ_{stab}^{e}
dppm	6.50, 6.92	9.20	*c*, 10.00	7.79	2.21
dppe	6.48, 6.87	9.12	*c*, 10.00	7.86	2.14
depm	6.59, 7.07		9.15, 9.55	8.21	1.34
depe	6.64, 7.05		9.17, 9.67	8.26	1.41
dmpm	6.69, 7.19		9.40, 9.80	8.51	1.29
dmpe	6.74, 7.15		9.40, 9.95	8.47	1.48

^{a}The W(5d) band is split due to spin–orbit coupling. ^{b}The σ(W–P) has both A$_1$ and B$_2$ components. ^{c}The first component of this band is predicted to overlap with the Ph(π) band. ^{d}n(P) refers to the ionization energy of the phosphorus lone pair in the free ligand. ^{e}The stabilization energy of the phosphorus lone pair upon coordination is calculated such that Δ_{stab} = IE[σ(W–P)] – IE[n(P)].

structure of the free and coordinated phosphine ligands. The ionization energy, IE, of the phosphorus lone pair in a series of free phosphines and the IE of the σ(M–P) bond in the corresponding complexes allow for the evaluation of the stabilization energy of the phosphorus lone pair upon coordination, Δ_{stab}. Previous studies on the L = $PMe_{3-n}Ph_n$ (n = 0–3) ligands and the square-planar complexes, such as [AuMe$_3$L], strongly support a trend of increasing basicity of these phosphines as phenyl (Ph) groups replace methyl (Me) groups: $PMe_3 < PMe_2Ph < PMePh_2 < PPh_3$.[13,14]

These results have also been supported by gas-phase proton affinity measurements for this series of ligands.[15] However, this is the opposite basicity trend expected from electronegativity arguments and the trend that is observed in the pK_a's of the conjugate acids, BH$^+$, in aqueous solution.[16] This led to controversy over the basicity trend,[13-17] and it is obvious that basicity trends in this series cannot be explained by any single cumulative substituent factor such as inductive effect.[18] Rather, π-bonding effects, steric effects, and solvation effects may all be important factors.[19,20]

In this work we have studied the spectroscopic properties of the complexes [W(CO)$_5$($PMe_{3-n}Ph_n$)] (n = 0–3) and [W(CO)$_4$(LL)] (LL = Me$_2$PCH$_2$PMe$_2$, dmpm; Me$_2$P(CH$_2$)$_2$PMe$_2$, dmpe; Et$_2$PCH$_2$PEt$_2$, depm; Et$_2$P(CH$_2$)$_2$PEt$_2$, depe, Ph$_2$PCH$_2$PPh$_2$, dppm; Ph$_2$P(CH$_2$)$_2$PPh$_2$, dppe) by IR, ^{13}C NMR, and UP spectroscopy in order to compare the substituent effects of Me and Ph groups on phosphine ligands. A preliminary account of parts of this work has been published.[17]

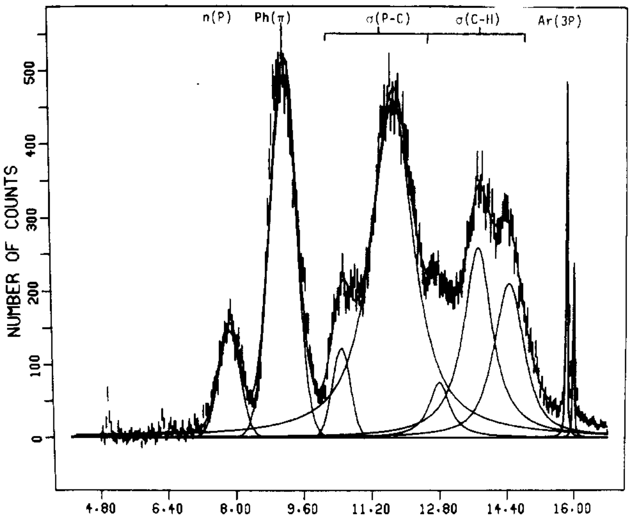

Figure 1. He I photoelectron spectrum of Ph$_2$PCH$_2$PPh$_2$ (dppm).

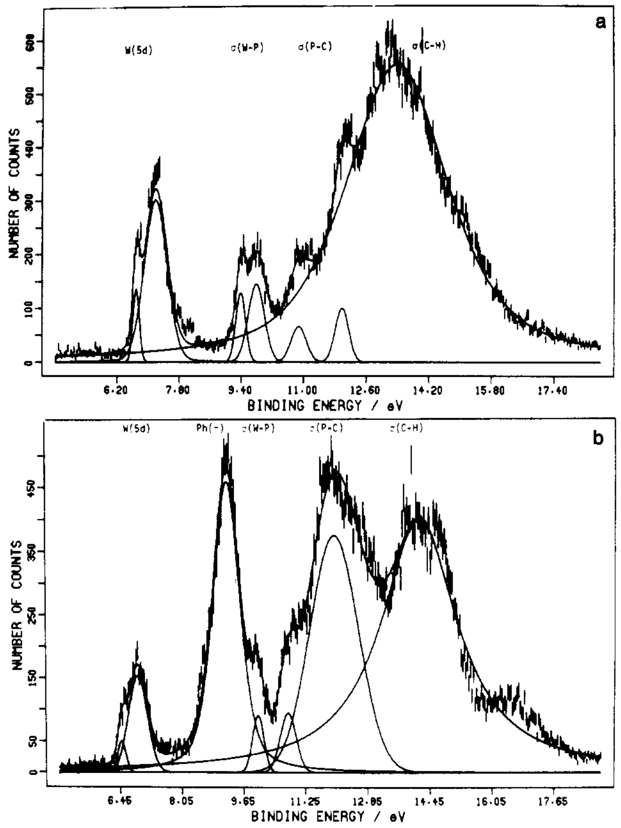

Figure 2. He I photoelectron spectra of (a) [W(CO)$_4$(dmpm)] and (b) [W(CO)$_4$(dppm)]. The $5\sigma+\pi$(CO) ionizations are also expected to be under the broad envelope labeled σ(CH).

Experimental Section

Materials. Tungsten hexacarbonyl and all the ligands except PMe$_3$ and depm were commerical products and were used without further purification. PMe$_3$[21] and depm[22] were prepared by literature methods and purified by distillation under dry nitrogen. The tungsten complexes [W(CO)$_5$L] (L = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$) and [W(CO)$_4$(LL)] (LL = dmpm, dmpe, depm, depe, dppm, dppe) were prepared by literature methods.[5,23,24] These complexes were then purified by recrystallization and characterized with the use of literature melting points and mass, IR, and NMR spectroscopic data.

Spectroscopic Measurements. Infrared spectra were obtained from dilute solutions in a 0.1-mm NaCl solution cell by using an IBM IR/32 FTIR spectrometer. Raman spectra of the complexes [W(CO)$_5$L] (L = $PMe_{3-n}Ph_n$, n = 0–3) were also measured (488.0-nm exciting line; 100-μm slits; in cyclohexane) in order to determine the Raman active ν(B$_1$) band positions. These Raman spectra were calibrated by using the neon lines at 1769.67 and 1777.3 cm^{-1}. ^{13}C NMR spectra were recorded with a Varian XL-300 instrument operating at 300 MHz. Saturated CDCl$_3$ solutions were run overnight (~25 000 transients) in order to

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Table II. Vertical Ionization Energy (eV) from the He I Photoelectron Spectra of $[W(CO)_5(PMe_{3-n}Ph_n)]$ (n = 0–3)

$[W(CO)_5L]$ L	W(5d)[a]	Ph(π)	σ(W–P)	n(P)[b]	Δ_{stab}
PPh_3	7.20, 7.41, 7.67	8.75, 9.37	10.44	7.80	2.64
$PMePh_2$	7.23, 7.42, 7.71	8.83, 9.42	10.33	8.28	2.05
PMe_2Ph	7.34, 7.56, 7.81	c, 9.49	10.28	8.32	1.96
PMe_3	7.46, 7.64, 7.90		10.08	8.62	1.46
PEt_3[d]	7.41, 7.60, 7.82		9.75	8.31	1.44

[a] The W(5d) band is split due to spin–orbit coupling and ligand field splitting. [b] Reference 13. [c] Not resolved. [d] IE[n(P)] = 8.31 eV for PEt_3 is taken from ref 33.

bring out the ^{183}W satellites of the trans CO resonances. In all cases the deuterium signal of the solvent was used as an internal lock; $CDCl_3$ signals served as internal standards.

The He I photoelectron spectra of the compounds were run on a McPherson ESCA-36 photoelectron spectrometer using a hollow-cathode UV He lamp and computer fitted to Lorentzian–Gaussian line shapes.[25] Compounds that were not sufficiently volatile were heated to within 20 deg of their melting point to obtain spectra.[26] All spectra were calibrated with the Ar $3P_{3/2}$ line at 15.759 eV.

Results

Photoelectron Spectroscopy. The results of the UPS Study carried out on the $[W(CO)_4(LL)]$ series are summarized in Table I. The vertical IE of the mainly W(5d), Ph(π), σ(W–P), and n(P) bands are listed. The IE ranges of σ(P–C) (10.5–12.5 eV), σ(C–H) (12–15 eV), and 5σ+π(C–O) (16–17.5 eV) are not included in Table I since they are not well resolved in the spectra. Similarly, the IE for the $[W(CO)_5(PMe_{3-n}Ph_n)]$ series are summarized in Table II.

Representative samples of the fitted spectra are shown in Figures 1–3. Figure 1 is the argon-calibrated photoelectron spectrum of $Ph_2PCH_2PPh_2$ (dppm), which is assigned by referring to the similar spectra of the $PMe_{3-n}Ph_n$ series.[13] The lowest binding energy (BE) peak is due to the phosphorus lone pair, n(P), and is followed by the Ph(π) peak, the σ(P–C) band, and the σ(C–H) band. Our only interest is to measure accurately the IE of the n(P) peaks in the series of diphosphine ligands, and these are listed in Table I.

Parts a and b of Figure 2 are the PE spectra of $[W(CO)_4(dmpm)]$ and $[W(CO)_4(dppm)]$, respectively. The ordering of the BE peaks is W(5d) < Ph(π) < σ(W–P) < σ(P–C), σ(C–H), 5σ+π(C–O).[17] The first band, which is mainly due to the W(5d) level, is split by spin–orbit coupling, and we find the trend of these W(5d) BE values to be in the order dppm ~ dppe < depm ~ depe < dmpm ~ dmpe (Table I).

The second band in the Ph-substituted phosphines is the Ph(π) band. This band probably overlaps with one component of the σ(W–P) band in $[W(CO)_4(dppm)]$ and $[W(CO)_4(dppe)]$; therefore, only one component of the σ(W–P) band is listed in Table I for these compounds.

The third band due to σ(W–P) is clearly split into its two components,[27] as seen in $[W(CO)_4(dmpm)]$ (Figure 2a). The second component of this band was then consistently used in calculating the relative stabilization energies, Δ_{stab}, of the phosphorus lone pairs upon coordination, and the values are listed in Table I.

The PE spectra of $[W(CO)_5(PMe_3)]$ and $[W(CO)_5(PPh_3)]$ are shown in parts a and b, respectively, of Figure 3. In this series the W(5d) band could be resolved into its three components. The splitting is due to both spin–orbit coupling and ligand field splitting, which was predicted by Bursten[28] and later demonstrated in two subsequent studies.[29,30] The Ph(π) band is resolved into its a_2 and b_1 components (Figure 3b) due to the lowered symmetry of the benzene ring. Finally, the BE of the σ(W–P) peaks seen in parts a and b of Figure 3 can be used to calculate Δ_{stab} of the phosphorus lone pair (Table II).

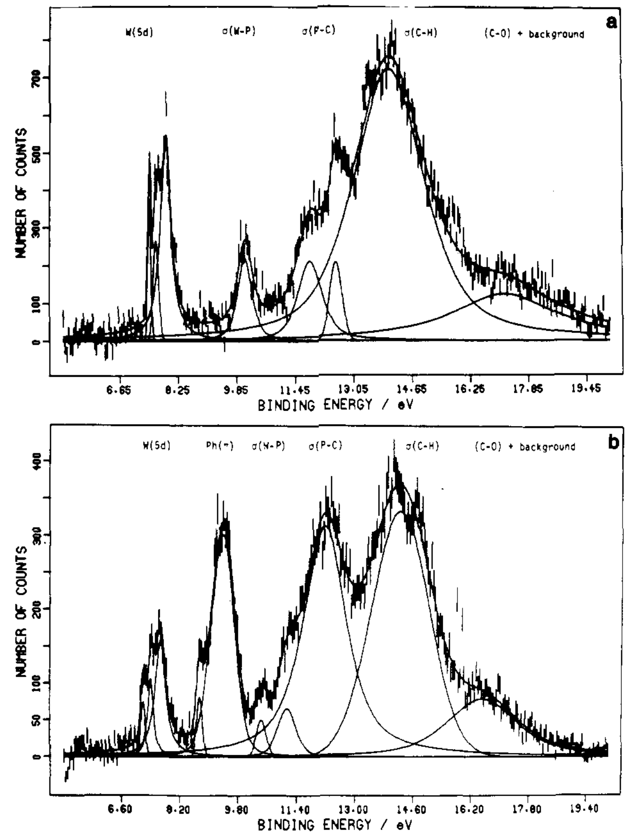

Figure 3. He I photoelectron spectra of (a) $[W(CO)_5(PMe_3)]$ and (b) $[W(CO)_5(PPh_3)]$.

IR Spectroscopy. It is of interest to look at the infrared spectroscopic properties of the tungsten complexes in cyclohexane since this nonpolar solvent is expected to approximate gas-phase properties. The measured carbonyl stretching frequencies, ν(CO), and the calculated Cotton–Kraihanzel force constants were determined and are summarized in Table III. The accepted interpretation of ν(CO) is that the substitution of CO by phosphine ligands (better σ donors but poor π acceptors) will lead to a greater W(dπ) → CO(π*) back-donation to the remaining CO's and lower ν(CO).[33]

In the $[W(CO)_5(PMe_{3-n}Ph_n)]$ series, the trend in $\nu(A_1{}^1)$ (the characteristic frequency) and k_2 (CO force constant cis to PR_3) indicates that PMe_3 is more basic than PPh_3. This trend has previously been noted in related systems such as the complexes $[Ni(CO)_3L]$, for which ν(CO) values are 2064.1, 2065.3, 2067.0, and 2068.9 cm^{-1} for L = PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3, respectively.[33] However, values for k_1, the CO force constant trans to PR_3 in $[W(CO)_5(PR_3)]$, would indicate the opposite order, i.e. that PPh_3 is more basic than PMe_3. The opposite trends in k_1 and k_2 values were also noted in the $[Mo(CO)_5L]$ and *cis*-$[Mo(CO)_4L_2]$ series.[32] The discrepancy between the trends based on $\nu(A_1{}^1)$ and k_1 arises because k_1 is determined by the frequency of all modes. However, it should be emphasized that $\nu(A_1{}^1)$ can be measured precisely but that there are likely to be errors associated with the calculation of k_1, partly because of the simplified

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Table III. CO Stretching Frequencies (cm^{-1}) and Force Constants (mdyn/Å) in Cyclohexane[a]

compd	$\nu(A_1^1)$	$\nu(B_1)$	$\nu(A_1^2)$	$\nu(E)$	k_1	k_2
$W(CO)_5(PPh_3)$	2071.8	1979.5	1942.0	1939.0	15.45	15.83
$W(CO)_5(PMePh_2)$	2071.8	1979.5	~1947	1939.5	15.53	15.83
$W(CO)_5(PMe_2Ph)$	2071.0	1973.0	1947.0	1938.0	15.52	15.79
$W(CO)_5(PMe_3)$	2069.5	1973.0	1946.5	1937.0	15.52	15.78
compd	$\nu(A_1^1)$	$\nu(A_1^2)$	$\nu(B_2)$	$\nu(B_1)$	k_1	k_2
$W(CO)_4(dppm)$	2020.7	1926.2	1912.7	1895.3	14.94	15.44
$W(CO)_4(dppe)$	2020.7	1924.2	1910.7	1898.2	14.95	15.42
$W(CO)_4(dmpm)$	2015.5	1921.3	1897.2	1897.2	14.96	15.23
$W(CO)_4(dmpe)$	2014.9	1919.4	1894.2	1894.2	14.93	15.20
$W(CO)_4(depm)$	2013.0	1918.4	1894.3	1894.3	14.91	15.19
$W(CO)_4(depe)$	2012.0	1918.4	1894.3	1894.3	14.91	15.18

[a] The convention of the modes for $[W(CO)_5L]$ follows that of ref 1 and for $[W(CO)_4L_2]$ follows that in: *J. Mol. Struct.* **1977**, *41*, 99.

Table IV. CO Stretching Frequencies (cm^{-1}) and Force Constants (mdyn/Å) in CS_2

compd	$\nu(A_1^1)$	$\nu(A_1^2)$	$\nu(B_2)$	$\nu(B_1)$	k_1	k_2
$W(CO)_4(dppm)$	2017.8	1919.4	1905.9	1883.7	14.80	15.35
$W(CO)_4(dppe)$	2017.8	1917.5	1903.8	1887.6	14.82	15.33
$W(CO)_4(dmpm)$	2011.0	1913.6	1889.	~1884 sh	14.80	15.13
$W(CO)_4(dmpe)$	2011.0	1911.7	1887.6	~1887.6	14.82	15.12
$Cr(CO)_4(dppe)$[a]	2009	1914	1899	1877	14.75	15.32
$Cr(CO)_4(dmpe)$[a]	2009	1921	1900	1894	14.83	15.30
$Mo(CO)_4(dppe)$[a]	2020	1919	1907	1881	14.87	15.48
$Mo(CO)_4(dmpe)$[a]	2020	1929	1909	1903	14.98	15.46

[a] $\nu(CO)$ and force constants as reported in ref 4.

Table V. ^{13}C NMR Data[a]

compd	$\delta(CO)_{trans}$	$\delta(CO)_{cis}$	$^1J(W-C)_{trans}$	$^1J(W-C)_{cis}$	$^2J(P-C)_{trans}$	$^2J(P-C)_{cis}$
$W(CO)_5(PPh_3)$	199.21	197.28	143.8	126.2	22.0	7.2
$W(CO)_5(PMePh_2)$	199.67	197.02	144.1	125.7	20.0	7.0
$W(CO)_5(PMe_2Ph)$	199.76	196.72	144.8	125.7	19.8	7.2
$W(CO)_5(PMe_3)$	200.05	196.92	144.9	125.2	18.7	7.7
$W(CO)_4(dppe)$	208.28	201.41	149.3	125.1	7.35, 25.0	6.9
$W(CO)_4(depe)$	208.84	201.86	148.0	124.0	6.1, 11.0	7.1
$W(CO)_4(dmpe)$	209.32	201.68	148.8	124.0	5.6, 11.0	7.1
$W(CO)_4(dppm)$	210.46	202.90	152.6	125.2	7.1, 22.0[b]	6.6
$W(CO)_4(dmpm)$	211.08	203.33	142.0	124.0	8.8, 10.7	7.3

[a] Coupling constants, *J*, are in Hz. Solvent: $CDCl_3$. [b] For $W(CO)_4(dppm)$ the $\delta(CO)_{trans}$ was observed to be a triplet rather than a doublet of doublets. The analysis is given in ref 43.

force field used and partly because of the difficulty in some cases to obtain precise values for the A_1^2 and E modes due to overlap of these peaks. This is unfortunate since k_1 represents the CO force constant trans to the phosphine ligand, and so trends in k_1 should give a more reliable estimate of the trend in donor ability of the phosphine ligands than of trends in $\nu(A_1^1)$.

We also report an IR study of the $[W(CO)_4(LL)]$ series in cyclohexane in Table III. In this series the $\nu(CO)$ and k_2 values are largest when Ph substituents are on the diphosphine ligands, but the k_1 values remain quite constant. These results indicate that the Ph substituents decrease the basicity of the ligands. However, in a recent study of similar Cr and Mo compounds in CS_2,[4] the opposite trend was reported. We decided to measure the $\nu(CO)$ of the W analogues in CS_2, as a check of this reported trend, and the results are summarized in Table IV. The IR measurements for $\nu(CO)$ and the calculated k_2 values were found to follow the same trend as is also observed in the cyclohexane solvent. The k_1 values remain constant for both sets of ligands: $k_1(dmpm) \sim k_1(dppm)$ and $k_1(dmpe) \sim k_1(dppe)$.

^{13}C NMR Spectroscopy. Recently, Buchner and Schenk studied the trans influence of ligands bonded to tungsten.[8] They found that a trans-influence series for ligands L was best derived from the one-bond coupling constant $^1J(^{183}W-^{13}C)$ of the axial or trans CO group of the monosubstituted tungsten carbonyl compounds $[W(CO)_5L]$. Buchner and Schenk reported that $^1J(^{183}W-^{13}C)_{trans}$ = 145 Hz for $[W(CO)_5(PMe_3)]$ and 140 Hz for $[W(CO)_5(PPh_3)]$. The smaller ^1J trans value indicated that PPh_3 is a stronger σ donor than PMe_3. However in order to be more conclusive, we have measured the ^{13}C NMR spectra for the series $[W(CO)_5(PMe_{3-n}Ph_n)]$ (n = 0–3), $[W(CO)_4(R_2P(CH_2)_2PR_2)]$ (R = Ph, Et, Me), and $[W(CO)_4(R_2PCH_2PR_2)]$ (R = Ph, Me). These results are summarized in Table V.

This study indicates that the range of values in $^1J(^{183}W-^{13}C)_{trans}$ is small (~1 Hz) for the series $[W(CO)_5L]$ although the trend does indicate that PPh_3 is the strongest donor, since it gives the lowest value of $^1J(WC)$. However, an independent series of trans influence can be obtained from the chemical shifts of the carbonyl ligands trans to the phosphine ligands, L. This series (Table V) indicates that PMe_3 is the strongest donor in the series PMe_nPh_{3-n}, in contrast to the above coupling constant trend. For the complexes $[W(CO)_4(R_2P(CH_2)_2PR_2)]$, both the trends in $\delta(CO)$ and $^1J(WCO)$ indicate that the methylphosphines are slightly stronger donors. Trends in $\delta(^{13}CO)$ and $^1J(^{183}W-^{13}C)$ for the carbonyl ligands cis to phosphorus are also too small to be conclusive. Therefore, it appears that the sensitivity of the ^{13}C NMR criterion of trans influence is too low to be able to make any conclusion on the trans influence and hence the σ-donor abilities of these phosphine ligands.

Discussion

The IE of the phosphorus lone pair (HOMO) in the series of ligands have been measured for the diphosphine ligands $R_2PCH_2PR_2$ and $R_2P(CH_2)_2PR_2$ (R = Ph, Me, Et), and in both series the IE decrease in the order Me > Et > Ph (Table I). This series is in accord with an earlier PES study of the $PMe_{3-n}Ph_n$ (n = 0–3) series,[13] and if we include the reported IE measurement for PEt_3,[33] the order remains Me > Et > Ph.

If Koopmans' theorem is assumed, these results indicate that, for example, PPh_3 should be a stronger donor than PMe_3. The trend is the opposite of the series expected from electronegativity arguments and from the known order of basicities in aqueous solution. However, a subsequent measurement of proton affinities confirmed that PPh_3 is indeed a stronger Brønsted base than PMe_3 under gas-phase conditions.[15] The lower Brønsted basicity of PPh_3 in aqueous solution can be rationalized in terms of the lower solvation energy[19,20] of the bulkier ion $[PPh_3H]^+$ compared to $[PMe_3H]^+$ and is therefore due primarily to steric rather than electronic effects. It can be argued that the observed trends are not due to ground-state effects but due to differential relaxation effects. Thus, for example, the phenyl groups could release charge on demand through conjugation of the π system with the n(P) orbital and hence stabilize the ion state $[Ph_3P]^+$ or the protonated $[Ph_3PH]^+$.

Relaxation effects in valence-band PES studies have nearly always been negelected because it is predicted that the total relaxation contribution is only ~1 eV.[34] Therefore, *differences* in relaxation contributions for *analogous* compounds should be considerably smaller than this. In fact, arguments based on ground-state effects have been used successfully in the interpretation of many UPS spectra. For example, ground-state arguments have been used to rationalize the shifts and splitting of the t_{2g} orbitals in d^6 $[M(CO)_{6-n}L_n]$ complexes.[28-30] In contrast, relaxation contributions in core level shifts are an order of magnitude larger.[34] However, the success of Jolly's LOIP method[35-37] for using core BE shifts to position nonbonding valence levels strongly suggests that, even in core levels, differences in relaxation energy for similar compounds are <1 eV, which also indicates that differences in valence-band relaxation energies are considerably less than 1 eV. Therefore, we conclude that trends in the lone-pair BE are not due to relaxation effects but accurately reflect relative molecular orbital energies. We also note that relaxation effects on ionization to $[PR_3]^+$ are likely to be similar to relaxation effects on protonation to give $[PR_3H]^+$ or on complexation to give $[W(CO)_5(PR_3)]$. Hence, even if relaxation effects were partly responsible for the lower IE of PPh_3 compared to that of PMe_3, similar effects should also make PPh_3 a stronger σ donor.[13]

The trends in binding energies of the W(5d) electrons (Tables I and II) both for $[W(CO)_5(PMe_nPh_{3-n})]$ and for $[W(CO)4(R_2P(CH_2)_nPR_2)]$ follow the same sequences as for the n(P) level of the free phosphines; that is, they follow the series R = Me > Et > Ph. Again, it is easier to oxidize the phenyl- rather than the methylphosphine derivatives under gas-phase conditions. Again it could be argued that this is a relaxation effect, but the simplest rationalization is that the phenylphosphines are slightly stronger donors than corresponding methylphosphines, as predicted above. We emphasize that the differences in W(5d) binding energies are small and would not be expected to lead to major differences in chemical reactivity. Where such effects are observed it would be more logical to explain them in terms of the much greater differences in steric effects. For example, the heats of reaction of $[Mo(CO)_3(toluene)]$ with the ligands L = PMe_nPh_{3-n} to give $[Mo(CO)_3L_3]$ have been measured recently and are for $n = 3$, −47.1, for $n = 2$, −43.8, for $n = 1$, −37.2, and for $n = 0$, −37.2 kcal mol^{-1}.[38] The differences between the values were factored into steric and electronic contributions, and the best fit predicted that ~10 kcal mol^{-1} was due to steric effects and only ~1 kcal mol^{-1} (i.e. within the limits of error of the fit) was due to electronic effects for the PMe_3 and PPh_3 derivatives. The possibility that the basicity series of complexes such as $[W(CO)_5(PMe_nPh_{3-n})]$ may be different in the gas phase and in solution, especially in polar solvents, should also be considered since the effect is known to be of great importance for the free phosphine ligands.[15]

A second useful parameter from the photoelectron spectra is the stabilization energy of the phosphorus lone pair on coordination, Δ_{stab} (Table I and II). In general, ligands forming the strongest σ bonds may be expected to give the largest values of Δ_{stab}, although there are several complicating factors. One possible complicating factor is associated with differences in CPC bond angles in free and coordinated phosphines, which depend greatly on the steric effects of substituents on phosphorus.[33] The data in Table I and II indicate that there are only very small differences in Δ_{stab} for trimethylphosphine and triethylphosphine (as well as for the phosphines dmpm, dmpe, depm, depe) and so suggest that the steric effects of substituents do not have a major effect. Δ_{stab} values for phenylphosphines are very much greater, consistent with them being the stronger donors. However, as discussed previously,[17,39,40] the very strong mixing of the n(P) level of the free phenylphosphine derivature or the σ(W–P) level of the coordinated phosphine with the p_π orbitals of the phenyl rings is expected to destabilize the n(P) level but to stabilize the σ(W–P) level and hence lead to large values of Δ_{stab}. Since it is not possible to factor the Δ_{stab} for the phenylphosphines into the σ-bonding and π-conjugation[41] components, the larger Δ_{stab} values for the phenylphosphines do not necessarily indicate stronger σ bonding compared to the methyl- or ethylphosphine analogues.

π-Bonding effects may also be of importance in determining what controls the basicity trends in these phosphine ligands. Although $M(d\pi) \rightarrow CO(\pi^*)$ back-bonding in carbonyl complexes is strong,[1] the $M(d\pi) \rightarrow P(d\pi)$ in M–P bonds are believed to be quite weak.[2] In an earlier study we noted that the ligand field splitting in the W(5d) level was directly related to π-back-bonding effects and found this splitting to be constant through the $[W(CO)_5(PMe_nPh_{3-n})]$ series.[15,42] Hence, π-back-bonding effects are probably similar for this ligand series.

We have also examined the vibrational spectra and ^{13}C NMR spectra of the complexes. Previous IR studies in the ν(CO) region indicated that the donor ability of methylphosphines is greater than that of phenylphosphines,[2] in contrast to the results from PE spectroscopy, and so a careful study of the IR and Raman spectra of the tungsten carbonyl complexes was carried out. In agreement with previous work, we find that $\nu(A_1{}^1)$ for the CO group trans to phosphorus in $[W(CO)_5(PMe_nPh_{3-n})]$ is higher for the phenylphosphine compared to methylphosphine ligands (Table III). However, the range of values is only ~2 cm^{-1} for the series of phosphines, indicating only a slight difference in electronic effects. Further, the trend in the Cotton–Kraihanzel force constants k_1 is irregular (Table III) and would suggest that PPh_3 is the strongest donor of the series of phosphines. Our conclusion is that the differences in electronic effects between the ligands PMe_nPh_{3-n} are too small to be determined by the technique of vibrational spectroscopy. Similarly, the trends in the ^{13}C NMR parameters δ(CO) and $^1J(^{183}W-^{13}C)$ for carbonyls trans to phosphorus in the complexes $[W(CO)_5(PR_3)]$ or $[W(CO)_4(R_2P(CH_2)_2PR_2)]$ (Table V) are not particularly useful. For $[W(CO)_5(PMe_nPh_{3-n})]$ the trend in δ(CO) indicates that methylphosphines are the stronger donors whereas the trend in $^1J(^{183}W-^{13}C)$ indicates that phenylphosphines are.

Because PE spectroscopy gives the most direct information about electronic energy levels in complexes, we believe that phenylphosphines are slightly stronger donors than methylphosphines. In the gas phase, it can be predicted that the proton affinity of $[W(CO)_5(PPh_3)]$ will be greater than that of $[W(CO)_5(PMe_3)]$, because of the good correlation of proton affinities with ionization energies. However, in solution the chemical reactivity of complexes is likely to be dominated by differences in steric effects between phenyl- and methylphosphines. Such effects will decrease the reactivity of phenyl- compared to methyl-

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phosphine in reactions occurring by associative mechanisms (such as oxidative addition or protonation) by direct steric interactions, and differences in solvation energies due to steric effects in either ground or transition states could also have a great effect on chemical reactivity. Other techniques, such as IR and ^{13}C NMR spectroscopy, give conflicting evidence on the relative donor abilities of phenyl- vs. methylphosphines. However, the commonly held view among inorganic and organometallic chemists that methylphosphines are significantly stronger donor ligands than phenylphosphines is, in our opinion, no longer tenable.

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Registry No. dppm, 2071-20-7; W(CO)$_5$(PPh$_3$), 15444-65-2; W(CO)$_5$(PMePh$_2$), 18534-36-6; W(CO)$_5$(PMe$_2$Ph), 42565-94-6; W(CO)$_5$(PMe$_3$), 26555-11-3; W(CO)$_4$(dppm), 41830-14-2; W(CO)$_4$(dppe), 29890-05-9; W(CO)$_4$(dmpm), 90624-10-5; W(CO)$_4$(dmpe), 40544-99-8; W(CO)$_4$(depm), 103884-73-7; W(CO)$_4$(depe), 97284-98-5; ^{183}W, 14265-81-7; ^{13}C, 14762-74-4.

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Isomerization Processes Observed for Chromium Compounds by Using the Gas Chromatographic Reactor

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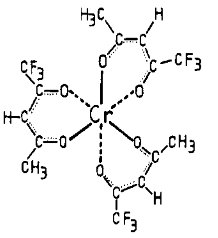
Two volatile chromium compounds, tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) [Cr(tfa)$_3$] and (2-methylnaphthalene)tricarbonylchromium [2-MenaphCr(CO)$_3$], have been studied gas chromatographically. The resolution of geometrical isomers of Cr(tfa)$_3$ using gas chromatography at sufficiently high temperatures (150–200 °C) permitted the dynamic interconversion process of the isomers to be studied. The use of high-resolution capillary columns aided this study. The activation energy for cis $\rightarrow$ trans isomerization was estimated to be ca. 130 ± 10 kJ mol^{-1}, and the twist mechanism was believed to be operative. Successful gas chromatographic separation of isomers of a bicyclic polyene–M(CO)$_3$ system is reported for the first time. The rearrangement of the –Cr(CO)$_3$ group can be followed in the gas chromatographic reactor; however, direct on-column injection is necessary in order to overcome decomposition of the compound, and this makes extraction of thermodynamic data less straightforward. An intramolecular (nondissociative) mechanism for the rearrangement is supported, and activation energies for isomer interconversion were estimated at 94 ± 7 and 100 ± 10 kJ mol^{-1}, respectively.

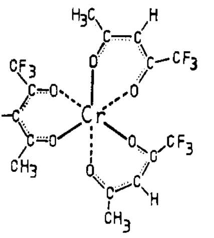
Introduction

The gas chromatographic resolution of the cis and trans geometric isomers of Cr(tfa)$_3$ (**1a** and **1b**) has been well documented.[1-3] The resolution of the isomers is a function of chromatographic parameters such as temperature, liquid phase, carrier flow rate, and overall plate count (efficiency) of the column; on capillary columns the resolution is much greater by virtue of the higher efficiency achievable. Each geometric isomer is enantiomeric, existing in Δ and Λ optically isomeric forms; however, these are not resolved in the GC experiment since the liquid phase is nondiscriminating toward these isomers [and so cis(Δ) and cis(Λ) coelute]. The mechanism of interconversion from cis to trans and vice versa for Cr(tfa)$_3$ and indeed many analogous systems such as [M(unsymmetrical bidentate)$_3$], [M(unsymmetrical bidentate)$_2$(symmetrical bidentate)], etc. has been the subject of much interest over the past few decades. Thus, these complexes may undergo isomerization as well as racemization. Any mechanism proposed to account for this dynamic behavior must take cognizance of all possible pathways that can lead to isomerization–racemization and fit this to experimental observation. This has been discussed by Gordon and Holm[4] in general terms and also for the Co(III) complex with 5-methylhexane-2,4-dione, and the mechanisms are also presented in advanced-level textbooks.[5]

1b



1a



Nuclear magnetic resonance methods have been applied to study the isomerization process. Fay and Piper used ^{19}F and ^{1}H NMR to characterize and in some cases obtain coalescence of the trifluoromethyl and methyl resonances, respectively, in M(tfa)$_3$ complexes and M(tfa)$_n$(acac)$_{3-n}$ systems.[6-8] Time-dependent intensties of NMR signals were also employed to study the inert Co complex. More recently, Grossmann and Haworth used the dynamic ^{1}H NMR method to study coalescence of methyl resonances of labile M(tfa)$_3$ (M = Al^{3+}, Ga^{3+})[9] and from the activation parameters proposed mechanisms for ligand interchange for *trans*-M(tfa)$_3$. Hence, both time-dependent and dynamic NMR procedures have been utilized.

Gas chromatography has been used almost exclusively for the volatile and thermally stable paramagnetic Cr(tfa)$_3$ complex, for which NMR methods are unsuited. The procedure is essentially a time-dependent one, with Cr(tfa)$_3$ heated at different temperatures and the solution sampled at intervals in order to estimate rate constants and activation parameters for the isomerization. Fontaine et al.[10] dissolved the complex in both 1,2,4-trimethyl-

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