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A Fourier Transform Carbon-13 NMR Study of the Electronic Effects of Phosphorus, Arsenic, and Antimony Ligands in Transition-Metal Carbonyl Complexes

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Received September 14, 1979

^{13}C NMR spectra have been obtained for 116 $\text{LNi}(\text{CO})_3$ complexes of phosphorus, arsenic, and antimony ligands as well as analogous $\text{LCr}(\text{CO})_5$, $\text{LMo}(\text{CO})_5$, and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ derivatives. Analysis of the carbonyl chemical shift data yields electronic effect parameters which characterize the ratio of the σ basicity to π acidity of the ligands. These parameters are in close agreement with the electronic parameters for phosphorus ligands derived by Tolman and Kabachnik. The donor/acceptor ratio for phosphorus ligands increases in the order: $\text{PCl}_3 < \text{P}(\text{OPh})_3 < \text{P}(\text{SR})_3 < \text{P}(\text{OR})_3 < \text{PPh}_3 < \text{P}(\text{NR}_2)_3 \leq \text{PR}_3$. The donor/acceptor ratio for phosphite ligands increases (1) with the replacement of aryl by alkyl substituents, (2) with the replacement of caged phosphites by open-chained analogues, and (3) with increasing chain length for alkyl substituents. The donor/acceptor ratio for phosphines increases (1) with decreasing unsaturation in alkyl substituents, (2) with increasing alkyl chain length, and (3) with increasing substitution at the α carbon. Comparison of data for phosphine, arsine, and stibine ligands suggests that the range of donor/acceptor ratios is largest for phosphines and smallest for stibines. Furthermore, variations in the donor/acceptor ratio due to changes in the R group in ER_3 ligands are significantly larger than variations due to changes in the nature of the group 5A element. Our data suggest that the donor/acceptor ratio for ER_3 ligands increases in the order: $\text{AsR}_3 < \text{PR}_3 < \text{SbR}_3$. The magnitude of the $^2J_{^{13}\text{C}^{31}\text{P}}$ through-metal coupling to the trans carbonyl in $\text{LMo}(\text{CO})_5$ complexes appears to increase with increasing electron-withdrawing power for the substituents on the phosphorus ligand, a behavior more commonly associated with directly bound coupling constants such as the $^1J_{^{31}\text{P}^{13}\text{W}}$ coupling in $\text{LW}(\text{CO})_5$ derivatives.

Introduction

A linear correlation between the ^{13}C NMR carbonyl chemical shift and the infrared stretching force constant for the carbonyl mode was apparent from the earliest studies of the ^{13}C NMR spectra of transition-metal carbonyl complexes.^{1,2} An increase in the stretching force constant appears to be reflected by a *shielding* of the carbonyl resonance, a shift to higher field strengths. This correlation has now been extended to a wide variety of metal-carbonyl systems and appears valid for most complexes where calculations of the infrared stretching force constants are not contentious.³⁻⁷

The Darensbourgs⁸ have argued that an increase in the carbonyl stretching force constant in metal carbonyl complexes may result from either an increase in the σ basicity or a decrease in the π acidity of the carbonyl. Therefore they suggest that an increase in the stretching force constant must mirror an increase in the positive charge on the carbonyl carbon. If variations in the ^{13}C NMR carbonyl chemical shift are dominated by contributions from either *local* diamagnetic shielding⁹ or the dependence of the *local* paramagnetic shielding¹⁰ on electron density, we should expect a *deshielding* of the carbonyl resonance with increasing force constant rather than the shielding that is observed.

Our studies of $(\eta^6\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$ complexes suggested a net donation of electron density from the arene ring to the $\text{Cr}(\text{CO})_3$ fragment¹¹ and a deshielding of the carbonyl resonance with increasing donation to the $\text{Cr}(\text{CO})_3$ moiety.⁴ Since the extent of transition metal \rightarrow carbonyl π back-donation is expected to increase with increasing electron density on the transition metal, we⁴⁻⁷ and others¹² have attributed this deshielding of the carbonyl resonance to a decrease in the magnitude of the separation between the electronic ground state and the lowest lying excited states with increased back-bonding. This hypothesis is supported by the observation that the carbonyl resonance in $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ complexes ($\text{M} = \text{Cr}^-, \text{Mn}^0, \text{Fe}^+$) is deshielded with increasing negative charge,⁴ in accord with the results of molecular orbital calculations which suggest an increase in the metal \rightarrow carbonyl π back-donation with increasing negative charge.¹³ This hypothesis is further supported by the excellent correlation (r

$= 0.991$) between the carbonyl chemical shift and the Cr-C bond lengths in $\text{Cr}(\text{CO})_6$, $\text{LCr}(\text{CO})_5$, and $\text{L}_2\text{Cr}(\text{CO})_4$ complexes.⁴

If the carbonyl resonance is deshielded with increasing electron density at the transition metal, then the carbonyl chemical shift should reflect the electronic effects of ligands introduced into these complexes. Since the electron density at the metal in $\text{LNi}(\text{CO})_3$ complexes should increase as the σ basicity of L increases and decrease as the π acidity increases, the carbonyl chemical shift in $\text{LNi}(\text{CO})_3$ complexes should be a measure of the ratio of the σ -donor to π -acceptor character of the ligand. By subtracting the chemical shift of the parent $\text{Ni}(\text{CO})_4$ complex from the chemical shift of $\text{LNi}(\text{CO})_3$ derivatives, we can define an electronic effect parameter in which L is compared to the CO ligand. The sign convention is such that an increase in the magnitude of this parameter implies an increase in the ratio of the σ basicity to π acidity or a net increase in the electron-donor ability of the ligand.

We wish to report herein the results of a study of 116 different $\text{LNi}(\text{CO})_3$ derivatives, thereby significantly expanding our earlier study.⁶ We have investigated the extent to which these electronic effect parameters can be transferred to other systems such as $\text{LCr}(\text{CO})_5$, $\text{LMo}(\text{CO})_5$, and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ complexes.

Experimental Section

$\text{P}(\text{OR})_3$ ligands ($\text{R} = \text{Pr}, i\text{-Pr}, \text{Bu}$) were synthesized by the reaction

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of phosphorus trichloride with the corresponding alcohol in the presence of a slight excess of dimethylaniline.¹⁴ (RO)PCl₂ and (RO)₂PCl (R = Me, Et, *i*-Pr, Bu, Ph) were synthesized by using stoichiometric amounts of the alcohol in the presence of an equimolar amount of dimethylaniline.¹⁵ P(NR₂)₃ (R = Me, Et), PhP(NMe₂)₂, and Ph₂P(NMe₂) were synthesized through the reaction of PCl₃, PhPCl₂, or Ph₂PCl with a twofold amount of dialkylamine.¹⁶ PhP(OR)₂ and Ph₂P(OR) (R = Me, Et, *i*-Pr, Bu, Ph) were synthesized by the alcoholysis of either PhP(NMe₂)₂ or Ph₂P(NMe₂).¹⁷

ER₃ ligands (E = P, R = Pr, *i*-Pr, pentyl, hexyl, heptyl, octyl; E = As, R = Et, Bu; E = Sb, R = Et) were synthesized via the dropwise addition of an ether solution of the trihalide to a slight excess of the Grignard reagent in ether solution.¹⁸ PhSbCl₂ and Ph₂SbCl were synthesized by the metathesis of stoichiometric mixtures of Ph₃Sb and SbCl₃.¹⁹ PhER₂ and Ph₂ER (E = P, R = Me, Et, Pr, Bu; E = As, R = Me, Et, Bu; E = Sb, R = Me, Et) were synthesized via reaction of the PhECl₂ or Ph₂ECl intermediate with a Grignard reagent in ether solution.²⁰

These ligands were purified through vacuum distillation or fractional recrystallization, when possible, and characterized by infrared and proton magnetic resonance spectroscopy. Other ligands were purchased or obtained as gifts and were used without further purification.

Ni(CO)₄ was purchased from Matheson Gas Products and used without further purification. Particular attention must be paid to the extreme toxicity of Ni(CO)₄. All manipulations were carried out in a well-ventilated hood tested with a smoke bomb before use to ensure that no fumes leaked into other laboratories. For minimization of toxicity through a reduction in the vapor pressure, Ni(CO)₄ was dispensed directly into CDCl₃ to form a 4 M solution which was handled by syringe. All nickel carbonyl complexes were destroyed immediately after use by reaction with bromine. LNi(CO)₃ complexes were prepared by the addition of a 2-mL aliquot of 4 M Ni(CO)₄ in CDCl₃ to an argon- or nitrogen-purged NMR tube containing 8 mmol of the ligand in 1 mL of CDCl₃. The samples were allowed to stand for 10–15 min and then agitated until CO evolution ceased. Preliminary ¹³C NMR spectra were obtained to determine the extent of complexation. If complexation appeared complete, an 0.2-mL aliquot was removed, diluted with 15 mL of chloroform, and used for infrared characterization of the complex. Approximately 2 mmol of excess Ni(CO)₄ was then added to the sample, and the ¹³C NMR spectrum was accumulated until the signal-to-noise ratio for the carbonyl region was between 50 and 100 to 1. The ¹³C NMR chemical shifts are reported in ppm downfield from the internal Ni(CO)₄ reference and are the result of at least two independent measurements with a precision of ±0.03 ppm.

LCr(CO)₃ complexes were synthesized by the reaction of an excess of the hexacarbonyl with the ligand in refluxing diglyme solution²¹ or by photolysis of the hexacarbonyl with a high-pressure mercury lamp in the presence of a hexane solution of the ligand.²² LMo(CO)₅ derivatives were synthesized by the reaction of an excess of the hexacarbonyl with the ligand in refluxing methylcyclohexane.²³ Excess metal hexacarbonyl was removed by vacuum sublimation or fractional recrystallization, and the complex was characterized by infrared spectroscopy. Preliminary ¹³C NMR spectra were recorded in CDCl₃ solution, excess hexacarbonyl was dissolved in the solution, and the ¹³C NMR carbonyl chemical shifts were measured relative to the internal metal hexacarbonyl reference with a precision of ±0.06 ppm.

(η⁶-C₆H₆)Cr(CO)₂L complexes were synthesized by photolysis of the parent (arene)tricarbonylchromium(0) complex with a high-pressure mercury lamp in either benzene or hexane solution in the

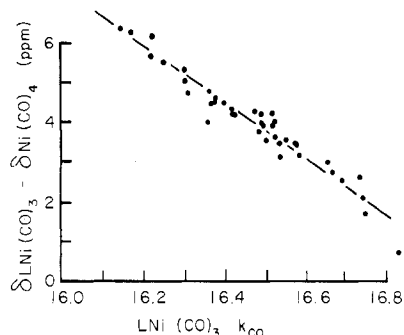


Figure 1. A plot of the ¹³C NMR carbonyl chemical shifts in ppm downfield from Ni(CO)₄ for 40 LNi(CO)₃ complexes vs. the infrared stretching force constants in mdyin/Å for the carbonyl mode (*r* = 0.962). Force constants were calculated from the data of C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970), on the basis of the Cotton–Kraihanzel approximations, F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962), under an assumed local symmetry of C_{3v}.

presence of a slight excess of the respective ligand.²⁴ (η⁶-C₆H₆)Cr(CO)₃ was synthesized by the method of Rausch et al.²⁵ All complexes were characterized by infrared spectroscopy.

¹³C NMR spectra were obtained with a JEOL FX-60-FT spectrometer operating at 15 MHz, or a Varian XL-100-FT spectrometer operating at 25 MHz, using an internal deuterium lock. The technique of equilibrium saturation was used to overcome the long T₁ relaxation time for the carbonyl resonance.²⁶ We used pulse widths that correspond to flip angles on the order of 30–40° and a repetition rate on the FX-60 of 2.2 seconds.

For maximum precision in carbonyl chemical shift measurements, an internal reference was used whose chemical shift was as close as possible to that of the complex under investigation. These data may be converted to a Me₄Si reference by using the approximate conversions:

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{Ni}(\text{CO})_4} + 191.64 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{Cr}(\text{CO})_6} + 211.28 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{Mo}(\text{CO})_6} + 200.77 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3} + 233.34 \text{ ppm}$$

Results

The ¹³C NMR spectra of LNi(CO)₃ complexes in CDCl₃ solution exhibit a single sharp resonance at low field assigned to the geometrically equivalent carbonyls and a pattern of resonances at high field analogous to the free ligand. For the vast majority of the complexes studied, the magnitude of the ²J_{13C31P} through-metal nuclear spin–spin coupling constant was less than 1 Hz and could not be resolved. There is no obvious relationship between the magnitude of this coupling constant, when observed, and the nature of the ligand. The carbonyl chemical shift (δ_{CO}) and coupling constant data for 116 LNi(CO)₃ complexes of phosphorus, arsenic, and antimony ligands are given in Table I.

If we derive substituent constants for the X groups in X₃ENi(CO)₃ complexes by dividing δ_{CO} by three, we can use these substituent constants to predict the carbonyl chemical shift in X₂YENi(CO)₃ derivatives. The correlation between the predicted and experimental values of δ_{CO} for 49

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Table I. ^{13}C NMR Chemical Shifts for $\text{LNi}(\text{CO})_3$ Complexes, in Ppm Downfield from $\text{Ni}(\text{CO})_4^a$

no.	ligand	chem shift	no.	ligand	chem shift
1	$\text{P}(\text{OMe})_3$	3.18	59	$\text{PhP}(\text{OBU})_2$	4.20
2	$\text{P}(\text{OCH}_2)_3\text{CEt}$	2.60	60	$\text{PhP}(\text{OPh})_2$	2.54
3	$\text{P}(\text{OEt})_3$	3.61	61	$\text{PhP}(\text{NMe}_2)_2$	4.69
4	$\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	2.76	62	PhPCL_2	0.69
5	$\text{P}(\text{OPr})_3$	3.94	63	PhPH_2	3.54
6	$\text{P}(\text{O-}i\text{-Pr})_3$	3.90	64	PhPMe_2	4.76
7	$\text{P}(\text{O-allyl})_3$	3.43	65	PhPET_2	5.36
8	$\text{P}(\text{OBu})_3$	3.95 (1.4) ^b	66	PhPVy_2	4.25
9	$\text{P}(\text{OPh})_3$	1.69	67	PhPPr_2	5.29
10	$\text{P}(\text{OPh-}p\text{-Cl})_3$	1.32	68	PhPBu_2	5.29
11	$\text{P}(\text{O-lauryl})_3$	3.98	69	$\text{PhP}(\text{c-Hx})_2$	5.80
12	$\text{P}(\text{S-lauryl})_3$	2.50 (3.0)	70	$\text{PhP}(\text{c-C}_5\text{H}_{10})$	4.94
13	$\text{P}(\text{NMe}_2)_3$	5.68	71	$\text{Ph}_2\text{P}(\text{OMe})$	3.96
14	$\text{P}(\text{NEt}_2)_3$	5.68	72	$\text{Ph}_2\text{P}(\text{OEt})$	4.27
15	PCl_3	-1.41 (12.0)	73	$\text{Ph}_2\text{P}(\text{O-}i\text{-Pr})$	4.26
16	PMe_3	5.05	74	$\text{Ph}_2\text{P}(\text{OBu})$	4.30
17	PET_3	5.54	75	$\text{Ph}_2\text{P}(\text{OPh})$	3.46
18	$\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$	3.47	76	$\text{Ph}_2\text{P}(\text{NMe}_2)$	4.34
19	PVy_3^c	4.22	77	Ph_2PCL	2.49
20	PPr_3	5.62	78	Ph_2PH	3.93
21	$\text{P-}i\text{-Pr}_3$	6.20	79	Ph_2PMe	4.53
22	$\text{P}(\text{allyl})_3$	4.92	80	Ph_2PEt	4.78
23	PBu_3	5.69	81	Ph_2PVy	4.26
24	$\text{P-}i\text{-Bu}_3$	5.40	82	Ph_2PPr	4.76
25	$\text{P-}s\text{-Bu}_3$	6.23 (1.2)	83	Ph_2PBu	4.74
26	$\text{P-}t\text{-Bu}_3$	6.37 (1.2)	84	$\text{Ph}_2\text{P-}t\text{-Bu}$	4.80
27	$\text{P}(\text{SiMe}_3)_3$	5.67	85	$\text{Ph}_2\text{PC}_6\text{F}_5$	3.13
28	$\text{P}(\text{pentyl})_3$	5.70	86	$\text{Ph}_2\text{P}(\text{c-Hx})$	5.07
29	$\text{P}(\text{hexyl})_3$	5.70	87	$(\text{NCCH}_2\text{CH}_2)_2\text{PH}_2$	3.13 (1.7)
30	$\text{P}(\text{heptyl})_3$	5.69	88	$(\text{NCCH}_2\text{CH}_2)_2\text{PH}$	3.33 (1.5)
31	$\text{P}(\text{octyl})_3$	5.66 (1.0)	89	$(\text{c-Hx})\text{PH}_2$	4.07
32	$\text{P}(\text{c-Hx})_3^c$	6.32 (1.5)	90	$(\text{c-Hx})_2\text{PH}$	5.35
33	PPh_3	4.30	91	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	4.39
34	$\text{P}(\text{benzyl})_3$	3.98	92	$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	4.29
35	$\text{P}(\text{naphthyl})_3$	4.33	93	$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	4.60
36	$\text{P}(\text{Ph-}p\text{-CH}_3)_3$	4.50	94	$(\text{Ph}_2\text{P})_2\text{CH}_2$	3.52
37	$\text{P}(\text{Ph-}p\text{-OCH}_3)_3$	4.43	95	$\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2^d$	7.79
38	$\text{P}(\text{Ph-}p\text{-F})_3$	3.77	96	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2^e$	4.15, 4.36
39	$\text{P}(\text{Ph-}p\text{-Cl})_3$	3.54	97	$\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2$	4.19
40	$\text{P}(\text{Ph-}p\text{-NMe}_2)_3$	5.35	98	$(\text{Ph}_2\text{As})_2\text{CH}_2$	3.33
41	$\text{P}(\text{Ph-}o\text{-CH}_3)_3$	3.67	99	AsMe_3	4.46
42	$\text{P}(\text{Ph-}m\text{-CH}_3)_3$	4.48	100	AsEt_3	5.33
43	$\text{P}(\text{Ph-}o\text{-OCH}_3)_3$	5.37	101	AsBu_3	5.26
44	$(\text{MeO})\text{PCl}_2$	0.17	102	AsPh_3	4.16
45	$(\text{EtO})\text{PCl}_2$	0.30	103	PhAsMe_2	4.34
46	$(i\text{-PrO})\text{PCl}_2$	0.38	104	PhAsEt_2	4.89
47	$(\text{BuO})\text{PCl}_2$	0.40	105	PhAsBu_2	4.90
48	$(\text{PhO})\text{PCl}_2$	-0.33	106	Ph_2AsMe	4.19
49	$(\text{MeO})_2\text{PCl}$	1.69	107	Ph_2AsEt	4.47
50	$(\text{EtO})_2\text{PCl}$	2.00	108	Ph_2AsBu	4.48
51	$(i\text{-PrO})_2\text{PCl}$	2.15	109	SbMe_3	4.99
52	$(\text{BuO})_2\text{PCl}$	2.20	110	SbEt_3	5.89
53	$(\text{PhO})_2\text{PCl}$	0.74	111	SbBu_3	5.85
54	$(\text{PhO})\text{P}(\text{OCH}_2)_2$	2.08	112	SbPh_3	4.86
55	$\text{EtP}(\text{OMe})_2$	4.36	113	PhSbMe_2	4.94
56	$\text{PhP}(\text{OMe})_2$	3.48	114	PhSbEt_2	5.52
57	$\text{PhP}(\text{OEt})_2$	4.04	115	Ph_2SbMe	4.89
58	$\text{PhP}(\text{O-}i\text{-Pr})_2$	4.23	116	Ph_2SbEt	5.16

^a Chemical shifts were measured in CDCl_3 solution and are reported in ppm downfield from $\text{Ni}(\text{CO})_4$. All data are the result of duplicate measurements with a precision of ± 0.03 ppm. Part of these data were reported by G. M. Bodner, *Inorg. Chem.*, **14**, 1932 (1975).

^b $^2J_{13\text{C}31\text{P}}$ through-metal nuclear spin-spin coupling constant in Hz, ± 0.2 Hz. ^c Vy = vinyl, c-Hx = cyclohexyl. ^d This is the chemical shift for the $\text{LNi}(\text{CO})_2$ complex; no evidence was found in the ^{13}C NMR spectrum for the $\text{LNi}(\text{CO})_3$ derivative. ^e Excess $\text{Ni}(\text{CO})_4$ was added to ensure complexation at both ends of this bidentate ligand. Thus, two nonequivalent $\text{LNi}(\text{CO})_3$ environments were observed.

$\text{X}_2\text{YENi}(\text{CO})_3$ complexes is excellent (r , linear correlation coefficient, = 0.997).

Tolman²⁷ has derived analogous electronic effect parameters for phosphorus ligands in $\text{LNi}(\text{CO})_3$ complexes by measuring the A_1 infrared stretching frequency. It is significant that a linear correlation ($r = 0.962$) has been observed between δ_{CO} and both the A_1 stretching frequencies and the stretching force constants calculated from the data of Tolman (Figure 1). It should be noted, however, that the ratio of the range of the carbonyl chemical shifts to the precision of measurement is

$2^{1/2}$ times larger than the equivalent ratio for the infrared stretching frequencies.

A linear correlation has been reported between δ_{CO} for $\text{LNi}(\text{CO})_3$ complexes and the cis carbonyl chemical shift ($\delta_{\text{CO}}^{\text{cis}}$) in analogous $\text{LM}(\text{CO})_5$ complexes of Cr, Mo, and W.⁷ Data for an extended set of $\text{LCr}(\text{CO})_5$ and $\text{LMo}(\text{CO})_5$ complexes are given in Table II. The excellent correlations shown in Figures 2 and 3 between δ_{CO} for $\text{LNi}(\text{CO})_3$ complexes and $\delta_{\text{CO}}^{\text{cis}}$ for $\text{LCr}(\text{CO})_5$ ($r = 0.983$) and $\text{LMo}(\text{CO})_5$ ($r = 0.993$) complexes suggest that electronic effect parameters obtained

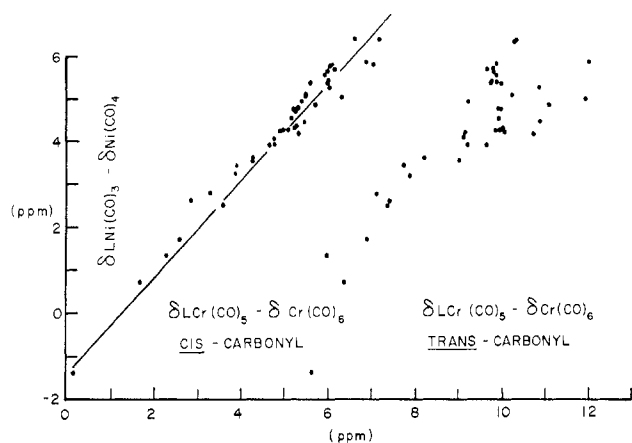


Figure 2. A plot of the ^{13}C NMR carbonyl chemical shifts in ppm downfield from $\text{Cr}(\text{CO})_6$ for the cis and trans carbonyl resonances for 42 $\text{LCr}(\text{CO})_5$ complexes vs. the ^{13}C NMR carbonyl chemical shifts in ppm downfield from $\text{Ni}(\text{CO})_4$ for the analogous $\text{LNi}(\text{CO})_3$ complexes. Correlation coefficients are 0.983 and 0.856 for the cis and trans carbonyl resonances, respectively.

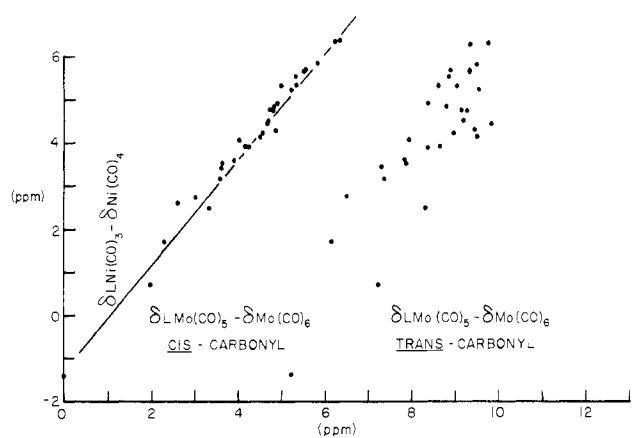


Figure 3. A plot of the ^{13}C NMR carbonyl chemical shifts in ppm downfield from $\text{Mo}(\text{CO})_6$ for the cis and trans carbonyl resonances for 30 $\text{LMo}(\text{CO})_5$ complexes vs. the ^{13}C NMR carbonyl chemical shifts in ppm downfield from $\text{Ni}(\text{CO})_4$ for the analogous $\text{LNi}(\text{CO})_3$ complexes. Correlation coefficients are 0.993 and 0.852 for the cis and trans carbonyl resonances, respectively.

from the study of $\text{LNi}(\text{CO})_3$ complexes may be applied to other metal-carbonyl systems. The analogous correlations for the trans carbonyl chemical shift ($\delta_{\text{CO}}^{\text{trans}}$) are not as good. We have reported difficulty with the analysis of $\delta_{\text{CO}}^{\text{trans}}$ in $\text{LM}(\text{CO})_5$ complexes of Cr, Mo and W,⁷ Webb and Graham²⁸ have reported similar problems with $\delta_{\text{CO}}^{\text{trans}}$ in $\text{XRe}(\text{CO})_5$ derivatives, and Woodard, Angelici, and Dombek²⁹ have reported difficulties with the interpretation of both $\delta_{\text{CO}}^{\text{trans}}$ and $\delta_{\text{CS}}^{\text{trans}}$ in $\text{LW}(\text{CO})_4(\text{CS})$ complexes. It is therefore interesting to note that predictions of δ_{CO} for $\text{X}_2\text{YPCr}(\text{CO})_5$ derivatives from data for $\text{X}_3\text{PCr}(\text{CO})_5$ and $\text{Y}_3\text{PCr}(\text{CO})_5$ complexes lead to linear correlations between the calculated and experimental chemical shifts for both the cis ($r = 0.980$) and trans carbonyl ($r = 0.964$) resonances. A linear correlation has also been observed between δ_{CO} for analogous $\text{LCr}(\text{CO})_5$ and $\text{LMo}(\text{CO})_5$ complexes for both the cis ($r = 0.993$) and trans carbonyl ($r = 0.932$) resonances.

Substituent constants from $\text{LNi}(\text{CO})_3$ complexes can also be applied to $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ derivatives for which δ_{CO}

data are reported in Table III. The correlation between these data and δ_{CO} for analogous $\text{LNi}(\text{CO})_3$ complexes is relatively good ($r = 0.956$).

Carbonyl Chemical Shifts for Metal Carbonyl Complexes of Phosphorus Ligands

The replacement of one or more carbonyls in $\text{M}(\text{CO})_m$ complexes with trivalent phosphorus ligands leads to a deshielding of the carbonyl resonance for the remaining CO ligands and therefore an increase in δ_{CO} relative to the parent $\text{M}(\text{CO})_m$ complex. Since there is an apparent deshielding of the carbonyl resonance with increasing metal \rightarrow carbonyl π back-bonding, and back-bonding increases as electron density on the metal increases, the carbonyl chemical shift in these complexes should reflect the donor/acceptor character of the phosphorus ligand.

Data for $\text{LNi}(\text{CO})_3$ complexes suggest an increase in the donor/acceptor ratio for phosphorus ligands in the order: $\text{PCl}_3 < \text{P}(\text{OPh})_3 < \text{P}(\text{SR})_3 < \text{P}(\text{OR})_3 < \text{PPh}_3 < \text{P}(\text{NR}_2)_3 \leq \text{PR}_3$; the net donation of electron density increases as the electron-withdrawing power of the substituents on phosphorus decreases.³⁰ Within the phosphite ligands, the donor/acceptor ratio increases in the order: $\text{P}(\text{O}-p\text{-CIPh})_3 < \text{P}(\text{OPh})_3 < \text{P}(\text{OCH}_2)_3\text{CR} < \text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3 < \text{P}(\text{OMe})_3 < \text{P}(\text{OCH}_2\text{C}=\text{H}=\text{CH}_2)_3 < \text{P}(\text{OEt})_3 < \text{P}(\text{OR})_3$ in accord with the relative basicities of phosphite ligands as determined from studies of $^1J_{\text{H}^{31}\text{P}}$ coupling constants, the ν_{BH} stretching frequency in borane adducts, CNDO calculations, and studies of the ν_{NO} stretching frequency in $\text{Ni}(\text{NO})\text{L}_3^+$ complexes.³¹⁻³⁵

The donor/acceptor ratio for phosphine ligands increases in the order: $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 < \text{P}(\text{CH}=\text{CH}_2)_3 < \text{PPh}_3 < \text{P}(\text{CH}_2\text{CH}=\text{CH}_2)_3 < \text{PMe}_3 < \text{P-}i\text{-Bu}_3 < \text{PET}_3 < \text{PPr}_3 < \text{PR}_3$ ($\text{R} = \text{butyl, pentyl, hexyl, heptyl, octyl}$) $< \text{P-}i\text{-Pr}_3 \leq \text{P-}s\text{-Bu}_3 < \text{P}(\text{-}i\text{-Hx})_3 \leq \text{P-}t\text{-Bu}_3$. This ratio appears to increase as the unsaturation of the alkyl substituent decreases, as the alkyl chain length increases, and as substitution at the α -carbon atom increases. These data are in agreement with the predictions of studies of gas-phase basicity, NMR band-shape analyses of exchange in borane adducts, and molecular orbital calculations³⁶⁻³⁸ as well as with classical assumptions of the relative electron-donor character of alkyl substituents obtained from studies of carbonium ion stability.

To investigate the transmission of aromatic substituent effects through metal carbonyl complexes, we have analyzed the δ_{CO} data for $(p\text{-XPh})_3\text{PNi}(\text{CO})_3$ complexes by using the field (F) and resonance (R) substituent parameters of Swain and Lupton.³⁹ The δ_{CO} data were fit by using the equation

$$\int_{\text{X}}^{\text{H}} \text{CO} = fF + rR$$

- (30) We have used the field (F) and resonance (R) substituent parameters of Swain and Lupton³⁹ as a rough estimate of the electron-withdrawing power of substituents on phosphorus. A multiple linear regression analysis of δ_{CO} for eight $\text{X}_3\text{PNi}(\text{CO})_3$ complexes led to a linear correlation ($r = 0.965$) between experimental and calculated chemical shifts when the contribution to δ_{CO} from field or inductive effects (69.3%) was assumed to dominate resonance effects (30.7%).
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Table II. ^{13}C NMR Chemical Shifts in Ppm for the Cis and Trans Carbonyl Resonances in $\text{LCr}(\text{CO})_5$ and $\text{LMo}(\text{CO})_5$ Complexes^a

no.	ligand	$\text{LCr}(\text{CO})_5$		$\text{LMo}(\text{CO})_5$	
		cis CO	trans CO	cis CO	trans CO
1	$\text{P}(\text{OMe})_3$	3.89 (21) ^b	7.90 (4)	3.60 (14)	7.39 (40)
2	$\text{P}(\text{OCH}_2)_3\text{CEt}$	2.88 (22.0)	7.43 ^c	2.62 (14.0)	<i>d</i>
3	$\text{P}(\text{OEt})_3$	4.28 (21.3)	8.24	3.92 (13.3)	7.85 (39.9)
4	$\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	3.31 (20.7)	7.13 (3.6)	3.04 (13.3)	6.52 (41.5)
6	$\text{P}(\text{O}-i\text{-Pr})_3$	4.67 (20.8)	9.22	4.25 (13.3)	8.38 (38.7)
7	$\text{P}(\text{O-allyl})_3$	3.90 (20.7)	7.76	3.66 (12.9)	7.31 (40.4)
9	$\text{P}(\text{OPh})_3$	2.59 (20)	6.93	2.32 (13)	6.15 (46)
10	$\text{P}(\text{OPh-}p\text{-Cl})_3$	2.29 (20.1)	6.01		
13	$\text{P}(\text{NMe}_2)_3$	6.17 (17.1)	9.67 (7.4)	5.52 (11.6)	9.34 (29.9)
	PH_3	3.96 (13.5)	8.43 (7)		
15	PCl_3	0.18 (16.4)	5.66 (4.5)	-0.01 (11)	5.25 (66)
16	PMe_3	5.50 (14.0)	<i>d</i>		
17	PET_3	5.96 (14.5)	9.89 (8)	5.35 (9.4)	8.86 (20.7)
19	PVy_3	4.92 (13.4)	10.07		
20	PPr_3	6.03 (14.0)	9.83 (7.3)		
22	$\text{P}(\text{allyl})_3$	5.40 (13.4)	9.24 (6.7)	4.92 (9.5)	8.40 (23.2)
23	PBu_3	6.08 (14.5)	9.83 (8)	5.55 (9)	8.88 (21)
24	$\text{P-}i\text{-Bu}_3$	6.05 (13.4)	9.77 (7.9)		
26	$\text{P-}r\text{-Bu}_3$	6.66 (11.0)	10.36 (4.9)	6.22 (7.4)	9.74 (22.0)
32	$\text{P}(\text{c-Hx})_3$	7.19 (13.4)	10.28 (6.1)	6.37 (8.6)	9.32 (21.5)
33	PPh_3	5.25 (13.5)	10.06 (7)	4.89 (9)	9.44 (23)
61	$\text{PhP}(\text{NMe}_2)_2$	5.29 (15.2)	<i>d</i>		
62	PhPCl_2	1.71 (15.3)	6.39	2.01 (10.8)	7.24 (46.5)
63	PhPH_2	4.29 (13.7)	9.04 (7.3)	3.68 (9.1)	7.87 (24.1)
64	PhPMe_2	5.26 (13.7)	10.01 (8.6)	4.73 (9.1)	9.28 (21.6)
65	PhPET_2	5.59 (13.7)	10.01 (7.8)	5.00 (9.1)	9.06 (21.6)
66	PhPVy_2	5.00 (13.4)	9.87 (7.3)	4.61 (9.1)	8.95 (21.6)
69	$\text{PhP}(\text{c-Hx})_2$	7.05 (12.8)	9.91 (6.1)		
76	$\text{Ph}_2\text{P}(\text{NMe}_2)$	5.29 (13.9)	<i>d</i>		
77	Ph_2PCl	3.59 (14.0)	7.40	3.37 (10.0)	8.34 (31.5)
78	Ph_2PH	4.81 (13.7)	9.71 (6.8)	4.17 (9.1)	8.67 (23.2)
79	Ph_2PMe	5.20 (13.7)	9.95 (6.9)	4.72 (9.1)	9.20 (22.4)
80	Ph_2PEt	5.33 (13.7)	9.97 (6.8)	4.76 (8.3)	9.13 (22.0)
81	Ph_2PVy	5.14 (12.8)	9.97 (6.7)		
86	$\text{Ph}_2\text{P}(\text{c-Hx})$	5.50 (12.8)	10.25 (6.7)		
89	$(\text{c-Hx})\text{PH}_2$	4.80 (13.4)	9.16 (6.7)	4.05 (9.1)	7.96 (23.2)
90	$(\text{c-Hx})_2\text{PH}$	6.03 (12.8)	9.74 (6.1)	5.32 (8.3)	8.62 (21.6)
99	AsMe_3	5.44	10.89	4.69	9.83
101	AsBu_3	6.06	10.89	5.25	9.56
102	AsPh_3	5.37	10.76	4.52	9.49
	PhAsCl_2	1.26	7.96		
	Ph_2AsCl	3.23	9.34		
109	SbMe_3	6.34	11.94		
111	SbBu_3	6.89	12.03	5.86	9.49
112	SbPh_3	5.74	11.11	4.85	8.79
	$\text{C}_6\text{H}_{11}\text{NH}_2$	2.67	8.61		
	$\text{C}_2\text{H}_5\text{N}$	2.77	8.79		
	$\text{C}(\text{OMe})\text{Ph}$	4.83	12.87		
	$\text{C}(\text{NH}_2)\text{Ph}$	5.80	12.27		
	Cl^-	4.88	12.31		

^a Chemical shifts were measured in CDCl_3 solution and are reported in ppm downfield from the parent hexacarbonyl resonance. All data are the result of duplicate measurements with a precision of at least ± 0.06 ppm. Part of these data were reported by G. M. Bodner, *Inorg. Chem.*, **14**, 2694 (1975). ^b $^2J_{^{13}\text{C}^{31}\text{P}}$ through-metal nuclear spin-spin coupling constant in Hz, ± 0.6 Hz. ^c The magnitude of the $^2J_{^{13}\text{C}^{31}\text{P}}$ coupling constant to the trans carbonyl in $\text{LCr}(\text{CO})_5$ derivatives can become vanishingly small. ^d Data for the trans carbonyl chemical shift for samples in which problems with either solubility or sample size lead to a trans carbonyl resonance with insufficient signal-to-noise ratio are not included.

where $\int_{\text{X}}^{\text{HCO}}$ represents the carbonyl chemical shift for $(p\text{-XPh})_3\text{PNi}(\text{CO})_3$ relative to $\text{Ph}_3\text{PNi}(\text{CO})_3$. A multiple linear regression analysis of the data yields a linear correlation ($r = 0.997$) between experimental and calculated chemical shifts for values of f and r corresponding to 47.6% and 52.4%, respectively.

If δ_{CO} data for $\text{X}_3\text{PNi}(\text{CO})_3$ and $\text{Y}_3\text{PNi}(\text{CO})_3$ complexes can be used to predict δ_{CO} for $\text{X}_2\text{YPNi}(\text{CO})_3$ derivatives, we should be able to reverse this process to predict the chemical shift for complexes such as $\text{H}_3\text{PNi}(\text{CO})_3$, which are difficult to synthesize. Analysis of δ_{CO} data for six primary and secondary phosphine nickel tricarbonyl complexes yields a predicted δ_{CO} for $\text{H}_3\text{PNi}(\text{CO})_3$ of 3.17 ± 0.07 ppm. Extrapolation

of the linear correlation between $\delta_{\text{CO}}^{\text{cis}}$ for $\text{LCr}(\text{CO})_5$ complexes and δ_{CO} for analogous $\text{LNi}(\text{CO})_3$ derivatives yields a predicted value of δ_{CO} for the $\text{H}_3\text{PNi}(\text{CO})_3$ complex of 3.18 ppm. These data suggest that the donor/acceptor ratio for the H_3P ligand is smaller than any PR_3 ligand studied, approximately equal to the donor/acceptor ratio of $\text{P}(\text{OMe})_3$.

The δ_{CO} data for $\text{X}_3\text{PNi}(\text{CO})_3$ complexes can be transposed into a set of substituent parameters for the X groups on phosphorus, as described in Table IV. An excellent linear correlation ($r = 0.972$) exists between these substituent constants and the σ parameters for phosphorus ligands derived by Kabachnik from studies of the pK_a data for phosphoric acids of the type $\text{R}_1\text{R}_2\text{P}(\text{O})\text{OH}$.⁴⁰

Table III. ^{13}C NMR Chemical Shifts for $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{L}$ Complexes, in Ppm Downfield from $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3^a$

no.	ligand	chem shift	no.	ligand	chem shift
1	P(OMe) ₃	4.90 (32.4) ^b	63	PhPH ₂	5.65 (19.9)
3	P(OEt) ₃	5.34 (31.6)	69	PhP(c-Hx) ₂	9.76 (19.8)
4	P(OCH ₂ CH ₂ Cl) ₃	4.28 (31.6)	78	Ph ₂ PH	6.12 (20.6)
6	P(O- <i>i</i> -Pr) ₃	6.36 (32.0)	80	Ph ₂ P ⁺ Et	7.93 (20.6)
9	P(OPh) ₃	3.48 (32.7)	86	Ph ₂ P(c-Hx)	9.07 (19.8)
23	PBu ₃	7.89 (21.6)	89	(c-Hx)PH ₂	6.32 (19.8)
32	P(c-Hx) ₃	10.40 (19.9)	90	(c-Hx) ₂ PH	7.95 (19.9)
33	PPh ₃	7.88 (21.6)			

^a Chemical shifts were measured in CD₂Cl₂ solution and are reported in ppm downfield from $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$. All data are the result of duplicate measurements with a precision of at least ± 0.06 ppm. ^{13}C NMR carbonyl chemical shift data for $(\eta^6\text{-C}_6\text{H}_5\text{-X})\text{Cr}(\text{CO})_3$ derivatives have been reported previously; see G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 360, 1335 (1974).

^b $^2J_{^{13}\text{C}^{31}\text{P}}$ through-metal nuclear spin-spin coupling constants in Hz, ± 0.6 Hz.

Table IV. Substituent Parameters for X Substituents in Trivalent Phosphorus Compounds

X	σ	X	σ
<i>t</i> -Bu	-1.06 ^a	benzyl	-0.27
c-Hx	-1.05	O-lauryl	-0.27
<i>s</i> -Bu	-1.02	OBu	-0.26
<i>i</i> -Pr	-1.01	OPr	-0.25
Bu	-0.84	O- <i>i</i> -Pr	-0.24
NMe ₂	-0.83	Ph- <i>p</i> -F	-0.20
SiMe ₃	-0.83	OEt	-0.14
Pr	-0.81	Ph- <i>p</i> -Cl	-0.12
Et	-0.79	CH ₂ CH ₂ CN	-0.10
<i>i</i> -Bu	-0.74	O-allyl	-0.08
Ph- <i>p</i> -NMe ₂	-0.72	OMe	0.00
CH ₃	-0.62	H	0.00
allyl	-0.58	OCH ₂ CH ₂ Cl	0.14
Ph- <i>p</i> -CH ₃	-0.44	S-lauryl	0.23
Ph- <i>p</i> -OCH ₃	-0.42	OPh	0.50
naphthyl	-0.38	OPh- <i>p</i> -Cl	0.62
Ph	-0.37	Cl	1.53
Vy	-0.35		

^a The substituent parameters were calculated by dividing δ_{CO} in the X₃PNi(CO)₃ complex by three, reversing the sign of the parameter so that substituents which are electron withdrawing relative to H have positive values of σ , and then scaling these data so that the substituent parameter for H is equal to zero.

There has been some concern about the analysis of $\delta_{\text{CO}}^{\text{trans}}$ data for LM(CO)₅ complexes of Cr, Mo, and W^{7,29} and XRe(CO)₅ complexes.²⁸ Correlations between $\delta_{\text{CO}}^{\text{trans}}$ and the trans carbonyl stretching force constant (k_1) have met with only marginal success, perhaps reflecting assumptions inherent in the calculation of k_1 . The data in Table II suggest several conclusions. First, predictions of $\delta_{\text{CO}}^{\text{trans}}$ on the basis of the additivity of substituent effects lead to a correlation between calculated and experimental chemical shifts ($r = 0.964$) essentially as good as the correlation for $\delta_{\text{CO}}^{\text{cis}}$ data ($r = 0.980$). Second, the mean value of $\delta_{\text{CO}}^{\text{trans}}$ (9.47) is almost exactly twice the mean value of $\delta_{\text{CO}}^{\text{cis}}$ (4.77) for LCr(CO)₅ complexes. Third, variations in either $\delta_{\text{CO}}^{\text{cis}}$ or $\delta_{\text{CO}}^{\text{trans}}$ are significantly larger than variations in $\delta_{\text{CO}}^{\text{trans}} - \delta_{\text{CO}}^{\text{cis}}$. Fourth, linear correlations exist between the σ substituent constants in Table IV and both $\delta_{\text{CO}}^{\text{trans}}$ ($r = -0.930$) and $\delta_{\text{CO}}^{\text{cis}}$ ($r = -0.918$) for X₃PCr(CO)₅ complexes. Finally, there is a reasonable correlation between $\delta_{\text{CO}}^{\text{trans}}$ and $\delta_{\text{CO}}^{\text{cis}}$ ($r = 0.923$) for phosphine complexes of LCr(CO)₅, $\delta_{\text{CO}}^{\text{trans}}$ is relatively small when $\delta_{\text{CO}}^{\text{cis}}$ is small; however, $\delta_{\text{CO}}^{\text{trans}}$ does not increase as rapidly as $\delta_{\text{CO}}^{\text{cis}}$.

Comparison of the Donor/Acceptor Character of PR₃, AsR₃, and SbR₃ Ligands

Analysis of δ_{CO} data for R₃ENi(CO)₃ complexes (E = P, As, Sb; R = Me, Et, Bu, Ph) yield several generalizations.

First, the effect of variation of the R substituent on the donor/acceptor ratio of ER₃ ligands decreases in the order: PR₃ > AsR₃ > SbR₃. Second, the donor/acceptor ratio decreases in the order: Bu \approx Et > Me > Ph, regardless of E. Third, variations in the donor/acceptor ratio of ER₃ ligands due to changes in the R group are significantly larger than variations due to changes in the nature of the group 5A element. Finally, the donor/acceptor ratio for these ligands appears to decrease in the order: SbR₃ > PR₃ > AsR₃.

Gas-phase proton affinity measurements suggest that the intrinsic basicity of PH₃ is greater than that of AsH₃.⁴¹ Enthalpy data for the gas-phase reaction of group 5A ligands with BX₃ Lewis acids suggest a decrease in the basicity of these ligands in the order: PR₃ > AsR₃ > SbR₃,⁴² as have studies of the photoelectron spectra of the free ligands.⁴³ These data may explain the relative donor/acceptor ratios for PR₃ and AsR₃ ligands, but they are inconsistent with the observation that the donor/acceptor ratio for SbR₃ is larger than for either PR₃ or AsR₃ ligands.

It might be tempting to invoke either steric effects, or through-space shielding effects, to explain this apparent anomalous behavior. No steric effect on δ_{CO} has been seen, however, even in the sterically crowded $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{P}(\text{c-Hx})_3$ complex. Furthermore, neighboring diamagnetic screening would shield the carbonyls in stibine complexes relative to their arsine and phosphine analogues, just as δ_{CO} for W(CO)₆ is shielded relative to Mo(CO)₆ or Cr(CO)₆.⁷

It is therefore of interest to note that X-ray crystallographic studies of Ph₃ECr(CO)₅ complexes (E = P, As, Sb, Bi) imply an increase in both the bond order and the s character of the group 5A element in the Cr-E bond in these complexes in the order: P < As < Sb < Bi.⁴ The anomalously large donor/acceptor ratio for stibine ligands may therefore be due to the strength of the σ interaction between the group 5A element and the transition metal. It should also be noted that Brill has found an increase in the donor/acceptor ratio for E(OR)₃ ligands in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ complexes in the order: Sb(OR)₃ > P(OR)₃ > As(OR)₃.⁴⁵

²J_{13C31P} Through-Metal Nuclear Spin-Spin Coupling Constants

The magnitude of the ²J_{13C31P} through-metal nuclear spin-spin coupling to the trans CO in LM(CO)₅ complexes of Mo and W is significantly larger than that of the analogous coupling to the cis CO, whereas in LCr(CO)₅ complexes the converse is true, coupling to the cis CO exceeds the coupling to the trans CO.⁷ Similar behavior has been reported for the ²J_{31P31P} coupling for *cis*- and *trans*-L₂M(CO)₄ complexes of the group 6B metals.⁴⁶ The data in Table I reinforced our initial suggestion that ²J_{13C31P} coupling in LM(CO)₅ complexes of Cr, Mo, and W mirrors the behavior observed for the ²J_{31P31P} coupling in L₂M(CO)₄ complexes of these metals.

The magnitude of the ²J_{13C31P} coupling to the trans CO in LMo(CO)₅ derivatives increases in the order: PR₃ \leq PPh₃ < P(OR)₃ < P(OPh)₃ < PCl₃, the order of increasing electron-withdrawing power of the substituents on phosphorus. A similar observation has been reported for both the ¹J_{31P9597Mo} and ¹J_{31P183W} coupling in LM(CO)₅ complexes, where a linear correlation has been observed between the magnitude of these coupling constants and the electronegativity of the substituents on phosphorus.⁴⁶⁻⁴⁸

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The approximate theory for directly bound coupling⁴⁹

$${}^1J_{XY} \propto \frac{1}{\Delta E} \alpha_X^2 \alpha_Y^2 |\psi_X(0)|^2 |\psi_Y(0)|^2$$

suggests that directly bound coupling constants should increase with increasing *s* character (α^2) of the hybrid orbitals used to form the X–Y bond or with increasing electron density at the nucleus ($|\psi(0)|^2$).⁵⁰ There are two factors which can lead to an increase in the magnitude of ${}^1J_{PM}$ coupling with increasing electron-withdrawing power for the substituents on phosphorus. An increase in the electron-withdrawing power of the substituents leads to a decrease in the electron density on the phosphorus and therefore an increase in the effective nuclear charge on the phosphorus atom. The increased nuclear charge draws electrons in the metal–phosphorus bond toward the nucleus of the phosphorus atom, thereby increasing $|\psi_P(0)|^2$, leading to an increase in the magnitude of the phosphorus–metal coupling. Bent has argued that the introduction of an electron-withdrawing substituent concentrates *s* character in orbitals directed toward the groups of lowest electronegativity.⁵¹ Thus, as the electron-withdrawing power of the substituents on phosphorus increases, α_P^2 for the metal–phosphorus bond increases, and the coupling constant increases as well.

The linear correlations between the trans ${}^2J_{13C^{31}P}$ coupling constants in $LMo(CO)_5$ complexes and both the ${}^1J_{31P^{95}Mo}$ coupling in $LMo(CO)_5$ complexes ($r = 0.987$) and the ${}^1J_{31P^{183}W}$ coupling in $LW(CO)_5$ complexes ($r = 0.907$) would suggest that the metal-mediated trans ${}^2J_{13C^{31}P}$ coupling behaves much as one might expect directly bound ${}^1J_{13C^{31}P}$ coupling to behave.

Acknowledgment. We gratefully acknowledge the financial support provided by a Cottrell College Science Grant from the Research Corp. as well as grants from Sigma Xi and the Missouri Academic of Sciences which made this work possible. We are indebted to D. E. Troutner and M. S. Feather of the University of Missouri at Columbia for providing access to infrared and nuclear magnetic resonance spectrometers which greatly facilitated completion of this work. We also acknowledge our debt to C. A. Tolman, E. I. du Pont de Nemours and Co., D. Forster, Monsanto Co., and S. Searles, Jr., University of Missouri at Columbia, for providing generous samples of various ligands. Finally we acknowledge our debt to the School of Chemical Sciences at the University of Illinois for the use of their FT NMR spectrometers.

Registry No. $P(OMe)_3Ni(CO)_3$, 17099-58-0; $P(OCH_2)_3CETi(CO)_3$, 72868-01-0; $P(OEt)_3Ni(CO)_3$, 18558-97-9; $P(OCH_2CH_2Cl)_3Ni(CO)_3$, 18559-00-7; $P(OPr)_3Ni(CO)_3$, 72868-02-1; $P(O-i-Pr)_3Ni(CO)_3$, 55333-41-0; $P(O-allyl)_3Ni(CO)_3$, 72868-03-2; $P(OBu)_3Ni(CO)_3$, 18558-98-0; $P(OPh)_3Ni(CO)_3$, 18474-92-5; $P(OPh-p-Cl)_3Ni(CO)_3$, 72868-04-3; $P(O-lauryl)_3Ni(CO)_3$, 72868-05-4; $P(S-lauryl)_3Ni(CO)_3$, 72868-06-5; $P(NMe_2)_3Ni(CO)_3$, 30512-95-9; $P(NEt_2)_3Ni(CO)_3$, 72868-07-6; $PCl_3Ni(CO)_3$, 18474-97-0; $PMe_3Ni(CO)_3$, 16406-99-8; $PEt_3Ni(CO)_3$, 18555-45-8; $P(CH_2CH_2CN)_3Ni(CO)_3$, 72881-54-0; $P(Vy)_3Ni(CO)_3$, 72881-55-1; $PPr_3Ni(CO)_3$, 72881-56-2; $P-i-Pr_3Ni(CO)_3$, 18475-09-7; $P(allyl)_3Ni(CO)_3$, 72881-57-3; $PBu_3Ni(CO)_3$, 15698-54-1; $P-i-Bu_3Ni(CO)_3$, 72881-58-4; $P-s-Bu_3Ni(CO)_3$, 18475-00-8; $P-t-Bu_3Ni(CO)_3$, 22955-41-5; $P(SiMe_3)_3Ni(CO)_3$, 16010-24-5; $P(pentyl)_3Ni(CO)_3$, 72881-59-5; $P(hexyl)_3Ni(CO)_3$, 72868-08-7; $P(heptyl)_3Ni(CO)_3$, 72868-09-8; $P(octyl)_3Ni(CO)_3$, 72868-10-1; $P(c-Hx)_3Ni(CO)_3$, 18475-08-6; $PPH_3Ni(CO)_3$, 14917-13-6; $P(benzyl)_3Ni(CO)_3$, 18558-95-7; $P(naphthyl)_3Ni(CO)_3$, 72868-11-2; $P(Ph-p-CH_3)_3Ni(CO)_3$, 52729-09-6; $P(Ph-p-OCH_3)_3Ni(CO)_3$, 52729-08-5; $P(Ph-p-F)_3Ni(CO)_3$, 25493-

52-1; $P(Ph-p-Cl)_3Ni(CO)_3$, 52151-06-1; $P(Ph-p-NMe_2)_3Ni(CO)_3$, 72868-12-3; $P(Ph-o-CH_3)_3Ni(CO)_3$, 28796-13-6; $P(Ph-m-CH_3)_3Ni(CO)_3$, 72868-13-4; $P(Ph-o-OCH_3)_3Ni(CO)_3$, 62945-86-2; $(MeO)PCl_2Ni(CO)_3$, 72868-14-5; $(EtO)PCl_2Ni(CO)_3$, 72868-15-6; $(i-PrO)PCl_2Ni(CO)_3$, 72868-16-7; $(BuO)PCl_2Ni(CO)_3$, 72868-17-8; $(PhO)PCl_2Ni(CO)_3$, 72868-18-9; $(MeO)_2PCINi(CO)_3$, 72868-19-0; $(EtO)_2PCINi(CO)_3$, 72868-20-3; $(i-PrO)_2PCINi(CO)_3$, 72868-21-4; $(BuO)_2PCINi(CO)_3$, 72868-22-5; $(PhO)_2PCINi(CO)_3$, 72868-23-6; $(PhO)P(OCH_2)_2Ni(CO)_3$, 72868-24-7; $EtP(OMe)_2Ni(CO)_3$, 72868-25-8; $PhP(OMe)_2Ni(CO)_3$, 55333-40-9; $PhP(OEt)_2Ni(CO)_3$, 62945-82-8; $PhP(O-i-Pr)_2Ni(CO)_3$, 72868-26-9; $PhP(OBu)_2Ni(CO)_3$, 72868-27-0; $PhP(OPh)_2Ni(CO)_3$, 55333-54-5; $PhP(NMe_2)_2Ni(CO)_3$, 72868-28-1; $PhPCl_2Ni(CO)_3$, 18474-95-8; $PhPH_2Ni(CO)_3$, 72868-29-2; $PhPMe_2Ni(CO)_3$, 55333-45-4; $PhPEt_2Ni(CO)_3$, 62945-89-5; $PhPVy_2Ni(CO)_3$, 72868-30-5; $PhPPr_2Ni(CO)_3$, 72868-31-6; $PhPBu_2Ni(CO)_3$, 18555-44-7; $PhP(c-Hx)_2Ni(CO)_3$, 72868-32-7; $PhP(c-C_6H_{10})Ni(CO)_3$, 72868-33-8; $PhP(OMe)Ni(CO)_3$, 55333-43-2; $Ph_2P(OEt)Ni(CO)_3$, 72868-34-9; $Ph_2P(O-i-Pr)Ni(CO)_3$, 72868-35-0; $Ph_2P(OBu)Ni(CO)_3$, 72868-36-1; $Ph_2P(OPh)Ni(CO)_3$, 55333-39-6; $Ph_2P(NMe_2)Ni(CO)_3$, 72868-37-2; $Ph_2PCINi(CO)_3$, 18559-01-8; $Ph_2PHNi(CO)_3$, 72868-38-3; $Ph_2PMeNi(CO)_3$, 55333-44-3; $Ph_2PETNi(CO)_3$, 69970-14-5; $Ph_2PVyNi(CO)_3$, 72868-39-4; $Ph_2PPrNi(CO)_3$, 72868-40-7; $Ph_2PBuNi(CO)_3$, 18705-97-0; $Ph_2P-t-BuNi(CO)_3$, 72868-41-8; $Ph_2PC_6F_5Ni(CO)_3$, 72868-42-9; $Ph_2P(c-Hx)Ni(CO)_3$, 72868-43-0; $(NCCH_2CH_2)_2PHNi(CO)_3$, 72868-44-1; $(NCCH_2CH_2)_2PHNi(CO)_3$, 72868-45-2; $(c-Hx)_2PH_2Ni(CO)_3$, 72868-46-3; $(c-Hx)_2PHNi(CO)_3$, 72868-47-4; $Ph_2P(CH_2)_2PPh_2Ni(CO)_3$, 62945-84-0; $Ph_2P(CH_2)_3PPh_2Ni(CO)_3$, 62945-85-1; $Ph_2P(CH_2)_4PPh_2Ni(CO)_3$, 72868-48-5; $(Ph_2P)_2CH_2Ni(CO)_3$, 62945-83-9; *cis*- $Ph_2PCH=CHPPh_2Ni(CO)_2$, 21044-41-7; $Ph_2P(CH_2)_2AsPh_2Ni(CO)_3$ (P bonded), 72868-49-6; $Ph_2As(CH_2)_2AsPh_2Ni(CO)_3$, 72868-50-9; $(Ph_2As)_2CH_2Ni(CO)_3$, 72868-51-0; $AsMe_3Ni(CO)_3$, 16407-00-4; $AsEt_3Ni(CO)_3$, 72868-52-1; $AsBu_3Ni(CO)_3$, 72868-53-2; $AsPh_3Ni(CO)_3$, 37757-32-7; $PhAsMe_2Ni(CO)_3$, 72868-54-3; $PhAsEt_2Ni(CO)_3$, 72868-55-4; $PhAsBu_2Ni(CO)_3$, 72881-60-8; $Ph_2AsMeNi(CO)_3$, 72868-56-5; $Ph_2AsEtNi(CO)_3$, 72868-57-6; $Ph_2AsBuNi(CO)_3$, 72868-58-7; $SbMe_3Ni(CO)_3$, 72868-59-8; $SbEt_3Ni(CO)_3$, 16787-29-4; $SbBu_3Ni(CO)_3$, 72868-60-1; $SbPh_3Ni(CO)_3$, 52151-12-9; $PhSbMe_2Ni(CO)_3$, 72868-61-2; $PhSbEt_2Ni(CO)_3$, 72868-62-3; $Ph_2SbMeNi(CO)_3$, 72868-63-4; $Ph_2SbEtNi(CO)_3$, 72868-64-5; $P(OMe)_3Cr(CO)_5$, 18461-34-2; $P(OCH_2)_3CETr(CO)_5$, 42194-79-6; $P(OEt)_3Cr(CO)_5$, 18461-32-0; $P(OCH_2CH_2Cl)_3Cr(CO)_5$, 18461-35-3; $P(O-i-Pr)_3Cr(CO)_5$, 65774-61-0; $P(O-allyl)_3Cr(CO)_5$, 72868-65-6; $P(OPh)_3Cr(CO)_5$, 18461-39-7; $P(OPh-p-Cl)_3Cr(CO)_5$, 72868-66-7; $P(NMe_2)_3Cr(CO)_5$, 15137-66-3; $PH_3Cr(CO)_5$, 18116-53-5; $PCl_3Cr(CO)_5$, 18461-41-1; $PMe_3Cr(CO)_5$, 26555-09-9; $PEt_3Cr(CO)_5$, 21321-30-2; $PVy_3Cr(CO)_5$, 65338-52-5; $PPr_3Cr(CO)_5$, 72868-67-8; $P(allyl)_3Cr(CO)_5$, 72868-68-9; $PBu_3Cr(CO)_5$, 18497-59-1; $P-i-Bu_3Cr(CO)_5$, 72868-69-0; $P-t-Bu_3Cr(CO)_5$, 23046-54-0; $P(c-Hx)_3Cr(CO)_5$, 15603-93-7; $PPH_3Cr(CO)_5$, 14917-12-5; $PhP(NMe_2)_2Cr(CO)_5$, 72868-70-3; $PhPCl_2Cr(CO)_5$, 18461-40-0; $PhPH_2Cr(CO)_5$, 72868-71-4; $PhPMe_2Cr(CO)_5$, 72881-35-7; $PhPET_2Cr(CO)_5$, 72868-72-5; $PhPVy_2Cr(CO)_5$, 72868-73-6; $PhP(c-Hx)_2Cr(CO)_5$, 72868-74-7; $Ph_2P(NMe_2)Cr(CO)_5$, 72881-36-8; $Ph_2PClCr(CO)_5$, 18461-36-4; $Ph_2PHCr(CO)_5$, 18399-60-5; $Ph_2PMeCr(CO)_5$, 18497-53-5; $Ph_2PETCr(CO)_5$, 18497-54-6; $Ph_2PVyCr(CO)_5$, 72868-75-8; $Ph_2P(c-Hx)Cr(CO)_5$, 72868-76-9; $(c-Hx)_2PH_2Cr(CO)_5$, 72868-77-0; $(c-Hx)_2PHCr(CO)_5$, 72868-78-1; $AsMe_3Cr(CO)_5$, 31238-08-1; $AsBu_3Cr(CO)_5$, 72868-79-2; $AsPh_3Cr(CO)_5$, 29742-98-1; $PhAsCl_2Cr(CO)_5$, 58448-94-5; $Ph_2AsClCr(CO)_5$, 72881-61-9; $SbMe_3Cr(CO)_5$, 59136-89-9; $SbBu_3Cr(CO)_5$, 72868-80-5; $SbPh_3Cr(CO)_5$, 29985-15-7; $C_6H_{11}N-H_2Cr(CO)_5$, 15134-57-3; $C_3H_5NCH_2Cr(CO)_5$, 14740-77-3; $C(OMe)-PhCr(CO)_5$, 27436-93-7; $C(NH_2)_3NCH_2Cr(CO)_5$, 32370-44-8; $ClCr(CO)_5$, 14911-56-9; $P(OMe)_3Mo(CO)_5$, 15631-20-6; $P(OCH_2)_3CETMo(CO)_5$, 15665-65-3; $P(OEt)_3Mo(CO)_5$, 15603-75-5; $P(OCH_2CH_2Cl)_3Mo(CO)_5$, 72868-83-8; $P(O-i-Pr)_3Mo(CO)_5$, 34369-19-2; $P(O-allyl)_3Mo(CO)_5$, 72868-84-9; $P(OPh)_3Mo(CO)_5$, 15711-66-7; $P(NMe_2)_3Mo(CO)_5$, 14971-43-8; $PCl_3Mo(CO)_5$, 19212-18-1; $PEt_3Mo(CO)_5$, 19217-79-9; $P(allyl)_3Mo(CO)_5$, 72868-85-0; $PBu_3Mo(CO)_5$, 15680-62-3; $P-t-Bu_3Mo(CO)_5$, 22955-40-4; $P(c-Hx)_3Mo(CO)_5$, 15603-94-8; $PPH_3Mo(CO)_5$, 14971-42-7; $PhPCl_2Mo(CO)_5$, 21485-20-1; $PhPH_2Mo(CO)_5$, 72868-86-1; $PhPMe_2Mo(CO)_5$, 24554-78-7; $PhPET_2Mo(CO)_5$, 72868-87-2; $PhPVy_2Mo(CO)_5$, 72868-88-3; $Ph_2PClMo(CO)_5$, 23581-74-0;

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72868-96-3; (η^6 -C₆H₆)Cr(CO)₂PBu₃, 12278-02-3; (η^6 -C₆H₆)Cr(CO)₂P(c-Hx)₃, 12278-74-9; (η^6 -C₆H₆)Cr(CO)₂PPh₃, 12278-67-0; (η^6 -C₆H₆)Cr(CO)₂PhPH₂, 72868-97-4; (η^6 -C₆H₆)Cr(CO)₂PhP(c-Hx)₂, 72868-98-5; (η^6 -C₆H₆)Cr(CO)₂Ph₂PH, 72868-99-6; (η^6 -C₆H₆)Cr(CO)₂Ph₂P(c-Hx), 72869-00-2; (η^6 -C₆H₆)Cr(CO)₂Ph₂P(c-Hx)₂, 72869-01-3; (η^6 -C₆H₆)Cr(CO)₂(c-Hx)PH₂, 72869-02-4; (η^6 -C₆H₆)Cr(CO)₂(c-Hx)₂PH, 72869-03-5; Ph₂P(CH₂)₂AsPh₂Ni(CO)₃ (As bonded), 72869-04-6.

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Infrared Metal-Ligand Vibrations of Hexaaquametal(III) Ions in Alums

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Received November 2, 1979

The infrared spectra of mulls of the cesium β -alums CsM^{III}(SO₄)₂·12H₂O (M^{III} = Al, Ti, V, Cr, Fe) and of the ammonium and potassium α -alums of Al^{III} and Cr^{III} are reported between 300 and 1200 cm⁻¹ at ambient temperature, together with that of the α -alum CsCo(SO₄)₂·12H₂O between 450 and 1200 cm⁻¹ at about 80 K. Only two bands are observed to shift appreciably with change in the trivalent metal ion; these are assigned to the antisymmetric metal-ligand stretch ν_3 and the antisymmetric metal-ligand bend ν_4 of the M(H₂O)₆³⁺ complex. These assignments are confirmed by the observation of metal isotope shifts of 5 and 1 cm⁻¹, respectively, between cesium chromium alums enriched in ⁵⁰Cr and ⁵³Cr.

Introduction

There have been remarkably few vibrational studies of the M(H₂O)₆³⁺ species¹⁻⁷ and assignments of the M^{III}-OH₂ stretching frequencies remain elusive. Most reports are on individual compounds, and, although some assignments have been aided by deuteration, few comparative studies have been reported. The alums, of composition M^I(H₂O)₆M^{III}(H₂O)₆(XO₄)₂, provide a series of compounds in which the trivalent metal ion can be systematically varied, usually in isomorphous structures. This advantage is somewhat offset, however, by the presence of the M(H₂O)₆⁺ species, which contributes additional vibrations due to the coordination sphere of the monovalent cation.

This study reports the infrared mull spectra of the cesium sulfate alums of Al, Ti, V, Cr, Fe, and Co. Comparison of these spectra allows a clear assignment of the two infrared active M^{III}-OH₂ vibrations. The cesium alums were chosen because it is possible to obtain stable specimens containing the Co(H₂O)₆³⁺ species⁸ and because crystal structure determinations of all of the compounds are available.⁹⁻¹¹ This series

does not contain the Sc alum, and we were unable to obtain reliable spectra of the Mn alum, which decomposed under the conditions used in recording the other spectra.

Experimental Section

The cesium alums were prepared from reagent grade chemicals either by using methods described in the literature (Al,⁹ V,⁸ Cr,⁸ Fe⁸) or by the procedures described below. They were recrystallized from 1 M H₂SO₄ unless stated otherwise and characterized by their infrared spectra, by single-crystal X-ray structure determinations, and in some cases by their melting points. The ammonium and potassium alums were recrystallized commercially. The isotope-enriched chromium alums were prepared by oxidizing enriched chromium(III) oxide obtained from Oak Ridge National Laboratory with perchloric acid to chromium(VI) oxide and then proceeding as above.

The cesium titanium alum was prepared under an inert atmosphere. Cesium sulfate (1 g) was dissolved in 30 mL of deoxygenated 1 M sulfuric acid. Addition of 7 mL of a deoxygenated 15% w/v solution of titanium trichloride gave a violet solution. Storage under refrigeration gave violet crystals which were collected, washed with 1 M sulfuric acid, and recrystallized from 1 M sulfuric acid. The crystals are unstable in air and were stored under a nitrogen atmosphere.

The cesium manganese alum¹² was prepared by adding with stirring a solution of 3.6 g of cesium sulfate in 5 mL of 30% sulfuric acid to a solution of 5.3 g of freshly prepared manganese(III) acetate¹³ in 30 mL of 30% sulfuric acid cooled to 0 °C. The mixture was kept at 3 °C for 3 days while crystallization occurred. The product is very susceptible to decomposition by heat and by dehydration but can be kept in the mother liquor at low temperatures.

The cesium cobalt alum⁸ was prepared by electrolysis of cobalt(II) sulfate for 5 h at 0.2 A, producing a large deposit of blue microcrystals. Aging these under refrigeration for 1 week produced larger crystals which were collected by filtration and washed with 17 M acetic acid followed by dry ether.

Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrometer, generally using cesium iodide plates. With the manganese and cobalt alums, oxidation of the iodide in the plates occurs.

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