

# Electron Donor–Acceptor Properties of Phosphorus Ligands. Substituent Additivity

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**Abstract:** A rapid method is described for determining electron donor–acceptor properties of triply connected phosphorus ligands based on the  $A_1$  carbonyl stretching frequency of  $Ni(CO)_3L$  in  $CH_2Cl_2$ . Data are given for 70 ligands and a substituent additivity rule is proposed. Forty-seven substituent parameters  $\chi_i$  are derived and found to correlate well with Kabachnik's  $\sigma$  parameters, based on ionization constants of phosphorus acids.

It has been known for some time that replacement of one or more CO's of a transition metal carbonyl with a triply connected phosphorus ligand causes the CO stretching frequencies of the remaining carbonyls to fall, by an amount depending on the number and nature of the phosphorus ligands.<sup>1–6</sup> Horrocks and Taylor proposed a "spectrochemical series" for  $\pi$ -bonding ligands based on their work with cobalt nitrosyl carbonyls.<sup>5</sup> Similar series have been found in substituted group VI carbonyls<sup>6</sup> and in other tetrahedral metal carbonyl–nitrosyl complexes.<sup>7</sup> More recently Strohmeier and Müller have shown that phosphorus ligands can be ranked in a " $\pi$ -acceptor strength" series which is generally valid for a wide variety of monosubstituted transition metal carbonyls.<sup>8</sup>

In the course of studies of homogeneous catalysis involving transition metal–phosphorus complexes, it was of interest to determine the relative ranking of a number of new phosphorus ligands. It was anticipated that the electron donor–acceptor properties of the ligands in the complexes would influence their catalytic behavior. An example of this is the dramatic change in hydrogenation activity on changing *para* substituents on rhodium chloride tris(triphenylphosphine), reported by Wilkinson.<sup>9</sup> We expect that reactions in a catalytic sequence in which the formal oxidation state of the transition metal changes will be particularly influenced by changes in the electronic nature of the ligand. This sort of effect has been mentioned for oxidative addition reactions of  $H_2$  to  $d^8$  complexes.<sup>10</sup>

We wish to report here a rapid and convenient infrared method for determining electron donor–acceptor properties of triply connected phosphorus based on measurement of the  $A_1$  carbonyl stretching frequency of 0.05 *M* solutions of  $Ni(CO)_3L$  in  $CH_2Cl_2$ . Data for 70

monodentate phosphorus ligands are presented. A substituent additivity rule is proposed so that the frequency  $\nu_{CO}(A_1)$  of a complex  $Ni(CO)_3PX_1X_2X_3$  can be accurately predicted by adding the contributions  $\chi_i$  of the substituents  $X_i$ . Finally, the results are discussed in terms of the bonding between nickel and phosphorus.

## Experimental Section

In attempting to repeat experiments by Strohmeier and Müller,<sup>8</sup> who had measured CO stretching frequencies of  $Ni(CO)_3L$  complexes in  $CS_2$ , we got undesirable black precipitates with carbon disulfide solutions of  $Ni(CO)_4$ , even in the absence of added ligand.

We found that methylene chloride was an ideal solvent by virtue of (a) dissolving a wide variety of phosphorus-containing ligands, (b) being transparent in the CO stretching region of interest, and (c) not giving precipitates.

In these experiments deoxygenated reagent  $CH_2Cl_2$  was used as solvent. The  $Ni(CO)_4$  was purchased from Matheson. The ligand samples from commercial sources were used without further purification. Others were prepared from  $PPh_{3-n}Cl_n$  by standard reactions with Grignard reagents<sup>11</sup> or alcohols;<sup>12</sup> the purities were checked by elemental analyses and <sup>31</sup>P nmr spectra.

The  $Ni(CO)_3L$  complexes were not isolated but were prepared in solution by the reaction of ligand with  $Ni(CO)_4$ . To a small serum-capped test tube containing 0.1 mmol of ligand in 0.5 ml of  $CH_2Cl_2$  was added 0.5 ml of 0.2 *M*  $Ni(CO)_4$  in  $CH_2Cl_2$  by syringe. The tube was shaken and allowed to stand at room temperature for 10 min. Any unreacted  $Ni(CO)_4$  was then removed by pumping on the solution for 10 min by means of a hypodermic needle connected to a ligand nitrogen trap. The remaining solution was then diluted to 2 ml of 0.05 *M*  $Ni(CO)_3L$  solution by adding fresh  $CH_2Cl_2$ .

Infrared spectra over the region of 2200–1900  $cm^{-1}$  were recorded with a Perkin-Elmer 221 spectrometer using a 5- $cm^{-1}/cm$  abscissa. After each solution had been run in a 0.1-mm NaCl cell, the spectrum was calibrated using CO gas at 0.1 atm in a 10-cm cell.<sup>13</sup> Band centers could be measured with a precision of  $\pm 0.5$   $cm^{-1}$  or better for the sharp higher frequency  $A_1$  band and  $\pm 2$   $cm^{-1}$  for the broad lower frequency E band of each  $Ni(CO)_3L$  compound.<sup>14</sup>

## Results and Discussion

The measured frequencies for the 70 ligands are shown in Table I. Examination of these data shows that successive replacement of one substituent on phosphorus by another causes  $\nu_{CO}(A_1)$  to change by nearly constant increments. This is shown most clearly by complexes of the type  $PPh_{3-n}X_n$  in Figure 1.

This observation suggests that it should be possible to assign to each substituent on phosphorus a contri-

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(14) The assignments were easily made based on the work of ref 4a and 8.

**Table I.** Infrared CO Stretching Frequencies of Ni(CO)<sub>3</sub>L in CH<sub>2</sub>Cl<sub>2</sub>

	Ligand	$\nu_{\text{CO}}$ (A <sub>1</sub> ), cm <sup>-1</sup>	$\nu_{\text{CO}}$ (E), cm <sup>-1</sup>	Ligand	$\nu_{\text{CO}}$ (A <sub>1</sub> ), cm <sup>-1</sup>	$\nu_{\text{CO}}$ (E), cm <sup>-1</sup>	
1	P( <i>t</i> -Bu) <sub>3</sub> <sup>a</sup>	2056.1	1971	36	P( <i>m</i> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>	2074.1	1999
2	P(cyclohexyl) <sub>3</sub>	2056.4	1973	37	PPh(OEt) <sub>2</sub>	2074.2	1997
3	P( <i>o</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	2058.3	1974	38	PPh <sub>2</sub> (OPh)	2074.6	1998
4	P( <i>i</i> -Pr) <sub>3</sub>	2059.2	1977	39	PPh <sub>2</sub> C <sub>6</sub> F <sub>5</sub>	2074.8	1998
5	PBu <sub>3</sub>	2060.3	1976	40	P( <i>O-i</i> -Pr) <sub>3</sub>	2075.9	1996
6	PEt <sub>3</sub>	2061.7	1978	41	PPh <sub>2</sub> ( <i>O-o</i> -C <sub>6</sub> H <sub>4</sub> Cl)	2076.1	2001
7	PPhEt <sub>2</sub>	2063.7	1982	42	P(OEt) <sub>3</sub>	2076.3	1996
8	PPh(piperidyl) <sub>2</sub>	2064.0	1982	43	PPhH <sub>2</sub>	2077.0	1998
9	PMe <sub>3</sub>	2064.1	1982	44	P(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	2077.9	2000
10	PPhMe <sub>2</sub>	2065.3	1982	45	PhP(OCH <sub>2</sub> ) <sub>2</sub>	2078.7	2000
11	PPh <sub>2</sub> ( <i>o</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sup>a</sup>	2066.1	1986	46	P(OCH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>3</sub>	2078.7	2000
12	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>3</sub>	2066.1	1987	47	P(OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> ) <sub>3</sub>	2079.3	1998
13	P(CH <sub>2</sub> Ph) <sub>3</sub>	2066.2	1986	48	P(OMe) <sub>3</sub>	2079.5	2000
14	P( <i>o</i> -tolyl) <sub>3</sub>	2066.6	1986	49	PPh(OPh) <sub>2</sub> <sup>a</sup>	2079.8	2005
15	PPh <sub>2</sub> Et	2066.7	1986	50	PPh <sub>2</sub> Cl	2080.7	2006
16	P( <i>p</i> -tolyl) <sub>3</sub>	2066.7	1987	51	PMe <sub>2</sub> CF <sub>3</sub>	2080.9	2004
17	PPh <sub>2</sub> Me	2067.0	1987	52	P( <i>O-2,4</i> -[CH <sub>3</sub> ] <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>3</sub>	2083.2	2011
18	PPh <sub>2</sub> (piperidyl)	2067.0	1988	53	P(OCH <sub>2</sub> CH <sub>2</sub> Cl) <sub>3</sub>	2084.0	2005
19	P( <i>m</i> -tolyl) <sub>3</sub>	2067.2	1989	54	P( <i>O-p</i> -tolyl) <sub>3</sub>	2084.1	2009
20	PPh <sub>2</sub> (2,4,6-[CH <sub>3</sub> ] <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sup>a</sup>	2067.4	1988	55	P( <i>O-p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>3</sub>	2084.1	2009
21	PPh(CH <sub>2</sub> Ph) <sub>2</sub>	2067.6	1988	56	P( <i>O-o</i> -tolyl) <sub>3</sub>	2084.1	2011
22	PPh <sub>2</sub> ( <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sup>a</sup>	2068.2	1989	57	P(OPh) <sub>3</sub>	2085.3	2012
23	PPh <sub>2</sub> (CH <sub>2</sub> Ph)	2068.4	1989	58	PhOP(OCH <sub>2</sub> ) <sub>2</sub>	2086.5	2011
24	PPh <sub>3</sub>	2068.9	1990	59	P(OCH <sub>2</sub> ) <sub>3</sub> CPr	2086.8	2010
25	PPh <sub>2</sub> (CH=CH <sub>2</sub> )	2069.3	1990	60	P(OCH <sub>2</sub> ) <sub>3</sub> CEt	2086.8	2010
26	P(CH=CH <sub>2</sub> ) <sub>3</sub>	2069.5	1990	61	P(OCH <sub>2</sub> ) <sub>3</sub> CMe	2087.3	2011
27	PPh <sub>2</sub> ( <i>p</i> -C <sub>6</sub> H <sub>4</sub> F)	2069.5	1991	62	P(OCH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	2087.6	2011
28	PPh <sub>2</sub> ( <i>m</i> -C <sub>6</sub> H <sub>4</sub> F)	2070.0	1991	63	P( <i>O-p</i> -Cl- <i>o</i> -tolyl) <sub>3</sub>	2088.2	2018
29	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>	2071.3	1995	64	P( <i>O-p</i> -C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub>	2089.3	2019
30	PPh <sub>2</sub> (OEt)	2071.6	1994	65	P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> <sup>b</sup>	2090.9	<i>b</i>
31	PPh <sub>2</sub> (OMe) <sup>a</sup>	2072.0	1995	66	P(OCH <sub>2</sub> CCl <sub>3</sub> ) <sub>3</sub>	2091.7	2018
32	PPh( <i>O-i</i> -Pr) <sub>2</sub>	2072.2	1995	67	PPhCl <sub>2</sub>	2092.1	2016
33	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub> <sup>a</sup>	2072.8	1996	68	P( <i>O-p</i> -C <sub>6</sub> H <sub>4</sub> CN) <sub>3</sub>	2092.8	2024
34	PPh <sub>2</sub> H	2073.3	1995	69	PCl <sub>3</sub> <sup>b</sup>	2097.0	<i>b</i>
35	PPh(OBu) <sub>2</sub>	2073.4	1997	70	PF <sub>3</sub> <sup>b</sup>	2110.8	<i>b</i>

<sup>a</sup> These compounds were provided through the courtesy of Dr. O. F. Vogl. Syntheses, characterization, and <sup>31</sup>P nmr studies of these compounds will be published by him in a separate paper. <sup>b</sup> Solutions of these ligands were not pumped on either because of a low equilibrium concentration of Ni(CO)<sub>3</sub>L or because of its volatility. The E bands were obscured by the very strong broad Ni(CO)<sub>4</sub> band centered at 2035 cm<sup>-1</sup>.

tribution to the CO stretching frequency given by the ligand. This substituent contribution is designated  $\chi_i$ , and has a magnitude (in cm<sup>-1</sup>) such that for any Ni(CO)<sub>3</sub>PX<sub>1</sub>X<sub>2</sub>X<sub>3</sub>

$$\nu_{\text{CO}}(\text{A}_1) = 2056.1 + \sum_{i=1}^3 \chi_i \text{ cm}^{-1}$$

The frequency 2056.1 cm<sup>-1</sup> is that of tri-*t*-butylphosphine, the most basic ligand in the series. Writing the equation in this way sets the origin of the scale such that  $\chi_i = 0$  for *t*-butyl. Values for the other substituents are given in Table II. Using the substituent parameters in Table II, it is possible to calculate frequencies of the 70 compounds in Table I with an average deviation of  $\pm 0.3$  cm<sup>-1</sup>.

The value of the additivity rule, of course, is that values of  $\nu_{\text{CO}}(\text{A}_1)$  given by other ligands can be predicted even when direct data are not available. For example,  $\nu_{\text{CO}}(\text{A}_1)$  for PH<sub>3</sub> can be confidently predicted at 2081.0 cm<sup>-1</sup>, placing PH<sub>3</sub> between P(OMe)<sub>3</sub> and P(OPh)<sub>3</sub>.

Other additive relationships can be seen in the entries in Table II. Successive replacement of hydrogens on -CH<sub>3</sub> by methyl groups decreases  $\chi_i$  by a nearly constant 0.9 cm<sup>-1</sup> for each substitution on going from -CH<sub>3</sub> to -CH<sub>2</sub>CH<sub>3</sub> to -CH(CH<sub>3</sub>)<sub>2</sub> to -C(CH<sub>3</sub>)<sub>3</sub>; <sup>15</sup> substitution

(15) The regular behavior on successive substitutions, even in the case of the very bulky *t*-butylphosphine, as well as the similarity in  $\chi_i$  for *o*- and *p*-tolylphosphine, indicates that steric effects are unimportant in determining the carbonyl stretching frequencies.

on methyl by two propyl groups (in cyclohexyl) has twice the effect of one propyl (in *n*-butyl), the decrements in  $\chi_i$  being 2.5 and 1.2 cm<sup>-1</sup>, respectively. Replacement of hydrogens on -OPh by methyl groups decreases  $\chi_i$  by 0.3 cm<sup>-1</sup> for *o*-CH<sub>3</sub> and 0.4 cm<sup>-1</sup> for *p*-CH<sub>3</sub>; -*O-2,4*-[CH<sub>3</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub> has a value of  $\chi_i$  which is 0.7 cm<sup>-1</sup> less than that of -OPh.

A further correlation with predictive value is illustrated by Table III. Insertion of oxygen between an organic group R and phosphorus increases  $\chi_i$  by an increment of about 5 cm<sup>-1</sup> for most groups.

The high CO stretching frequencies associated with the strained bicyclic phosphite esters have been mentioned previously by Verkade.<sup>16</sup> It is interesting that the five-membered phosphite ring derived from ethylene glycol exhibits a similarly high contribution to  $\nu_{\text{CO}}$  (9.8 cm<sup>-1</sup>).<sup>17</sup>

Among the highly electronegative substituents the order of electron withdrawal was found to be CF<sub>3</sub> > F > Cl > C<sub>6</sub>F<sub>5</sub>, the values of  $\chi_i$  being 19.6, 18.2, 14.8, and 11.2 cm<sup>-1</sup>, respectively.

### The Nature of the Nickel-Phosphorus Bond

The term " $\pi$ -acceptor strength" has come into common usage to describe rank ordering of ligands in series based on carbonyl stretching frequencies in substituted

(16) J. G. Verkade, R. E. McCarley, D. C. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

(17) Substituent no. 34 in Table II.

**Table II.** Substituent Contribution to  $\nu_{\text{CO}}$  ( $A_1$ ) of  $\text{Ni}(\text{CO})_3\text{PX}_1\text{X}_2\text{X}_3$ 

	$\nu_{\text{CO}} (A_1) = 2056.1 + \sum_{i=1}^3 \chi_i$	$\chi_i, \text{cm}^{-1}$
1	- <i>t</i> -Bu	0.0
2	-Cyclohexyl	0.1
3	- <i>o</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	0.9
4	- <i>i</i> -Pr	1.0
5	-Bu	1.4
6	-Et	1.8
7	-Piperidyl	2.0
8	-Me	2.6
9	-2,4,6-[CH <sub>3</sub> ] <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	2.7
10	- <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	3.4
11-13	- <i>p</i> -Tolyl, - <i>o</i> -tolyl, -CH <sub>2</sub> Ph	3.5
14	- <i>m</i> -Tolyl	3.7
15	-Ph	4.3
16	-CH=CH <sub>2</sub>	4.5
17	- <i>p</i> -C <sub>6</sub> H <sub>4</sub> F	5.0
18	- <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	5.6
19	- <i>m</i> -C <sub>6</sub> H <sub>4</sub> F	6.0
20	- <i>o</i> - <i>i</i> -Pr	6.3
21	-OBu	6.5
22	-OEt	6.8
23	-CH <sub>2</sub> CH <sub>2</sub> CN	7.3
24-26	-OMe, -OCH <sub>2</sub> CH=CH <sub>2</sub> , -OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	7.7
27	-H	8.3
28	-O-2,4-[CH <sub>3</sub> ] <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	9.0
29-31	-OCH <sub>2</sub> CH <sub>2</sub> Cl, -O- <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> , -O- <i>p</i> -tolyl	9.3
32	-O- <i>o</i> -tolyl	9.4
33	-OPh	9.7
34	-(OCH <sub>2</sub> ) <sub>2</sub> /2 <sup>a</sup>	9.8
35	-(OCH <sub>2</sub> ) <sub>3</sub> CPr/3 <sup>a</sup>	10.2
36	-(OCH <sub>2</sub> ) <sub>3</sub> CEt/3 <sup>a</sup>	10.2
37	-(OCH <sub>2</sub> ) <sub>3</sub> CMe/3 <sup>a</sup>	10.4
38	-OCH <sub>2</sub> CH <sub>2</sub> CN	10.5
39	-O- <i>p</i> -Cl- <i>o</i> -tolyl	10.7
40	-O- <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	11.1
41	-C <sub>6</sub> F <sub>5</sub>	11.2
42	-O- <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl	11.4
43	-OCH <sub>2</sub> CCl <sub>3</sub>	11.9
44	-O- <i>p</i> -C <sub>6</sub> H <sub>4</sub> CN	12.2
45	-Cl	14.8
46	-F	18.2
47	-CF <sub>3</sub>	19.6

<sup>a</sup> This notation is meant to indicate the effect of one end of a poly-functional substituent.

**Table III.** The Difference between  $\chi_{\text{OR}}$  and  $\chi_{\text{R}}$ 

R	$\chi_{\text{OR}}, \text{cm}^{-1}$	$\chi_{\text{R}}, \text{cm}^{-1}$	$\chi_{\text{OR}} - \chi_{\text{R}}, \text{cm}^{-1}$
- <i>i</i> -Pr	6.3	1.0	5.3
-Et	6.8	1.8	5.0
-Me	7.7	2.6	5.1
- <i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	9.3	3.4	5.9
- <i>p</i> -Tolyl	9.3	3.5	5.8
-Ph	9.7	4.3	5.4
- <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	11.1	5.6	5.5
-CH <sub>2</sub> CH <sub>2</sub> CN	10.5	7.3	3.2
Av			5.2 ± 0.5

transition metal carbonyls.<sup>6-8,18</sup> We have chosen to use the more empirical term "electron donor-acceptor property." An exact description of the bonding between a transition metal and phosphorus cannot, of course, be obtained from a single frequency. (Note that  $A_1$  and E modes are highly correlated in Table I.) The earliest evidence for multiple bond character in Ni-P bonds seems to be the work of Chatt and Hart,<sup>3</sup> who observed

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 744.

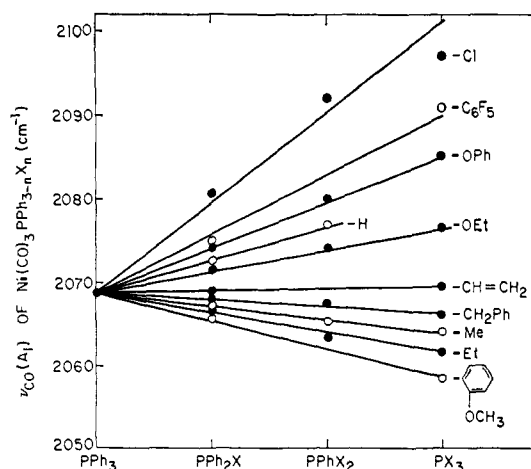


Figure 1. Effect of successive replacement of Ph by -X on  $\nu_{\text{CO}}$  ( $A_1$ ) of  $\text{Ni}(\text{CO})_3\text{PPh}_{3-n}\text{X}_n$ .

dipole moments in phosphine-substituted nickel carbonyls to be smaller than expected on the basis of complete donation of two electrons. They explained the smaller values in terms of substantial back donation of electrons from Ni to P, giving an estimated bond order of 1.3 to 1.7. Most authors seem to have adopted this notion. On the other hand, Bigorne<sup>4f</sup> has argued that changes in  $\sigma$  bonding can account for the observed changes in CO frequencies and that there is little if any  $\pi$  bonding to any of the phosphorus ligands. The basis of his argument is a fair correlation between CO stretching frequencies and Taft's inductive substituent parameter  $\sigma$ .<sup>19</sup> He has also argued that force constants of Ni-P bonds were not large enough to suggest substantial double bonding.<sup>4c</sup>

Recently Graham<sup>20</sup> and Stewart and Treichel<sup>21</sup> have attempted to separate  $\sigma$  and  $\pi$  bonding between M and P in molecules of the type  $\text{LM}(\text{CO})_5$  by using the different CO stretching force constants for carbonyls *cis* and *trans* to L. Using the same type of data, Angelici and Malone have argued that variations in  $\nu_{\text{CO}}$  can be explained in terms of  $\sigma$  bonding alone.<sup>22</sup>

A major objection to correlations of CO stretching frequencies with inductive parameters like Taft's  $\sigma$  is that these parameters are based on transmission of inductive effects through carbon. It is not surprising that substituents can behave somewhat differently when attached to phosphorus. The best example of this is the substituent -H. Its presence on phosphorus gives a much higher CO stretching frequency than one could expect based on its usual inductive effect on carbon, as any attempt to correlate  $\chi_i$  with carbon-based parameters like Taft's  $\sigma$  readily shows. The same sort of behavior of -H (making phosphorus a poor  $\sigma$  donor) is evident in the failure by Henderson and Streuli to obtain a single correlation for  $\text{p}K_a$ 's of phosphonium ions obtained from  $\text{PR}_3$ ,  $\text{PHR}_2$ , and  $\text{PH}_2\text{R}$  with  $\Sigma\sigma$ .<sup>23</sup>

It would be more sensible to have a group of substituent parameters based on their electronic effects on phosphorus. Such parameters (designated as  $\sigma$ ) have

(19) R. W. Taft in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 619.

(20) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(21) R. P. Stewart and P. M. Treichel, *ibid.*, **7**, 1942 (1968).

(22) R. J. Angelici and M. D. Malone, *ibid.*, **6**, 1731 (1967).

(23) W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

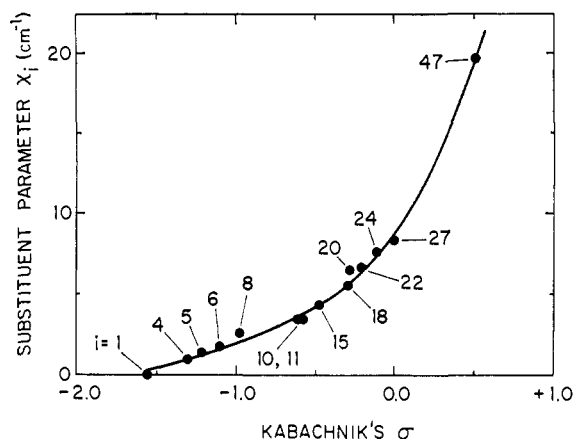
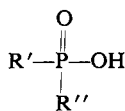


Figure 2. Correlation of substituent parameter  $\chi_i$  with Kabachnik's  $\sigma$  from ref 24. The substituent indices refer to Table II.

been proposed by Kabachnik, based on acid ionization constants in water of phosphorus acids of the type<sup>24</sup>



He subsequently found an excellent correlation (correlation coefficient  $r = 0.95$ ) between these parameters and the phosphonium ion  $\text{p}K_a$ 's of  $\text{HPR}_3^+$  reported by Henderson and Streuli,<sup>23</sup> with the points for  $\text{PR}_2\text{H}$  and  $\text{PRH}_2$  phosphines falling on the same line.<sup>25</sup> The ex-

(24) M. I. Kabachnik, *Dokl. Akad. Nauk. SSSR*, **110**, 393 (1956); *Proc. Acad. Sci. USSR, Chem. Sect.*, **110**, 577 (1956).

cellent correlation between our substituent parameters based on CO stretching frequencies and Kabachnik's  $\sigma$  values<sup>24</sup> is shown in Figure 2. We have found a similar correlation between  $\chi_i$  and the phosphonium  $\text{p}K_a$ 's. It is clear that in the reaction of  $\text{H}^+$  with  $\text{PR}_3$  to form a phosphonium ion, it is the  $\sigma$  donor ability of the phosphorus which determines the equilibrium constant, since  $\pi$  bonding cannot be involved between H and P.

While it is clear that more electron-withdrawing substituents give higher CO stretching frequencies, there does not appear to be sufficient evidence at this time to say to what extent the reduced electron density on nickel is to be attributed to a reduced  $\sigma$  donation or an enhanced  $\pi$ -acceptor behavior of phosphorus in the complexes.

It might be expected that double bond character in the Ni-P bonds might reflect itself in greater strength of the bonds and in more stability of the complexes. The effect of electronic changes in phosphorus ligands on the stability of their Ni(0) complexes will be considered in the following paper.<sup>26</sup>

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## Phosphorus Ligand Exchange Equilibria on Zerovalent Nickel. A Dominant Role for Steric Effects

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**Abstract:** Ligand exchange on Ni(0) was carried out using 24 phosphorus ligands L and 12  $\text{NiL}_4$  complexes. The new complexes  $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$ ,  $\text{Ni}[\text{P}(\text{OCH}_2\text{CCl}_3)_3]_4$ , and  $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$  are disclosed.  $^{31}\text{P}$  nmr data on the starting ligands and complexes and on a number of mixed complexes of the type  $\text{NiL}_{4-n}\text{L}'_n$  are reported. From the product distributions after toluene solutions of  $\text{NiL}_4$  and  $4\text{L}'$  were equilibrated, the ligands can be ranked in a series according to the stability of the complexes. A quantitative measure of steric effects in phosphorus-transition metal complexes is proposed, based on measurements on atomic models. It is shown that steric effects are much more important than electronic effects in determining the exchange equilibria among phosphorus ligands on Ni(0), as well as in determining the degree of substitution of CO from  $\text{Ni}(\text{CO})_4$  by these ligands. Implications of these results for other transition metal complexes are discussed. Spectroscopic evidence indicates that  $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$  and  $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$ , the complexes with the largest ligands, are extensively dissociated in solution; the other complexes are not.

Since the discovery of  $\text{Ni}[\text{PCl}_3]_4$ <sup>1</sup> and  $\text{Ni}[\text{PF}_3]_4$ <sup>2</sup> in 1951, a variety of zerovalent nickel complexes with phosphorus ligands have been described in the litera-

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ture. Little appears to be known, however, about the relative stabilities of the complexes or about the factors which are important in determining the stability. We wish to report the results of a series of experiments which indicate the relative importance of electronic and