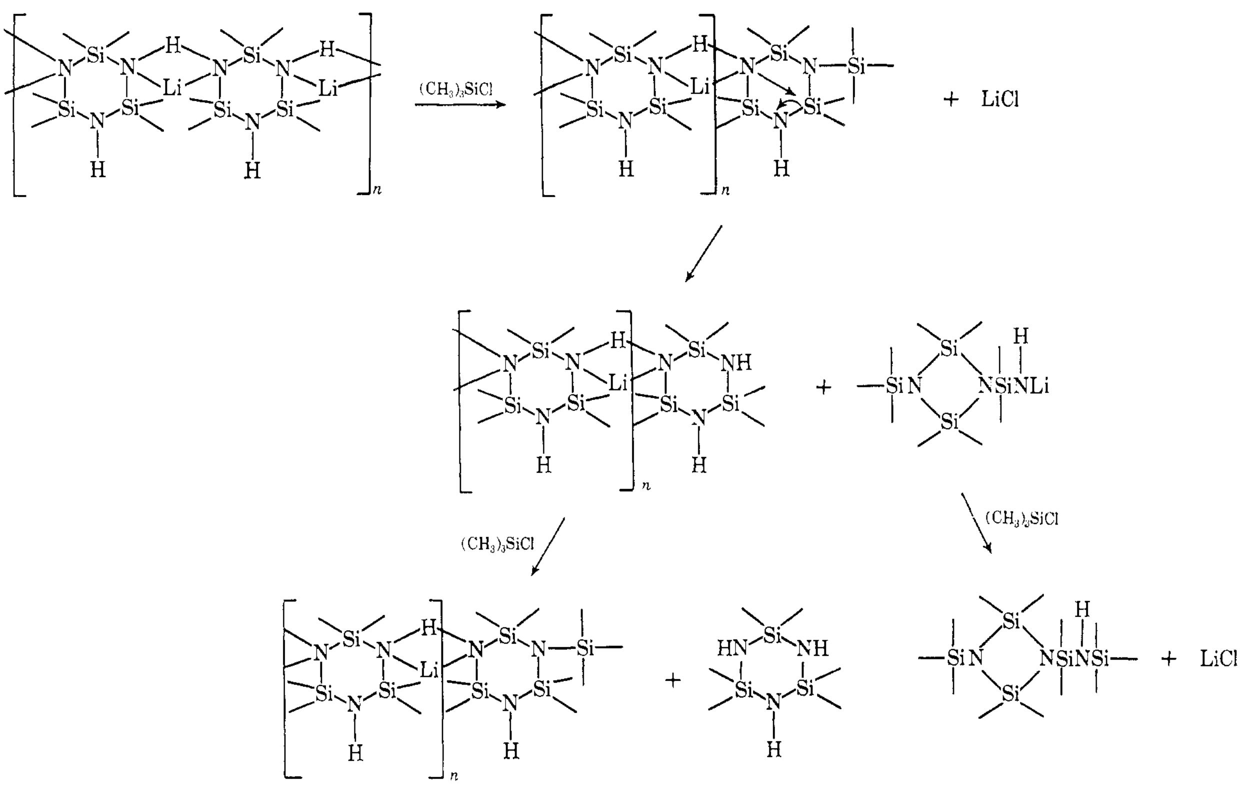
SCHEME I



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Correspondence

σ and π Effects of Phosphines, Pyridines, and Amines in $LW(CO)_5$ Complexes

Sir:

In a recent paper Graham[1] has defined inductive (σ) and resonance (π) effects of a ligand or group L in terms of the effect of L on ν_{CO} of $LM(CO)_5$ complexes (M = Mn, Mo). Using eq 1 and 2 relative σ and π parameters were derived for various L groups from the differences between the CO stretching force constants[2,3] of the compound $LM(CO)_5$ and a reference compound $RM(CO)_5$. A positive value of the σ (or π) parameter

$$\Delta k_1 = \sigma + 2\pi \qquad (1)$$

$$\Delta k_1 = \sigma + \pi \qquad (2)$$

implies that L is a σ (or π) acceptor, while a negative σ (or π) parameter implies that L is a σ (or π) donor compared to the reference group R, for which $\sigma = \pi = 0$

From the similar decrease in carbonyl stretching frequencies and force constants with increasing pK_a of L in $LW(CO)_5$ complexes (L = amine, pyridine, or phosphine) it has been suggested earlier that only changes in W–L σ bonding affect the CO stretching force constants,[4] though for at least the phosphine ligands this would seem to be a controversial conclusion in view of earlier studies.[5] We wish to observe here that these published data on $LW(CO)_5$ complexes can be evaluated using Graham's method. This treatment of these data assumes that both inductive and resonance effects are operative in determining carbonyl band positions and hence contradicts the suggestion that σ bonding alone is influential in these spectra. As a result of this treatment one sees the difference in k_1 between the phosphine and amine complexes appears to reflect the π component of M–L bonding. While application of this model[1] is not a proof, *a priori*, that π bonding plays a significant part in determining this observed effect of a ligand, one

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[1] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

[2] CO stretching force constants are those obtained from the Cotton–Kraihanzel method;[3] k_1 is the force constant associated with the CO group *trans* to L and k_2 is the force constant of the CO groups *cis* to L.

[3] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[4] R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

[5] W. D. Horrocks, Jr., and R. C. Taylor, *ibid.*, **2**, 723 (1963); F. A. Cotton, *ibid.*, **3**, 702 (1964), and references therein.

TABLE I

GRAHAM σ AND π PARAMETERS FOR $LW(CO)_5$ COMPLEXES[a]

Ligand L	pK_a	k_1	k_2	Δk_1	Δk_2	σ[b]	π[c]
$(C_6H_5)_3P$	2.7	15.57	15.89	0.50	0.14	−0.22	0.36
$3\text{-}BrC_5H_4N$	2.8	15.16	15.85	0.09	0.10	0.11	−0.01
$4\text{-}BrC_6H_4NH_2$	3.9	15.15	15.83	0.08	0.08	0.08	0.00
$(p\text{-}CH_3C_6H_4)_3P$	4.0	15.54	15.86	0.47	0.11	−0.25	0.36
$(p\text{-}CH_3OC_6H_4)_3P$	4.5	15.53	15.85	0.46	0.10	−0.26	0.36
$C_6H_5NH_2$	4.6	15.11	15.82	0.04	0.07	0.10	−0.03
C_5H_5N	5.2	15.11	15.80	0.04	0.05	0.06	−0.01
$4\text{-}CH_3OC_6H_4NH_2$	5.3	15.07	15.80	0.00	0.05	0.10	−0.05
$4\text{-}CH_3C_5H_4N$	6.0	15.07	15.77	0.00	0.02	0.04	−0.02
$(C_6H_5)(C_2H_5)_2P$	6.3	15.51	15.82	0.44	0.07	−0.30	0.37
C_4H_9NO	8.3	15.12	15.77	0.05	0.02	−0.01	0.03
$(n\text{-}C_4H_9)_3P$	8.4	15.47	15.78	0.40	0.03	−0.34	0.37
$(CH_3)_3N$	9.8	15.08	15.76	0.01	0.01	0.01	0.00
$(CH_3)_2CHNH_2$	10.6	15.07	15.75	0.00	0.00	0.00	0.00
$C_6H_{11}NH_2$	10.7	15.07	15.75	0.00	0.00	0.00	0.00
$(CH_3)_2NH$	10.7	15.11	15.74	0.04	−0.01	−0.06	0.05
$HC(CH_2CH_2)_3N$	10.9	15.05	15.72	−0.02	−0.03	−0.04	0.01

[a] Data taken from ref 4; cyclohexane solution; force constants and parameters in mdyn/Å. [b] Estimated experimental uncertainty ±0.12.[1] [c] Estimated experimental uncertainty ±0.08.[1]

can assume that it strongly favors such a view, especially since it allows these data to be correlated so well with previous studies and with the generally accepted intuitive model.[5]

The σ and π parameters were calculated for the $LW(CO)_5$ complexes from the reported carbonyl stretching force constants[4] and are shown in Table I. The reference compound was taken as $C_6H_{11}NH_2W(CO)_5$, analogous to the choice of $C_6H_{11}NH_2Mo(CO)_5$ as reference in the $LMo(CO)_5$ series.[1]

It is immediately obvious from Table I that there is no general correlation of the basicity of L with the value of its σ parameter,[6] although there is a trend toward lower σ values (increasing σ-donor ability) with increased pK_a of L in two *separate* series: (1) amines and pyridines and (2) phosphines. The values of the σ parameters indicate that the amines and pyridines are weak σ acceptors (in three cases weak donors) while the phosphines are all strong σ donors. Considering inductive effects alone in $LW(CO)_5$ compounds, one would predict lower force constant values when L = phosphine than when L = amine or pyridine. The observation that k_1 values of the amine complexes are lower than those of phosphine complexes of the same pK can be interpreted in terms of either the inductive effect being operative through the π system[7] or a resonance effect contributing to the net result. In both cases one has to evoke π-bonding changes in explaining this variation.

Although there is no correlation of σ values with the basicities of the ligands L in $LW(CO)_5$ complexes, there is clearly a relationship of pK_a with k_2 (observed by Angelici[4]) and with Δk_2. However the value of Δk_2, which varies in the same way as k_2,[8] is, by definition, $\sigma + \pi$, and, if one accepts this definition, changes in k_2 for $LW(CO)_5$ would of necessity involve *both* σ- and π-bonding changes in the W–L bond. The significance of the observed correlation of pK_a and k_2 then becomes less clear. However it would seem to be the near constancy of the *sum* of these two effects for a ligand of given pK_a which is to be related to the variation of k_2 with pK_a for L = amine, pyridine, or phosphine in these tungsten complexes. This constancy was previously noted as evidence for the synergistic relationship of σ and π bonds in these complexes.[1]

The dependence of k_1 on pK_a in the $LW(CO)_5$ complexes was found[4] to be practically the same as that of k_2, although k_1 values for the amine and pyridine complexes are lower than for the phosphine complexes. This result would be predicted by the Graham method and the fact that the dependence of k_2 (or Δk_2) on pK_a is the same for all three types of ligands. From eq 1 and 2 relation 3 may be derived. For L = amine or

$$\Delta k_1 = \Delta k_2 + \pi \tag{3}$$

pyridine, $\pi \approx 0$ (Table I) so $\Delta k_1 = \Delta k_2$, and, thus, Δk_1 would be expected to have the same behavior as Δk_2 when pK_a is varied. In the case where L = phosphine, the value of π is seen to be approximately constant (+0.36).[9–11] Hence eq 3 becomes $\Delta k_1 = \Delta k_2 + 0.36$. It is clear that Δk_1 will have the same dependence as Δk_2 on pK_a because Δk_1 and Δk_2 differ only by a constant. However, the effect of the positive π parameter when L

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(6) A similar conclusion was reached by Graham[1] for the LMo(CO) series.

(7) We consider the σ parameter of any group to reflect the net charge transfer from ligand to metal, in both the σ- and π-bonding systems, owing to the electronegativity of the group. Thus, in bonding to a metal, an amine transfers very little electron density to a metal relative to a phosphine ligand (which has a negative σ value). It is important that this concept of σ value is not confused with the concept of Brønsted basicity, in which one also refers to good or poor donors in a different sense.

(8) Note here and in the following discussion that any variation in k_1 or k_2 with pK_a is the same as that for Δk_1 and Δk_2, respectively, since corresponding k and Δk differ only by a linear scale change.

(9) It is possible that this result is fortuitous. For the analogous molybdenum compounds, the values of π vary significantly, and several other studies[10,11] also suggest this. We do not express concern over this, since this manner of evaluation of σ and π effects is only approximate[1] and since the similarities of k_1 (Δk_1) were observed only qualitatively.[4] More important, however, is the fact that this is a question more or less peripheral to the main point under consideration.

(10) G. R. VanHecke and W. D. Horrocks, *Inorg. Chem.*, **5**, 1968 (1966).

(11) S. O. Grim, D. O. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

= phosphine results in the values of Δk_1 for phosphines that lie consistently higher than those of the latter ligands with comparable pK_a's.

One cannot help but note the fact that relatively large changes in pK_a of a ligand lead to a vanishingly small net change in k_1 and k_2. In fact the accuracy of these latter calculated values is such that we can say that the observed trend is barely significant. However, the effect of the π parameter of the phosphine ligands on k_1, which is assigned to lead to a net variation of approximately 0.40 mdyn/Å above the k_1 for amines, is large indeed.

In agreement with previous work,[1,4,5] the Graham method indicates that W-L π bonding in LW(CO)$_5$ (L = amine or pyridine) is of little importance when compared with W-L σ bonding. The σ and π parameters calculated by this method show that these ligands behave as weak σ and π acceptors or donors in the tungsten complexes. Phosphines, however, are shown to be strong σ donors and even stronger π acceptors from the values of their σ and π parameters. Using the Graham method it is clear that the inductive (σ) effect is important, as Angelici concludes;[4] however it is not possible in terms of tungsten–phosphine σ bonding *alone* to explain the reported dependence of the CO stretching frequencies and force constants on ligand basicity as was previously done.[4]

It is of interest that a recent paper by Darensbourg and Brown[12] is in some accord with these conclusions. These workers suggest that the net transfer of electrons from the ligand to the metal in the σ system leads to the shift in ν_{CO} for amine and phosphine complexes to lower frequency. One would anticipate that this shift would be greater for the phosphine complexes than for the amine complexes if this were the only effect since phosphines are strong donors,[8] *i.e.*, $\sigma < 0$; however, back-bonding to the phosphine ligand lowers the energy of the metal d orbitals and in turn results in less back-bonding in these complexes (than in the corresponding amine system).[13] In a sense the result of this interpretation is that σ and π bondings in phosphine metal complexes do indeed reinforce each other, and it is the sum of these two effects which leads to the observed results.

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[12] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).

[13] One must take care in assigning these ν_{CO} effects as being due to π bonding only, even though direct correlations can be made.

[14] NASA Traineeship holder, 1966–1968.

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RECEIVED FEBRUARY 26, 1968