The Aryl Effect in Disubstituted Dimanganese and Dicobalt Carbonyls

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The energies of the intense bands in the near-UV−vis spectra of a number of axially substituted $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$ complexes containing non-π-acid phosphine substituents have been measured in solution. When combined with data reported previously, the trends show unambiguously that a major contributor to the energies is Giering and Prock's aryl effect (quantifiable by E_{ar} values that are almost proportional to the number of aryl groups attached to the donor P atom). The equation $h\nu = \alpha + \beta\chi + \gamma\theta + \omega E_{ar}$ gives an excellent empirical description of the data ($100(1 - R^2) = 0.5\%$ and 2.6% for the Mn_2 and Co_2 complexes, respectively) where χ is the Tolman/Bartik measure of the σ-basicity and θ is the Tolman cone angle of the ligands. The values of $h\nu$ increase with increasing σ-basicity and decrease with increasing ligand size and increasing numbers of aryl groups. The maximum increase of 1650 cm^{-1} in the $h\nu$ values of the Mn_2 complexes is found when L = $P(p\text{-}F_3CC_6H_4)_3$ is replaced by $P(n\text{-}Bu)_3$, and this is made up of 49 ± 4% contribution by the less unfavorable aryl effect, 33 ± 5% due to the greater basicity, and 18 ± 1% due to the smaller size of the $P(n\text{-}Bu)_3$ ligands. In the Co_2 complexes the aryl and steric effects contribute 82 ± 11% and 16 ± 3%, respectively, but the electronic effect is small and not well defined. The dominant contributions of the aryl effect are striking. Indeed, the correlation of the data with the aryl effect *alone* leads to R^2 values of 0.827 and 0.845 for the Mn_2 and Co_2 complexes, respectively. The effect of σ-donicity is ascribed to the greater concentration of electron density in the region of the M−P bond when the electron is in the σ^* orbital, and the effect of ligand size is ascribed to a lengthening of the M−M and M−P bonds, the former decreasing σ-orbital overlap and the latter decreasing the effective σ-donicity. No explanation is yet available for the origins of the empirically well established aryl effect even though it shows up in a wide range of physicochemical measurements.

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Introduction

The range of P-donor ligands available as substituents in organometallic compounds, or as nucleophiles in their associative substitution reactions, is very large,[1] and correlations of physicochemical properties of the complexes with electronic and steric effects of such ligands is widespread.[1,2] Their electronic and steric properties can be of enormous practical importance in determining the reactivity of substituted complexes, and this is illustrated by the classical observation that $Rh(PPh_3)_3Cl$ is a very effective homogeneous catalyst for hydrogenation of alkenes whereas the closely related trialkylphosphine complexes are not.[3] The presence of P-donor substituents can also modify the behavior of other catalysts in important ways that are dependent on the particular P-donors present.[3a,4]

The separation of electronic and steric effects of participating P-donor or other similar ligands was begun by Basolo[5] and steadily became more quantitative, particularly after the introduction by Tolman of cone angles, θ, as a measure of the effective size of those ligands,[1,6] and the recognition by Giering et al.[7] that there could be sharp cone angle thresholds, θ_{th}, such that steric effects only become evident when $\theta > \theta_{th}$. Equation 1 is a typical example[2e] of equations that

$$\log k_2 = \alpha + \beta pK_a' + \gamma(\theta - \theta_{th})\lambda \qquad (1)$$

quantitatively describe the dependence of a physicochemical parameter on the electronic and steric properties of ligands involved. In this case the physicochem-

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(1) Tolman, C. A. *Chem. Rev.* **1976**, *76*, 313.

(2) For example: (a) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951. (b) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet.Chem.* **1984**, *272*, 29. (c) Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742 and references cited therein. (d) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *36*, 95. Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286. (e) Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265. Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238 and references cited therein.

(3) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 28. (b) Montelatici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1054.

(4) Hegedus, L. S.; Collman, J. P.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransitionmetal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. Wood, C. D.; Garrone, P. E. *Organometallics* **1984**, *3*, 170. Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147.

(5) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.

(6) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(7) Prock, A.; Giering, W. P.; Greene, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479 and references therein.

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Table 1. Ligand and Spectroscopic Parameters for the Bis-Axial Complexes $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$

				$Mn_2(CO)_8L_2$				$Co_2(CO)_6L_2$			
						$h\nu$ (cm^{-1})				$h\nu$ (cm^{-1})	
L	θ^a	χ^b	$E_{ar}{}^c$	$\nu_{CO}{}^d$ (cm^{-1})	λ^d (nm)	exptl	calcd^e	$\nu_{CO}{}^f$ (cm^{-1})	λ^d (nm)	exptl	calcd^e
PEt_3 (**1**)	132	6.30	0	(1950)	(356)	20 090	(28 090)				
$P(n\text{-}Bu)_3$ (**2**)	132	5.25	0	(1950)	(356)	28 090	(28 120)	(1950)	(371)	26 950	(27 030)
$PPhEt_2$ (**3**)	136	9.30	1	(1951)	(363)	27 550	(27 580)	(1957)	(376)	26 600	(26 490)
PPh_2Et (**4**)	140	11.30	2	(1958)	(369)	27 100	(27 120)	(1958)	(385)	25 970	(25 950)
$P(i\text{-}Bu)_3$ (**5**)	143	5.70	0	1942	358	27 930	(27 850)				
$P(p\text{-}CF_3\phi)_3{}^g$ (**6**)	145	20.2	2.7	1962	378	26 460	(26 470)	1965	392	25 510	(25 520)
$P(p\text{-}Cl\phi)_3$ (**7**)	145	16.80	2.7	1958	376	26 600	(26 590)	1949			
$P(p\text{-}F\phi)_3$ (**8**)	145	15.70	2.7	1953	372			1952			
PPh_3 (**9**)	145	13.25	2.7	1954	374	26 740	(26 720)	1945	392	25 510	(25 540)
$P(p\text{-}tol)_3$ (**10**)	145	11.50	2.7	1950	374	26 740	(26 790)	1943	394	25 380	(25 540)
$P(p\text{-}MeO\phi)_3$ (**11**)	145	10.50	2.7	1950	372	26 880	(26 830)	1943	390	25 640	(25 540)
PPh_2Cy (**12**)	153	9.30^h	2	1953	372	26 880	(26 890)	1950	388	25 770	(25 720)
$P(i\text{-}Pr)_3$ (**13**)	160	3.45	0	1941	363	27 550	(27 540)				
$PPhCy_2$ (**14**)	162	5.35^h	1		368	27 170	(27 120)				
PCy_3 (**15**)	170	1.40	0	1939	366	27 320	(27 380)	1946	380	26 320	(26 330)

[a] Tolman cone angle. [b] From ref 2b. [c] Giering's aryl parameter. [d] Numbers in parentheses are from ref 10b and were measured in hydrocarbon solvents. Others were measured in CH_2Cl_2. [e] Values are given to four significant figures to avoid rounding errors. Calculated values were obtained as in text. [f] Values in parentheses were from ref 10 and were measured in hydrocarbon solvents. Others were measured with compounds in suspension in parafin oil. [g] $\phi = C_6H_4$ here and below. [h] Bartik et al.[2b] provided no values of χ for these ligands and these values are interpolated between χ values for PPh_3 and PCy_3.

ical parameter is the value of log k_2 for the associative reactions of metal carbonyls with a series of P-donor nucleophiles of different σ-donicity, pK_a', and cone angle. The switching factor, λ, is zero when $\theta \leq \theta_{th}$,[7] and no steric effects are operative, and unity when $\theta > \theta_{th}$. The equation implies that electronic and steric effects (when the latter exist) are linear functions of the chosen electronic and steric parameters of the nucleophiles and that these parameters are transferable from one system to another. Data for associative reactions of over 50 metal carbonyls are found to be represented closely by this equation,[2e,7,8] and well over 100 sets of data that include a variety of other types of physicochemical measurements have also been successfully analyzed by analogous equations.[2c,9]

It was recently discovered, however, that a number of important and diverse sets of data could not be satisfactorily analyzed in terms of simple electron donicity and steric parameters alone.[2c] The cause of the difficulty was found to be the involvement of ligands containing varying numbers of aryl groups. Separation of the data into sets, each containing ligands with the same number of aryl groups, led to satisfactory fits of each data set, and differences between the sets of data were almost linearly related to the number of aryl groups. The addition of a term including an "aryl parameter" $E_{ar} = 0$, 1, 2, and 2.7 depending on whether the number of aryl groups in the ligands was 0, 1, 2, and 3, respectively, resolved the problem completely. The scale of this aryl effect can be very significant. Thus the vertical ionization potentials of phosphines can vary by *ca*. 1.4 eV depending on the number of aryl groups, and the rate constants for nucleophilic displacement of I^- from EtI by P donors would increase by 10^3 as E_{ar} changes from 0 to 2.7 if other effects remained constant. Even though the effect is empirically demonstrable, there is no real understanding of the physical reasons why such a variety of physicochemical phenomena are affected, or why the effect does not seem to be dependent on the presence of any substituents in the aryl groups.[2c]

That being so, any further demonstration that the effect is empirically genuine would be of value, particularly if the demonstration involved a physicochemical property quite different from any studied before. We present an extension of a previous study[10] of the electronic and steric effects of axially disposed P-donor ligands in the metal−metal-bonded carbonyls $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$. This showed semiquantitatively that the energies of the intense bands that were then assigned[11a] to the $\sigma \rightarrow \sigma^*$ transitions in these compounds appeared to depend on the σ-donicity, π-acidity, and size of the substituents. These transitions were believed to involve the bonding and antibonding molecular orbitals located along the metal−metal bond axes and lead to characteristic allowed transitions in the near-UV spectra.[11] The new data for phosphine substituents, which are σ-donors only, allow the energies to be analyzed quantitatively in a way that is only successful if a dominant aryl effect is allowed for. The effects of σ-donicity and ligand size are compared quantitatively with the aryl effect.

Experimental Section

$Mn_2(CO)_{10}$ and $Co_2(CO)_8$ (Strem) were used as received. The ligands L were obtained and purified as described elsewhere.[8] The complexes $Mn_2(CO)_8L_2$ were prepared by photolysis[12] of $Mn_2(CO)_{10}$ in toluene with a medium-pressure Hg lamp and a small excess of the ligand ($L = P(p\text{-}XC_6H_4)_3$; $X = CF_3$, F, Cl, Me, MeO; PEt_3, $P(i\text{-}Bu)_3$, and $P(i\text{-}Pr)_3$), or by thermal reaction of $Mn_2(CO)_8(PPh_3)_2$ with a 10-fold excess of L (PCy_3, PCy_2Ph, $PCyPh_2$) in cyclohexane at 60 °C for ca. 5 h. In both cases completion of reaction was verified by the absence of reactant bands in the IR spectra. Neither method was successful with $L = P(CH_2C_6H_5)_3$, $P(CH_2CH_2CN)_3$, $P(NMe_2)_3$, or $P(t\text{-}Bu)_3$ when ill defined insoluble products were formed, and the photochemical method was not successful with PCy_2Ph or $PCyPh_2$ when mixtures of products were formed. The products were characterized by their FTIR spectra which showed only one strong band in the C−O stretching region (Table 1). The IR frequencies showed a good correlation with Bartik's χ values[2b]

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(8) Poë, A. J.; Zheng, Y. *Inorg. Chim. Acta* **1996**, *252*, 311 and references cited therein.

(9) Giering, W. P. Personal communication.

(10) (a) Jackson, R. A.; Poë, A. J. *Inorg. Chem.* **1978**, *17*, 2330. (b) Jackson, R. A. Ph.D. Thesis, University of Toronto, Canada, 1977.

(11) (a) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; Chapter 2.

(12) Jackson, A. R.; Poë, A. J. *Inorg. Chem.* **1978**, *17*, 997 and references therein.

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(ν_{CO} = (1937.2 ± 1.5) + (1.20 ± 0.12)χ cm^{-1}; RMSD[13] = 1.9 cm^{-1}, R^2 = 0.926) provided only data based on a common solvent, CH_2Cl_2, are used.

The complexes $Co_2(CO)_6L_2$ (L = P(p-$XC_6H_4)_3$; X = H, Cl, F, CF_3, Me, and MeO) were prepared by thermal reaction[14] of $Co_2(CO)_8$ (0.85 mg, 0.25 mmol) with 2 molar equiv of L in freshly distilled toluene (40 mL) at 90−100 °C under argon for ca. 5 h when reddish-brown solid products finally separated. These were filtered under Ar and dried under vacuum (yield: 80−90%). The complexes with X = Cl or F were insoluble in polar or nonpolar organic solvents. The complex $Co_2(CO)_6(PCyPh_2)_2$ was prepared in a similar way, but in lower yields (20−30%), the reaction solution being reduced in volume by ca. two-thirds before addition of sufficient 3:1 hexane/MeOH to effect precipitation of the brown product. The products were characterized by their FTIR spectra (one strong band in the C−O stretching region[14]). The trends shown by the ν_{CO} values are not as regular as those shown in the Mn_2 complexes, but the frequencies for the (p-$XC_6H_4)_3P$ compounds show a gradient of 2.2 ± 0.4 (RMSD = 2.8 cm^{-1}; R^2 = 0.86) when plotted against Bartik's χ values.

The FTIR spectra were measured with a Nicolet 10DX spectrophotometer, and the UV−vis spectra of the products were measured with a Hewlet-Packard 8452A diode array spectrophotometer. UV−vis data for the new complexes were obtained in CH_2Cl_2, rather than parafin hydrocarbon solvents for solubility reasons, but in those cases where the UV−vis spectra of the compounds had been measured previously,[10,11,15] closely similar results were obtained when the solvents were CH_2Cl_2 or parafin hydrocarbons. Values of $h\nu$ found in acetonitrile were, however, usually slightly higher by up to 300 cm^{-1}, but the trends, such as they are with a smaller set of ligands, are similar. As expected,[11] all the products showed a characteristic strong band in the near-UV with a weaker high-wavelength shoulder, and the wavelengths and energies ($h\nu$, cm^{-1}) of the strong band are shown in Table 1.

Discussion

Dependence of $h\nu$ on the Electronic and Steric Properties of the Phosphine Ligands. As will be shown below, the values of $h\nu$ in Table 1 for the phosphine-substituted Mn_2 and Co_2 compounds can be described very successfully by eq 2 with the term ωE_{ar}, related to the aryl effect, being dominant for both sets of complexes. There is no steric threshold above the

$$h\nu = \alpha + \beta\chi + \gamma\theta + \omega E_{ar} \tag{2}$$

minimum cone angle of 132° and the same steric effect, quantified by γ, is operative over the whole range of cone angles used. The parameter χ is a measure of the relative σ-donicity of the ligands, and the coefficients β and ω quantify the sensitivity of the $h\nu$ values to the σ-donicity and the aryl effect, respectively, while α is simply the value of $h\nu$ when χ, θ, and E_{ar} are all zero.

In analyzing the fit of the data to eq 2 we follow exactly the protocol established by Giering et al.[2c,7] Considering first the data for the Mn_2 complexes we can obtain a value of β from the dependence of $h\nu$ on χ for the series of ligands P(p-$XC_6H_4)_3$ which all have the same value of θ (145°)[1,6] and three aryl groups, but whose χ values cover quite a wide range. The graph in Figure 1 shows that $h\nu$ decreases linearly with χ with the exception of the value for X = F which deviates from the trend set by the others. A linear least squares analysis of the data for the latter five substituents gives β = −33.8 ± 8.7 with RMSD = 54 cm^{-1} and R^2 = 0.836. The deviation of the data for the P(p-$FC_6H_4)_3$ ligand from the correlation is +260 cm^{-1}, or nearly 5 times the value of the RMSD, so the deviation is quite significant. This value β can now be used to examine the steric effect by plotting $h\nu$ + 33.8χ vs θ as is done in Figure 2, and this immediately shows the unavoidable need to include a third parameter in the data analysis. If there were no such need, then all the data would be expected to fall on a typical steric profile,[2c,e,7,8] i.e. all the values of $h\nu$ + 33.8χ should decrease linearly with θ if θ_{th} < 132°, or they should be constant up to a steric threshold after which they should decrease linearly. The data for PEt_3, P(n-$Bu)_3$, P(i-$Pr)_3$, P(i-$Bu)_3$, and PCy_3 treated separately show that $h\nu$ + 33.8χ decreases linearly with increasing θ (i.e. θ_{th} < 132°) and a value of γ = −26.3 ± 1.3 cm^{-1} deg^{-1} (RMSD = 35 cm^{-1}; R^2 = 0.992) can be obtained

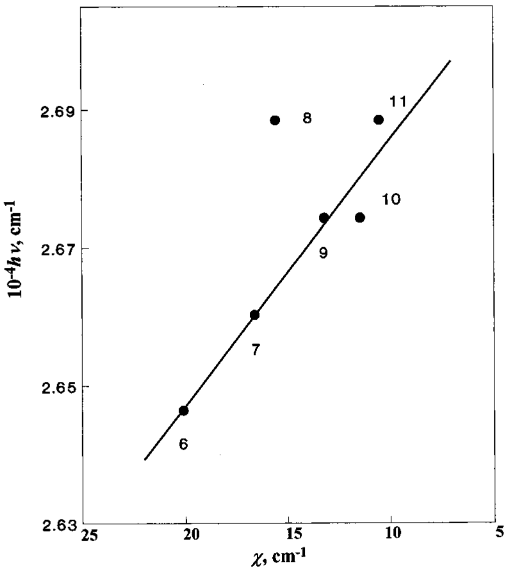

Figure 1. Dependence of $h\nu$ for $Mn_2(CO)_8L_2$ on the σ-basicity parameter, χ, for the isosteric substituents P(p-$XC_6H_4)_3$ (θ = 145°). Basicity increases with decreasing values of χ. The ligand numbering, here and elsewhere, is as in Table 1.

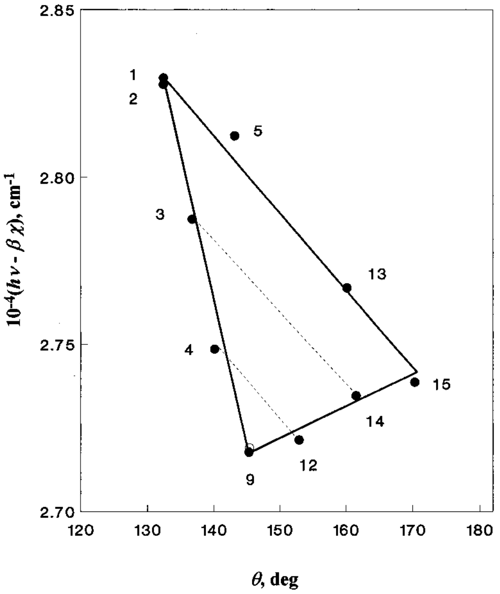

Figure 2. Dependence of $h\nu - \beta\chi$ on θ for $Mn_2(CO)_8L_2$ (β = −33.8). The open circle represents the average value for the P(p-$XC_6H_4)_3$ substituents.

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[13] Root mean square deviation.

[14] Bonati, F.; Cenini, S.; Morelli, D.; Ugo, R. *J. Chem. Soc. A* **1966**, 1052.

[15] Balch, A. L.; Benner, L. S. *J. Organomet. Chem.* **1977**, *134*, 121.

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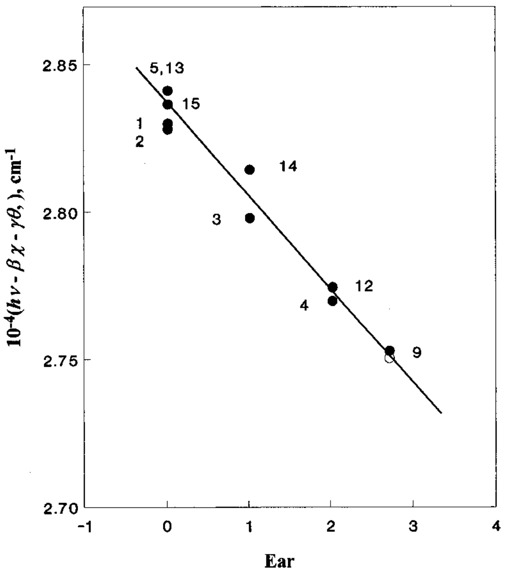

Figure 3. Dependence of $h\nu - \beta\chi - \gamma\theta$ on E_{ar} for $Mn_2(CO)_8L_2$ ($\beta = -33.8$; $\gamma = -26.3$ cm^{-1} deg^{-1}). The open circle at $E_{ar} = 2.7$ is the average value for the $P(p\text{-}XC_6H_4)_3$ substituents.

Table 2. Spectroscopic Parameters from the Multivariant Least Squares Analysis of the *hν* Values According to Eq 2

	β	γ (cm^{-1} deg^{-1})	ω (cm^{-1})	RMSD (cm^{-1})	R^2
Mn_2	−36.8 ± 5.4	−23.3 ± 1.3	−297 ± 22	38.4	0.995
Co_2	−2.0 ± 14.0	−18.5 ± 3.9	−457 ± 60	80	0.974

from the gradient. The lines joining the pairs of data for $PPhEt_2$ and $PPhCy_2$, and PPh_2Et and PPh_2Cy have similar gradients (−20 and −22 cm^{-1} deg^{-1}), respectively) but are progressively displaced below the first line to an extent dependent on the number of aryl groups in the ligands. The average value of $h\nu + 33.8\chi$ for the ligands $P(p\text{-}XC_6H_4)_3$, each with three aryl groups, lies even lower. It can therefore be concluded that the extra parameter that Figure 2 shows to be unambiguously needed is indeed the aryl parameter, E_{ar}. A plot of $h\nu + 33.8\chi + 26.3(\theta - 132)$ vs E_{ar} is shown in Figure 3, and the gradient leads to a value of $\omega = -326 \pm 19$ cm^{-1} (RMSD = 78 cm^{-1}; $R^2 = 0.960$).

This stepwise analysis of the data shows that they can be well described by the model represented by eq 2, and the data can therefore be analyzed by a multivariant least squares program[16] with the results indicated in Table 2. The parameters obtained from the program are in excellent agreement with those obtained by the stepwise analysis. The adequacy of the model used to fit the data can be expressed, for example, by the steric profile shown in Figure 4 and by comparison of the values of $h\nu$(expt) and $h\nu$(calc) in Table 1. The value of $R^2 = 0.995$ shows that less than 1% of the variation in $h\nu$ from complex to complex is unaccounted for by the model expressed by eq 2 and the values of the coefficients given in Table 2.[17] The RMSD value of 38 cm^{-1} corresponds to an uncertainty of ≤±1 nm in the determination of λ_{max}. Even the introduction of the data for L = $P(p\text{-}FC_6H_4)_3$ into the analysis only reduces R^2 to 0.987 and increases the RMSD to 64 cm^{-1} without appreciably affecting values of β, γ, or ω.

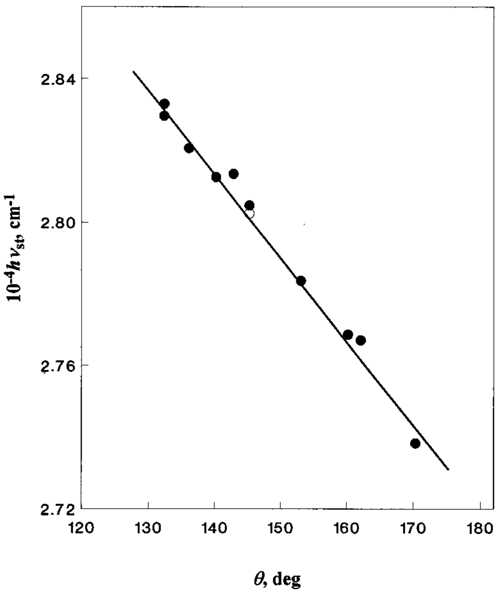

Figure 4. Dependence of $h\nu_{st} = h\nu - \beta\chi - \omega E_{ar}$ on θ for $Mn_2(CO)_8L_2$. (Values of β and ω taken from Table 2.) The open circle is the average value for the $P(p\text{-}XC_6H_4)_3$ substituents.

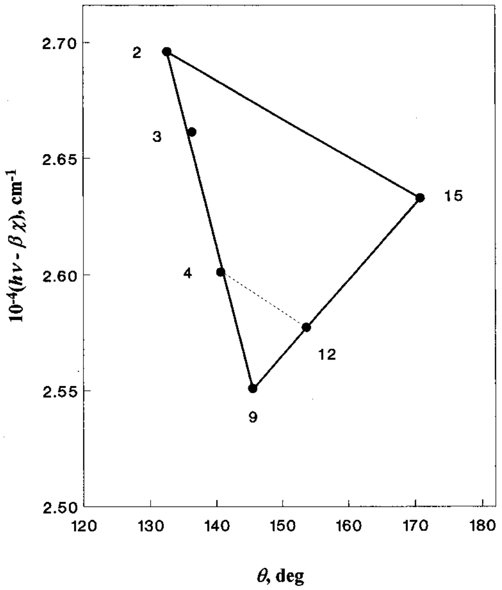

Figure 5. Dependence of $h\nu - \beta\chi$ on θ for $Co_2(CO)_6L_2$ ($\beta = -2.0$).

The same procedures can be carried out with the somewhat less extensive data for the Co_2 compounds. A value of $\beta = -2.6 \pm 12.4$ is found from the data for the three $P(p\text{-}XC_6H_4)_3$ complexes that were soluble enough for reliable UV−vis spectra to be obtained. A plot of $h\nu + 2.6\chi$ vs θ is shown in Figure 5 to be of exactly the same form as that in Figure 2, and the existence of the aryl effect in these Co_2 complexes is also clear. The coefficients obtained by fitting the data to eq 2 are given in Table 2, and the values of $h\nu$(calc) are included in Table 1. The fit is only slightly less good than that for the Mn_2 complexes.

The Relative Contributions of σ-Donicity, Ligand Size, and the Aryl Effect to *hν*. The relative importance of each ligand property in contributing to the variation in $h\nu$ for the Mn_2 complexes can be assessed as follows. The dependence of $h\nu$ on each property taken

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[16] We are grateful to Professor W. P. Giering for providing us with a copy of his program.

[17] Achen, C. H. *Interpreting and Using Regression*; Sage University Paper Series on Quantitative applications in the social sciences, Series No. 29; Sage Publications: Beverly Hills and Lonon, 1982; p 58.

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Table 3. Maximum Contributions in cm^{-1} ($kJ\ mol^{-1}$) of the Ligand Effects to $h\nu$

	σ-basicity	size effects	aryl effects
Mn_2	$+684 \pm 158$ (8.2 ± 1.9)	-942 ± 76 (11.3 ± 0.9)	-823 ± 92 (9.8 ± 1.1)
Co_2	$+37 \pm 259$ (0.4 ± 3.1)	-701 ± 150 (8.4 ± 1.8)	-1234 ± 162 (14.8 ± 1.9)

separately can be determined, and the correlations are found to improve in the following order: θ ($R^2 = 0.10$, $\gamma = -16 \pm 14$ cm^{-1} deg^{-1}) < χ ($R^2 = 0.51$, $\beta = -77 \pm 22$) < E_{ar} ($R^2 = 0.827$, $\omega = -410 \pm 54$ cm^{-1}). The major contributor is clearly the E_{ar} parameter, and the value of ω obtained when only the aryl effect is allowed for is quite close to that when all three properties are allowed to contribute. This is even more true for the Co_2 complexes where $R^2 = 0.845$ and $\omega = -441 \pm 71$ cm^{-1} when the data are correlated with the E_{ar} parameter alone.

Of the various combinations of two ligand properties it turns out that use of E_{ar} and θ gives the best fit ($R^2 = 0.964$) for the Mn_2 complexes. Use of the ligand parameters χ and θ alone leads to $R^2 = 0.881$, but this value, and the values of β and γ, are left quite unchanged if an *irrelevent* third parameter such as the molecular weight of L is included.[18] The value found for β is about 3 times that found from the isosteric $P(p\text{-}XC_6H_4)_3$ ligands, which also shows how inadequate this two-parameter fit is. By contrast, inclusion of the E_{ar} values of the ligands increases the R^2 value to 0.995 (Table 2), and the value of β is now in excellent agreement with that found from the $P(p\text{-}XC_6H_4)_3$ ligands. Again, the two parameters θ and E_{ar} are the best *pair* of parameters in accounting for the Co_2 data ($R^2 = 0.976$), and in this case the introduction of the electronic parameter χ has essentially no effect.

Since the coefficients β, γ, and ω in Table 2 do not all have the same units, the ratios of their numerical values are not meaningful in describing the relative contributions of the various factors to the resultant values of $h\nu$. However, the maximum effects caused by the variation of χ, θ, and E_{ar} for the particular selection of ligands used can be estimated, and these are given in Table 3. For the Mn_2 complexes an increase in E_{ar} from 0 to 2.7 contributes approximately as much to a decrease in $h\nu$ as the maximum increase in the steric effect, while the effect of increasing σ-donicity (i.e. decreasing χ) is in the opposite direction but perceptibly smaller. It is the balance between the steric and aryl effects that leads to the linear decrease of the steric profiles in Figure 2 between ligands 1 and 9, where the increasing steric and aryl effects both contribute to a decrease in $h\nu$, and the smaller linear increase between ligands 9 and 15, where the decreasing aryl effect increases $h\nu$, but this is partially offset by the increasing steric effect. Another way of looking at the relative contributions is to calculate the extent to which the different terms contribute to the difference between the highest and lowest values of $h\nu$. These correspond, respectively, to L = $P(n\text{-}Bu)_3$ and $P(p\text{-}F_3CC_6H_4)_3$, which show a difference in their calculated values of 1650 cm^{-1} in $h\nu$. This is made up of 802 ± 60, 303 ± 17, and 550 ± 80 cm^{-1} for decreases in the aryl effect, decrease in size, and increase in the basicity, respectively; i.e. the contributions decrease in the order $49 \pm 4\%$, $33 \pm 5\%$, and $18 \pm 1\%$ for the aryl, basicity, and steric effects, respectively. The covariance is such that if ω is decreased numerically by 1 standard deviation, the value of β becomes numerically larger by ca. 1 standard deviation and that of γ larger, but only by ca. one-third of its standard deviation.

For the Co_2 complexes, the data in Table 3 show that the aryl effect is clearly larger than the steric effect and the σ-donicity effect is much smaller, although there is a reasonable probability that it could be almost half that shown by the Mn_2 complexes. The maximum difference in the calculated values of $h\nu$ is 1510 cm^{-1} for L = $P(n\text{-}Bu)_3$ and $P(p\text{-}F_3CC_6H_4)_3$, made up of 1234 ± 162 cm^{-1} from the decreasing aryl effect, 241 ± 51 cm^{-1} from the decreasing steric effect, and ca. 30 cm^{-1} from the increasing basicity effect; i.e. the relative contributions are in the order aryl effect ($82 \pm 11\%$) $\gg$ steric effect ($16 \pm 3\%$) $\gg$ basicity effect (ca. 2%). The covariance is such that if ω is decreased numerically by 1 standard deviation, then γ is barely affected but β becomes numerically significant and ca. one-third of β for the Mn_2 complexes.

These analyses of the values of $h\nu$ in terms of eq 2 are completely empirical. In themselves they do not depend on the nature of the transition that gives rise to the observed intense bands which are simply observables dependent on the nature of the particular ligands present. The values of λ_{max} determined from the spectra are unlikely to be appreciably affected by the presence of the weak shoulders on their high wavelength side, but any such effect must evidently by systematic. The analyses follow the same procedure as that followed successfully elsewhere with a wide variety of kinetic and other data (see above). They make use of σ-donicity and steric parameters, χ and θ, respectively, that have been used widely before, but because of the frequently observed and quite close correlations between these and other electronic and steric parameters (at least when only phosphine ligands are involved[2]), the nature of the analyses would not be affected qualitatively by the choice of other parameters. In these analyses it is clear that χ and θ alone are not sufficient to account for all the changes in the observed data, and the quite newly discovered aryl effect parameter, E_{ar}, is also essential. Indeed the dominant role played by the aryl effect is shown by the fact that the data can even be accounted for reasonably well by the aryl effect alone! The analyses have a potentially useful predictive quality that can be illustrated by supposing that data for the Mn_2 complex with L = $PPhCy_2$ had not been obtained before the analysis was undertaken. All of the other data were fitted to eq 2 and the parameters obtained used to estimate a value of $h\nu = 27\,110$ cm^{-1} for the $PPhCy_2$ complex, a value very close to the value 27 170 cm^{-1} "subsequently" measured. This procedure would have worked well for 13 of the other 14 ligands involved but not for the $P(p\text{-}FC_6H_4)_3$ complex which is clearly deviant in this respect.

Physical Origins of the Basicity, Size, and Aryl Effects. Although it has been stressed that the need for the three parameters in fitting the data is quite empirical, the direction and magnitude of the effects

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[18] A reviewer has commented that we could "...just add another term to your equation and eventually you can fit anything". This is simply not ture, since R^2 values cannot be improved by any number of *noncorrelating* parameters that might be added.

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should, of course, depend on the nature of the transitions and the ways in which the various ligand properties affect the measured transition energies.

The original explanation offered[10] for the σ-donicity effect, for instance, was based on the belief that the intense band corresponded to a $\sigma \rightarrow \sigma^*$ transition.[11] An electron promoted to the σ^* from the σ orbital would spend more of its time close to the P-donor substituent than it did when in the σ orbital. This has recently been supported by calculations of electron distributions in the σ and σ^* orbitals of $Mn_2(CO)_{10}$.[19] The excited electron would be expected to be more destabilized by stronger σ donors which would therefore increase the value of $h\nu$. However, doubt has been cast on the assignment of the more intense UV–vis band in $Mn_2(CO)_{10}$ to the $\sigma \rightarrow \sigma^*$ transition,[19,20] and it is possible, though this remains to be confirmed,[19] that its assignment should be changed to $d\pi \rightarrow \sigma^*$, the shoulder on the low energy side of this band being due to the $\sigma \rightarrow \sigma^*$ transition. If the assignments are in doubt for the unsubstituted complex, then they must also be problematical for the substituted ones, although it is, in principle, possible that they could be correctly assigned to $\sigma \rightarrow \sigma^*$ in the latter.[21] However, if they are all $d\pi \rightarrow \sigma^*$ transitions, it is not quite as obvious why an increase in σ-donicity increases the energy of the transitions. It would remain true that the electron in σ^* orbital would be close to the P-donor atom, but whether the transition involves enough electron transfer in that direction to account for the observed changes is not clear. Because of the poorly resolved nature of the low-energy shoulders in the $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$ complexes, it was not possible to investigate the way in which this transition depended on the electronic and steric natures of the substituents. It is interesting that the value of β is so much lower in the $Co_2(CO)_6L_2$ complexes. These also show weak shoulders on the low-energy side of the very intense bands, and the same problem with assignments presumably arises. It is possible that the values of β could provide evidence for the assignments, low values indicating $d\pi \rightarrow \sigma^*$ with less electron transfer toward the P-donor ligand, and higher values indicating $\sigma \rightarrow \sigma^*$ with more electron transfer.

The values of β obtained in correlations such as these represent the efficiency with which the system responds to the changing σ-donicity of the P-donor ligands involved. For the particular ligands used here, we can compare the σ-basicity effect with the basicity toward the proton in kJ mol^{-1} as defined by pK_a'.[2e] This varies by up to 73 kJ mol^{-1}, whereas the $h\nu$ values vary by up to 8 kJ mol^{-1} for the Mn_2 complexes, and the energies of the C–O stretching frequencies vary by only 0.3 kJ mol^{-1}. These values can be compared, for example, with those for associative reactions of P-donor nucleophiles with metal carbonyls where the values of $\Delta G^\ddagger$ can vary by up to 44 kJ mol^{-1} for the same series of ligands; i.e. β values of up to ca. 0.6 are observed.[2e,24] The efficiencies of response to the varying σ-donicities therefore lie in the order: "protonation", 100%; associative reactions, ≤60%; $h\nu$ in $Mn_2(CO)_8L_2$, ca. 10%; and ν_{CO} in $Mn_2(CO)_8L_2$, ca. 0.4%.

The origin of the steric effects observed here probably lies in increases in the M–M and/or M–P bond lengths with increasing ligand size. The latter would act by preventing the ligand from exerting its full σ-donicity, and the former would act by decreasing σ orbital overlap. The effect can be put in absolute energetic terms in the following way. The maximum cone angle range of 38° corresponds to a difference of 230 kJ mol^{-1} in the calculated interligand repulsion energies, E_R, between the ligands in $Cr(CO)_5L$[2d] so that the sensitivity of $h\nu$ in $Mn_2(CO)_8L_2$ to this change in ligand size (11.3 kJ mol^{-1}; Table 3) is only ca. 5% of this reference sensitivity. Structures are known for the complexes $Mn_2(CO)_8L_2$ ($L = PEt_3$ and $P(NMe_2)_3$; $\theta = 132°$ and $157°$, respectively).[25] The Mn–P distance is 15 pm longer when the substituent is larger, and the Mn–Mn distance is 43 pm longer. The steric effect can therefore be concluded to originate in both Mn–Mn and Mn–P bond lengthening, with the former probably being the more important. Several unsuccessful attempts were made in this laboratory to obtain crystals of the complex $Mn_2(CO)_8(PCy_3)_2$, containing the even larger PCy_3 substituent.

The origin of the aryl effect in general[2c] remains obscure. It seems likely that the magnitude of the effect will be found sometimes to depend on the nature of substituents in the aryl ring, so the deviation of the data for the *p*-fluoro complex in Figure 1 may be an example of things to come. As it is, the effect is empirically a substantial contributor to a number of very diverse physicochemical measurements. Converting to common units, three aryl groups bring about (i) a decrease of up to 15 kJ mol^{-1} in the energies of the transitions studied here, (ii) a decrease of 120 kJ mol^{-1} in the vertical ionization potentials of phosphines, and (iii) a decrease of ca. 16 kJ mol^{-1} in the activation free energy for nucleophilic attack by phosphines on EtI.[2c] Clearly, such a wide-ranging effect needs further attention from both an experimental and a theoretical point of view.[26]

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(19) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1995**, *34*, 3425.

(20) Mayer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. Márquez, A.; Sanz, J. F.; Gelizé, M.; Dargelos, A. *J. Organomet. Chem.* **1992**, *434*, 235.

(21) It is interesting that no low-energy shoulder is observed in $Re_2(CO)_{10}$, and it was suggested that this transition is buried beneath the more intense band.[22] However, $Re_2(CO)_8(PPh_3)_2$ shows a clear low-energy shoulder.[23]

(22) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

(23) DeWit, D. G.; Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans* **1975**, 2065. Lemoine, P.; Gross, M. *J. Organomet. Chem.* **1977**, *133*, 193.

(24) Farrar, D. H.; Poë, A. J.; Zheng, Y. *J. Am. Chem. Soc.* **1994**, *116*, 6252.

(25) Churchill, M. R.; Holladay, A. *Cryst. Struct. Commun.* **1981**, *10*, 1263. Hunt, J. J.; Duesler, E. N.; Paine, R. T. *J. Organomet. Chem.* **1987**, *320*, 307.

(26) It is interesting that an aryl effect of some sort is evident in the values of E_R where an empirical correction had to be made in calculating them for phenyl-containing ligands in order to "improve correlations with kinetics data".[2d] The need for this correction was ascribed to repulsions between the π electrons on the aryl rings and the neighboring CO ligands.