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Reinvestigation of the Oxidative Addition of MeI, H_2, and O_2 to $Ir(CO)(Cl)L_2$. Quantitative Analysis of Ligand Effects (QALE)

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Kinetic data for the oxidative addition of MeI and H_2 to $Ir(CO)(Cl)L_2$, as well as the data for the association and dissociation of O_2, were analyzed satisfactorily in terms of the three stereoelectronic parameters χ, θ, and E_{ar} of the phosphine ligands according to the following equation: $\log k = a\chi + b\theta + cE_{ar} + d$. Literature data for MeI and H_2 addition have been supplemented with data from our laboratories. The addition of MeI involves the most polar transition state of the group, whereas the addition of H_2 involves the least polar transition state based on the size of the coefficients of χ. All the reactions show a significant dependence on E_{ar}, including the addition of H_2, which shows little dependence on χ. The steric sensitivity (coefficient of θ) is greatest for the addition of MeI and least for H_2. The coefficients of both χ and E_{ar} for the MeI reaction are smaller in acetone compared to those in benzene, whereas the steric sensitivity shows a smaller variation on changing solvent. The addition of H_2 is insensitive to the nature of the solvent. The dissociation of O_2 from $Ir(CO)(Cl)L_2(O_2)$ is insensitive to both θ and χ but does show a statistically significant dependence on E_{ar}.

Introduction

The chemistry of the iridium complexes $Ir(CO)(Cl)L_2$ (Vaska's complexes) is a paradigm of organometallic chemistry.[1] In particular, the oxidative addition of MeI to $Ir(CO)(Cl)L_2$ (eq 1) has been studied extensively.[2] There

$$Ir(CO)(Cl)L_2 + MeI \xrightarrow{k_1} Ir(CO)(Cl)L_2(Me)(I) \quad (1)$$

seems to be agreement that the reaction proceeds by nucleophilic displacement of iodide to form the transient complex $Ir(CO)(Cl)L_2(Me)^+$. The ligand-effect studies of Thompson and Sears[3] and Ugo et al.[4] appear to support this conclusion. Both groups observed that the rate of addition of MeI to the $P(p\text{-}XPh)_3$ complexes increases as the electron-donor capacity of the ligands increases. In addition, both groups noted that the reactivity pattern for the PEt_xPh_{3-x} complexes was curiously $PEtPh_2 > PEt_2Ph > PPh_3$; this pattern correlates with neither the size (θ) nor the electron-donor capacity (χ or pK_a) of the ligands.

For several years now, we have been interested in the interpretation of ligand-effect data.[5] A growing body of evidence suggests that ligand-effect data can be separated into steric and electronic components.[5–7] This can be accomplished by graphical methods or by linear regression analysis according to eq 2 if there are no steric thresholds, as is the case for the systems described herein.[8] In eq 2, χ is an electronic parameter derived from the infrared data for $Ni(CO)_3L$,[9] θ is the cone angle of the phosphorus

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$$\log k = a\chi + b\theta + cE_{ar} + d \qquad (2)$$

ligand,[10] and E_{ar} is an electronic parameter, the magnitude of which depends on the number of aryl groups attached to the phosphorus(III) ligand.[8]

Application of this graphical method (using χ and θ only) to the literature data for the addition of MeI[3,4] or O_2[11a] to $Ir(CO)(Cl)L_2$ (eqs 1 and 3) does not give satisfactory results.[5] Thus, our graphical analysis of the kinetic data

$$Ir(CO)(Cl)L_2 + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Ir(CO)(Cl)L_2(O_2) \qquad (3)$$

for the MeI reaction affords a steric profile that resembles a scatter diagram (Figure 1). Attempts to separate the stereoelectronic components of the kinetics of addition of O_2 to $Ir(CO)(Cl)L_2$ (in terms of the pK_a values of HPR_3^+ and θ) led to a curious steric profile that suggested steric acceleration for small ligands and steric inhibition for the PCy_3 complex.[51]

In order to understand why the data for reactions 1 and 3 do not correlate with χ and θ, we embarked on a program to extend the set of kinetic data for the addition of MeI to $Ir(CO)(Cl)L_2$. It was our hope that an interpretable pattern of reactivity would emerge. In this paper, we report the results of this study and compare these results to those of our reinvestigation of the addition of H_2[12] to $Ir(CO)(Cl)L_2$ (eq 4), which appears to proceed via a nonpolar transition state.

$$Ir(CO)(Cl)L_2 + H_2 \xrightarrow{k_4} Ir(CO)(Cl)L_2H_2 \qquad (4)$$

Results

The literature kinetic data for the addition of MeI[2i,3] and H_2[12c,e] to $Ir(CO)(Cl)L_2$ in several solvents has been supplemented by measurements made in our laboratories. For the addition of MeI, we found good second-order kinetics with no evidence of complicating side reactions except for the complexes where L = $PPh_2(t\text{-}Bu)$ and PPh_2Cy. In each of these cases it appears that the initially formed product undergoes further reaction. These side reactions do not appear to influence the kinetics of the initial addition of MeI. We were unsuccessful in our attempts to characterize the decomposition products. For the reactions that afforded stable adducts, we characterized the products by ^1H NMR and IR spectroscopy. We were unable to measure the rates of reaction of a few of the complexes in the more polar solvents because of their insolubility. Thus, we were not able to study the PCy_3 or $P(p\text{-}Me_2NPh)_3$ complexes in DMF or acetone. All data are presented in Table I.

The resulting kinetic data were analyzed in terms of the phosphorus stereoelectronic parameters χ, θ, and E_{ar}. Only the data for the $PPhCy_2$ complex did not fit the analyses.

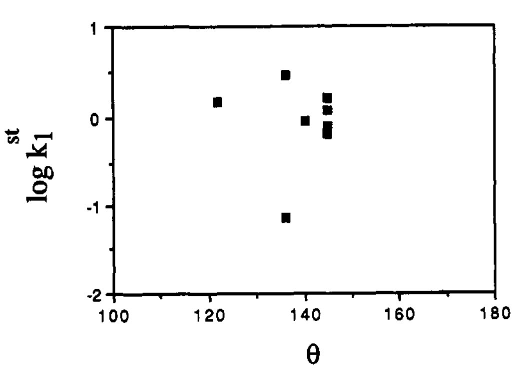

Figure 1. Steric profile for the addition of MeI to $Ir(CO)(Cl)L_2$ (eq 3). The profile is based on the analysis (in terms of χ and θ) of the kinetic data reported by Thompson and Sears.[4]

Discussion

There are a number of cases where the simple graphical separation of kinetic data in terms of χ and θ provides insightful results.[5] The analysis of the decarbonylation of $(\eta\text{-}Cp)Mo(CO)_2LCOMe$ (eq 5) is a relevant example.[13]

$$(\eta\text{-}Cp)Mo(CO)_2LCOMe \xrightarrow{k_5} (\eta\text{-}Cp)Mo(CO)_2LMe + CO \qquad (5)$$

The electronic profile for this first-order reaction is a scatter diagram (Figure 2a) showing no particular pattern. The line drawn through the points for complexes containing the isosteric ligands $P(p\text{-}XPh)_3$ does show that the reaction is slightly accelerated as the electron-donor capacity of the ligands decreases (larger χ). Importantly, the data point for $P(i\text{-}Bu)_3$, which is virtually isosteric (θ = 143°) with $P(p\text{-}XPh)_3$ (θ = 145°), falls on the line determined by the data for the $P(p\text{-}XPh)_3$ complexes. The steric profile of the reaction (constructed by plotting versus θ the deviations of the data from the line in Figure 2a) shows that the reaction is sterically accelerated and that steric effects appear to be continuously operative over the entire range of θ for this set of ligands. The fact that $P(p\text{-}XPh)_3$ points fall on the steric profile indicates that E_{ar} makes an insignificant contribution to the rate of this reaction (vide infra).[8] The stereoelectronic demands of this decarbonylation reaction are consonant with a process where the rate-determining step involves primarily the dissociation of a π-acid ligand.

We could not analyze the kinetic data for the addition of MeI to $Ir(CO)(Cl)L_2$ (eq 1) in this manner. The difficulty arises because there is a second electronic effect, the aryl effect[8] (E_{ar}), which assumes significance here. The importance of the aryl effect can be readily appreciated when the analysis of $\log k_1$ for the addition of MeI is performed graphically in terms of χ and θ alone. In Figure 3a, we show the electronic profile for the addition of MeI to $Ir(CO)(Cl)L_2$. There are several features to note about this electronic profile. First, examination of the $P(p\text{-}XPh)_3$ data shows that the rate of reaction is dramatically enhanced as the electron-donor capacity of the ligand increases (smaller χ). Second, all the other data fall below the line defined by the $P(p\text{-}XPh)_3$ complexes. For example, the data point for $P(i\text{-}Bu)_3$, which is a strong electron-donor ligand and nearly isosteric with $P(p\text{-}XPh)_3$,

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Table I. Stereoelectronic Parameters (χ, θ, and E_{ar}) for the Phosphine Ligands, Infrared Data (ν_{CO}) for $Ir(CO)(Cl)L_2$, and Kinetic Data for the Addition of MeI, O_2, and H_2 to $Ir(CO)(Cl)L_2$

entry no.	phosphine	χ^a	θ^b	$E_{ar}{}^c$	$\nu_{CO}{}^d$	$10^3k_1{}^e$	$10^3k_1{}^f$	$10^2k_3{}^g$	$10^5k_{-3}{}^g$	$10^2k_4{}^h$	$10^2k_4{}^i$	$10^6k_5{}^j$
1	PMe_2Ph	10.6	122	1.0	1954.7	50^k						3.63
2	PEt_3	6.3	132	0	1942.0	23	128	33.8	1.57	42		
	PEt_3					29^k						
3	PEt_2Ph	9.3	136	1.0	1951.0	11.5^l				19		
4	$PMePh_2$	12.1	136	2.0	1959.4	17.7^l						6.76
5	PBu_3	5.25	136	0	1940.1			26.1	3.90	26		3.89
6	$PEtPh_2$	11.3	140	2.0	1955.5	13.6^l	45	14.2	6.75	27		
7	$P(i\text{-}Bu)_3$	5.7	143	0	1938.9	0.55	30			2.7		5.62
8	$P(Me_2NPh)_3$	5.25	145	2.7	1951.9							
9	$P(p\text{-}MeOPh)_3$	10.5	145	2.7	1960.6	25.3^l	107	48.4	12.5	93	170	9.55
10	$P(p\text{-}MePh)_3$	11.5	145	2.7	1961.5	13.2^l		21.6	12.2	64.0^n	175	10.7
11	PPh_3	13.25	145	2.7	1964.7	3.6	21	13.9	13.9	36	140	13.5
	PPh_3					3.5^k	20^m			44.0^n	175	
12	$PPh_2(p\text{-}ClPh)$	14.4	145	2.7		0.449^l						
13	$P(p\text{-}FPh)_3$	15.7	145	2.7	1968.0	0.0854^l	3.3			49	61	
14	$PPh(p\text{-}ClPh)_2$	15.6	145	2.7		0.0932^l						
15	$P(p\text{-}ClPh)_3$	16.8	145	2.7	1969.8	0.0144^l	1.3	3.10	8.67	38	67	
16	$P(p\text{-}CF_3Ph)_3$	20.5	145	2.7	1974.9		0.25			17	67	
17	$P(i\text{-}Pr)(Ph)_2$	10.1	150	2.0								23.4
18	$PCyPh_2$	9.3	153	2.0	1949.5	4.9	40			2.8		
19	$P(t\text{-}Bu)Ph_2$	8.8	157	2.0	1950.4	0.18	16			9.1		
20	$P(i\text{-}Pr)_3$	3.45	160	0	1936.3	0.19	0.96			0.59		
21	PCy_2Ph	5.35	161	1.0	1948.7	<0.002	0.26			1.3		
22	PCy_3	1.4	170	0	1931.7	0.31		0.127	5.85	0.079		46.8

[a] χ (cm^{-1}) values were taken or calculated from data presented in ref 10. [b] Values of θ (deg) were taken or calculated from data presented in ref 9. [c] Reference 8. [d] Measurements were made on dilute methylene chloride solutions of complex; values are given in cm^{-1}. [e] k_1 in units of $M^{-1}\ s^{-1}$; in benzene. [f] Acetone. [g] k_3 in units of $M^{-1}\ s^{-1}$ and k_{-3} in s^{-1}; data taken from ref 11a (chlorobenzene). [h] k_4 in units of $M^{-1}\ s^{-1}$; in toluene. [i] Dimethylformamide. [j] k_5 in units of s^{-1}; data taken from ref 13. [k] Data taken from ref 21. [l] Data taken from ref 3. [m] Data point taken from ref 2j. [n] Data taken from ref 12e.

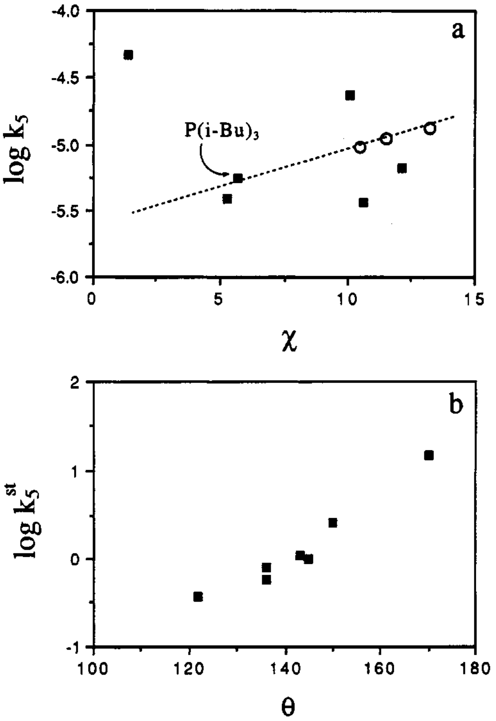

Figure 2. Electronic (a) and steric (b) profiles for the decarbonylation of (η-Cp)Mo(CO)LCOMe. Data are taken from Table I.

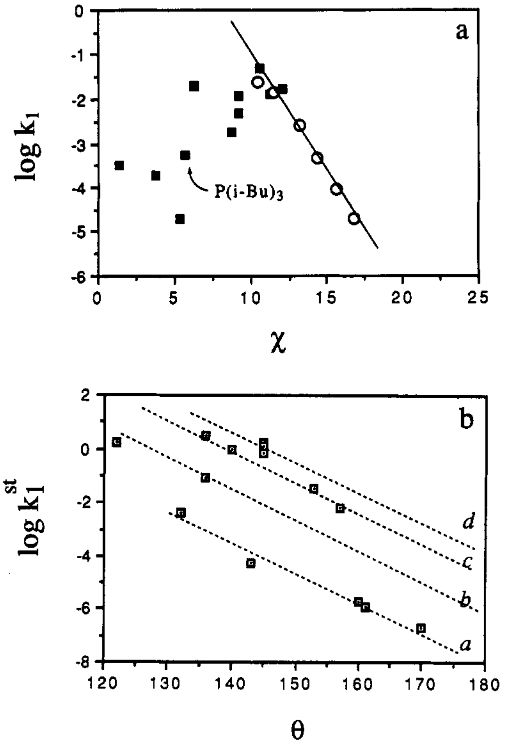

Figure 3. (a) Plot of log k_1 for the addition of MeI to $Ir(CO)(Cl)L_2$. The line is drawn through the data for complexes containing $P(p\text{-}XPh)_3$ (open circles). (b) Steric profile for the reaction above, which was created by plotting the difference between the data and the line shown in Figure 3a. The lines are drawn through families of complexes that contain phosphine ligands which bear 0 (*a*), 1 (*b*), 2 (*c*), or 3 (*d*) aryl groups.

should fall near the line in Figure 3a as it does in Figure 2b. Surprisingly, the $P(i\text{-}Bu)_3$ complex is 4 decades less reactive than predicted. Likewise, the PEt_3 complex is less reactive than predicted by the analysis of the $P(p\text{-}XPh)_3$ data even though PEt_3 is smaller and more basic than any of the $P(p\text{-}XPh)_3$ ligands.

A steric profile (Figure 3b) of reaction 1 was generated by plotting the deviations of the data from the line in Figure 3a versus θ. At first glance, it resembles a scatter diagram, until it is recognized that the data fall along three parallel lines that are distinguished by the number of aryl groups attached to the phosphorus. The data for the $P(p\text{-}XPh)_3$ groups form a separate cluster. It is clear from this

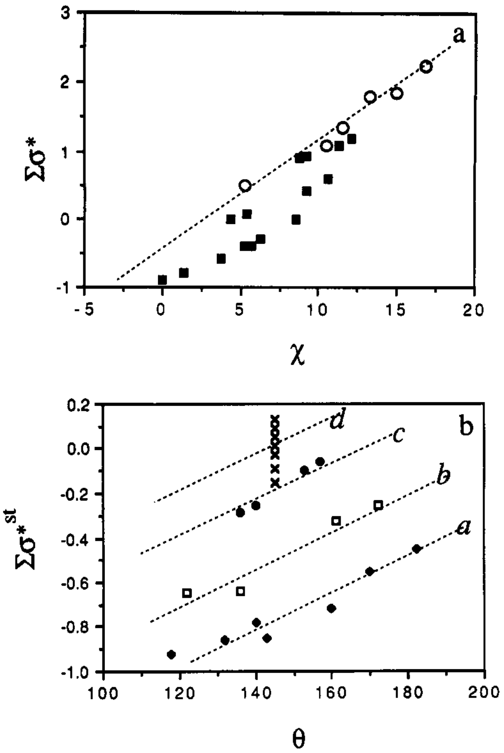

Figure 4. (a) Electronic profile for the correlation of $\Sigma\sigma^*$ with χ. (b) Deviation of the data from the line defined by the data (open circles) for $P(p\text{-}XPh)_3$ in Figure 4a, plotted against θ. The lines are drawn through families of ligands that possess 0 (*d*), 1 (*c*), 2 (*b*), and 3 (*a*) aryl groups.

steric profile that the attachment of phenyl groups incrementally enhances the reactivity of the complexes toward MeI.

This is a pattern that we had seen previously in our correlation of $\Sigma\sigma^*$ with χ and θ (Figure 4).[8] The steric profile (Figure 4b) shows the separation of the ligands according to the number of phenyl groups attached to the phosphorus. This separation forms the basis of our assignment of E_{ar} as described in ref 8.

These observations led us to analyze the data for the addition of MeI, O_2, and H_2 in terms of χ, θ, and E_{ar} via eq 2. In Figure 5, we show the electronic profiles for the addition of MeI to $Ir(CO)(Cl)L_2$ in benzene (a) and acetone (b), the addition (c) and dissociation (d) of O_2 in chlorobenzene, and the addition of H_2 in toluene (e). The coefficients and statistical data resulting from the analysis of the kinetic data for each reaction according to eq 2 are displayed in Table II. In none of the examples do we find evidence for a steric threshold.

Interpretation of the data displayed in Table II reinforces our current views[2-4,11,12] of the mechanisms of the oxidative-addition reactions of $Ir(CO)(Cl)L_2$ and gives us some new insights into the chemistry of these complexes. Several trends are obvious. First, the coefficients of χ (Table II) increase by a factor of 10 on going from the addition of H_2 (toluene) to the addition of MeI (benzene) (Figure 6 shows plots of log *k* ($L = P(p\text{-}XPh)_3$) versus χ, which clearly show the relative dependence of the rate data on χ for the three reactions). This observation is consistent with a highly polar transition state for the MeI reaction and a nonpolar transition state for the addition of H_2. Significantly, the coefficient for the addition of O_2 is only 40% as large as that of the MeI reaction, suggesting that the polarity of its transition state is probably considerably less than that of the MeI addition.

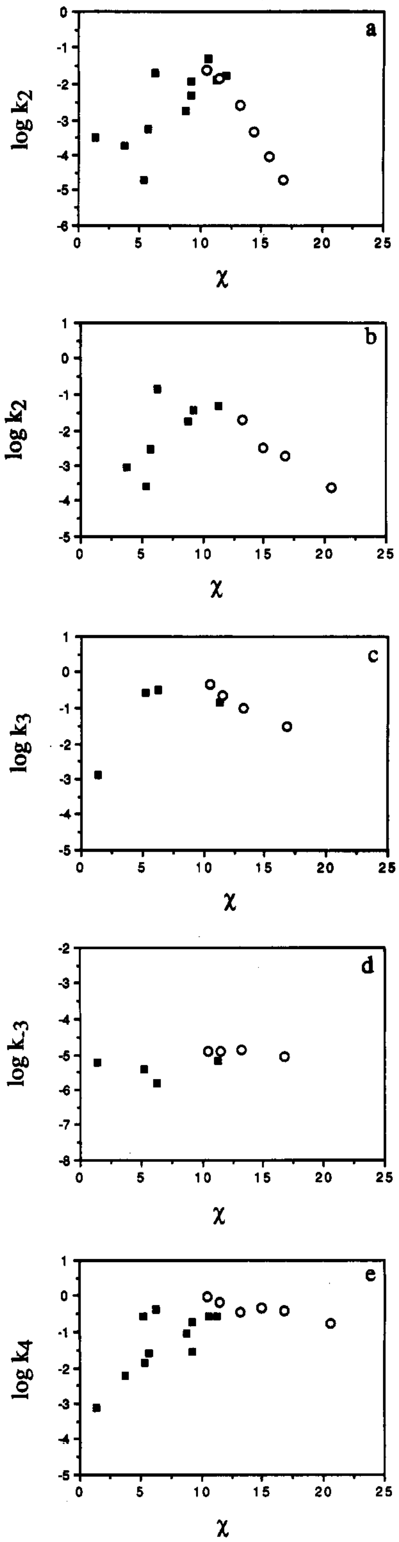

Figure 5. Electronic profiles for the reactions of $Ir(CO)(Cl)L_2$: (a) addition of MeI in benzene; (b) addition of MeI in acetone; (c) the addition of O_2 in chlorobenzene; (d) elimination of O_2; (e) addition of H_2 in toluene. Data are taken from Table I. The data for the complexes containing $P(p\text{-}XPh)_3$ are shown as open circles.

Second, steric factors are of major importance in controlling the reactivity of $Ir(CO)(Cl)L_2$ toward any of the addends. (The steric profiles for the reactions 1 (in benzene and acetone) and 3 and 4 (in aromatic solvents) are shown in Figure 7.) For example, the rate of addition of MeI in benzene is attenuated by 10^4 over the range of 38° spanned by the ligands. Not surprisingly, the steric

Table II. Data for the Linear Regression Analysis of Kinetic Data (Table I) According to Eq 2

entry no.	reacn	solvent	*a*	*b*	*c*	*d*	*n*	r^2
1	MeI[a]	benzene	−0.50 ± 0.04			3.9 ± 0.6	4	0.985
2	MeI	benzene	−0.54 ± 0.05	−0.120 ± 0.008	1.6 ± 0.2	17.5 ± 1.5	17	0.941
3	MeI[a]	acetone	−0.25 ± 0.03			1.5 ± 0.5	4	0.965
4	MeI	acetone	−0.30 ± 0.04	−0.091 ± 0.013	0.94 ± 0.15	12.9 ± 2.0	11	0.926
5	O_2[a]	chlorobenzene	−0.18 ± 0.02			1.5 ± 0.3	4	0.967
6	O_2	chlorobenzene	−0.18 ± 0.03	−0.086 ± 0.005	0.72 ± 0.10	12.0 ± 0.9	8	0.986
7	O_2[a] (dissociation)	chlorobenzene	−0.025 ± 0.014			4.6 ± 0.2	4	0.606
8	O_2 (dissociation)	chlorobenzene	−0.029 ± 0.036	0.008 ± 0.005	0.30 ± 0.09	−6.5 ± 0.9	8	0.909
9	H_2[a]	toluene	−0.062 ± 0.013			0.54 ± 0.20	6	0.84
10	H_2	toluene	−0.053 ± 0.029	−0.071 ± 0.008	0.56 ± 0.12	9.1 ± 1.3	15	0.927
11	H_2[a]	DMF	−0.05 ± 0.02			0.7 ± 0.2	6	0.704

[a] Data for the $P(p\text{-}XPh)_3$ complexes only.

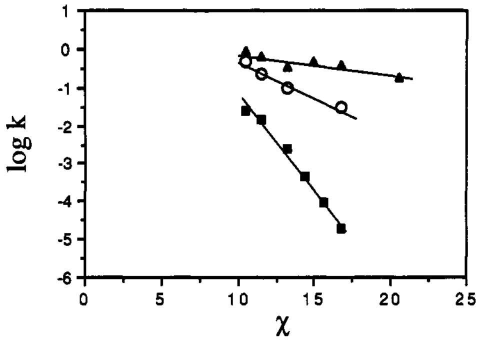

Figure 6. Plots of log *k* versus χ for the addition of MeI (benzene, filled squares), O_2 (chlorobenzene, open circles), and H_2 (toluene, filled triangles) to $Ir(CO)(Cl)L_2$ ($L = P(p\text{-}XPh)_3$). Data are taken from Table I.

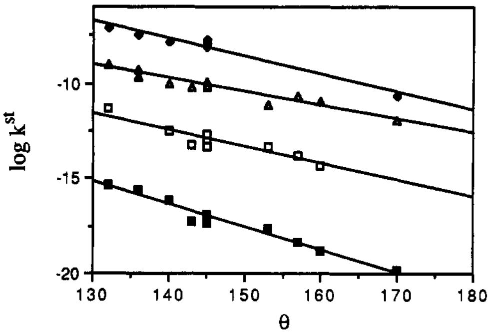

Figure 7. Steric profiles for the addition of O_2 (chlorobenzene, filled diamonds), H_2 (toluene, open triangles), MeI (acetone, open squares), and MeI (benzene, filled squares) to $Ir(CO)(Cl)L_2$. For the sake of clarity, constants have been added to or subtracted from the actual steric profiles in order to separate the profiles.

effect diminishes on going to O_2 and diminishes still further on going to H_2. These observations suggest that the steric effect is at least in part a result of complex–addend interaction. However, the steric sensitivities of these reactions are rather similar, suggesting that a portion of the steric inhibition might be independent of the addend and attributable to compression of the ancillary ligands.

The dramatic enhancement of these oxidative-addition reactions by E_{ar} is noteworthy. For example, in benzene, E_{ar} contributes nearly 10^4 to the rate of addition of MeI to the $P(p\text{-}XPh)_3$ complexes. The magnitude of the aryl effects appears to parallel that of χ. However, in the addition of H_2, the coefficient of χ is close to zero but the coefficient of E_{ar} remains large and positive.

The significant involvement of the aryl effect in the addition of MeI explains the unusual reactivity pattern ($PEtPh_2 > PEt_2Ph > PPh_3$) for PEt_xPh_{3-x} complexes noted both by Thompson and Sears[3] and by Ugo et al.[4] The reason for this is that E_{ar} is not directly proportional to the number of aryl groups attached to the phosphorus (Table I). Thus, as one goes from PEt_2Ph to $PEtPh_2$, the decrease in rate resulting from increases in χ and θ is more than offset by the increase in E_{ar}. On the other hand, as one goes from $PEtPh_2$ to PPh_3, the rate decrease resulting from the further increases in χ and θ is not offset by the relatively small increase in E_{ar}.

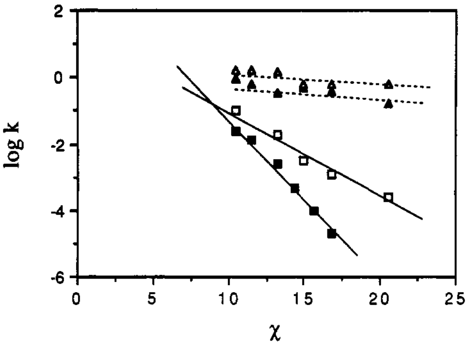

Figure 8. Plots of log *k* for the addition of MeI to $Ir(CO)(Cl)L_2$ ($L = P(p\text{-}XPh)_3$) in benzene (filled squares) and in acetone (open squares) and for the addition of H_2 in toluene (filled triangles) and in DMF (open triangles).

Changing solvents seems to have the largest effect on the electronic parameters and a lesser impact on the steric component of the reactions. Thus, we find for the addition of MeI that the coefficient of χ is attenuated by 60% on going from benzene to acetone. (The electronic profiles ($L = P(p\text{-}XPh)_3$) for the addition of MeI in benzene and acetone and the addition of H_2 in toluene and DMF are shown in Figure 8.) It should be noted that enhancement of the rate of reaction as one goes to a more polar solvent is often taken as an indication of a polar transition state. Inspection of the curves in Figure 8 for the addition of MeI shows that the curve for the acetone reaction intersects the curve for benzene at $\chi = 9.5$. If an experiment were performed with a ligand having a χ value less than 9.5, one would expect the reaction to be slower in acetone than in the less polar benzene. (We attempted to measure the rate of reaction of the $P(p\text{-}Me_2NPh)_3$ complex ($\chi = 5.25$) in benzene but found that the complex is insoluble in this solvent.) Thus, interpretation of data for one ligand in two different solvents can be dangerous. The change in *slope* of the electronic profile as one goes from a nonpolar to a polar solvent might be a better measure of the difference in charge between the ground and transition states. In support of this assertion, the change in slope is large for the MeI addition on replacing benzene with acetone. In contrast, for the addition of H_2 ($L = P(p\text{-}XPh)_3$) the change in slope of the electronic profile is very small when toluene is replaced by DMF, even though the reaction is slightly faster in DMF.

The coefficient of E_{ar} for the addition of MeI is also reduced in acetone and is about 70% of that in benzene. The relative change in the steric coefficient for the addition of MeI in acetone is smaller than the change in the electronic coefficients on going from benzene to acetone, and the change is hardly significant statistically.

The results of the analysis of the addition of O_2 shed some light on the mechanism of this reaction. The addition of triplet O_2 to singlet Ir(CO)(Cl)L_2 to form a singlet product requires a stepwise process. There appear to be three reasonable mechanisms, as outlined in Schemes I–III. A comparison of the χ coefficients for the addition of MeI (benzene) and O_2 (chlorobenzene) reveals that the MeI reaction, which is thought to involve the formation of Ir(CO)(Cl)L_2(Me)$^+$, has a more polar transition state than the O_2 reaction. Therefore, we believe that we can exclude Scheme I, since this process would generate Ir(CO)(Cl)L_2^+ by an initial electron transfer. We expect that the χ dependence for the formation of Ir(CO)(Cl)L_2^+ would be greater than that for the addition of MeI.

Scheme I

$$\mathrm{Ir(CO)(Cl)L_2 + O_2 \rightleftarrows Ir(CO)(Cl)L_2^+ + O_2^-}$$

$$\mathrm{Ir(CO)(Cl)L_2^+{-}O{-}O^- \rightleftarrows Ir(CO)(Cl)L_2(O_2)}$$

Scheme II

$$\mathrm{Ir(CO)(Cl)L_2 + O_2 \rightleftarrows Ir^{\bullet}(CO)(Cl)L_2{-}O{-}O^{\bullet}}$$

$$\mathrm{Ir(CO)(Cl)L_2^+{-}O{-}O^- \rightleftarrows Ir(CO)(Cl)L_2(O_2)}$$

Scheme III

$$\mathrm{Ir(CO)(Cl)L_2 + O_2 \rightleftarrows Ir^{\bullet}(CO)(Cl)L_2{-}O{-}O^{\bullet}}$$

$$\mathrm{Ir^{\bullet}(CO)(Cl)L_2{-}O{-}O^{\bullet} \rightleftarrows Ir(CO)(Cl)L_2(O_2)}$$

Analysis of the kinetics for the dissociation of O_2 from Ir(CO)(Cl)L_2(O_2) (reading any of the schemes backwards) reveals that the transition state for this process is virtually independent of χ and θ, although there is a significant dependence on E_{ar}. We believe that this is indicative of a nonpolar transition state, which provides further evidence for rejecting Scheme I as well as also excluding Scheme II. Thus, we are left with the radical addition shown in Scheme III.

The data for the PCy_2Ph complex does not fit the analysis for the addition of MeI. The complex behaves as though the aryl effect were not operative. It is also interesting to note that ν_{CO} for PCy_2Ph also correlates with the PR_3 complexes rather than with the family of PR_2Ph complexes. These observations suggest to us that conformational effects may be important in determining how the aryl effect is transmitted to the reaction center. We are currently pursuing this idea.

Conclusion

Excellent correlations of kinetic data with the stereoelectronic parameters χ, θ, and E_{ar} have been obtained for the addition of MeI, H_2, and O_2 to Ir(CO)(Cl)L_2. These analyses lead to interpretations that are intuitively reasonable and in agreement with current views of these reactions. Importantly, the aryl effect plays a dominant role in determining the reactivity of Ir(CO)(Cl)L_2.

The question arises whether a single electronic parameter could exist that incorporates χ and E_{ar}. For example, let us suppose that we have such a new electronic parameter, χ', with which we can get an excellent correlation for the MeI addition to Ir(CO)(Cl)L_2 according to

$$\log k = a'\chi' + b\theta + d \tag{6}$$

We already know that there is excellent correlation using eq 2, which we rewrite as

$$\log k = a(\chi + (c/a)E_{ar}) + b\theta + d \tag{7}$$

Therefore, χ' must correlate closely with $\chi + (c/a)E_{ar}$. For this system we know that c/a is -10.3 ± 1.9. In contrast, when we examine ν_{CO} for Ir(CO)(Cl)L_2 we find the relationship

$$\nu_{CO} = (1.56 \pm 0.13)\chi - (1.03 \pm 0.04)\theta + (4.4 \pm 0.5)E_{ar} + (1945.9 \pm 5.9)$$

$$n = 18 \qquad r^2 = 0.986$$

The value of c/a for ν_{CO} is $+2.8 \pm 0.5$. In the two examples there is no statistically significant overlap between the values of c/a and they even have opposite signs. Clearly, if χ' were used in the correlation of ν_{CO}, the fit would be poor because χ' incorrectly estimates the effect of E_{ar}.

Even on the basis of only the results reported in previous work[8] *and in this paper, we reach the inescapable conclusion that two stereoelectronic parameters (e.g. χ and θ) are not sufficient to describe generally the properties of phosphines and phosphine complexes.* By including E_{ar} along with χ and θ, we have analyzed 80 sets of data for phosphines, silanes, thioethers, and alkyl compounds. We find excellent correlation with a median r^2 of 0.97. In many of these correlations E_{ar} makes a significant contribution that enhances or opposes the effect of χ. In other correlations E_{ar} does not make a significant contribution at all.

It is the involvement of more than one electronic parameter and the insistence of many researchers to use only one electronic parameter that has led to such a proliferation of electronic substituent constants (χ, δ, pK_a, $\sum\sigma^{Ph}$, $\sum\sigma^*$) even in organometallic chemistry.

Experimental Section

The complexes Ir(CO)(Cl)L_2 were prepared by literature methods from $IrCl_3(H_2O)_x$ and the appropriate phosphine.[14] All phosphines were used as received from Organometallics Inc., Aldrich Chemical Co., and Strem Chemicals. All solvents were purified by standard methods, and solutions were routinely deaerated by the freeze–thaw method.[15] Iodomethane (Lancaster Synthesis) was washed with a solution of distilled water and sodium thiosulfate to remove excess iodine and then distilled over Drierite. Most of the iridium complexes are known compounds which were characterized by comparison of their spectroscopic properties to appropriate literature values.

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[14] (a) Bushweller, C. H.; Rithner, C. D.; Butcher, D. J. *Inorg. Chem.* 1984, *23*, 1967. (b) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* 1967, *89*, 844.

[15] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Ed.; Pergamon Press: New York, 1988.

Kinetic Measurements for the Addition of MeI to Ir(CO)(Cl)L_2. All measurements were made on argon- or nitrogen-purged solutions with concentrations of complex between 10^{-4} and 10^{-5} M. The concentration of MeI was always at least 100 times greater than the concentration of complex. The rates of reaction were measured by monitoring the disappearance of the absorption of the starting material, Ir(CO)(Cl)L_2, in the region between 379 and 388 nm using a Cary 210 UV–vis spectrophotometer equipped with a thermostated cell which was set at 25 °C. For the extremely O_2 sensitive compounds all procedures were carried out under a constant pressure of N_2. The measurements were routinely made at three or more concentrations of MeI. Second-order rate constants were obtained in the standard manner by plotting the pseudo-first-order rate constants versus the concentration of MeI. The errors in the second-order rate constants were generally less than 10%, with intercepts close to zero. A few of the literature experiments were repeated as a check of our method. Our results for Ir(CO)(Cl)L_2 (L = PEt_3, PPh_3) and the literature results are in close agreement, as shown in Table I.

Kinetic Measurements for the Addition of H_2. The measurements of the rate of addition of H_2 to Ir(CO)(Cl)L_2 were performed in the same manner as the MeI experiments, except that the toluene and DMF solutions were saturated with H_2. Concentrations of H_2 in these solvents at 25 °C were calculated via the Bunsen coefficients. Measurements were made on three samples with the same concentration of H_2.

Analysis of Data. The statistical analyses of the kinetic and spectroscopic data were performed according to the protocol described previously.[8]

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