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Steric and Electronic Effects in Associative Substitution Reactions of Dodecacarbonyltetrairidium

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The kinetics of reactions of $Ir_4(CO)_{12}$ with L = P-*n*-Bu_3, $P(OEt)_3$, $P(OCH_2)_3CEt$, and $P(C_6H_{11})_3$ have been shown to be first order in [L], and activation parameters for these associative reactions have been derived. Combination of the second-order rate constants with published values for PPh_3 and $P(OPh)_3$ enables all the rate data to be expressed in terms of a linear free energy relationship involving electronic effects (quantified relative to the half-neutralization potentials, ΔHNP) and steric effects (quantified relative to Tolman's cone angles, θ). This behavior is shown to be a limiting case of a more general relationship for associative reactions of metal carbonyls in which steric effects are negligible at relatively low cone angles and can become linearly dependent on θ at higher values. This general relationship provides a number of parameters indicative of the intrinsic susceptibility of a metal carbonyl to nucleophilic attack (given by log k_2 for a hypothetical, very small ligand with ΔHNP = 0) and electronic and steric effects. $Ir_4(CO)_{12}$ is shown to have a very high susceptibility to nucleophilic attack, and this is rationalized by a simple model for the transition state in which formation of a strong Ir–P bond is encouraged by decreasing the number of electrons involved in bonding the Ir_4 cluster from 12 to 10. The importance of the consequent flexibility of the coordination sphere around the Ir atom undergoing nucleophilic attack is emphasized in regard to steric effects, as is the importance of the cluster bond strength in regard to intrinsic reactivity.

Introduction

Electronic effects in associative substitution reactions of metal carbonyls[1a,b] with P-donor nucleophiles were first clearly established by Basolo et al. for reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$[1c] and $Co(CO)_3(NO)$.[1d] In both cases good linear free energy plots of log k_2 vs. ΔHNP were obtained, where ΔHNP is a measure of the proton basicity of the nucleophiles.[1d] These studies were quickly extended to include reactions of $Mn(CO)_4(NO)$[1e] and $Fe(CO)_2(NO)_2$,[1f] and a common feature that emerged was the deviations from the LFER of data for tricyclohexylphosphine (PCy_3). This was ascribed to an unfavorable steric effect. Similar results were obtained[2] when data[3] for $Mo(CO)_6$ and $W(CO)_6$ were plotted in the same way, but in these cases, data for PPh_3 deviated from the LFER.

Associative reactions of $Ru_3(CO)_{12}$ also show a reasonably good LFER for several smaller nucleophiles, but data for both PPh_3 and PCy_3 deviate, the latter by much more than the former.[2,4] It was suggested[4] that the gradients of such LFER and the extent of any deviations observed for larger nucleophiles would provide a good quantitative measure of the relative extents of bond making in the transition states, especially for complexes of similar stereochemistry. Steric deviations should be related, at least semiquantitatively, to the size of the nucleophiles as measured by their cone angles.[5] It was pointed out that less good LFER are to be expected the greater the importance of steric effects since deviations will then be expected even for nucleophiles with smaller cone angles than PPh_3 and PCy_3. An extreme example of this has been provided recently by the reactions of $(\eta^5\text{-}Me_5C_5)M(CO)_2$ (M = Co, Rh) where the rates are dominated by steric effects.[6]

$Ir_4(CO)_{12}$ is also known to undergo associative substitution with P donors,[7,8] and the rate of reaction with PPh_3 is slower than that with the less basic but smaller $P(OPh)_3$. Reaction with the much more basic P-*n*-Bu_3 was shown qualitatively to be much faster,[8] so both electronic and steric effects are important. We report below quantitative data for reactions with P-*n*-Bu_3 and other P donors that enable a quantitative analysis of electronic and steric effects to be made, and we suggest a general approach to the systematics of such reactions.

Experimental Section

Dodecacarbonyltetrairidium (Strem Chemicals) was used as received. Chlorobenzene (BDH, AnalaR grade) and heptane (Baker "Analyzed") were stored over molecular sieves, and tetrachloroethylene (BDH Assured) was distilled and stored over molecular sieves. Triethyl phosphite (Eastman Kodak) and P-*n*-Bu_3 (Aldrich) were distilled over sodium under nitrogen. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($P(OCH_2)_3CEt$, etpb, Strem Chemicals) was sublimed and stored under vacuum.

If heated to ca. 100 °C for 10 min, chlorobenzene, tetrachloroethylene, and decalin will dissolve sufficient $Ir_4(CO)_{12}$ to give $\lesssim 10^{-4}$ M solutions. Solubility in heptane is somewhat lower. The UV–vis spectra show a maximum at 320 nm (ϵ ca. 6×10^3 M^{-1} cm^{-1}) and the IR spectra show bands at 2072 (s) and 2032 (m) cm^{-1} in C_2Cl_4 and decalin, and closely similar bands in C_6H_5Cl.

Solutions of $Ir_4(CO)_{12}$ for kinetic study were made up by heating suspensions to 80–100 °C for ca. 10 min. Cooled solutions were mixed with accurately known volumes of fresh stock solutions of nucleophiles. Reactions with P-*n*-Bu_3 were usually followed in cells placed in the thermostated cell holder of a Cary 210 UV–vis spectrophotometer. Some reactions with P-*n*-Bu_3 and all reactions with the other nucleophiles were carried out in septa-sealed Schlenk tubes immersed in a thermostated oil bath and shielded from light. Solutions were bubbled with argon for ca. 10 min before running the reactions. Samples were withdrawn by syringe at known times and their IR spectra recorded with a Perkin-Elmer 298 spectrophotometer.

Results

Reactions with P-*n*-Bu_3 in C_2Cl_4 or heptane at 20–40 °C led cleanly to a product showing IR bands at 2060 (s), 2032 (s), 1996 (s), 1824 (m), and 1788 (m) cm^{-1} in excellent agreement with those reported for $Ir_4(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$.[9] Further reaction occurred only when the temperature was raised. The electronic spectra showed a general increase in absorbance throughout the reactions. The final spectra showed ill-defined shoulders at ca. 300 and 335 nm and were quite stable, the absorbance at 320 nm having increased by ca. 100%. First-order rate plots were linear for at least 2 half-lives, and the observed rate constants are clearly first order in [P-*n*-Bu_3]. Values of $k_2 = k_{obsd}/[P\text{-}n\text{-}Bu_3]$ are given in Table I.

Reactions with PCy_3 in decalin proceeded at 100 °C with growth of IR bands at 2033 (s), 1985 (s), 1980 (s), 1780 (s, br),

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Table I. Rate Constants for Associative Reactions of $Ir_4(CO)_{12}$

L	T, °C	10^2[L], M	10^3k_2,[a] M^{-1} s^{-1}				
P-n-Bu_3[b]	20.0	5.0–10.0	2.82	2.83	3.13		
	25.0	3.0–10.0	4.60	4.86	4.39	4.60	
	31.5	1.0–15.0	6.70	6.60	7.50	6.67	6.63
	31.5	5.80	8.00[c]	8.05[c]	6.33[d]		
	31.5	8.0–15.0	9.79[e]	9.17[e]	9.39[e]		
	35.6	1.0–10.0	10.3	9.70	8.62	8.67	8.76
	40.0	3.0–10.0	11.2	11.6	11.6	11.3	
PCy_3[f]	79.6	4.8–10.0	1.12	1.26	1.23		
	88.4	5.0–10.0	2.10	2.26	2.09		
	99.4	10.0	3.07				
	99.5	3.0	3.05				
	109.3	4.9–9.9	9.22	9.90			
etpb[g]	40.0	0.50–1.01	1.88	2.05	2.22		
	50.1	0.20–1.01	4.27	4.63	4.59	4.77	4.42
	59.6	0.20–0.61	7.83	8.22	8.62	9.25	7.70
$P(OEt)_3$[g]	31.5	5.00–10.0	5.04	5.00			
	35.3[h]	5.00–15.0	5.88	4.84	4.47	4.97	
	40.0	5.00–10.0	11.1	12.2			

[a] $k_2 = k_{obsd}/[L]$ except for reaction with PCy_3 for which $k_2 = (k_{obsd} - k_1)/[L]$ where values of k_1 were estimated from data for reactions with $AsPh_3$ given in ref 8, viz. 2 × 10^{-6} (79.6), 7 × 10^{-6} (88.4), 2 × 10^{-5} (99.4), and 6 × 10^{-5} s^{-1} (109.3 °C). [b] In C_6H_5Cl and with UV–vis monitoring unless otherwise indicated. [c] In C_2Cl_4 with IR monitoring. [d] In C_2Cl_4. [e] In heptane. [f] In C_6H_5Cl. [g] In C_2Cl_4 unless otherwise indicated. [h] In C_6H_5Cl.

and 1765 (sh) cm^{-1}. These are very close to the bands shown by $Ir_4(CO)_9(P\text{-}i\text{-}Pr_3)_3$.[10] Further reaction led to slow, rather complex changes in the spectrum. The kinetics were followed by monitoring the decreasing absorbance in C_6H_5Cl of the band at 2072 cm^{-1} due to $Ir_4(CO)_{12}$. Excellent rate plots were obtained, and the second-order rate constants were estimated from $(k_{obsd} - k_1)/[PCy_3]$ and are given in Table I. The values of k_1 for the dissociative path are significant, though still small, only for these reactions that require higher temperatures. Values of k_1 were estimated from data published for the reaction with $AsPh_3$.[8]

Reactions with etpb in C_2Cl_4 at 20–40 °C were accompanied by rather complex changes in the IR spectra. One clear feature was the growth and decay of a band at 2060 cm^{-1}, a band characteristic of $Ir_4(CO)_{11}\{P(OMe)_3\}$.[11] However, no band comparable to that due to the latter complex at 2095 cm^{-1} was observed. The final spectra showed bands at 2060 (sh), 2050 (m), 2030 (vs), 2012 (s), and 1975 (s) cm^{-1}, with a broad, structured band at 1810–1850 cm^{-1}. These do not correspond simply to spectra reported for $Ir_4(CO)_{10}\{P(OMe)_3\}_2$[11] or $Ir_4(CO)_9\{P(OPh)_3\}_3$[9] alone. Although there are some features in common, no band at 2070 cm^{-1} was evident. In view of the possibility of isomerism in such complexes, we conclude that a mixture of various substitution products was obtained. The absence of any product band at 2070 cm^{-1} enabled the kinetics to be followed by monitoring the decreasing absorbance at 2072 cm^{-1}, and very good plots of ln A vs. time were obtained. Reactions with $P(OEt)_3$ showed very similar changes in the IR spectra although no growth and decay of a band at 2060 cm^{-1} was observed. The kinetics were followed as for reactions with etpb, and the second-order rate constants for reactions with these phosphites were estimated from $k_{obsd}/[L]$ (Table I).

Discussion

All the values of k_{obsd} show a strong dependence on [L], and apart from the reaction with PCy_3, values of k_2 were estimated from $k_{obsd}/[L]$. At the temperatures needed for reactions with PCy_3 the dissociative path must play a small part in the reaction. Values of k_2 were, therefore, obtained from $(k_{obsd} - k_1)/[L]$, where k_1 was estimated from data for reactions with $AsPh_3$.[8] Solvent effects on k_2 are quite small. Relative rate constants for reaction with P-n-Bu_3 at 31.5 °C are 1.0 (C_6H_5Cl), 1.1 ± 0.1 (C_2Cl_4), and 1.4 ± 0.1 (heptane), and for reaction with $P(OEt)_3$ at 35.3 °C, they are 1.0 (C_6H_5Cl) and 1.5 ± 0.2 (C_2Cl_4). Values of ΔH_2^* and ΔS_2^* (Table II) were estimated in the usual way.

Table II. Activation Parameters[a] for Associative Reactions of $Ir_4(CO)_{12}$

L	ΔH_2^*, kcal mol^{-1}	ΔS_2^*, cal K^{-1} mol^{-1}
P-n-Bu_3	11.67 ± 0.38	−30.2 ± 1.3
PCy_3	16.5 ± 1.6	−26 ± 4
etpb	14.08 ± 0.53	−21.4 ± 1.6
$P(OEt)_3$	18.2 ± 1.1	−10 ± 4
PPh_3[b]	20.5 ± 0.4	−16 ± 1
$P(OPh)_3$[b]	17.3 ± 0.2	−25 ± 1

[a] Uncertainties are standard deviations derived so that 95% confidence limits can be obtained by doubling them. [b] Parameters recalculated by using values of k_{obsd} from ref 8 and values of k_1 based on data for reaction with $AsPh_3$.

Table III. Values of log k_2 Estimated from the Activation Parameters in Table II

		log k_2			
no.	L (ΔHNP, V; θ, deg)	T = 40 °C	T = 60 °C	T = 80 °C	T = 100 °C
1	P-n-Bu_3 (0.131; 132)	−1.926	−1.410	−0.951	−0.541
2	PCy_3 (0.033; 170)	−4.286	−3.567	−2.929	−2.347
3	etpb (0.650; 101)	−1.678	−1.062	−0.522	−0.046
4	$P(OEt)_3$ (0.520; 109)	−1.934	−1.147	−0.447	+0.180
5	PPh_3 (0.573; 145)	−4.939	−4.055	−3.270	−2.567
6	$P(OPh)_3$ (0.875; 128)	−4.133	−3.382	−2.714	−2.117

Table IV. Values of α, β, and γ in Eq 1

T, °C	α	β, V^{-1}	γ, deg^{-1}	R[a]
40	7.18	−3.17	−0.068	0.9900
60	7.28	−2.84	−0.064	0.9935
80	7.31	−2.69	−0.062	0.9943
100	7.48	−2.34	−0.058	0.9927

[a] Correlation coefficients.

The fact that reaction with P-n-Bu_3 proceeds to $Ir_4(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ without spectroscopic evidence for the mono-substituted intermediate is consistent with a larger value of k_2 for this intermediate compared with that for $Ir_4(CO)_{12}$.[12] No intermediates are seen during formation of $Ir_4(CO)_9(PCy_3)_3$ but whether this is due to larger values of k_2 for the mono- and bis-substituted intermediates or to sterically enhanced dissociative processes is not obvious, though the latter seems more likely. The observation of what is probably an $Ir_4(CO)_{11}$(etpb) intermediate suggests that, at least for this phosphite, the presence of one phosphite ligand stabilizes the cluster to some extent. Accumulation of $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ is noted in reactions of $Ru_3(CO)_{12}$ with etpb and $P(OPh)_3$.[4]

Values of log k_2 for the reactions of $Ir_4(CO)_{12}$ at various temperatures (Table III) can be calculated from the activation parameters. Plots of log k_2 at 80 °C against ΔHNP[6] for the various nucleophiles show no regular trend (Figure 1). However, $P(OPh)_3$ and P-n-Bu_3 have very similar cone angles,[5,13] and their values of log k_2 can be joined as shown, making allowances for the small differences in cone angle. This provides a measure of the electronic effect for nucleophiles of cone angle 130°. Deviations from this line of the values of log k_2 can be ascribed to steric effects, and those for reactions at 80 °C are plotted in Figure 2 against the relevant cone angles. Similar plots are obtained from data at other

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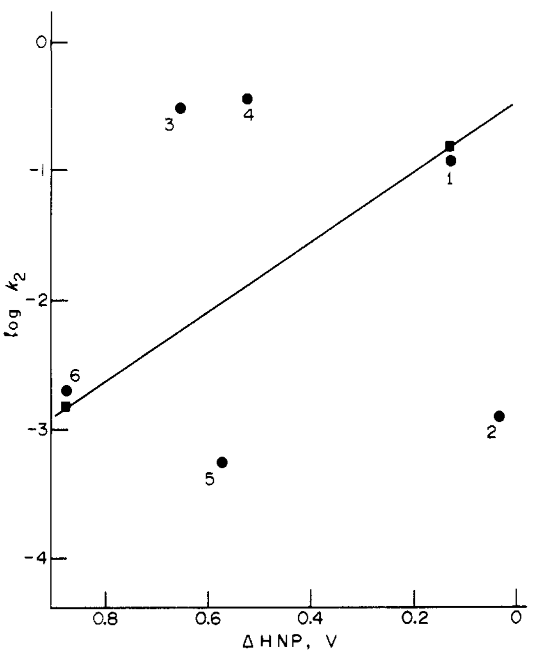

Figure 1. Dependence of log k_2 on ΔHNP at 80 °C: (●) log k_2; (■) log k_2 corrected for differences between cone angles for $P(OPh)_3$ and P-*n*-Bu_3 and 130°. ΔHNP is a measure of the relative proton basicity of the nucleophiles in nitromethane, and basicity increases with decreasing ΔHNP. Values of ΔHNP are taken from ref 6. Numbering of the nucleophiles is taken from Table III.

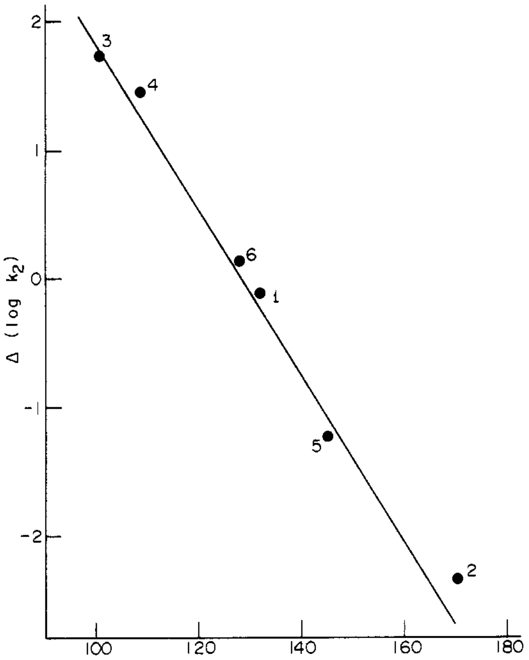

Figure 2. Deviations of values of log k_2 from the line drawn in Figure 1 plotted against the cone angles, θ, for the various nucleophiles (numbering from Table III).

temperatures, and the data can all be expressed in terms of the three parameters α, β, and γ in eq 1. Values for these parameters are given in Table IV.

$$\log k_2 = \alpha + \beta(\Delta HNP) + \gamma\theta \qquad (1)$$

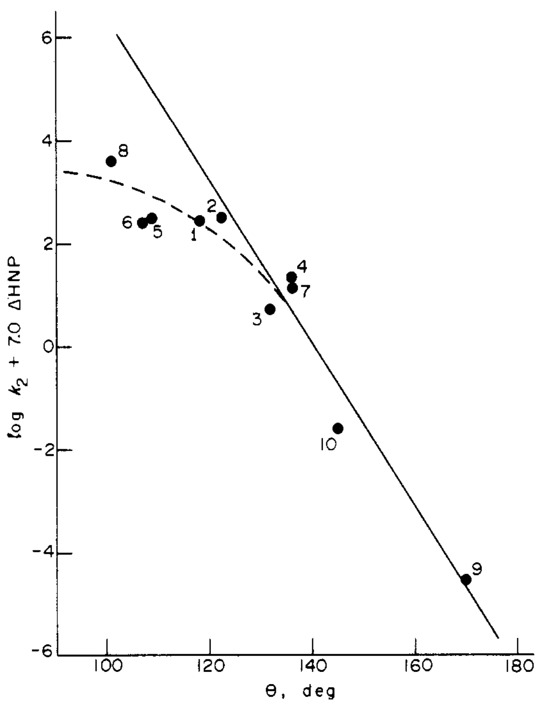

Figure 3. Dependence of log k_2 + 7.0(ΔHNP) on θ for reactions of $(N_4Me_2)Fe(CO)_3$ in toluene at 70 °C. Data and numbering taken from ref 19.

The fact that steric deviations of log k_2 are linearly dependent on cone angle from 170° down to 101° demonstrates the wide and systematic influence of steric effects for reactions of $Ir_4(CO)_{12}$. The question of how small a nucleophile would have to be for steric effects to become negligible is of interest. If they continue to be significant indefinitely as θ decreases, then the values of α in Table IV would correspond to values of log k_2 for a rather highly nucleophilic ligand (ΔHNP = 0) of negligible size. The temperature dependence of α corresponds to $\Delta H_2^{\ddagger}$ = ca. 2 kcal mol^{-1} and $\Delta S_2^{\ddagger}$ = ca. −20 cal K^{-1} mol^{-1}. It seems more likely, however, that steric effects will decrease and become negligible[14] somewhere between θ = 101 and 0°. This must be the case for the reactions at 25 °C of $(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NC_5H_4X)^+$ studied by Kochi et al.[15] These show a good fit to eq 2[16] for θ = 132–150°. At ΔHNP

$$\log k_2 = 19.6 - 3.4(\Delta HNP) - 0.12\theta \qquad (2)$$

= γ = 0, log k_2 is much greater than for a diffusion-controlled reaction, so the steric effect must decrease significantly as θ → 0°. This is also evidently the case for all those carbonyls that show linear plots of log k_2 against ΔHNP for smaller ligands but show significant steric deviations for larger ligands such as PPh_3 and/or PCy_3.[4,18]

Interesting examples of this type of behavior are given by $(N_4Me_2)Fe(CO)_3$[19] and $V(CO)_6$.[20] A reasonable LFER is given[19] for reactions of $(N_4Me_2)Fe(CO)_3$ at 70 °C with all the P donors with $\theta \lesssim 120°$, but when $\theta \gtrsim 130°$, significant deviations are observed. However, the data can be better analyzed if steric and electronic effects are separated more clearly. A plot of log k_2 + 7.0 (ΔHNP) is given in Figure 3 and shows a linear dependence on θ (γ = −0.16 deg^{-1}) when $\theta \gtrsim 130°$, but as θ decreases below this, some leveling off is observed. If β is taken as −9.0 V^{-1} a linear dependence on θ (γ = −0.13 deg^{-1}) is obtained for all the nucleophiles, but the fit is appreciably less good, the mean deviation

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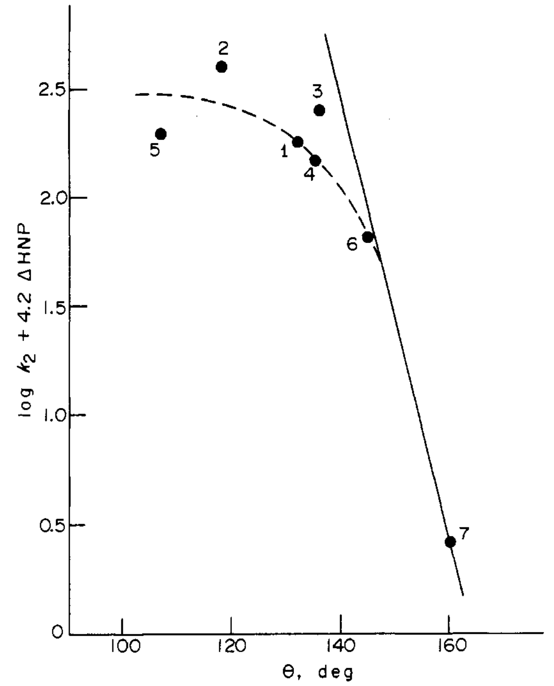

Figure 4. Dependence of log k_2 + 4.2(ΔHNP) on θ for reactions of $V(CO)_6$ in hexane at 25 °C. Data and numbering taken from ref 20.

of log $k_2 - \beta(\Delta HNP)$ from the line being 0.66 as compared with 0.45 for the data in Figure 3.

Quite a good LFER between log k_2 and ΔHNP is shown by all the P donors used for reactions of $V(CO)_6$ at 25 °C apart from P-*i*-Pr_3 (θ = 160 °C).[20] However, even some of the smaller nucleophiles show evidence for steric effects in that log k_2 for PPh_3 is ca. 0.45 less than that for $P(OMe)_3$, which has almost exactly the same basicity but is 38° smaller. If one uses this observation to make the necessary small steric adjustments, one can obtain a value of $-4.2\ V^{-1}$ for β from the values of log k_2 for P-*n*-Bu_3 (θ = 132°), $PMePh_2$ (θ = 136°), and P(O-*i*-Pr)$_3$ (θ = 135°). A plot of log k_2 + 4.2(ΔHNP) vs. θ is shown in Figure 4 where a clear leveling off at low cone angles is evident.

The form of these plots can be regarded as the paradigm for associative reactions of this type.[21] Data for $Ir_4(CO)_{12}$ and $(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NC_5H_4X)^+$[15] fall only on the portion where log $k_2 - \beta(\Delta HNP)$ decreases linearly with θ. Data for $(\eta^5\text{-}Me_5C_5)M(CO)_2$ (M = Co, Rh)[6] appear to behave similarly although they may begin to show some leveling off at lower θ.[22] Other carbonyls show the horizontal part of the plot, with some decrease at higher cone angles, provided sufficiently large nucleophiles were included in the study.

These plots provide a number of parameters that can be used to describe the susceptibility of the carbonyls to nucleophilic attack by P donors. The constant value of log $k_2 - \beta(\Delta HNP)$ at low enough cone angles is a measure of the intrinsic reactivity of the complex as given by a standard nucleophile with ΔHNP = 0. The constant β provides a measure of the electronic discrimination of the complex. This can be and often presumably is a good measure of the relative amount of bond making in the transition states for a group of closely related complexes. However, circumstances could arise where increased bond making with more basic nucleophiles is only allowed at the expense of a similar amount of bond weakening elsewhere so that the two effects cancel. (This implies, not a constant amount of bond making with all the nucleophiles used but an extent of bond making dependent on the particular nucleophile.) This could well be the case for reactions of $(\eta^5\text{-}Me_5C_5)M(CO)_2$[6] where β is very small. These complexes are believed[6] to undergo some degree of $\eta^5 \rightarrow \eta^3$ "slippage" on attack by a nucleophile. This requires energy, and the extra bond making involved with more basic nucleophiles may be offset by a greater degree of slippage.

Steric effects in associative reactions will be indicated both by the cone angle at which log $k_2 - \beta(\Delta HNP)$ begins to decrease and by the gradient, γ, of the linear portion of the decrease. They can also be quantified by the difference between the intrinsic reactivity and the value of log $k_2 - \beta(\Delta HNP)$ for a chosen ligand such as PPh_3 or PCy_3, as has been done before.[2,4]

Apart from these indicators, values of ΔH_2^* can also provide a measure of intrinsic reactivity, especially if they are available for nucleophiles not subject to steric effects. In this case, ΔH_2^* could be plotted against ΔHNP so as to give a value for the standard nucleophile with ΔHNP = 0.

Not all these parameters will necessarily be derivable for any one complex though many more of them could be obtained than are presently known. Thus, even for the archetypical $Co(CO)_3(NO)$,[1b,1d] reactions with nucleophiles with cone angles between 145 and 170° should show when steric effects become apparent and might also provide a value of γ.

The most widely known parameter is β,[4,15,18] and a reasonable number of estimates of steric deviations for PPh_3 and PCy_3 are available. Values of γ are known only for $(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NC_5H_4X)^+$ (-0.12 deg^{-1}),[15] $Ir_4(CO)_{12}$ (-0.06 to -0.07 deg^{-1}), $(N_4Me_2)Fe(CO)_3$ (-0.16 deg^{-1}, from Figure 3), $V(CO)_6$ (ca. -0.1 deg^{-1}, from Figure 4), and $(\eta^5\text{-}Me_5C_5)M(CO)_2$ (-0.1 deg^{-1}).[23] A considerable number of intrinsic reactivities are available from LFER plots, but these are spread out over a range of temperatures and only some are directly comparable. It is not our intention to review all available data here but only to compare $Ir_4(CO)_{12}$ with some other carbonyls of interest.

$Ir_4(CO)_{12}$ clearly has a much higher intrinsic reactivity than $W(CO)_6$[3] and $Os_3(CO)_{12}$.[24] It is of rather higher reactivity than $Ru_3(CO)_{12}$.[4] Although it has higher values of ΔH_2^* for most nucleophiles, the difference is negligible for P-*n*-Bu_3,[4,26] (ΔHNP close to 0). The difference is a maximum (5 kcal mol^{-1}) for PPh_3, the largest ligand in common, and this suggests that $Ir_4(CO)_{12}$ suffers from larger steric effects than $Ru_3(CO)_{12}$. This is not unexpected in view of their geometry,[27] and the data for P-*n*-Bu_3 probably imply a greater intrinsic reactivity for $Ir_4(CO)_{12}$ if it suffers from steric inhibition in its reactions with P-*n*-Bu_3 and $Ru_3(CO)_{12}$ does not. The electronic discrimination shown by $Ir_4(CO)_{12}$ at 60 °C is slightly greater[28] ($\beta = -2.8\ V^{-1}$) than that for $Ru_3(CO)_{12}$ ($\beta = -2\ V^{-1}$ when only log k_2 values for $P(OPh)_3$ and P-*n*-Bu_3 are considered).[29]

Comparison with $V(CO)_6$ is of interest since it is exceptionally susceptible to nucleophilic attack for an octahedrally coordinated binary carbonyl.[20] This is ascribed to its 17-electron nature, which allows for formation of a new two-center, three-electron bond to the nucleophile without any electronic weakening of the other bonds. The intrinsic reactivity of $Ir_4(CO)_{12}$ is probably almost as great when measured by log $k_2 - \beta(\Delta HNP)$ at low enough cone

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(21) This does not imply that all data should be in accord with such a trend but merely that it provides a model against which data can be compared, any deviations presumably requiring more subtle considerations than are incorporated into the simple model. See, for example, ref 6 and 22.

(22) Data for $P(OMe)_3$ and $P(OEt)_3$ in ref 6 (θ = 107 and 109°) lie well below the linear plot running from PMe_3 (θ = 118°) to P-*i*-Bu_3 (θ = 143°). It is not clear why data for these two phosphites should be deviant when data for P(O-*i*-Pr)$_3$ (θ = 130°) and $P(OCy)_3$ (θ = 135°) fit, since the ΔHNP values of the phosphites are not very different and electronic effects are small.

(23) Estimated in ref 15 from data in reference 6.

(24) ΔH_2^* for reaction of $Os_3(CO)_{12}$ with P-*n*-Bu_3 is higher[25] by ca. 8 kcal mol^{-1}, and this is unlikely to be due to steric differences.

(25) Brodie, N.; Poë, A. J.; Sekhar, V. *J. Chem. Soc., Chem. Commun.* **1985**, 1090–1091. Poë, A. J.; Sekhar, V. *Inorg. Chem.* **1985**, *24*, 4376–4380.

(26) Poë, A. J.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982–2985.

(27) Churchill, M. V.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655–2659. Churchill, M. V.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528–3535.

(28) Nucleophilicity increases as ΔHNP decreases and so β values are negative. Thus, electronic discrimination increases as β becomes more negative.

(29) This value of β is in agreement with that in ref 4 but considerably lower than that estimated in ref 18. The latter is incorrect because of a typographical error in Table 6 of ref 4. The column headed 10^5k_2 should have been headed 10^4k_2 as is evident from the data in Tables 1–5 and Table 7 of ref 4.

angles. This is ca. 2.5 for $V(CO)_6$ at 25 °C (Figure 4) and cannot be very much less than this for $Ir_4(CO)_{12}$ as judged by any reasonable extrapolation to $\theta = 0$ of a plot of log $k_2 - \beta(\Delta HNP)$ against θ for data at 25 °C, β being taken as $-3.5\ V^{-1}$ (see Table IV). Extrapolation to $\Delta HNP = 0$ of $\Delta H_2^{\ddagger}$ for the θ-independent reactions of $V(CO)_6$ with $P(OMe)_3$ and PMe_3 gives ca. 7 kcal mol^{-1} as a measure of its intrinsic reactivity. A similar extrapolation of $\Delta H_2^{\ddagger}$ for reaction of $Ir_4(CO)_{12}$ with etpb (using the dependence of $\Delta H_2^{\ddagger}$ for $P(OPh)_3$ and P-*n*-Bu_3 on ΔHNP) leads to ca. 9 kcal mol^{-1}, which would be an upper limit if steric effects contribute to $\Delta H_2^{\ddagger}$ for etpb to any extent. Both $Ir_4(CO)_{12}$ and $V(CO)_6$ are very much less reactive than $(\eta^5\text{-}MeC_5H_4)M(CO)_2(NC_5H_4X)^+$, which has $\Delta H_2^{\ddagger} = 4.4$ kcal mol^{-1} for reaction with PPh_3[15] in spite of its high susceptibility to steric effects (see above). This high intrinsic reactivity of the Mn complex is probably due to its relatively high oxidation state as well as to its 17-electron nature.

The electronic discrimination shown at 25 °C for $Ir_4(CO)_{12}$ (β = ca. $-3.4\ V^{-1}$) is less[28] than that for $V(CO)_6$ ($\beta = -4.2\ V^{-1}$)[30] so bond formation seems to be greater for the latter. Steric effects are harder to judge. The plot in Figure 2 shows them still to be operative for $Ir_4(CO)_{12}$ even with θ as low as 101°, and the gradient gives $\gamma = -0.06\ deg^{-1}$. Figure 4 shows that steric effects for $V(CO)_6$ do not become apparent until $\theta \gtrsim 120°$, but above that γ = ca. $-0.1\ deg^{-1}$. Steric effects will depend on metal–nucleophile bond lengths in the transition states. Perhaps these are[20] longer for the 17-electron $V(CO)_6$ even though the strength of the bonds is greater as suggested by the value of β. On the other hand, as θ increases, $V(CO)_6$ may eventually offer greater steric resistance by being less flexible. $Ir_4(CO)_{12}$ may prove to be quite flexible during associative reactions (see below) so that, although steric effects are apparent even for quite small nucleophiles, sensitivity to cone angle is not as great.

It would appear from these considerations that the susceptibility of the 18-electron $Ir_4(CO)_{12}$ to nucleophilic attack is not markedly less than that of the 17-electron $V(CO)_6$, and an understanding of its high susceptibility may be reached as follows. High intrinsic reactivity is usually related[1a,31] to facile changes in the bonding of other ligands attached to the metal, and an analogous explanation can be given for $Ir_4(CO)_{12}$. In simple valence bond terms, a given Ir atom can be envisaged as being bonded to the other three by use of three of its electrons. If only one of them is used in the transition state, it can be regarded as being in a single σ orbital directed toward the middle of the tetrahedron and overlapping with three singly occupied σ orbitals from the other Ir atoms. This will lead to multicenter four-electron bonding to the other Ir atoms instead of the six-electron bonding in the unperturbed cluster. However, the singular Ir atom will now have eight nonbonding electrons and will have one vacant dsp^3-type orbital to accommodate an electron pair from the nucleophile. Thus a full Ir–P bond can be made at the expense of weakening the bonding within the Ir_4 cluster by reducing the total number of cluster bonding electrons only from 12 to 10. This weakening of the cluster bonding has been shown to be an important feature of associative reactions of other clusters[25] and implies that the intrinsic reactivity should be closely related to the strength of bonding within the metal cluster. Further, the stereochemistry around the attacked Ir atom will have changed from quasi-octahedral d^2sp^3 to roughly dsp^3, and the OC-Ir-CO angles could therefore have opened up substantially. This analysis seems to provide a reasonable explanation of the various aspects of the observed reactivity.

Summary

Associative substitution reactions of $Ir_4(CO)_{12}$ with P-donor nucleophiles have been analyzed in terms of electronic and steric effects. A general approach to quantifying the various features of such reactions of metal carbonyls has been developed. The high susceptibility of $Ir_4(CO)_{12}$ to nucleophilic attack has been demonstrated by comparison with data for reactions of other highly susceptible metal carbonyls. It can be related to its ability to form quite strong Ir–P bonds at the expense of relatively slight weakening of the bonding within the Ir_4 cluster. This is accompanied by changes of the coordination around the Ir atom that is being attacked. These result in a relatively small, but always present, steric effect. The concept of the flexibility of the coordination spheres during associative reactions of metal carbonyls is emphasized.

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Note Added in Proof. After this paper was originally submitted, the work of Giering et al. came to our attention (Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–1991). This includes an analysis of published rate data for associative reactions that is essentially identical with that outlined here.

Registry No. $Ir_4(CO)_{12}$, 18827-81-1; P-*n*-Bu_3, 998-40-3; $P(OEt)_3$, 122-52-1; $P(OCH_2)_3CEt$, 824-11-3; $P(C_6H_{11})_3$, 2622-14-2.

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[30] A somewhat higher value was estimated in ref 15, but this did not account for any steric effects apart from that for P-*i*-Pr_3.

[31] Basato, M.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 456–459.

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Steric and Electronic Effects in Cobalt(II) Disproportionation with Phosphorus Ligands

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The disproportionation reaction $2Co^{2+} + 11PZ_3 \rightarrow CoL_5^+ + CoL_6^{3+}$ ($L = PZ_3$) is found to depend in a curious way upon the shape of the ligand (as well as on its steric bulk). Thus, for example $P(OMe)_3$ and $(MeO)_{ax}(\overline{POCHMe_{eq}CH_2CHMe_{eq}O})$ drive the reaction, but $P(OEt)_3$ and $(MeO)_{ax}\overline{POCH_2CMe_2CH_2O}$ do not. Secondly, the ligand must possess a minimum degree of basicity for disproportionation to occur. For example $P(OCH_2)_3CMe$ functions in this reaction, but the smaller and less basic ligands $\overline{P(OCH_2)_2CHO}$ and PF_3 do not. Thirdly, diastereomeric CoL_6^{3+} complexes of an unusual nature are detected by ^{59}Co NMR spectroscopy when L is *n*-$PrO\overline{POCH_2CH_2O}$ or *n*-$BuO\overline{POCH_2CH_2O}$. Finally, the sterically more crowded CoL_6^{3+} product prefers the larger but more basic ligand $P(OMe)_3$ while the CoL_5^+ species preferentially binds the smaller but better π acceptor $P(OCH_2)_3CEt$ when a mixture of the two ligands is employed in the disproportionation.

Introduction

$$2Co^{2+} + 11PZ_3 \rightarrow CoL_5^+ + CoL_6^{3+} \qquad (1)$$

The disproportionation reaction (1) in which $L = PZ_3$ has been known for over 25 years.[1] Except for the phosphite esters $P(OMe)_3$,[2] **4a**,[3] **4b**,[3] **6**,[3] **29**,[4] and **31**[5,6] and the chelating diphosphonites **35**[7] and **36**[7] (in Table I), which have been reported

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