The ^{31}P NMR spectrum of V is a characteristic AB_2 type in appearance, much resembling that of the free ligand.[13] The satellite spectrum can be compared to that of $Ph_2P(Se)CH_2CH_2P(Se)PhCH_2CH_2PPh_2(Se)$, which was recently analyzed.[18] It consists of the AB_2 part of an AB_2X spin system overlapping with the ABC part of an ABCX spin system. The center phosphorus resonance is found at 7.5 ppm ($^3J_{PP}$ = 34.7 Hz, J_{WP} = 239.4 Hz), and the terminal phosphorus atoms are found at 13.5 ppm (J_{WP} = 242.0 Hz).

In the course of this work we have found free radical additions to be useful and even preferred so long as at least one of the reactants is an uncoordinated phosphine. When both secondary phosphines and vinylphosphines were coordinated, the free radical method failed, but in those cases potassium *tert*-butoxide led to the desired addition. This observation has been noted in the preparation of diphos derivatives as well.[19]

The enormous potential of using addition reactions for ligation control becomes apparent in this study. Many complexes, until now considered chemical oddities because of their synthetic inaccessibility, will become commonplace and available for catalytic, mechanistic, and spectroscopic studies.

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Registry No. I, 79919-64-5; I (oxide), 79933-12-3; II, 79919-65-6; III, 79919-66-7; III (oxide), 79919-67-8; IV, 79919-68-9; IV (oxide), 79919-69-0; V, 79919-70-3; $(OC)_5WPPh_2CH_2CH_2PPh(O)CH_2CH_2PPh_2$, 79919-71-4; $(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2(O)$, 79919-72-5; $(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$, 79933-13-4; $(OC)_5WPPh(CH{=}CH_2)_2$, 79919-73-6; $(OC)_5WPPh_2H$, 18399-62-7; $(OC)_5WPPh_2(CH{=}CH_2)$, 64012-10-8; PPh_2H, 829-85-6.

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Kinetics and Mechanism of Oxidative Addition of Methyl Iodide to Four- and Five-Coordinate Iridium(I) Complexes

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Oxidative addition of methyl iodide to four-coordinate iridium and rhodium complexes is important in the Monsanto process[1] in the conversion of methanol to acetic acid, which was found to be catalyzed by iodide ions.[2,3] We have lately found some more oxidative-addition reactions that are catalyzed by iodide ions.[4]

Our interest lies in the reactivities of five-coordinated d^8 iridium complexes. Recently we presented the first evidence of dioxygen attacking a five-coordinate iridium(I) iodide complex,[4] and we also obtained evidence for direct attack of dihydrogen on the five-coordinate complex $IrH(CO)(PPh_3)_3$.[5]

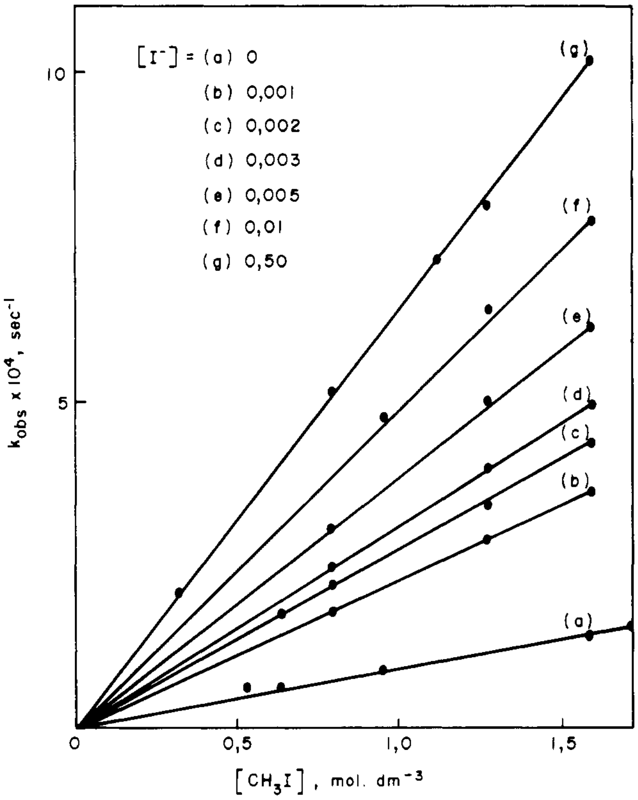

Figure 1. Plots of k_{obsd} vs. $[CH_3I]$ for different $[I^-]$ (in mol·dm^{-3}) at 25 °C. Experimental points were fitted to the theoretical lines obtained from the SPSS program.

We report here the kinetic results of the iodide-catalyzed reaction

$$[(cod)Ir(phen)]^+Cl^- + CH_3I \xrightarrow{[I^-]} [(cod)Ir(phen)(CH_3)(I)]^+ \qquad (1)$$

(cod = cycloocta-1,5-diene; phen = 1,10-phenanthroline). The four-coordinate $[Ir(cod)(phen)]^+Cl^-$ in the presence of iodide establishes equilibrium 2 in methanol solution. A K_e value

$$[(cod)Ir(phen)]^+Cl^- + I^- \underset{MeOH}{\overset{K_e}{\rightleftharpoons}} (cod)Ir(phen)I \qquad (2)$$

of 227 ± 5 cm^3·mol^{-1} (at 25 °C) was determined spectrophotometrically.

The rate of reaction 1 was found to be first order in both [complex] and [methyl iodide] and increased with increasing sodium iodide concentration. Under the conditions of the kinetic measurements all the reactions went to completion. Since the concentration of methyl iodide was always in sufficiently large excess to remain essentially constant throughout the reaction, the observed rate of disappearance of Ir(cod)(phen)X (X = Cl, I) in every case studied yielded linear semilog graphs. The data at 20, 30, and 35 °C are given in Table I.

Plots of k_{obsd} vs. $[CH_3I]$ at different concentrations of iodide at 25 °C are shown in Figure 1. A family of straight lines through the origin for the methyl iodide concentration range used was obtained. The slopes of these plots increase with increasing [NaI]. All the data conform to the rate law given in eq 3, which can be derived from Scheme I.

$$k_{obsd} = \left(\frac{k_1 + k_2K_e[I^-]}{1 + K_e[I^-]}\right)[CH_3I] \qquad (3)$$

The rate law given in eq 3 simplifies to $k_{obsd} = k_1[CH_3I]$ if the concentration of added iodide is zero. The slope of plot (a) in Figure 1 then gives the values of k_1 (Table II), the rate

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Table I. Summary of the Kinetic Data for the Reactions

$$[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})]^+ + \mathrm{CH_3I} \xrightarrow[\mu=0.01]{[\mathrm{I^-}]} [(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})(\mathrm{CH_3})(\mathrm{I})]\mathrm{X}\ (\mathrm{X} = \mathrm{Cl, I})$$

$[\mathrm{CH_3I}]$, mol·dm^{-3}	temp, °C	$[\mathrm{I^-}]$, mol·dm^{-3}	$10^4 \times k_{\mathrm{obsd}}$, s^{-1}	k_1, dm^3·mol^{-1} s^{-1}	k_2, dm^3·mol^{-1} s^{-1}
1.585	30	0.00	2.23	1.41×10^{-4}	
1.270			1.76	1.39×10^{-4}	
0.793			1.11	1.40×10^{-4}	
1.585	35		3.21	2.03×10^{-4}	
1.270			2.60	2.02×10^{-4}	
0.793			1.58	1.99×10^{-4}	
1.585	20		1.07	6.75×10^{-5}	
1.270			0.89	7.01×10^{-5}	
0.793			0.64	8.07×10^{-5}	
1.585	30	0.50	13.36		8.43×10^{-4}
1.270			10.63		8.37×10^{-4}
0.951			7.95		8.36×10^{-4}
1.585	35		17.82		1.12×10^{-3}
1.270			14.39		1.13×10^{-3}
0.793			9.28		1.17×10^{-3}
0.951			10.69		1.12×10^{-3}
1.585	20		7.13		4.50×10^{-4}
1.270			5.66		4.46×10^{-4}
0.793			3.51		4.43×10^{-4}

constant of methyl iodide attack on the four-coordinate $[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})]^+\mathrm{Cl}^-$. When the iodide concentration is taken to 0.50 mol·dm^{-3}, the only species in solution is the five-coordinated (cod)Ir(phen)I, so that rate law 3 becomes $k_{\mathrm{obsd}} = k_2[\mathrm{CH_3I}]$. These values of k_2 are given in Table II.

With use of all the data obtained at 25 °C, the rate and equilibrium constants were also obtained by using rate law 3 as the model in the SPSS nonlinear least-squares fit program[6] (Table II). From Table II it can be seen that good agreement was obtained between the k_1 and k_2 values obtained by experiment and by using the SPSS program. Also, the K_e values are in very good agreement.

The entropies of activation (Table II) are expectedly quite negative for reactions involving charged reactants and products and suggest a marked increase in polarity, or unusually stringent stereochemical restrictions, in going from reactants to the transition state. It is therefore reasonable to assume a transition-state configuration in which the iodide on the methyl group undergoes nucleophilic substitution by the iridium complex.

From the above data it is clear that oxidative addition of methyl iodide to the cationic $[\mathrm{Ir}(\mathrm{phen})(\mathrm{cod})]^+\mathrm{Cl}^-$ complex can proceed by two reaction mechanisms, i.e., either by electrophilic attack by the methyl group (followed by coordination of iodide) or by coordination of iodide (followed by methylation). Our results show unequivocably that the second path is preferred and consequently offers an explanation for iodide-catalyzed MeI oxidative-addition reactions.[1]

Experimental Section

Materials. Analytical grade methanol (Merck), distilled over magnesium and stored and transferred under nitrogen, was used for all the kinetic measurements.

The complexes Ir(cod)(phen)X (X = Cl, I) were prepared by published procedures,[7] and their reaction products with methyl iodide were characterized by microanalyses. Anal. Calcd for [(cod)Ir(phen)(CH$_3$)(I)]Cl: C, 37.4; H, 3.1; N, 4.36; I, 19.7; Cl, 5.5. Found: C, 37.3; H, 3.2; N, 4.5; I, 20.1; Cl, 5.7. Anal. Calcd for [(cod)Ir(phen)(CH$_3$)(I)]I: C, 32.7; H, 2.7; N, 3.8; I, 34.6. Found: C, 32.5; H, 2.9; N, 4.1; I, 35.0. Analytical grade sodium iodide and lithium chloride and reagent grade methyl iodide were obtained from Merck. Sodium iodide and lithium chloride were deaerated, dehydrated, and stored under nitrogen. Methyl iodide was extracted with aqueous sodium thiosulfate (to remove iodine), distilled under nitrogen, and stored over clean mercury. Purified nitrogen was supplied by the African Oxygen Co.

Scheme I

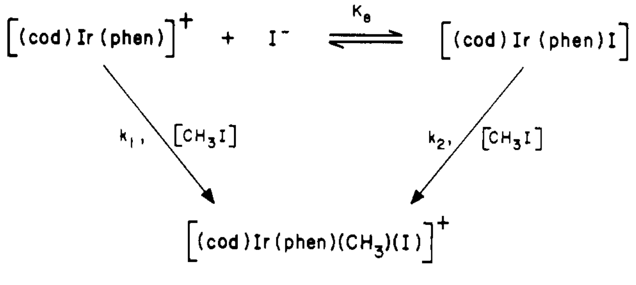

Table II. Summary of the Rate and Equilibrium Constants and Activation Parameters for the Reaction (25 °C)

$$[(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})]^+ + \mathrm{CH_3I} \xrightarrow[\mu = 0.01]{[\mathrm{I^-}]} [(\mathrm{cod})\mathrm{Ir}(\mathrm{phen})(\mathrm{CH_3})(\mathrm{I})]\mathrm{X}\ (\mathrm{X} = \mathrm{Cl, I})$$

	k_1, dm^3·mol^{-1}·s^{-1}	k_2, dm^3·mol^{-1}·s^{-1}	K_e, dm^3·mol^{-1}
	$(9.1 \pm 0.8) \times 10^{-5}$ [a]	$(6.5 \pm 0.1) \times 10^{-4}$ [a]	235 ± 15 [a]
	$(9.2 \pm 0.2) \times 10^{-5}$ [b]	$(6.4 \pm 0.1) \times 10^{-4}$ [b]	227 ± 5 [c]
$\Delta H^\ddagger$, kJ·mol^{-1}	51.9 ± 0.4	44.7 ± 1.7	
$\Delta S^\ddagger$, kJ·mol^{-1}·deg^{-1}	-146 ± 4	-159 ± 4	

[a] Values obtained by using the SPSS program with rate law 3 as model. [b] Values obtained for $[\mathrm{I^-}] = 0$ (k_1) and $[\mathrm{I^-}] = 0.5$ mol·dm^{-1} (k_2). [c] Determined spectrophotometrically.

Kinetics. Electronic absorption spectra were measured and the reactions were followed on a Cary 15 spectrophotometer with a thermostated cell compartment, at temperatures of (20, 25, 30, 35) ± 0.1 °C. Pseudo-first-order conditions were maintained by ensuring that the concentrations of the methyl iodide were at least a factor of 30 greater than that of the starting complexes.

The reactions were followed at λ 550 nm, which corresponds to studying the rate of disappearance of the starting complex. Data were obtained at iodide concentrations (1, 2, 3, 5, 10, 500) × 10^{-3} mol·dm^{-3}. The ionic strength was kept constant with lithium chloride at μ = 0.01.

The final UV–vis spectra of the reaction solutions were compared with those obtained from the prepared products and found to be identical. Also, the UV–vis spectra of [(cod)Ir(phen)(CH$_3$)(I)]X (X = Cl, I) were found to be identical.

Registry No. [Ir(cod)(phen)]Cl, 53522-11-5; [Ir(cod)(phen)]I, 80048-97-1; CH$_3$I, 74-88-4; [(cod)Ir(phen)(CH$_3$)(I)]Cl, 80041-65-2; [(cod)Ir(phen)(CH$_3$)(I)]I, 80041-66-3.

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Electron Paramagnetic Resonance Study of Nitrogen-Bridged Iron Porphyrin Dimers

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The determination of the physicochemical properties of μ-nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron], [(TPP)Fe]$_2$N, has been actively pursued,[1-7] as this is the first

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