The following compounds/mixtures of compounds were isolated (figures in parentheses represent the relative proportions of the isomers). $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3** (9) + **4** (1)): Anal. Calcd for $C_{19}H_{18}Cl_4ON_4P_4$: C, 39.1; H, 3.1; N, 9.6. Found: C, 39.5; H, 3.9, N, 9.4. $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**3**): mp 178 °C; R_f (TLC, silica gel, eluant benzene) 0.66. $N_3P_3(NPPh_3)(OCH_3)Cl_4$ (**4**): mp 174 °C, R_f 0.70. $N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ [**5** (4) + **6** (1)]: mp 149 °C; R_f 0.36. Anal. Calcd for $C_{20}H_{21}Cl_3O_2N_4P_4$: C, 41.1; H, 3.6. Found: C, 40.8; H, 3.6. $N_3P_3(NPPh_3)(OCH_3)_2Cl_3$ [**7** (15) + **8** (10) + **5** (1)]: mp 143 °C; R_f 0.36. Anal. Calcd for $C_{20}H_{21}Cl_3O_2N_4P_4$: C, 41.4; H, 3.6. Found C, 41.3; H, 3.7. $N_3P_3(NPPh_3)(OCH_3)_3Cl_2$ (**9**): mp 138 °C; R_f 0.08, 0.65 [eluant benzene–ethyl acetate (5:1)]. Anal. Calcd for $C_{21}H_{24}Cl_2O_3N_4P_4$: C, 43.8; H, 4.2. Found: C, 44.3; H, 4.6. $N_3P_3(NPPh_3)(OCH_3)_4Cl$ (**11**): mp 128 °C; R_f 0.26. Anal. Calcd for $C_{22}H_{27}ClO_4N_4P_4$: C, 46.3; H, 4.7. Found: C, 46.8; H, 5.0. $N_3P_3(NPPh_3)(OCH_3)_5$ (**12**): mp 150 °C, R_f 0.10 (for C, H, N analyses see ref 50).

The mass spectra of the mixture **5** (15) + **6** (18) + **7** (9) + **8** (11) + **9** (2) and of the compounds **9** and **12** were recorded. They show $[M]^+$ and $[M - H]^+$ peaks (M = molecular ion).

The purity of the fluoro derivatives **13–20** has been confirmed by mass spectrometry. They showed peak corresponding to $[M]^+$, $[M - H]^+$, $[M - Ph]^+$, $[M - OCH_3 - 2H]^+$, and $[PPh_2 - 2 H]^+$. The melting points and TLC R_f values of these compounds were as follows: $N_3P_3(NPPh_3)(OCH_3)F_4$ (**13**), mp 89 °C, R_f 0.62 (eluant benzene); $N_3P_3(NPPh_3)(OCH_3)F_4$ (**14**), mp 123 °C, R_f 0.66; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**15**), mp 126 °C, R_f 0.40; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**16**) (as a mixture with a small quantity of **15**), mp 105 °C, R_f 0.44; $N_3P_3(NPPh_3)(OCH_3)_2F_3$ (**17**), mp 78 °C, R_f 0.44; $N_3P_3(NPPh_3)(OCH_3)_3F_2$ (**18**) (as a mixture with **19**, a ratio 1:1), mp 89 °C, R_f 0.62 [eluant benzene–ethyl acetate (5:1)]; $N_3P_3(NPPh_3)(OCH_3)_3F_2$ (**19**), mp 92 °C, R_f 0.64; $N_3P_3(NPPh_3)(OCH_3)_4F$ (**20**), mp 152 °C, R_f 0.26.

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Supplementary Material Available: IR spectroscopic data for compounds **1–20** (Table V) (2 pages). Ordering information is given on any current masthead page.

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Spectral Characterization and Kinetics of Formation of Hypoiodous Acid in Aqueous Solution

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The UV–visible absorption spectrum of the transient HOI species was obtained by utilizing the anion-exchange capacity of the mercury carbide polymer $[Hg_3CO(ClO_4)]_n$. The spectrum of HOI exhibited an absorption maximum at 278 nm in agreement with a recently reported spectrum obtained by a different method. The kinetics of hydrolysis of iodine to form HOI and I^- were studied at 20 °C and an ionic strength of 0.1 M by temperature-jump spectrophotometry. In contrast to the halogens, Cl_2 and Br_2, the rate of hydrolysis is controlled by the disproportionation of the conjugate base, I_2OH^-, with a rate constant of 994 ± 36 s^{-1}.

Introduction

The halogens, Cl_2, Br_2, and I_2, are known to undergo rapid hydrolysis, or water-assisted disproportionation, according to the equation

$$X_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOX + X^- + H^+ \tag{1}$$

The only complete set of kinetic results for this reaction was provided by Eigen and Kustin,[1] whose temperature-jump experiments established the general rate law

$$k_{obsd} = k_1 + k_{-1}\{[HOX][X^-] + [H^+][X^-] + [HOX][H^+]\} \tag{2}$$

These results are summarized in Table I together with the values of the relevant equilibrium constants. For X = Cl and Br, the values of k_1 and k_{-1} were determined directly from the respective intercepts and slopes of plots of k_{obsd} vs. $[HOX][X^-] + [H^+][X^-] + [HOX][H^+]$, whereas for X = I, k_{-1} was considered to be so much greater than k_1 that the intercept could not be determined with accuracy by this method and therefore k_1 was calculated from the relationship

$$k_1 = K_1 k_{-1} \tag{3}$$

Table I. Summary of Rate and Equilibrium Constants at 20 °C and μ = 0.1 M

X	k_1, s^{-1}	k_{-1}, $M^{-2}\ s^{-1}$	K_1, M^2	ref
Cl	11.0	1.8×10^4	6.0×10^{-4}	1
	5.6^a			2
			$3.46 \times 10^{-4\,b}$	3
Br	110	1.6×10^{10}	6.9×10^{-9}	1
			4.46×10^{-9}	4
I	2.8^c	4.4×10^{12}	$4.3 \times 10^{-13\,b}$	1, 5
			$3.13 \times 10^{-13\,b,d}$	6

[a] A calorimetric flow technique was used at 9.5 °C. [b] $\mu \simeq 0$. [c] Differs slightly from 3.0 s^{-1} quoted in the original reference[1] because a different value for K_1 was used (i.e. 6.25×10^{-13} M^2). [d] Obtained from a quadratic fit of all the current literature data.

However, it should be noted that this k_1 value is two orders of magnitude smaller than would have been obtained from the actual intercept, which is ca. 450 s^{-1}. Preliminary stopped-flow experiments, in which solutions of iodine and carbonate buffers were mixed, indicate that hydrolysis must be complete within the mixing

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time of the instrument, thereby setting a low limit of ca. 10^3 s^{-1} on k_1. Although these measurements may be affected by base and/or buffer catalysis, a reinvestigation of iodine hydrolysis kinetics was deemed necessary.

Finally, in view of the importance of aqueous iodine chemistry to the nuclear industry, particularly with respect to the volatile hydrolysis products, the physical characterization of HOI has become a significant goal. The absorption maxima of HOI and OI^- in solution are now presented here.

Experimental Section

Commercially sublimed iodine was resublimed before use, although this precaution had no observable effects on the results. The mercuric carbide polymer $[Hg_3CO(ClO_4)]_n$ was prepared from the nitrate salt[7] by washing the solid with a $NaClO_4$ solution followed by repeated washing with a large volume of distilled water. All solutions were prepared from deionized, doubly distilled water.

The concentration of iodine in the stock solutions was determined by titration with a standardized sodium thiosulfate solution using a weight buret.

Hypoiodous acid was generated by rapidly stirring a slurry of the mercarbide polymer in a 10^{-3} M $HClO_4$ solution of iodine. After about 20 s the mixture was transferred to a 50-cm^3 glass syringe and filtered directly into a 5-cm quartz cell through a 1.2-μm Millipore filter. The cell was placed immediately into a spectrophotometer, and repetitive scans were recorded (500–230 nm). A 2-cm^3 aliquot of the filtered solution was immediately analyzed for its equivalent I_2 content by potentiostatic coulometry, i.e., by reduction of the total oxidized species to I^- at 0.1 V (vs. SCE) at a Pt working electrode. Note that the solution was reanalyzed at the completion of the experiment and the same total equivalent I_2 content was always found (i.e. to within ±1%).

Despite repeated washing of the mercarbide polymer prior to use, traces of HgI_2 were still present in the final HOI solution (eg. 1.5 ± 0.5 ppm or 7.5×10^{-6} M as determined by atomic absorption in a solution initially 4.00×10^{-4} M in HOI as determined coulometrically). As HgI_2 has an absorptivity of 4570 M^{-1} cm^{-1} at 265 nm, its contribution to the overall spectrum must be assessed. This was accomplished by sparging the "HOI solution" with argon to remove the volatile I_2 product of disproportionation until the final solution contains only HgI_2 and IO_3^-, where the spectral contribution of the latter only becomes important at shorter wavelengths, i.e. <240 nm. From the absorptivity of HgI_2 its concentration can be estimated at 5.6×10^{-6} M (in reasonable agreement with the atomic absorption value), which corresponds to a correction in the maximum absorptivity of HOI of ca. 15%. It is interesting to note that HOI was not purged from these solutions by the argon flow to any measurable extent, which is consistent with the assumed low volatility of HOI in aqueous solution.

The absorption spectrum of the hypoiodite ion was recorded with a rapid-scan, stopped-flow apparatus by mixing solutions of millimolar iodine and 1 M NaOH. The corresponding absorption maximum is listed in Table II.

The kinetics of reaction 1 were monitored at 350 nm with a Studiengesellschaft temperature-jump spectrophotometer, the output from which was stored on a Nicolet digital oscilloscope. The reaction chamber was Teflon-lined and contained either platinum or gold-plated platinum electrodes. These experiments were initiated by a capacitor discharge of 25–30 kV where the rise time was 1 μs. The pH of each solution was first adjusted to the desired value with either 0.1 M HNO_3 or 0.1 M NaOH. The spectrum of the solution was recorded immediately prior to the actual kinetic measurement. The ionic strength was maintained at 0.1 M with KNO_3. It should be noted that no secondary buffering of these solutions was attempted and that these conditions are exactly the same as outlined in the original study.[1]

Results and Discussion

Spectra. Hypoiodous acid was generated by the complete removal of iodide ions from the acidified iodine solution. Explicitly, the mercarbide polymer exchanges iodide for perchlorate ions, forcing eq 1 completely to the right at the expense of the otherwise stable iodine. The polymer $[Hg_3CO(X)]_n$, where X = Cl, Br, OH, NO_3, or ClO_4, is known[7,8] to have an extremely high distribution coefficient (>10^4) in favor of iodide ion. Moreover, this inorganic ion exchanger is not subject to oxidation by either I_2 or HOI as are commercial organic resins. The exchange is very rapid as evidenced by the immediate temporary loss of color, and hence I_2, by the solution. The lack of any spectral evidence for I_3^-, which exhibits intense peaks at 350 and 288 nm (absorptivities of 25 800 and 38 800 M^{-1} cm^{-1}, respectively),[9] attests to the completeness of the exchange. Indeed, it is the dominating presence of the triiodide ion that interferes with the direct spectral identifiction of HOI in I_2 solutions.

Table II. Absorption Maxima in the Spectra of Hypohalous Acids and Salts

acid	λ_{max}, nm ϵ, M^{-1} cm^{-1}	ref	anion	λ_{max}, nm ϵ, M^{-1} cm^{-1}	ref
HOCl	235 (100)	10–12	OCl^-	290 (360)	14
	235 (94)	13[a]		292 (350)	12
				293 (360)	15[a]
				295 (320)	11[a]
HOBr	260 (96)	13[a]	OBr^-	330 (303)	16
				331 (326)	17
				333 (173)	13[a]
HOI	278 (200)	this work	OI^-	370 (60)	15[a]
				365 (31)	18
				370 (60)	19
				365 (58)	this work

[a] Estimated from a figure in the referenced paper.

Following the initial exchange process, a further spectral change occurs over a period of many minutes with the reappearance of the peak at 460 nm characteristic of aquated iodine. However, there was no trace of the triiodide peaks. In addition, two isosbestic points were observed at 377 and 261 nm, consistent with a single rate-determining step governing the kinetics of disappearance of HOI. Qualitatively, at least, this behavior can be rationalized by either of the following reactions, or a combination thereof:

$$5HOI = 2I_2 + IO_3^- + H^+ + 2H_2O \qquad (4)$$

$$4HOI = 2I_2 + O_2 + 2H_2O \qquad (5)$$

Equation 4 represents the spontaneous disproportionation of HOI, while eq 5 results from the reduction by water. Both reactions are favored thermodynamically to go to completion under the prevailing conditions. However, the fact that the equivalent total iodine content of the solution (as determined by coulometry) remains constant during this reaction establishes eq 4 as being responsible for this spectral change. Moreover, the nonreappearance of iodide ion is only consistent with eq 4 due to the overriding Dushman reaction (viz. $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$).

The spectrum of HOI was derived by assuming that the absorption at 460 nm in the first scan is attributable solely to I_2, thus giving the concentration of I_2, whose contribution to the rest of the scan could then be subtracted, with the increase in $[I_2]$ during the time of the scan taken into account. The wavelength at the absorption maximum is given in Table II for comparison with HOX acids. The trend in λ_{max} values parallels that observed for the anion. More significantly, Paquette and Ford[19] have generated HOI in solution by the quantitative oxidation of I^- with HOCl and recorded its spectrum by stopped-flow rapid-scan spectrophotometry. This elegant method gave an absorption maximum at 285 nm (ϵ = 200 M^{-1} cm^{-1}), in reasonable agreement with our result, and they also observed isosbestic points at 377 and 261 nm.

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Table III. Summary of Kinetic Data Pertinent to Iodine Disproportionation

pH	$10^4[I_2]$, M	$10^5[I^-]$, M	$10^6[HOI]$, M	k_{obsd},[a] s^{-1}
2.95	6.82	3.50	0.0115	1020 ± 50
3.62	8.42	2.89	0.0759	970 ± 50
4.44	8.37	3.00	0.480	980 ± 20
5.27	8.96	3.19	3.28	970 ± 40
5.35	8.95	3.04	4.13	950 ± 70
5.36	8.71	2.93	4.25	980 ± 40
5.75	8.74	3.20	9.59	1040 ± 40
7.06	4.99	8.92	40.2	1050 ± 40

[a] Each k_{obsd} value is the mean of eight measurements, at 20 °C and $\mu = 0.1$.

The spectrum of HOI may be affected slightly by the presence of its conjugate acid, H_2OI^+, which has a reported K_a value of 0.03 at 25 °C.[20] However, as the pH of the measured solution was 3, H_2OI^+ would only represent ca. 3% of the total "I^+".

As a final comment on this procedure, the spectrum of HOBr in aqueous solution was also obtained by a procedure analogous to that described here for HOI and was found to agree with the literature value (see Table II) to within 7% at 260 nm.

Kinetics. As in the previous investigation,[1] the disproportionation of iodine was followed at 350 nm, which corresponds to an absorption maximum of I_3^-. Thus any perturbation of equilibrium 1 results in an adjustment of eq 6, which has been independently

$$I_2 + I^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} I_3^- \tag{6}$$

shown[21] to respond so rapidly that its kinetics do not influence the kinetics of the former (i.e., $k_6 = 6.2 \times 10^9$ M^{-1} s^{-1} and $k_{-6} = 8.5 \times 10^6$ s^{-1} at 25 °C and $\mu = 0.02$ M). As will be discussed later, it is pertinent that no change was detected at 460 nm (the absorption maximum of I_2) following the temperature jump, whereas the corresponding reactions of Cl_2 and Br_2 were readily monitored at their absorption maxima. This is despite the fact that the ΔH_1 value for X = I (69.9 kJ mol^{-1}) is larger than for X = Cl and Br (21.2 and 53.9 kJ mol^{-1}, respectively)[22] and the fact that the expected change in absorptivity for I_2 at its peak is also larger than the corresponding changes for the other two.

The solution conditions of the previous study[1] were also preserved (viz. total $[I_2]_0 \simeq 10^{-3}$ M, $\mu = 0.1$ M (KNO_3), and 20 °C). The initial series of experiments with platinum electrodes gave erratic results over the pH range 2.95–6.20, consistent with indications of irreversible decomposition upon discharge. When each experiment was conducted with a fresh solution, better reproducibility was achieved. However, the results proved to be highly reproducible with gold-plated electrodes. These data are summarized in Table III together with the calculated concentrations of the reactant species. These calculations were based on the absorptivities of I_2 and I_3^- at 350 nm (16.1 and 25 800 M^{-1} cm^{-1}) and 460 nm (731 and 972 M^{-1} cm^{-1}),[9] as well as the equilibrium constants K_1 (6.25×10^{-13})[23] and K_6 (698).[9]

It is immediately apparent from these results that, unlike the case for the previous study,[1] no pH dependence of k_{obsd} was observed. Although, of the five results reported by Eigen and Kustin[1] in a plot of $1/\tau$ vs. $[HOI][H^+] + [HOI][I^-] + [I^-][H^+]$, four (pH $\simeq 5$) show rate constants similar to those obtained here (e.g., ca. 660–980 s^{-1}), whereas the fifth at pH $\simeq 4$ is substantially higher (ca. 2300 s^{-1}). As these findings are not compatible with eq 2, particularly at lower pH where the $[H^+]$ terms in such a plot should dominate, an alternative mechanism is required. One possible reaction sequence could involve H_2OI^+ as an intermediate:

$$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^- \tag{7}$$

$$H_2OI^+ \rightleftharpoons H^+ + HOI \tag{8}$$

The equilibrium constants are $K_7 = 1.2 \times 10^{-11}$ (25 °C)[20] and $K_8 = K_1/K_7 = 0.05$. When the forward rate constant for disproportionation is allowed to equal the mean k_{obsd} value from Table III, viz. 994 ± 35 s^{-1} ($=k_7$), $k_{-7} = k_7/K_7 = 8 \times 10^{13}$ M^{-1} s^{-1}, which is well beyond the limits for a diffusion-controlled process. When we reject this path, as did Eigen and Kustin,[1] the alternative sequence can be considered:

$$I_2 + H_2O \rightleftharpoons I_2OH^- + H^+ \tag{9a}$$

$$I_2 + OH^- \rightleftharpoons I_2OH^- \tag{9b}$$

$$I_2OH^- \rightleftharpoons HOI + I^- \tag{10}$$

By the same logic applied above, with $k_{10} = 994$ and $K_{10} = 3.1 \times 10^{-3}$,[6] $k_{-10} = 3.2 \times 10^5$ M^{-1} s^{-1}. This translates into a k_{obsd} value at the maximum measured value of $[HOI] + [I^-] = 1.29 \times 10^{-4}$ M (the run at pH 7.06) of only 1035 M^{-1} s^{-1}. In other words, the range of [HOI] and $[I^-]$ is too narrow to observe the reverse reaction. Theoretically, this could be achieved either by raising the pH further, with the secondary disproportionation of HOI to I^- and IO_3^- becoming fast enough to bias the results, or by adding I^-. However, the latter would result in very high absorbance readings due to the predominance of I_3^- and would remove the sensitivity of eq 6 to small changes in $[I^-]$. $[I_2]$ is limited by the solubility of I_2, 1.326×10^{-3} M.[24] Nevertheless, it is at least indicative that a linear least-squares fit of k_{obsd} vs. $[HOI] + [I^-]$ yields $k_{10} = 963$ s^{-1} and $k_{-10} = 6.7 \times 10^5$ M^{-1} s^{-1} (cf. above $k_{-10} = 3.2 \times 10^5$ M^{-1} s^{-1}).

The preferred values for K_{9a} and K_{9b} are 2.0×10^{-10} M and 2.9×10^4 M^{-1},[6] based primarily on the estimates of Chia,[15] rather than those of Sigalla,[25] who reported a K_{9a} value of 4.5×10^{-11} M at 25 °C. Assuming diffusion-controlled rate constants for k_{-9a} and k_{9b} of ca. 10^{10} M^{-1} s^{-1}, then $k_{9a} \simeq 2$ s^{-1} and $k_{-9b} \simeq 3 \times 10^5$ M^{-1} s^{-1}. Under the pH conditions of the current experiments, the deprotonation equilibrium (eq 9a) is faster at low pH, while the base hydrolysis equilibrium (eq 9b) is faster and therefore dominates the two equilibria, at pH $\gtrsim 7$. More importantly, the acid–base equilibria (eq 9a and 9b) involved in the formation of I_2OH^- are significantly slower than the disproportionation of I_2OH^- (eq 10a) over the measured pH range of 2.95–7.06. This is consistent with the rate law suggested above, $k_{obsd} = k_{10} + k_{-10}\{[HOI] + [I^-]\}$.

The one difficulty with this mechanism is the very low concentrations of I_2OH^- that exist at low pH. Certainly, the magnitude of the change in absorbance accompanying the temperature jump increased with increasing pH, reflecting the increase in I_2OH^- concentration. Perhaps more significantly, as discussed earlier, the change in concentration for a given temperature increase is about 3 orders of magnitude smaller for the iodine system as compared to that for the other halogens. This was evidenced by the need to monitor the reaction via the magnifying effect of eq 6, despite the fact that ΔH_{10} is 20.5 kJ mol^{-1}, which is very similar to ΔH_1 for the chlorine system.

The reason for the shift in the rate-determining step for the sequence of reactions 9 and 10 in the disproportionation of iodine as compared to those of chlorine and bromine is not obvious. However, presumably the reduced strength of the X–X bond for X = I contributes by enhancing the rate of the disproportionation of X_2OH^-, where the X–X bond is broken. The greater basicity of iodine results in the acid–base equilibria responsible for I_2OH^- formation being significantly slower than for X = Cl and Br. Note that even if it were experimentally possible to extend the pH range beyond 7, it is conceivable that the equilibration of eq 9b for X = I would become fast enough to compete with the kinetics of

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eq 10 and thus shift the mechanism back to an overall third-order process for k_{-1}.

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A Convenient General Synthesis of *trans*-$[IrCl(CO)(PR_3)_2]$

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$[IrCl(cod)]_2$ is treated at room temperature with 4 mol equiv of PR_3 (R = Ph, C_6H_{11}, o-MeC_6H_4) and then CO to give the title complexes. In the case of PMe_3, $[IrCl(cod)]_2$ was converted to the new complex $[IrCl(cod)(PMe_3)_2]$, which on treatment with CO gave $[IrCl(CO)_2(PMe_3)_2]$. This readily loses CO in vacuo at 25 °C and in the solid state to give the title complex, which is a reversible CO carrier.

Vaska's complex[1] and its analogues have a special place in inorganic chemistry because of the importance of the oxidative-addition reactions that were discovered in this series. Surprisingly, the syntheses of these complexes[2–7] have almost always been carried out by reduction of Ir(III) or Ir(IV) precursors, often with a refluxing high-boiling solvent. In other cases, substitution reactions involving $[IrCl(CO)(PPh_3)_2]$ or $[Ir(CO)_3Cl]$ were used.[2,5,7a] For some recent investigations in alkane activation chemistry, we required a range of these complexes with different phosphines. We therefore investigated routes starting from the readily available Ir(I) species $[IrCl(cod)]_2$.

Two successful routes are described below, one for PMe_3 and the other for larger cone angle phosphines. A report by Labinger and Osborn[7b] describes a synthesis for the Vaska analogue containing PMe_2Ph, a case in which conventional syntheses fail. This synthesis, although unsuitable as a general method because of the alcohol solvents used, is similar to the route described here. The PMe_3 complex has also been prepared by the same authors[7a] from $[Ir(CO)(PMe_3)_4]Cl$ by repeated sublimations to drive off two of the PMe_3 ligands. Our methods involve only room-temperature, ambient-pressure reactions and are high-yield, rapid, and convenient. In each case the starting material is the commercially available $[IrCl(cod)]_2$.[8]

Results and Discussion

Equation 1 shows the general method for the synthesis of $[IrCl(CO)L_2]$ derivatives. We have not yet found a case where this method does not work, apart from that of PMe_3, for which we also report a second, closely related method. We find that the use of hexanes is essential to both methods because it prevents, or at least minimizes, the expulsion of the chloride ion from the coordination sphere of the metal to give ionic byproducts. This occurs particularly easily with the smaller, more basic phosphines. In contrast to previous methods,[2–7] all the steps involve only room-temperature reactions. In a nonionizing solvent, the larger tertiary phosphines are known[9,10] only to break the chloro bridge of $[IrCl(cod)]_2$ (**1**) to give the monomeric species **2**. The value of n in **2** can be 1 or 2 according to the size of the phosphine and whether the material has been recrystallized or not. Only when CO is added, is cod displaced. Complexes of type **3** are formed in quantitative yield over 1 h and can be crystallized to give the isolated materials in 85–95% yield, depending on the solubility of the product.

$$\underset{\mathbf{1}}{[Ir(cod)Cl]_2} \xrightarrow{PR_3} \underset{\mathbf{2}}{[IrCl(cod)(PR_3)_n]} \xrightarrow{CO} \underset{\mathbf{3}}{[IrCl(CO)(PR_3)_2]} \quad (1)$$

This method is not applicable to the case of PMe_3, and so we were forced to consider alternatives. The best method requires isolating the intermediate of type **2** and is shown in eq 2 and 3.

$$\underset{\mathbf{1}}{[IrCl(cod)]_2} \xrightarrow{PMe_3} \underset{\mathbf{2}}{[IrCl(PMe_3)_2(cod)]} \quad (2)$$

$$\underset{\mathbf{2}}{[IrCl(PMe_3)_2(cod)]} \xrightarrow{CO} \underset{\mathbf{4}}{[IrCl(PMe_3)_2(CO)_2]} \quad (3)$$

$$\underset{\mathbf{4}}{[IrCl(PMe_3)_2(CO)_2]} \xrightarrow[\text{in vacuo}]{-CO} \underset{\mathbf{3}}{[IrCl(CO)(PMe_3)_2]} \quad (4)$$

Again, the first two steps are carried out in hexanes. Non-alkane solvents appeared to react with **2** to give uncharacterized materials and so were unsuitable. In the first step, some $[Ir(cod)(PMe_3)_3]Cl$ was also formed as a white precipitate but could be removed by filtration. Either the new complex **2** can be isolated at this stage, or, more conveniently, the solution can be treated with CO directly without isolation. The second step forms the dicarbonyl complex **4**. This is particularly convenient to isolate because, unlike **3**, it is relatively insoluble in hexanes. This complex (**4**) appears to be a classical 5-coordinate species and is fluxional on the NMR time scale down to −70 °C. It shows two bands in the IR spectrum at 1909 and 1970 cm^{-1} corresponding to the asym and sym stretching vibrations, with an intensity ratio appropriate to a ca. 120° interligand angle (calculated angle from IR data 123°). The

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