

Binding and Activation of Halocarbons by Iron(II) and Ruthenium(II)

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A series of cyclopentadienylruthenium(II) and -iron(II) complexes contain intact iodoalkanes, *p*-iodotoluene, or chelating (P, X) (*o*-halophenyl)diphenylphosphine (X = Cl, Br) ligands. The halocarbons coordinate via σ -donation of a halogen lone pair and retain their carbon-halogen bonds. The complexes are synthesized from the halocarbon, metal halide, and silver(I) ion. Full characterization shows that they are Ru(II) complexes of intact halocarbons rather than Ru(IV) products of oxidative addition. The crystal and molecular structure of one such complex, $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{IC}_6\text{H}_4\text{-}p\text{-CH}_3)]\text{PF}_6$, is reported ($P1$, $a = 10.976$ (3) Å, $b = 11.329$ (3) Å, $c = 13.666$ (4) Å, $\beta = 102.62$ (3)°, $Z = 2$, $R_1 = 0.054$, $R_2 = 0.065$). The iodoalkanes are activated by coordination, and the complexes cleanly and rapidly alkylate a wide range of inorganic and organic nucleophiles. In particular, carbon-carbon bonds can be formed with C-nucleophiles such as enamines. The halocarbon complex can be much more selective than free halocarbon for C-alkylation over N-alkylation. The iodoalkane complexes undergo ligand substitution with common coordinating solvents to produce the corresponding solvento complexes. The haloarene complexes are displaced only by nucleophiles. Equilibrium experiments demonstrate that the order of binding is chelated *o*-bromoarene > chelated *o*-chloroarene > iodomethane > *p*-iodotoluene. The presence of carbonyl groups on Ru makes the metal more electrophilic, resulting in slower ligand exchange and less selective alkylations.

Introduction

Molecules that bind to transition metals either tend to be good σ -bases, in which case significant binding to the proton is also observed, or are good π -acids, in which case they often form stable oxides. For example, the σ -base NH_3 forms the NH_4^+ ion, and the π -acid CO readily forms CO_2 , a stable "complex" with the oxygen atom. Some ligands, such as PET_3 , do both. Very few molecules are known to act as ligands that do not fall into one of these two categories. The fact that PR_3 is an excellent ligand and SR_2 is a moderately good one encouraged us in 1981 to begin a study of the group 17 analogues, the halocarbons RX . These do not protonate, and the oxides $\text{RX}=\text{O}$ are known only for R = aryl and X = I and even then are not very stable, being excellent oxidants. It was therefore not obvious that halocarbons would bind to metals.

Halocarbons more commonly oxidatively add to metal complexes to give alkyl- or arylmetal halides. In this, they form a small but significant group of X-Y ligands, such as H_2 and $\text{R}_3\text{Si-H}$, for which both nondissociative (M-X-Y) and dissociative (X-M-Y) binding has been observed but for which the latter is more common. For HO-H, Ph-H, $\text{Ph}_2\text{P-H}$, and $\text{R}_2\text{N-H}$, in contrast, both types of binding are known, but the nondissociative type is more common, and for alkanes, R-H, only dissociative binding is known. In all the cases examined, nondissociative binding leads to an activation of the X-Y ligand by making it more acidic (e.g., H_2 , H_2O , R_2NH) or more subject to nucleophilic attack (e.g., MeI, $\text{R}_3\text{Si-H}$, PhH), as a result of depletion of electron density on X-Y by the Lewis acidic metal fragment.

We chose the chelating haloarenes $o\text{-C}_6\text{H}_4\text{X}_2$ for our initial studies and were able to demonstrate binding to Ir(III) by an unambiguous crystallographic study.^{1a} Previous suggestions for halocarbon binding either proved misconceived on detailed crystallographic study or were

based on IR data alone. Even iodoalkanes can bind,^{1d} and complexation was shown to accelerate nucleophilic attack at the halocarbon α -carbon by a factor of ca. 10^5 – 10^6 . We^{1c-f} and others² have shown that ligands such as $\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-X}$ (X = Br, Cl) can chelate via both the phosphorus and the ortho-halogen atom to iridium and rhodium, as demonstrated by X-ray crystallography. Gladysz has also seen halocarbon binding,³ but to Re(I), and has even characterized both the Re(I) haloalkane complex and an alkyl Re(III) halide. Recent examples of haloalkane coordination to Ru(II)⁴ and Ag(I)⁵ have been reported, in addition to several examples of secondary bonding⁶ between haloarenes⁷ and transition metals.

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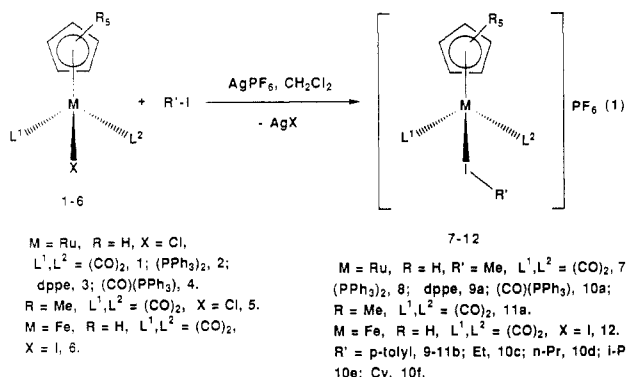
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We now report halocarbon binding to Fe(II) and Ru(II), together with structural data in one case. The ready reaction of these new complexes with a variety of nucleophiles, including carbon nucleophiles, makes them interesting candidates for organic synthetic applications. We find large rate enhancements and useful changes in selectivity in reactions with enamines. Some of this work has appeared as a communication.^{1e}

Results and Discussion

We wanted to see what metals can form halocarbon complexes. Since examples from groups 7 and 9 are known, we chose the group 8 Lewis acids $[\text{CpML}_2(\text{L}')^+]$ because they form many stable cationic complexes, are relatively resistant toward oxidative addition, are easily handled and characterized, and are convenient for IR and NMR studies.⁸ In addition, these complexes have received wide attention as reagents in organic synthesis because of their ability to coordinate and activate π -bonds toward nucleophilic attack⁹ as well as to stabilize alkylidene¹⁰ and vinylidene¹¹ groups.

Synthesis, Characterization, and Physical Properties. We prepared the halocarbon complexes shown in eq 1 by standard halide abstraction from the halocarbon (10–20 equiv), the neutral starting material $(\text{C}_5\text{R}_5)(\text{L}^1)(\text{L}^2)\text{MX}$, and AgPF_6 in dichloromethane.



For the secondary iodoalkane complexes (10e and 10f), we had to add the halocarbon after addition of silver salt in order to prevent iodide abstraction from the organic compound by Ag^+ . After filtration through Celite, the yellow-to-red microcrystalline complexes are isolated in 60–80% yields by precipitation with diethyl ether or alkanes. They are moderately air sensitive in solution but can be stored under N_2 at -10°C . The mixed carbonyl phosphine complexes 10a–f are more stable than the all-phosphine analogues, which darken upon exposure to air in solution. The dicarbonyl complexes appear to be less thermally stable; elemental analyses were variable and inconsistent with spectroscopic data. All other complexes gave satisfactory combustion analyses (see Experimental Section).

The structures of these complexes follow directly from the spectroscopic data and in one case (10b) an X-ray crystal structure determination. In general, formation of the cationic products induces a downfield shift in the ^1H

NMR resonance of +0.34 to +0.46 ppm (Cp) and +0.22 ppm (Cp*), compared to the halide starting materials. Similar shifts are observed in complexes of these metal fragments containing other ligands, such as the acetonitrile complexes discussed below. The halocarbon resonances also generally shift downfield upon coordination; for example, $\Delta\delta(\text{MeI})$ for the MeI complexes are +0.52 ppm for 7, +0.23 ppm for 10a, +0.45 ppm for 11a, and +0.40 ppm for 12. Exceptions occur in those complexes having two phosphorus ligands (i.e., 8, 9a, $\Delta\delta(\text{MeI}) = -0.02, -0.98$ ppm), in which upfield shifts are observed, presumably due to anisotropic effects of the aryl rings.

In the bis(triphenylphosphine) iodomethane complex 8, both the Cp and MeI resonances are broad, presumably due to rapid exchange of the MeI at room temperature. The iodoethane, 1-iodopropane, and 2-iodopropane complexes 10c–e show diastereotopic methylene (10c,d) and methyl (10e) resonances, because of the presence of a chiral metal center; the 2-iodopropane complex shows a diastereotopic chemical shift of 0.016 ppm. The *p*-iodotoluene complexes show downfield shifts in the para-methyl resonance ($\Delta\delta(p\text{-MeC}_6\text{H}_4\text{I}) = +0.02$ ppm for 10b, +0.04 ppm for 11b) while the dppe complex 9b has $\Delta\delta(p\text{-MeC}_6\text{H}_4\text{I}) = -0.09$ ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 10a–f show $\Delta\delta(\text{PPh}_3) = +2\text{--}4$ ppm relative to the neutral chloride. The infrared stretching frequencies in carbonyl complexes 7, 10a–f, 11a,b, and 12 appear at higher energy than in the neutral complexes ($\Delta\nu(\text{CO}) = 20\text{--}35\text{ cm}^{-1}$) and are all indicative of the formation of cationic Ru(II) or Fe(II) complexes. In addition, a strong band at 844 cm^{-1} , diagnostic for hexafluorophosphate anion, is present in the IR spectrum of each complex.

At no time have we seen oxidative addition to form cationic Ru(IV) complexes. All of them are clearly Ru(II) species containing intact halocarbon ligands for several reasons.

(1) In those complexes containing one or two phosphine ligands, we do not observe phosphorus coupling in the ^1H NMR resonances of the protons α to iodine in the halocarbon. Had oxidative addition occurred in MeI complexes 9a or 10a to give, for example, the as yet unreported ruthenium(IV) complexes $[\text{Cp}(\text{dppe})\text{Ru}(\text{I})(\text{Me})]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) or $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{I})(\text{Me})]^+$, the methyl resonance would show coupling to ^{31}P , as has been observed in all other ruthenium(II) and -(IV) (alkyl)(phosphine) complexes.¹²

(2) In those complexes containing one or two carbonyl groups, the carbonyl stretching frequencies are in the range expected for cationic Ru(II) or Fe(II) complexes. For example, the ν_{CO} is 1993 cm^{-1} in $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{MeCN})]\text{PF}_6$, a complex in which oxidative addition of MeCN to form a Ru(IV) species does not occur;¹³ the same stretching frequency is observed in the analogous MeI complex 10a. Relatively few Ru(IV) carbonyl complexes have been reported, none of them cationic. All of the neutral Ru(IV) complexes show ν_{CO} at substantially higher energy relative to the Ru(II) analogues (e.g., 2050 cm^{-1} in $(\text{C}_5\text{Me}_4\text{Et})\text{Ru}(\text{CO})\text{Br}_3$ compared to 2030 and 1982 cm^{-1} in $(\text{C}_5\text{Me}_4\text{Et})\text{Ru}(\text{CO})_2\text{Br}^{14}$). Johnston and Baird have re-

(12) For example: ^1H NMR $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuMe}$, δ 0.07 (d, $^3J_{\text{PH}} = 5.3$ Hz, Me);^{12a} $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\text{Me})(\text{H})]\text{BF}_4$, δ 0.35 (t, $^3J_{\text{PH}} = 6.3$ Hz, Me).^{12b} (a) Howell, J. A. S.; Rowen, A. J. *J. Chem. Soc., Dalton Trans.* 1980, 1845. (b) Heinekey, D. M.; Chinn, M. S., private communication.

(13) (a) A similar complex, $[(\text{C}_5\text{H}_4\text{R}^*)\text{CO}(\text{PPh}_3)\text{Ru}(\text{MeCN})]\text{PF}_6$ ($\text{R}^* = \text{neomenthyl}$),^{13b} has recently been crystallographically characterized.^{13b} (b) Cesarotti, E.; Angoletta, M.; Walker, N. P. C.; Hursthouse, M. B.; Vefghi, R.; Schofield, P. A.; White, C. J. *Organomet. Chem.* 1985, 286, 343.

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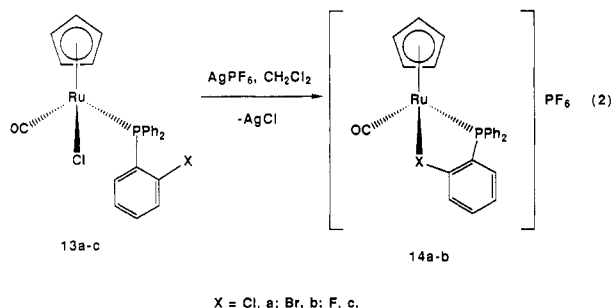
cently observed a $\Delta\nu(\text{CO})$ of $+143\text{ cm}^{-1}$ relative to the Os(II) precursor $\text{Cp}^*(\text{CO})(\text{PMe}_2\text{Ph})\text{OsBr}$ for the cationic Os(IV) carbonyl complex $[\text{Cp}^*(\text{CO})(\text{PMe}_2\text{Ph})\text{Os}(\text{Me})(\text{Br})]\text{Br}$.¹⁵

(3) The X-ray crystal structure of **10b** shows an intact C–I bond, with the Ru–I distance within the sum of the covalent radii (see below).

In solution, the carbonyl phosphine complexes **10a–f** decompose over several hours to several days to free halocarbon and several unidentified diamagnetic Cp-containing products, having C_5H_5 chemical shifts in the range expected for neutral complexes, as well as at somewhat lower field (i.e., δ 4.8–5.1). We observe exactly the same resonances upon performing the synthesis in neat CH_2Cl_2 omitting iodocarbon, and so these products arise from decomposition of the coordinatively unsaturated fragment $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}]^+$.¹⁶ We have not obtained evidence for dichloromethane complexes.⁵

We have not been able to prepare analogous chloro- or bromoalkane or -arene complexes, except in the cases of the chelating (*o*-halophenyl)diphenylphosphine complexes (see below). Attempted syntheses from reactions of $\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{RuCl}$ and AgPF_6 in the presence of RX ($\text{R} = p$ -tolyl, Pr^n ; $\text{X} = \text{Cl}, \text{Br}$) led to decomposition products similar to those formed from complexes **10a–f** as noted above. However, the ^1H NMR spectrum of iodoalkane complex **10d** ($\text{R}' = \text{Pr}^n$) in the presence of excess 1-bromopropane shows new resonances that may be attributable to the bromoalkane complex. We conclude that bromo- and chlorocarbon complexes are not accessible at room temperature via halide abstraction, consistent with the expected lower basicity of these halocarbons. Gladysz and co-workers have observed coordination of chloro- and bromocarbons^{3a,d} to $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}]^+$, but the resulting complexes are, as expected, less stable than the iodocarbon analogues.

We¹ and others² have previously shown that (*o*-halophenyl)diphenylphosphine ligands can chelate to transition-metal fragments via the phosphine and halogen atoms. Silver(I)-mediated halide abstraction from complexes **13a,b** yields cationic chelated chloro- and bromoarene complexes **14a,b** (eq 2), which are characterized by IR, ^1H and ^{31}P

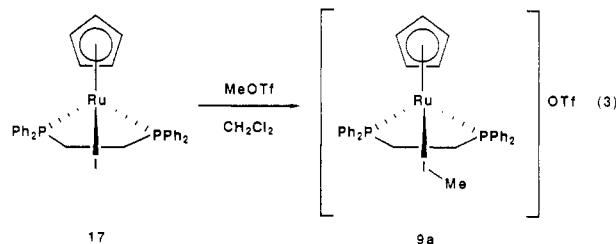


NMR, and elemental analysis. The Cp resonances shift downfield ($\Delta\delta(\text{C}_5\text{H}_5) = +0.38\text{ ppm}$), the carbonyl stretching frequencies shift to higher energy ($\Delta\nu(\text{CO}) = +42\text{ cm}^{-1}$), and ν_{PF} is seen at 844 cm^{-1} , consistent with the formation of cationic complexes. Direct evidence for chelation of the ortho-halo substituent arises from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which show downfield chelation shifts¹⁷ of $+23.5$

ppm for **14a** and $+27.2\text{ ppm}$ for **14b**, both characteristic of five-membered chelate rings. Had cyclometalation occurred to form four-membered chelate rings, upfield shifts ranging from -40 to -70 ppm would have been observed.¹⁸ In addition, we previously noted^{1f} that chelation leads to the disappearance of an aryl multiplet at ca. 6.7 ppm in the proton NMR, tentatively assigned to the proton ortho to halogen. In this case, the multiplet is observed in the spectra of **13a,b** but not **14a,b**, confirming chelation. Complexes **13a,b** and **14a,b** show excellent air and thermal stability and give satisfactory elemental analyses (see Experimental Section). Since *p*-chloro- and *p*-bromotoluene do not form stable ruthenium(II) complexes under the same conditions, the added stability of the chelate effect is necessary in order to observe chloro- and bromoarene binding.

The analogous (*o*-fluorophenyl)diphenylphosphine complex **13c** reacts with AgPF_6 to yield a complex mixture of several CpRu-containing products similar to the decomposition products of complexes **10a–f** noted above; none of them can clearly be identified as the fluorine-bound analogue of **14a,b**. Apparently the fluorophenyl group is insufficiently nucleophilic to coordinate to the open site. An open site is present, because treatment of the crude reaction mixture with excess $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in an NMR tube cleanly regenerates the starting chloro species **13c**. We have previously noted similar nonchelating behavior in the related complex $(\text{COD})\text{IrCl}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-F})$ ($\text{COD} = 1,5\text{-cyclooctadiene}$),^{1f} but in the fluorine-chelated complex $[\text{IrH}_2(\text{PPh}_3)_2(\eta^2(N,F)\text{-}8\text{-fluoroquinoline})]\text{SbF}_6$,^{7f} the rigidity of the quinoline ring apparently enforces a close Ir...F contact, characteristic of secondary bonding. Cruz-Garritz et al.,^{7g} however, have observed a similar interaction in the solid-state structure of the neutral Ru(III) complex $\text{Ru}(\eta^1(\text{S})\text{-SC}_6\text{F}_5)_2(\eta^2(\text{S},F)\text{-SC}_6\text{F}_5)(\text{PMePh}_2)_2$. So far, secondary bonding between fluoroarenes and transition metals has been found only in chelating cases.

We have briefly explored alternate synthetic routes to halocarbon complexes. Direct methylation of the iodide complex **15** with excess methyl trifluoromethanesulfonate (MeOTf , CH_2Cl_2 , overnight), yields the MeI complex **9a** in 85% yield (eq 3). This conversion may be significant



for the development of catalytic reactions involving halocarbons, because it provides a way to regenerate the MeI complex from the iodide.

The efficiency of this reaction depends markedly upon the electronic environment of the metal center. Reaction of the iodide complex $\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{RuI}$ with MeOTf in an NMR tube initially produces a small amount of MeI complex **10a**. Subsequently, free MeI and several new Cp-containing species (δ 5.02, 4.99, and 4.90 ppm) appear at the expense of both the iodide complex and the MeI complex **10a**. After several hours at room temperature,

(15) Johnston, L. G.; Baird, M. C. *Organometallics* 1988, 7, 2469.

(16) (a) These products may include formation of the PF_6^- complex, the aquo or hydroxo complex (from trace water), or the dimeric bridging halide complexes $[\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-X})]^+$ ($\text{X} = \text{Cl}, \text{I}$), similar to the halide-bridged Re dimers recently reported by Gladysz et al.,^{16b} although we have not yet identified any of these by isolation or independent synthesis. (b) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *Organometallics* 1989, 8, 219.

(17) Garrou, P. E. *Chem. Rev.* 1981, 81, 229.

(18) (a) For example, in the orthometallated Ru(II) complex $\text{RuH}(\text{Ph}_2\text{PC}_6\text{H}_4)(\text{PPh}_3)_2(\text{Et}_2\text{O})$,^{18b} the ring phosphorus nucleus resonates at -71.4 and -77.5 ppm upfield of those in the nonmetallated ligands. (b) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1977, 797.

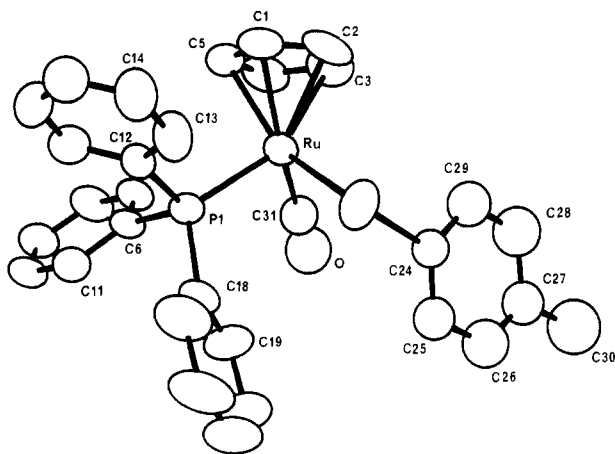
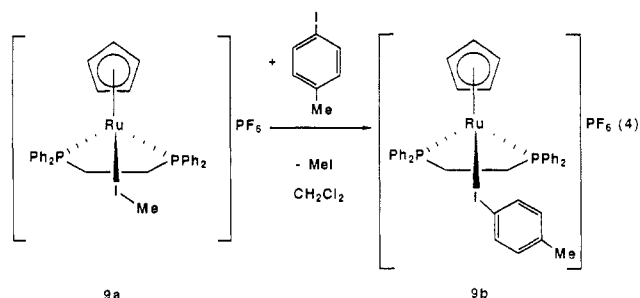


Figure 1. X-ray crystal structure of the major conformer of $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{IC}_6\text{H}_4\text{-p-Me})]\text{PF}_6$ (**10b**).

only the three new Cp-containing complexes and MeI are present; neither the iodide complex nor the MeI complex remain. This probably indicates the displacement of MeI from the initially formed **10a** by other ligands present in the solution to yield free MeI. The metal-containing products may include $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}_2(\mu\text{-I})]^+$ and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuOSO}_2\text{CF}_3$.

Evidence for the presence of the triflate complex is provided by the reaction of *p*-iodotoluene complex **10b** with excess $[\text{Bu}_4\text{N}]\text{CF}_3\text{SO}_3$. After 30 min at room temperature, the NMR spectrum shows complete displacement of iodotoluene and a major new Cp resonance at δ 4.90, matching one of the three products formed the methyl triflate reaction. Recently, Simpson and co-workers⁴ have described the reaction of $\text{Cp}(\text{PPh}_3)(\text{CN}^t\text{Bu})\text{RuI}$ with methyl trifluoromethanesulfonate to yield MeI and a coordinatively unsaturated Ru(II) complex, which recombine to produce the corresponding MeI complex. These observations suggest that direct alkylation of halide complexes may be a general route to halocarbon complexes.

Halocarbon complexes are also available via direct ligand displacement. For example, treatment of the MeI complex **9a** with excess *p*-iodotoluene, followed by evaporation and recrystallization, yields the *p*-iodotoluene complex **9b** in 65% yield (eq 4). Although the haloarene binds to ru-



thenium more weakly than does MeI (see equilibrium measurements below), the greater volatility of the MeI results in complete displacement to form **9b**. This process fails, however, for displacement of more volatile but also more strongly binding ligands such as ethylene. Simpson has recently utilized a similar procedure in the synthesis of $[\text{Cp}(\text{PPh}_3)(\text{CN}^t\text{Bu})\text{Ru}(\text{IME})]\text{OTf}^4$ from the corresponding dihydrogen complex.

Any reaction that generates an open coordination site at a transition-metal center can in principle be applied in the synthesis of halocarbon complexes, providing that no better ligand is present. For example, Gladysz et al.^{3a,d}

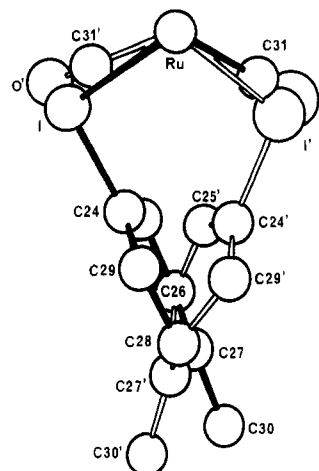
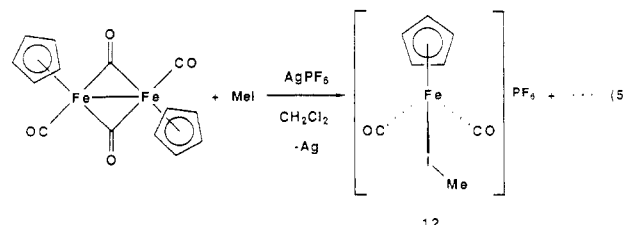


Figure 2. Unusual disorder present in the crystal of **10b**.

have synthesized halocarbon complexes by protonolysis of a rhenium-methyl species, generating methane and a 16-electron Lewis acidic fragment. We and others have prepared solvento complexes by protonation of molybdenum, tungsten, and rhenium polyhydrides.¹⁹ We now find that the oxidation of a metal-metal bond to form two coordinatively unsaturated mononuclear fragments in the presence of halocarbon forms the halocarbon complex. Treatment of $[\text{CpFe}(\text{CO})_2]_2$ with 2 equiv of silver(I) in the presence of MeI causes immediate formation of black Ag(s) and a lighter red solution (eq 5).



The red crystalline material, isolated from the filtrate in ca. 30% yield, consists of the MeI complex **12**, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{IME})]\text{PF}_6$ (50%), and another, as yet unidentified product, which has a Cp resonance at δ 5.14. Because of the low yield, we have not investigated this route further.

X-ray Crystal Structure of $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{IC}_6\text{H}_4\text{-p-CH}_3)]\text{PF}_6$ (10b**).** Although many of the previously reported haloarene complexes have been characterized crystallographically,^{1a,c,d,f,2,3a,d,4,5} all contain a chelating haloarene ligand. The metal-halogen-carbon angles probably reflected chelate geometry restraints. We therefore decided to investigate the crystal structure of the simple haloarene complex **10b** in order to determine the preferred coordination geometry at the halogen atom and to confirm nondissociative binding in a nonchelating case.

Diffraction-quality crystals of complex **10b** were grown by slow diffusion of ether into a concentrated dichloromethane solution at -5°C overnight. Data were collected as summarized in Table I, and the analysis, as described in the Experimental Section, yielded the structure shown in Figure 1. Positional and thermal parameters for non-hydrogen atoms are given in Table II. Bond distances and angles are given in Tables III and IV, respectively. Disorder of the *p*-iodotoluene iodine atom and the carbonyl

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Table I. Crystallographic Data for X-ray Diffraction Studies of $[\eta^5\text{-(C}_6\text{H}_5)_3\text{Ru(CO)(P(C}_6\text{H}_5)_3)_2\text{(IC}_6\text{H}_5\text{CH}_3)]\text{PF}_6$

Crystal Parameters at $23 \pm 2^\circ\text{C}$	
formula	$\text{Ru}_2\text{I}_2\text{P}_2\text{F}_6\text{O}_1\text{C}_{31}\text{H}_{28}$
space group	$P\bar{1}$ (no. 2)
a , Å	10.976 (3)
b , Å	11.329 (3)
c , Å	13.666 (4)
α , deg	100.82 (3)
β , deg	102.62 (3)
γ , deg	102.17 (2)
V , Å ³	1571.5 (1.9)
fw	819.47
ρ_{calcd} , g/cm ³	1.734 ($Z = 2$)
(B) Intensity Measurements	
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
radiation	Mo $K\alpha$ (0.71073 Å)
rlfns measd	$+h, \pm k, \pm l$
max 2θ	50
no. rlfns measd	5801
(C) Structure Solution and Refinement	
data used, $F^2 > 3\sigma(F^2)$	4075
parameters refined	358
abs coeff, cm ⁻¹	16.2
cryst dimen	$0.79 \times 0.32 \times 0.16$
abs corr	empirical
	min 0.519, max 1.327
p factor	0.02
final residuals R_1, R_2	0.054, 0.065
esd of unit wt	3.54
convergence, largest shift/error	0.06

ligand is present, but this disorder was successfully modeled as shown in Figure 2. The bold lines represent bonds within the 80% occupancy sites, while the lighter lines show bonds in the 20% occupancy groups. The primed distances and angles in Tables III and IV refer to atoms in the 20% occupancy groups. The solution of the structure is discussed in the Experimental Section.

Complex **10b** adopts the three-legged piano-stool coordination geometry. The *p*-iodotoluene ligand coordinates to the ruthenium ion via the iodine atom. In view of the disorder problems, we do not wish to overemphasize the distances, but these are very reasonable. The Ru–I distance of 2.6213 (1) Å is within the sum of the covalent radii (2.66 Å)²⁰ and is in fact significantly shorter ($\Delta(\text{Ru–I}) = 0.10\text{--}0.16$ Å) than terminal ruthenium–iodide distances in other organometallic iodo complexes of ruthenium(II) (2.72–2.78 Å).²¹ The covalent radius of iodine in an iodoarene is expected to be significantly smaller than that in iodide ion, because the latter bears a full negative charge. Simpson has also observed a shorter Ru–I bond length ($\Delta(\text{Ru–I}) = 0.054$ Å) in an MeI complex⁴ compared to the analogous iodide complex. The C–I distance in complex **10b** is 2.093 (9) Å, noticeably longer than that observed in free iodotoluene, 2.0548 Å.²² Gladysz et al.^{3a} noted a lengthening of the C–I bond in the rhenium complex of $\text{Me}_3\text{SiCH}_2\text{I}$ ($\Delta(\text{C–I}) = 0.04$ Å). The metal–iodine distances in the three other reported iodoarene complexes lie in the same range, namely, Ir–I = 2.744 (1), 2.781 (1) Å in

Table II. Positional and Thermal Parameters for $[\eta^5\text{-(C}_6\text{H}_5)_3\text{Ru(CO)(PPh}_3)_2\text{(IC}_6\text{H}_5\text{CH}_3)]\text{PF}_6$

atom	x/a	y/b	z/c	B_{eqv} , Å ²
I	0.37480 (7)	0.3347 (7)	0.44433 (5)	5.49 (2)
I'	0.0273 (3)	0.2964 (3)	0.4155 (2)	6.47 (7) ^a
Ru	0.16749 (6)	0.17421 (5)	0.31614 (4)	3.65 (1)
P(1)	0.1708 (2)	0.2836 (2)	0.1885 (1)	3.52 (4)
P(2)	0.6520 (2)	0.0552 (2)	0.3390 (2)	4.66 (5)
F(1)	0.7207 (5)	0.1159 (5)	0.2640 (4)	8.9 (2)
F(2)	0.5754 (7)	0.1542 (6)	0.3442 (5)	12.3 (2)
F(3)	0.5415 (6)	−0.0255 (7)	0.2421 (5)	10.9 (2)
F(4)	0.5825 (6)	−0.0103 (6)	0.4104 (4)	9.9 (2)
F(5)	0.7573 (7)	0.1366 (7)	0.4350 (5)	11.9 (2)
F(6)	0.7318 (7)	−0.0404 (6)	0.3309 (6)	14.9 (2)
O(1)	0.0060 (8)	0.3079 (7)	0.3963 (6)	7.6 (2) ^a
O'	0.402	0.351	0.417	5.0 ^a
C(1)	0.2346 (8)	0.0105 (7)	0.2531 (6)	5.4 (2)
C(2)	0.2416 (9)	0.0160 (7)	0.3581 (7)	7.1 (3)
C(3)	0.118 (1)	0.0027 (8)	0.3718 (7)	7.4 (3)
C(4)	0.0322 (8)	−0.0107 (7)	0.2718 (7)	5.9 (2)
C(5)	0.1038 (8)	−0.0071 (6)	0.2032 (6)	5.0 (2)
C(6)	0.0155 (6)	0.2654 (6)	0.0980 (5)	3.5 (2)
C(7)	−0.0939 (7)	0.1784 (6)	0.0965 (5)	4.5 (2)
C(8)	−0.2116 (7)	0.1604 (7)	0.0243 (6)	5.1 (2)
C(9)	−0.2205 (7)	0.2293 (7)	−0.0504 (6)	5.0 (2)
C(10)	−0.1093 (7)	0.3196 (6)	−0.0490 (6)	4.8 (2)
C(11)	0.0072 (7)	0.3372 (7)	0.0239 (5)	4.3 (2)
C(12)	0.2699 (6)	0.2351 (6)	0.1059 (5)	3.5 (2)
C(13)	0.3958 (7)	0.2340 (8)	0.1526 (5)	5.3 (2)
C(14)	0.4772 (7)	0.1966 (8)	0.0933 (6)	5.5 (2)
C(15)	0.4327 (7)	0.1598 (8)	−0.0092 (6)	5.3 (2)
C(16)	0.3072 (8)	0.1573 (8)	−0.0567 (6)	5.3 (2)
C(17)	0.2280 (7)	0.1955 (7)	−0.0006 (6)	4.5 (2)
C(18)	0.2338 (8)	0.4538 (6)	0.2339 (5)	4.8 (2)
C(19)	0.169 (1)	0.5166 (8)	0.2911 (7)	7.2 (3)
C(20)	0.220 (1)	0.6465 (9)	0.3358 (8)	9.5 (4)
C(21)	0.332 (1)	0.7085 (9)	0.3205 (9)	10.0 (4)
C(22)	0.392 (1)	0.6488 (8)	0.2625 (9)	8.9 (3)
C(23)	0.3445 (8)	0.5173 (8)	0.2166 (7)	6.9 (3)
C(24)	0.3074 (9)	0.3896 (8)	0.5731 (6)	4.3 (2) ^a
C(25)	0.297 (1)	0.509 (1)	0.5592 (7)	5.4 (2) ^a
C(26)	0.257 (1)	0.5438 (9)	0.6939 (7)	7.1 (2) ^a
C(27)	0.227 (1)	0.464 (1)	0.7501 (8)	6.0 (2) ^a
C(28)	0.233 (1)	0.336 (1)	0.7185 (8)	7.9 (3) ^a
C(29)	0.278 (1)	0.301 (1)	0.6259 (8)	6.3 (3) ^a
C(30)	0.190 (1)	0.499 (1)	0.850 (1)	10.0 (4) ^a
C(31)	0.0528 (9)	0.2572 (9)	0.3689 (7)	4.9 (2) ^a
C(24')	0.128 (3)	0.363 (3)	0.567 (3)	4.4 (8) ^a
C(25')	0.190 (6)	0.488 (5)	0.595 (4)	9 (2) ^a
C(27')	0.268 (4)	0.455 (4)	0.783 (3)	5.4 (9) ^a
C(29')	0.134 (5)	0.280 (5)	0.623 (4)	8 (1) ^a
C(30')	0.326 (5)	0.506 (4)	0.898 (3)	7 (1) ^a
C(31')	0.323	0.291	0.383	5.0 ^a

^a Refined isotropically. The carbonyl and iodotoluene ligands were disordered. The primed atoms were included at 20% occupancy and their unprimed counterparts at 80% occupancy.

$[\text{IrH}_2(\text{PPh}_3)_2(\text{Ime})_2]\text{SbF}_6$,^{1d} Re–I = 2.678 (1) Å in $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{ICH}_2\text{SiMe}_3)]\text{BF}_4$,^{3a} and Ru–I = 2.670 (2) Å in $[\text{Cp}(\text{PPh}_3)(\text{CN}^t\text{Bu})\text{Ru}(\text{Ime})]\text{PF}_6$.⁴

The small Ru–I–C(24) angle of 101.8 (2)° is similar to C–X–M angles previously observed in chelating haloarene complexes^{1a,2a–g} and suggests that σ -donation occurs predominantly through an iodine orbital of high *p*-character, rather than an sp^3 hybrid. Small C–I–C bond angles of ca. 95° have been observed in trivalent iodonium complexes.²³

The torsional angle of 67.5° between the plane of the *p*-iodotoluene ligand and the plane defined by Ru–I–C(24) demonstrates that the donor *p*-type orbital is that which is also in conjugation with the ligand aromatic ring and

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(21) For example, Ru–I = 2.719 Å in $\text{RuI}_2(\text{CO})_4$,^{21a} Ru–I = 2.766 (2) Å in $\text{RuI}(\text{COMe})(\text{CO})(\text{PPh}_3)_2$,^{21b} Ru–I = 2.708 (1) Å in $(\text{C}_6\text{H}_5\text{R}^*)\text{Ru}(\text{CO})(\text{PPh}_3)\text{I}^{21c}$ ($\text{R}^* = \text{neomenthyl}$). (a) Dahl, L. F.; Wampler, D. L. *Acta Crystallogr.* **1962**, *15*, 946. (b) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46. (c) Cesarotti, E.; Chiesa, A.; Ciani, G. F.; Sironi, A.; Vefghi, R.; White, C. J. *Chem. Soc., Dalton Trans.* **1984**, 653.

(22) Ahn, C.-T.; Soled, S.; Carpenter, G. B. *Acta Crystallogr.* **1972**, *B28*, 2152.

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Table III. Bond Distances (Å) for $[\eta^5\text{-(C}_5\text{H}_5\text{)Ru(CO)(PPh}_3\text{)(IC}_6\text{H}_5\text{CH}_3\text{)PF}_6]$

Ru-I	2.6213 (1)	C(18)-C(19)	1.37 (1)
Ru-P(1)	2.324 (2)	C(18)-C(23)	1.37 (1)
Ru-C(1)	2.232 (9)	C(19)-C(20)	1.42 (1)
Ru-C(2)	2.235 (9)	C(20)-C(21)	1.36 (2)
Ru-C(3)	2.221 (9)	C(21)-C(22)	1.32 (2)
Ru-C(4)	2.186 (7)	C(22)-C(23)	1.44 (1)
Ru-C(5)	2.196 (6)	C(24)-C(25)	1.37 (1)
Ru-C(31)	1.91 (1)	C(24)-C(29)	1.37 (2)
I-C(24)	2.093 (9)	C(25)-C(26)	1.47 (2)
P(1)-C(6)	1.821 (6)	C(26)-C(27)	1.32 (2)
P(1)-C(12)	1.821 (8)	C(27)-C(28)	1.46 (2)
P(1)-C(18)	1.838 (7)	C(27)-C(30)	1.51 (2)
C(31)-O	0.93 (1)	C(28)-C(29)	1.47 (2)
C(1)-C(2)	1.41 (1)	Ru-C(31')	1.85 ^a
C(1)-C(5)	1.40 (1)	Ru-I'	2.689 (4)
C(2)-C(3)	1.39 (2)	I'-C(24')	2.04 (3)
C(3)-C(4)	1.44 (1)	C(31')-O'	0.94 ^a
C(4)-C(5)	1.35 (1)	C(24')-C(25')	1.38 (7)
C(6)-C(7)	1.378 (9)	C(24')-C(29')	1.31 (7)
C(6)-C(11)	1.41 (1)	C(26)-C(25')	1.35 (5)
C(7)-C(8)	1.394 (9)	C(26)-C(27')	1.72 (5)
C(8)-C(9)	1.40 (1)	C(27')-C(30')	1.51 (5)
C(9)-C(10)	1.41 (1)	C(28)-C(27')	1.39 (4)
C(10)-C(11)	1.390 (9)	C(28)-C(29')	1.44 (4)
C(12)-C(13)	1.39 (1)	P(2)-F(1)	1.573 (6)
C(12)-C(17)	1.380 (9)	P(2)-F(2)	1.537 (8)
C(13)-C(14)	1.41 (1)	P(2)-F(3)	1.561 (6)
C(14)-C(15)	1.33 (1)	P(2)-F(4)	1.564 (7)
C(15)-C(16)	1.38 (1)	P(2)-F(5)	1.530 (6)
C(16)-C(17)	1.36 (1)	P(2)-F(6)	1.533 (8)

^a Not refined. The C(31') position was obtained from a difference Fourier peak. The O' position and distance were calculated.

thus expected to be less basic. However, inspection of the structure shows that decreasing the Ru-I-C(24)-C(29) angle (i.e., rotation about the I-C(24) bond axis), while allowing for donation from a more basic p-orbital orthogonal to the aromatic ring, would also lead to prohibitive steric repulsions between the metal center and the ortho C-H groups of the aromatic ring and is thus unlikely. The P1-Ru-I-C(24) torsion angle of 113.5° places the tolyl group in a conformation anti to the triphenylphosphine and syn to the carbonyl. If d-σ* backbonding were important in order to backbond with the more basic d-orbital, the halocarbon ligand might become syn to the PPh₃. Gladysz and Fenske have recently performed Fenske-Hall molecular orbital calculations^{3e} on [Cp(NO)(PH₃)Re(ICH₃)]⁺ and [Cp(NO)(PH₃)Re(ClCH₂Cl)]⁺ and conclude that, in these aliphatic cases, backbonding is negligible. All other intramolecular distances and angles are normal, and no close intermolecular contacts are apparent.

Alkylation of Nucleophiles by Iodoalkane Complexes. Free haloalkanes are widely employed as electrophilic alkylating agents for many different organic and inorganic nucleophiles. Methyl, primary alkyl, and sometimes also secondary alkyl halides react by the S_N2 mechanism, via nucleophilic attack at the carbon-based lobe of the C-X σ* orbital.²⁴ Earlier, we found that coordination of MeI to iridium(III) enhances the electrophilicity of the ligand, resulting in an increase of 10⁵ in the rate of nucleophilic attack by triethylamine. Other nucleophiles such as acetate and chloride displaced MeI.^{1d} Similarly, Gladysz and co-workers demonstrated that MeI complex [Cp(NO)(PPh₃)Re(IME)]⁺ methylates triphenylphosphine with a similar rate increase.^{3d} We wanted to see whether our Ru(II) system is also effective with a range of nucleophiles and the selectivities for nucleophile

Table IV. Bond Angles (deg) for $[\eta^5\text{-(C}_5\text{H}_5\text{)Ru(CO)(PPh}_3\text{)(IC}_6\text{H}_5\text{CH}_3\text{)PF}_6]$

Ru-I-C(24)	101.8 (2)	P(1)-C(18)-C(19)	117.6 (6)
Ru-I'-C(24')	108 (1)	P(1)-C(18)-C(23)	122.6 (7)
Ru-C(31)-O(1)	172.0 (0)	C(19)-C(18)-C(23)	119.8 (7)
I-Ru-I'	{87.43 (6)}	C(18)-C(19)-C(20)	119.8 (9)
I-Ru-P(1)	92.68 (4)	C(19)-C(20)-C(21)	120.2 (9)
I-Ru-C(31)	93.3 (2)	C(20)-C(21)-C(22)	120.1 (9)
I-Ru-C(31')	{11.40 (2)}	C(21)-C(22)-C(23)	121.5 (9)
I'-Ru-P(1)	97.15 (9)	C(18)-C(23)-C(22)	118.7 (9)
I'-Ru-C(31)	7.6 (3)	I-C(24)-C(25)	119.2 (8)
I'-Ru-C(31')	94.60 (6)	I-C(24)-C(29)	116.2 (8)
P(1)-Ru-C(31)	92.1 (3)	C(25)-C(24)-C(29)	124.7 (9)
P(1)-Ru-C(31')	83.0	C(24)-C(25)-C(26)	116.6 (9)
C(1)-Ru-C(2)	36.8 (3)	C(25)-C(26)-C(27)	116.6 (9)
C(1)-Ru-C(5)	36.9 (3)	C(25)-C(26)-C(27)	122.9 (9)
C(2)-Ru-C(3)	36.2 (4)	C(26)-C(27)-C(28)	120 (1)
C(3)-Ru-C(4)	38.2 (3)	C(26)-C(27)-C(30)	124 (1)
C(4)-Ru-C(5)	35.9 (4)	C(28)-C(27)-C(30)	116 (1)
C(31)-Ru-C(31')	99.7 (2)	C(27)-C(28)-C(29)	118 (1)
Ru-P(1)-C(6)	116.2 (2)	C(24)-C(29)-C(28)	118 (1)
Ru-P(1)-C(12)	111.6 (2)	I'-C(24')-C(25')	114 (3)
Ru-P(1)-C(18)	116.2 (3)	I'-C(24')-C(29')	117 (3)
C(6)-P(1)-C(12)	103.8 (3)	C(25')-C(24')-C(29')	129 (4)
C(6)-P(1)-C(18)	102.6 (3)	C(26)-C(25')-C(24')	120 (5)
C(12)-P(1)-C(18)	105.1 (4)	C(25')-C(26)-C(27')	119 (3)
C(2)-C(1)-C(5)	106.3 (8)	C(26)-C(27')-C(28)	101 (2)
C(1)-C(2)-C(3)	109.0 (8)	C(26)-C(27')-C(30')	125 (3)
C(2)-C(3)-C(4)	106.7 (9)	C(28)-C(27')-C(30')	133 (4)
C(3)-C(4)-C(5)	107.6 (8)	C(27')-C(28)-C(29')	131 (3)
C(1)-C(5)-C(4)	110.4 (7)	C(28)-C(29')-C(24')	109 (3)
P(1)-C(6)-C(7)	121.4 (6)	F(1)-P(2)-F(2)	89.7 (4)
P(1)-C(6)-C(11)	119.8 (5)	F(1)-P(2)-F(3)	88.2 (3)
C(7)-C(6)-C(11)	118.8 (6)	F(1)-P(2)-F(4)	177.7 (3)
C(6)-C(7)-C(8)	121.5 (7)	F(1)-P(2)-F(5)	92.4 (3)
C(7)-C(8)-C(9)	120.2 (7)	F(1)-P(2)-F(6)	87.7 (4)
C(8)-C(9)-C(10)	118.7 (7)	F(2)-P(2)-F(3)	87.8 (4)
C(9)-C(10)-C(11)	120.4 (7)	F(2)-P(2)-F(4)	91.9 (4)
C(6)-C(11)-C(10)	120.3 (6)	F(2)-P(2)-F(5)	90.5 (4)
P(1)-C(12)-C(13)	118.3 (5)	F(2)-P(2)-F(6)	177.4 (5)
P(1)-C(12)-C(17)	124.6 (6)	F(3)-P(2)-F(4)	90.1 (3)
C(13)-C(12)-C(17)	117.1 (7)	F(3)-P(2)-F(5)	178.2 (5)
C(12)-C(13)-C(14)	121.2 (6)	F(3)-P(2)-F(6)	92.3 (4)
C(13)-C(14)-C(15)	119.5 (7)	F(4)-P(2)-F(5)	89.3 (3)
C(14)-C(15)-C(16)	120.1 (8)	F(4)-P(2)-F(6)	90.8 (4)
C(15)-C(16)-C(17)	121.1 (7)	F(5)-P(2)-F(6)	89.4 (4)
C(12)-C(17)-C(16)	121.0 (7)		

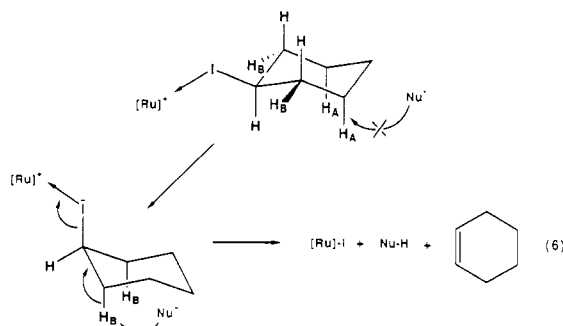
alkylation vs halocarbon displacement.

Each of the MeI complexes reported in this study, with one exception, reacts with chloride to yield chloromethane (having a ¹H NMR resonance at δ 3.02, identical with an authentic sample) and the corresponding metal iodide, as determined by in situ ¹H NMR experiments. In the case of the reaction with [CpRu(CO)(PPh₃)(IME)]⁺, the identity of the MeCl was also confirmed by GC (50 °C, Chromosorb 106). In all cases, the reaction occurred cleanly and rapidly, as noted by the color change from yellow to orange. In no case did side products account for more than a trace of Cp-containing products. Even the 2-iodopropane complex **10e** gave only nucleophilic displacement, to the exclusion of the base-induced elimination seen for the free halide. This reaction is rapid; isopropyl halides normally undergo S_N2 displacement reactions very slowly (e.g., *k* = 4.2 × 10⁻⁷ s⁻¹ (60 °C) for displacement in *i*-PrCl with KI/acetone²⁵), yet complex **10e** reacts essentially within the time of mixing.

Exceptionally, the iodocyclohexane complex **10f** reacts with these nucleophiles to give cyclohexene (identified by its characteristic ¹H NMR peaks at δ 1.65, 2.05, and 5.69) and protonated nucleophile. The axial H_a protons of the Cy group may block the incoming nucleophile in the chair conformation shown in eq 6 and so prevent nucleophilic

(24) Lowrey, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; Chapter 4.

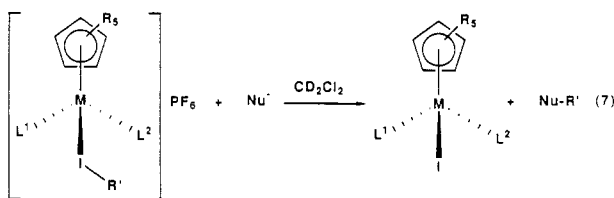
(25) Conant, J. B.; Hussey, R. E. *J. Am. Chem. Soc.* **1925**, *47*, 476.



displacement. This conformer also precludes E2 elimination,²⁶ but if the iodine becomes axial, the H_a protons also become axial and a favorable antiperiplanar arrangement can be attained. These restrictions do not apply in the isopropyl case, and so nucleophilic displacement occurs readily.

In the case of free CyX , reactions tend to be nonselective, e.g., acetolysis of cyclohexyl tosylate yields an 80:20 mixture of cyclohexene and cyclohexyl acetate.²⁷ In our case, the high reactivity ($t_{1/2}$ = seconds) and complete selectivity for elimination in **10f** suggest that halocarbon complexation may be useful in promoting dehydrohalogenation of cyclohexyl halides.

Several other nucleophiles, in addition to chloride, behave in a similar manner. Benzoate, triphenylphosphine, pyridine, fluoride ion, and *p*-toluenesulfonate ion all react with MeI complex **10a** to yield iodide complex $Cp(CO)(Ph_3)RuI$ and the corresponding methylated nucleophiles, in high yield (see eq 7 for details). These were identified by their characteristic 1H NMR spectra and by comparison with the authentic materials.



7: $Nu^- = Cl^-$, py; $R' = Me$

8: $Nu^- = Cl^-$; $R' = Me$

9a: $Nu^- = Cl^-$, $PhCO_2^-$, NEt_3 ; $R' = Me$

10a: $Nu^- = Cl^-$, F^- , py, $PhCO_2^-$

Ph_3P , *p*- TsO^- ; $R' = Me$

10c,d,e: $Nu^- = Cl^-$, py; $R' = Et$, *n*-Pr, *i*-Pr

11a: $Nu^- = Cl^-$, py; $R' = Me$

15: $M = Ru$, $R = H$, $L^1, L^2 = (CO)_2$

16: $M = Ru$, $R = H$, $L^1, L^2 = (PPh_3)_2$

17: $M = Ru$, $R = H$, $L^1, L^2 = dppe$

18: $M = Ru$, $R = H$, $L^1, L^2 = (CO)(PPh_3)$

19: $M = Ru$, $R = Me$, $L^1, L^2 = (CO)_2$

In each of these cases, the reaction proceeds cleanly and rapidly to form alkylated nucleophile and metal iodide complexes **6** and **15–19**. In all cases, reaction of the nucleophile with free MeI is slow at room temperature and not synthetically useful. Particularly notable is the reaction with *p*-toluenesulfonate anion, proving that the MeI complex **10a** is a more potent alkylating agent than methyl *p*-toluenesulfonate, a common reagent in organic synthesis.²⁸ The reaction with fluoride anion provides a mild method of introducing fluorine into organic molecules, an area of current interest.²⁹

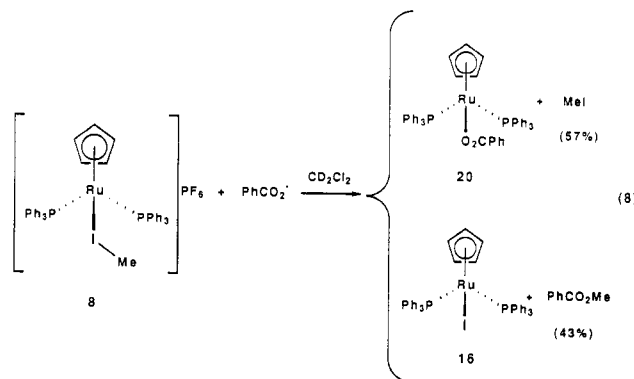
(26) Reference 24, Chapter 7.

(27) (a) Lambert, J. B.; Putz, G. J.; Mixan, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 5132. (b) Nordlander, J. E.; McCrary, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 5133.

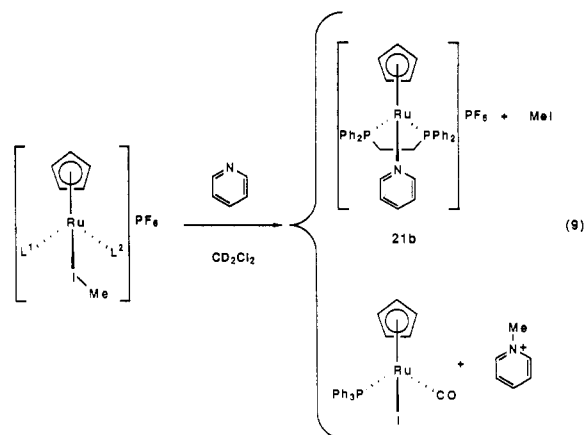
(28) For a review of trifluoromethanesulfonic acid and derivatives, including a discussion of applications of alkylsulfonates in organic synthesis, see: Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(29) For a review of fluorination methods in organic chemistry, see: Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647.

The bis(triphenylphosphine) MeI complex **8** reacts with benzoate to give both MeI displacement, yielding ruthenium(II) benzoate complex **20** and methyl benzoate, in a 1.3:1 ratio (eq 8). The same benzoate complex could also be prepared by direct reaction of $PhCOONa$ with $CpRuL_2Cl$. Conversely, reaction of MeI complex **8** with chloride produces MeCl exclusively (see eq 7).



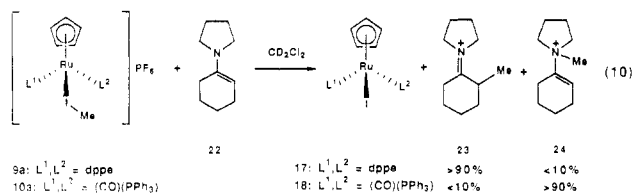
The difference in reactivity between the bis(tertiary phosphine) and phosphine carbonyl complexes is illustrated in the reaction of pyridine with MeI complexes **9a** and **10a** (eq 9). In the former case, MeI is displaced, and



the pyridine complex **21c** is formed; in the latter, rapid nucleophilic substitution occurs to give the iodo complex **18** and *N*-methylpyridinium ion. The difference in reactivity may be a result of the different electrophilicity of the two metal fragments. In the bis(phosphine) complex, dissociation of MeI is facile, and the 16-electron cationic species is trapped by incoming py. In contrast, the greater electrophilicity of the carbonyl complex slows the rate of dissociation, allowing nucleophilic attack at MeI.

Formation of Carbon–Carbon Bonds. In view of the significance of carbon–carbon bond formation in organic synthesis, we investigated the reactivity of MeI complexes toward carbon-centered nucleophiles. Consiglio's extensive studies on chirally modified $CpRu(II)$ complexes³⁰ made the prospect of employing chiral haloalkane complexes in asymmetric alkylations attractive. We find that the enamine 1-(*N*-pyrrolidinyl)cyclohexene, **22**, reacts rapidly in CD_2Cl_2 with the MeI complexes **9a** and **10a** to yield the iodo complexes **17** and **18** and mixtures of *N*- and *C*-alkylated products, in high overall yields (>90% by NMR, eq 10). Hydrolysis of the products with 0.5 M AcOH over 17 h at 20 °C gave a mixture of cyclohexanone and 2-methylcyclohexanone, which were determined by capillary GC on a Carbowax column and eluted with the same re-

(30) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761.

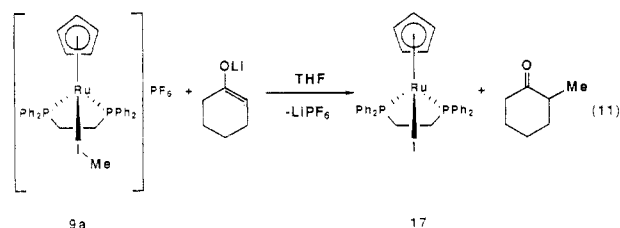


tention time as the authentic ketones.

The difference in selectivity between free and ruthenium-coordinated MeI is striking. Bound MeI in **9a** gives carbon alkylation to yield iminium salt **23**, identified by 1H NMR. Only a trace of N-alkylation product **24**, a common but undesired side product in enamine chemistry,³¹ is observed. In contrast, free MeI gives only the N-methylammonium salt, with less than 1% carbon alkylation, in an NMR experiment (CD_2Cl_2 , room temperature). On a preparative scale, the iminium ion formed from MeI complex **9a** salt yields, upon hydrolysis, 2-methylcyclohexanone in $>80\%$ yield.

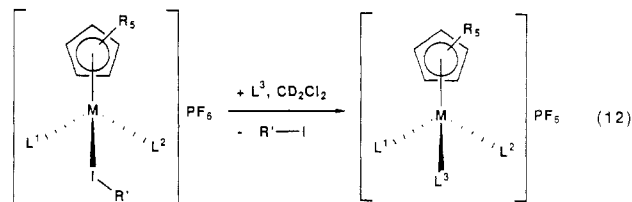
The enamine is also methylated by MeI complex **10a**, but with the opposite regioselectivity. At room temperature, the major product is the N-methyliminium salt ($>90\%$, 1H NMR), with only a trace of C-methylation. MeI complex **10a** reacts with the enamine on a preparative scale at low temperature to produce, after workup, 2-methylcyclohexanone, but in considerably lower yield than observed with the bis(diphenylphosphino)ethane complex **9a** (ca. 25–35%). The lower selectivity for C- vs N-alkylation with the carbonyl complex compared to the bis(tertiary phosphine) analogue is consistent with its greater electrophilicity and hence increased reactivity. Steric effects may also play an important role. The bulky dppe ligand may favor alkylation at the less sterically hindered carbon atom, increasing the observed selectivity for **23** compared to the (carbonyl)(phosphine) case. In the preparative scale reaction, the reactivity of **10a** is attenuated sufficiently by the low temperature to produce isolable but still not synthetically useful quantities of 2-methylcyclohexanone.

Other carbon nucleophiles are also alkylated by MeI complex **9a**. The lithium enolate of cyclohexanone reacts with MeI complex **9a** in THF to yield 2-methylcyclohexanone in 60% yield (eq 11). The enol silyl ether 1-



[(trimethylsilyl)oxy]cyclohexene, however, is insufficiently nucleophilic to react with the CO- or phosphine-containing MeI complexes **9a** and **10a**.

Ligand-Exchange Reactions. The reaction of the ruthenium haloalkane complexes with less reactive organic nucleophiles such as acetonitrile and acetone results in haloalkane displacement and generation of the corresponding solvent complex (eq 12). The supporting ligands are once again important. In the bis(tertiary phosphine) complex **9a**, substitution of MeI by acetonitrile occurs within the time of mixing, while in the carbonyl phosphine complex **10a**, the pseudo-first-order rate constant for displacement by acetonitrile is $(7.4 \pm 0.8) \times 10^{-4} s^{-1}$ at 300 K, corresponding to a free energy of activation

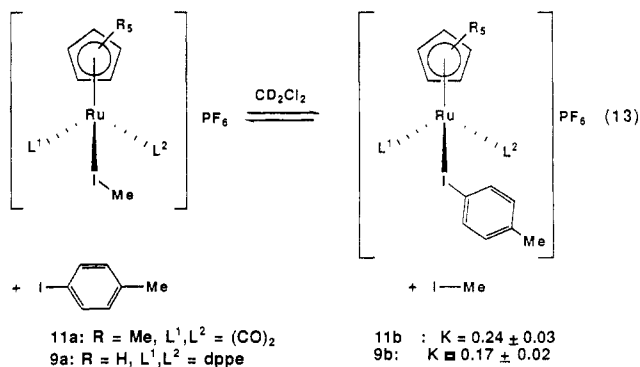


- 7: $R' = Me$
 9a: $R' = Me$
 10a: $R' = Me$
 10c-f: $R' = Et, n-Pr, i-Pr, Cy$
 11a: $R' = Me$
 12: $R' = Me$
- 25: $M = Ru, R = H, L^1, L^2 = (CO)_2, L^3 = MeCN$
 21a: $M = Ru, R = H, L^1, L^2 = dppe, L^3 = MeCN$
 21b: $M = Ru, R = H, L^1, L^2 = dppe, L^3 = py$
 26a: $M = Ru, R = H, L^1, L^2 = (CO)(PPh_3), L^3 = MeCN$
 26b: $M = Ru, R = H, L^1, L^2 = (CO)(PPh_3), L^3 = Me_2CO$
 26a: $M = Ru, R = H, L^1, L^2 = (CO)(PPh_3), L^3 = MeCN$
 27: $M = Ru, R = Me, L^1, L^2 = (CO)_2, L^3 = MeCN$
 28: $M = Fe, R = H, L^1, L^2 = (CO)_2, L^3 = MeCN$

$\Delta G^\ddagger = 21.9$ kcal/mol. The rate was independent of $[MeCN]$ over the range 5–40 equiv of MeCN/mol of **10a**. The observed rate dependence on the supporting ligands is consistent with a predominantly dissociative mechanism, as expected for an 18-electron organometallic complex. Associative mechanisms have been observed only in 18-electron complexes when they contain a ligand that can easily slip,³² e.g., η^5 - to η^3 -indene or linear ($3e^-$) to bent ($1e^-$) nitrosyl; no such ligands are present in complex **10a**. In a related system, White has reported that carbonyl substitution by phosphines in $(C_5R_5)(CO)_2RuBr$ is strictly dissociative.³³ The π -acidic carbonyl ligand in **10a** may strengthen the RI–Ru bond and slow dissociation. Alternatively, the lower barrier for displacement in the dppe complex may be a result of stabilization of the transition state by the better σ -donor phosphine ligand; this is how White explains faster CO substitution in $(C_5Me_4Et)Ru(CO)_2Br$ compared to the C_5H_5 case.³³ Steric effects may also increase the rates of ligand exchange in the dppe complex **9a** and of phosphine loss in $Cp(PPh_3)_2RuCl$.^{8b}

For a purely dissociative process, the activation enthalpy is approximately equal (the uncertainty being the enthalpic barrier to recombination) to the bond dissociation energy. Assuming a range in activation entropy of 5–20 cal/(mol K), we can estimate a ruthenium(II)–MeI bond dissociation energy of between 24 and 28 kcal/mol.

Ligand exchange can lead to an equilibrium mixture, favoring coordination of the better halocarbon ligand. For example, treatment of the MeI complex $[Cp^*(CO)_2Ru(IME)]PF_6$ (**11a**) with *p*-iodotoluene yields, after a few tens of minutes, an equilibrium mixture containing **11a** and *p*-iodotoluene complex **11b**, which favors MeI coordination ($K_{eq}(300 K) = 0.24 \pm 0.03$, 1H NMR, eq 13). The MeI



complex **9a** also reacts with *p*-iodotoluene to form an equilibrium mixture containing **9a** and *p*-iodotoluene complex **9b**, with a similar equilibrium constant ($K_{eq}(300 K) = 0.17 \pm 0.02$). These results are the first direct

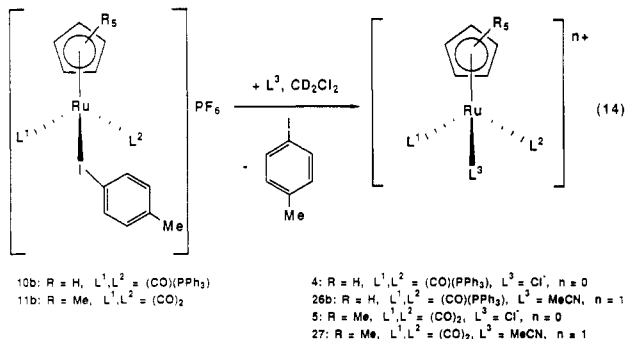
(31) (a) Curphey, T. J.; Hung, J. C.; Chu, C. C. C. *J. Org. Chem.* **1975**, *40*, 607. (b) Whitesell, J. K.; Whitesell, M. A. *Synthesis* **1983**, 517.

(32) Basolo, F. *Coord. Chem. Rev.* **1982**, *43*, 7.

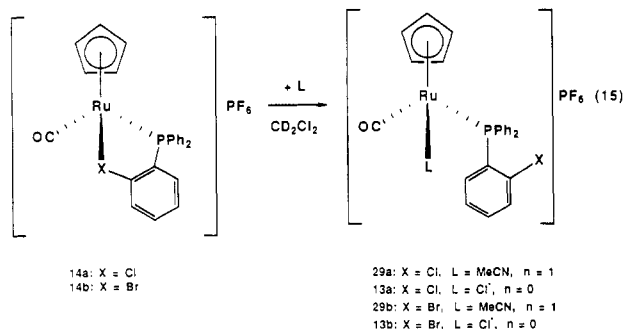
(33) Tabatabaian, K.; White, C. *Inorg. Chem.* **1981**, *20*, 2020.

quantification of relative ligating abilities of two different halocarbon ligands. In the case of dicarbonyls **11a** and **11b**, the K_{eq} value probably reflects the better σ -basicity of MeI, since steric effects are minimized with the small CO ligands. In the dppe case, however, it is difficult to separate steric and electronic effects, and both probably contribute. These equilibrium constants correspond to small Ru-IR bond energy differences (1.0 and 0.9 kcal/mol, respectively, neglecting entropic effects).

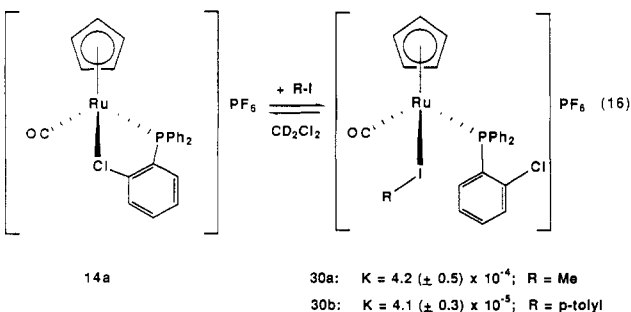
Haloareene complexes undergo displacement, whatever the nucleophile. For example, *p*-iodotoluene complexes **10b** and **11b** react with chloride and acetonitrile to yield free iodotoluene and the corresponding chloro or acetonitrile complexes, in quantitative yield (eq 14). Nucleophilic aromatic substitution was never seen.



The chelating (*o*-halophenyl)diphenylphosphine complexes **14a** and **14b** behave similarly. Upon treatment with excess MeCN, both yield the unchelated complexes (eq 15).



The acetonitrile complexes **29a** and **29b** show new Cp resonances appropriate for cationic complexes, multiplets in the δ 6.7–6.9 region assigned to the proton ortho to halogen in the unchelated ligands,^{1f} and resonances at δ 2.03, corresponding to coordinated acetonitrile. Reaction with chloride produces the chloro complexes **13a** and **13b**. In all cases, reaction occurs within time of mixing. Treatment of chloroarene complex **14b** with MeI or *p*-iodotoluene generates an equilibrium mixture of chelated and nonchelated halocarbon complexes (eq 16). The new



iodocarbon complexes **30a,b** were not isolated but have been identified by ¹H NMR. Both show Cp resonances

that correspond to cationic complexes (δ 5.21, **30a**; δ 5.14, **30b**) and resonances for coordinated iodocarbon (δ 2.49 (MeI), **30a**; δ 2.37 (ArMe), **30b**), which appear upfield of the free ligands. The equilibrium constants, determined by ¹H NMR, are $4.2 \times 10^{-4} (\pm 0.5 \times 10^{-4})$ for displacement by MeI and $4.1 \times 10^{-5} (\pm 0.3 \times 10^{-5})$ for displacement by *p*-iodotoluene. The chelating bromoarene complex **14b** does not react with MeI, implying that the ruthenium-bromoarene bond strength together with the chelate effect exceeds the bond dissociation energy of the Ru-MeI complex, ca. 24–28 kcal/mol.

Conclusion

The Fe and Ru Lewis acids $[(C_5R_5)(L^1)(L^2)M]^+$ (R = H, Me; $L^1, L^2 = PR_3, CO$) can coordinate a variety of iodoalkanes, *p*-iodotoluene, and chelating phosphine-haloarenes via halogen lone pairs to form stable, well-characterized complexes without oxidative addition of the halocarbon. MeI binds more strongly than *p*-iodotoluene. The iodoalkane complexes react with nucleophiles by attack at the α -carbon, resulting in alkylation of the nucleophile; the observed rate enhancements illustrate the polarizing effect of the cationic transition-metal fragment. By varying the ancillary ligands, we have also shown that the π -acidic CO increases the electrophilicity at Ru, and the strength of the metal-halocarbon bond. Most importantly, we have observed selective C-methylation of an enamine via an MeI complex, implying that such complexes may be useful in organic synthetic applications.

Experimental Procedure

General Considerations. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.³⁴ Solvents were purified according to standard procedures.³⁵ All reagents, unless otherwise noted, were purchased from Aldrich Chemical Co. and used as received. NMR spectra were obtained in CD₂Cl₂ with chemical shifts listed in ppm downfield of SiMe₄ (¹H and ¹³C) or 85% H₃PO₄ (³¹P), by using the following instruments: ¹H, Bruker WM-250 or JEOL FX-90Q; ¹³C, Bruker WM-250 operating at 62.8 MHz; ³¹P, Bruker WM-500 operating at 202.4 MHz or Varian CFT-20 operating at 32.0 MHz. Infrared spectra were obtained by using a Nicolet FT5-SX instrument, in dichloromethane solution. Elemental analyses were performed by Desert Analytics, Tucson, AZ. The starting materials [RuCl₂(CO)₂]₂,³⁶ Cp(PPh₃)₂RuCl (**2**),³⁷ Cp(dppe)RuCl (**3**),³⁸ Cp(CO)(PPh₃)RuCl (**4**),³⁹ Cp*(CO)₂RuCl (**5**),⁴⁰ and Cp(CO)₂FeI (**6**)⁴¹ were prepared according to literature procedures.

Complexes **13a–c** were synthesized by the same method as for Cp(CO)(PPh₃)RuCl, by using the ligands Ph₂P(C₆H₄-*o*-Br) (from Organometallics, Inc), Ph₂P(C₆H₄-*o*-Cl),⁴² and Ph₂P(C₆H₄-*o*-F).⁴³ Solvento complexes [Cp(CO)₂Ru(MeCN)]PF₆ (**25**),⁴⁴ [Cp(dppe)Ru(MeCN)]PF₆ (**21a**),⁴⁵ [Cp(dppe)Ru(py)]PF₆ (**21b**),⁴⁵ [Cp(CO)(PPh₃)Ru(MeCN)]PF₆ (**26a**),¹³ [Cp*(CO)₂Ru(MeCN)]PF₆

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(45) Davies, S. G.; Scott, F. J. *J. Organomet. Chem.* **1980**, 188, C42.

(27), and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{MeCN})]\text{PF}_6$ (28)⁴⁶ were prepared by the procedure described for MeI complex 10a, substituting acetonitrile for MeI.

The iodide complexes $\text{Cp}(\text{CO})_2\text{RuI}$ (15),³⁹ $\text{Cp}(\text{PPh}_3)_2\text{RuI}$ (16),⁴⁷ $\text{Cp}(\text{dppe})\text{RuI}$ (17), $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuI}$ (18),³⁹ and $\text{Cp}^*(\text{CO})_2\text{RuI}$ (19)^{48a} were prepared by refluxing the corresponding chloride with 10 equiv of NaI in methanol overnight. The products were isolated by evaporation, extraction with dichloromethane, and crystallization from toluene/pentane at -5°C .

Syntheses. **Chloro(cyclopentadienyl)dicarbonylruthenium(II)** (1). $\text{Cp}(\text{CO})_2\text{RuCl}$ was prepared by a modification of a literature procedure:⁴⁵ To a suspension of $[\text{RuCl}_2(\text{CO})_3]_2$ (1.74 g, 3.39 mmol) in THF (80 mL) in a 250-mL three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and magnetic stir bar was added CpTi (1.84 g, 6.84 mmol). The resulting suspension was refluxed under nitrogen for 20 h and evaporated in vacuo. The tan-yellow residue was extracted with toluene (4×30 mL), filtered through excess Celite, and evaporated. The orange residue, stirred in chloroform (30 mL) for 4–6 h in air, was evaporated and chromatographed on a Florisil (15×1 cm, CH_2Cl_2). Upon evaporation of the eluate, the resulting oil was triturated with excess pentane to yield solid $\text{Cp}(\text{CO})_2\text{RuCl}$ (1.00 g, 57%), identified by IR and ^1H NMR, which was used directly in the synthesis of complexes 4, 7, 13a–c, and 15 without further purification. We find this method to be superior to the method of Humphries and Knox⁴⁹ employing $\text{Ru}_3(\text{CO})_{12}$ and CpH , by which we obtain overall yields of <30%.

Carbonyl(cyclopentadienyl)(iodomethane)(triphenylphosphine)ruthenium(II) Hexafluorophosphate (10a). To a solution of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$ (200 mg, 0.41 mmol) and CH_3I (0.6 mL, 9.8 mmol, distilled and stored over Cu in the dark) in CH_2Cl_2 (20 mL) was added silver hexafluorophosphate (116 mg, 0.50 mmol). Silver chloride precipitated within minutes. The resulting suspension was stirred in the dark for 20–50 min and filtered through a column of Celite to remove AgCl . The resulting yellow solution was reduced in volume to ca. 3–5 mL, a layer of pentane (40 mL) was added, and the solution was stored at -5°C overnight. The resulting yellow microcrystals were collected on a medium-porosity frit, washed with pentane (3×5 mL), and dried in vacuo, yield 232 mg (77%).

All of the halocarbon complexes reported in this study were prepared in a similar manner, with the following exceptions: (1) For secondary iodoalkane complexes 10e and 10f, silver hexafluorophosphate was added to the solution of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$, causing AgCl to precipitate; the resulting suspension was stirred in the dark for 5–10 min prior to addition of iodoalkane and worked up in the manner described above. (2) The bisphosphine complexes 8, 9a, and 9b were precipitated rapidly by addition of ether (20 mL) and pentane (40 mL), rather than by slow crystallization, because of their greater air sensitivity.

Spectroscopic Data. $[\text{Cp}(\text{CO})_2\text{Ru}(\text{Ime})]\text{PF}_6$ (7): ^1H NMR δ 5.80 (s, C_5H_5), 2.69 (s, CH_3I); IR 2077, 2035 (s), 844 (s) cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_8\text{F}_6\text{IO}_2\text{PRu}^{1/4}\text{C}_5\text{H}_{12}$: C, 21.07; H, 2.08. Found: C, 21.40; H, 1.38. $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\text{Ime})]\text{PF}_6$ (8): ^1H NMR δ 7.70–6.90 (c, aryl), 4.56 (br s, C_5H_5), 2.14 (br s, CH_3I). Anal. Calcd for $\text{C}_{42}\text{H}_{38}\text{F}_6\text{IP}_3\text{Ru}$: C, 51.59; H, 4.51. Found: C, 51.73; H, 4.31. $[\text{Cp}(\text{dppe})\text{Ru}(\text{Ime})]\text{PF}_6$ (9a): ^1H NMR δ 7.70–7.25 (c, aryl), 4.96 (s, C_5H_5), 3.45, 3.76 (c, CH_2CH_2), 1.18 (s, CH_3I); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 132.4–129.4 (aryl), 81.60 (C_5H_5), 27.60 (CH_2), –11.97 (CH_3I); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 75.38. Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{F}_6\text{IP}_3\text{Ru}^{1/3}\text{C}_5\text{H}_{12}$: C, 43.21; H, 3.78. Found: C, 43.36; H, 3.77. $[\text{Cp}(\text{dppe})\text{Ru}(\text{I-}p\text{-tolyl})]\text{PF}_6$ (9b): ^1H NMR δ 7.75–7.20 (aryl), 6.65 (d, $^3J_{\text{HH}} = 8.1$ Hz, tolyl), 6.50 (d, $^3J_{\text{HH}} = 8.1$ Hz, tolyl), 4.90 (s, C_5H_5), 2.75–2.20 (c, CH_2CH_2), 2.25 (s, Ar CH_3).

$[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Ime})]\text{PF}_6$ (10a): ^1H NMR δ 7.60–7.20 (c, aryl), 5.23 (s, C_5H_5), 2.39 (s, CH_3I); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 200.91 (d, $^2J_{\text{PC}} = 17.1$ Hz, CO), 133.65–129.50 (aryl), 87.11 (C_5H_5), –6.88 (CH_3I); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 46.24; IR 1993 (s), 844 (s). Anal. Calcd for

$\text{C}_{25}\text{H}_{23}\text{F}_6\text{IO}_2\text{PRu}$: C, 40.39; H, 3.12. Found: C, 40.31; H, 2.97. $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{I-}p\text{-tolyl})]\text{PF}_6$ (10b): ^1H NMR δ 7.60–7.48, 7.39–7.25 (c, aryl), 7.06 (d, $^3J_{\text{HH}} = 8.75$ Hz, tolyl), 5.14 (s, C_5H_5), 2.36 (s, Ar CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 45.88; IR 1993 (s), 844 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{27}\text{F}_6\text{IO}_2\text{PRu}$: C, 45.44; H, 3.38. Found: C, 45.41; H, 3.30. $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{IET})]\text{PF}_6$ (10c): ^1H NMR δ 7.59–7.46, 7.34–7.26 (c, aryl), 5.23 (s, C_5H_5), 3.36 (m, ICH_2CH_3), 1.60 (t, $^3J_{\text{HH}} = 7.49$ Hz, ICH_2CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 46.18; IR 1993 (s), 844 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{F}_6\text{IO}_2\text{PRu}$: C, 41.23; H, 3.33. Found: C, 41.07; H, 3.25. $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{I-}p\text{-Pr})]\text{PF}_6$ (10d): ^1H NMR δ 7.59–7.47, 7.35–7.26 (c, aryl), 5.23 (s, C_5H_5), 3.36 (m, $\text{ICH}_2\text{CH}_2\text{CH}_3$), 1.67 (sextet, $^3J_{\text{HH}} = 6.95$ Hz, $\text{ICH}_2\text{CH}_2\text{CH}_3$), 0.95 (t, $^3J_{\text{HH}} = 7.3$ Hz, $\text{ICH}_2\text{CH}_2\text{CH}_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 46.30; IR 1993 (s), 844 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{F}_6\text{IO}_2\text{PRu}$: C, 42.04; H, 3.53. Found: C, 42.17; H, 3.49. $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{I-}i\text{-Pr})]\text{PF}_6$ (10e): ^1H NMR δ 7.70–7.15 (c, aryl), 5.25 (s, C_5H_5), 4.38 (sept, $^3J_{\text{HH}} = 6.88$ Hz, $\text{ICH}(\text{CH}_3)_2$), 1.695, 1.679 (d, $^3J_{\text{HH}} = 6.58$ Hz, $\text{ICH}(\text{CH}_3)_2$); IR 1985 (s), 844 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{F}_6\text{IO}_2\text{PRu}$: C, 42.04; H, 3.53. Found: C, 42.30; H, 3.69. $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{ICy})]\text{PF}_6$ (10f): ^1H NMR δ 7.94–7.78, 7.58–7.12 (c, aryl), 5.23 (s, C_5H_5), 4.42 (quintet, $^3J_{\text{HH}} = 4.38$ Hz, ICHR_2), 1.94, 1.58 (m, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 47.97; IR 1993 (s), 844 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{F}_6\text{IO}_2\text{PRu}$: C, 44.40; H, 3.85. Found: C, 44.71; H, 3.85. $[\text{Cp}^*(\text{CO})_2\text{Ru}(\text{Ime})]\text{PF}_6$ (11a): ^1H NMR δ 2.62 (s, CH_3I), 2.11 (s, $\text{C}_5(\text{CH}_3)_5$); IR 2056 (s), 2014 (s), 844 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_6\text{IO}_2\text{PRu}^{1/4}\text{C}_5\text{H}_{12}$: C, 30.25; H, 3.92. Found: C, 30.95; H, 3.36. $[\text{Cp}^*(\text{CO})_2\text{Ru}(\text{I-}p\text{-tolyl})]\text{PF}_6$ (11b): ^1H NMR δ 7.49 (d, $^3J_{\text{HH}} = 8.40$ Hz, tolyl), 7.12 (d, $^3J_{\text{HH}} = 8.05$ Hz, tolyl), 2.38 (s, Ar CH_3), 2.04 (s, $\text{C}_5(\text{CH}_3)_5$); IR 2056 (s), 2014 (s), 844 (s). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{F}_6\text{IO}_2\text{PRu}$: C, 34.82; H, 3.38. Found: C, 34.77; H, 3.34. $[\text{Cp}(\text{CO})_2\text{Fe}(\text{Ime})]\text{PF}_6$ (12): ^1H NMR δ 5.48 (s, C_5H_5), 2.57 (s, CH_3I); IR 2070 (s), 2028 (s), 844 (s). Anal. Calcd for $\text{C}_8\text{H}_8\text{FeIO}_2\text{PF}_6^{1/2}\text{C}_5\text{H}_{12}$: C, 25.22; H, 1.80. Found: C, 24.70; H, 1.72. $\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Cl})\text{RuCl}$ (13a): ^1H NMR δ 8.21 (m), 7.75–7.20 (c, 6.85–6.78 (m, aryl, ortho to Cl), 4.85 (s, C_5H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 44.25; IR 1971 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{Cl}_2\text{OPRu}$: C, 54.77; H, 3.64. Found: C, 54.39; H, 3.71. $\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Br})\text{RuCl}$ (13b): ^1H NMR δ 7.71–7.29 (m), 6.79 (m, aryl, ortho to Br), 4.86 (s, C_5H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 46.71; IR 1971 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{BrClOPRu}$: C, 50.50; H, 3.36. Found: C, 50.83; H, 3.34. $[\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Cl})\text{Ru}]\text{PF}_6$ (14a): ^1H NMR δ 7.95 (d, $J = 3.28$), 7.90 (d, $J = 3.30$), 7.61 (m), 7.33–7.24 (m, aryl), 5.23 (s, C_5H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 67.73; IR 2014 (s), 844 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{ClF}_6\text{OP}_2\text{Ru}$: C, 45.33; H, 3.01. Found: C, 45.40; H, 3.03. $[\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Br})\text{Ru}]\text{PF}_6$ (14b): ^1H NMR δ 8.11–7.97 (m), 7.71–7.16 (m, aryl), 5.24 (s, C_5H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 73.87; IR 2014 (s), 844 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{BrF}_6\text{OP}_2\text{Ru}$: C, 42.37; H, 2.82. Found: C, 42.26; H, 2.75. $\text{Cp}(\text{CO})_2\text{RuI}$ (15): ^1H NMR δ 5.47 (s, C_5H_5 , CD_2Cl_2). $\text{Cp}(\text{PPh}_3)_2\text{RuI}$ (16): ^1H NMR δ 7.72 (m, aryl), 4.19 (s, C_5H_5). $\text{Cp}(\text{dppe})\text{RuI}$ (17): ^1H NMR δ 7.88 (m), 7.41–7.09 (m, aryl), 4.66 (s, C_5H_5), 2.87–2.62 (m, CH_2CH_2). $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuI}$ (18): ^1H NMR δ 7.42 (m, aryl), 4.94 (s, C_5H_5); IR 1957 (s). $\text{Cp}^*(\text{CO})_2\text{RuI}$ (19): ^1H NMR δ 2.06 (s, C_5Me_5 , CD_2Cl_2). $\text{Cp}(\text{PPh}_3)_2\text{RuO}_2\text{CPh}$ (20): ^1H NMR δ 7.65 (d, $J = 1.8$ Hz), 7.57 (d, $J = 2.2$ Hz), 7.48 (s), 7.16 (m, aryl), 4.35 (s, C_5H_5); IR 1612 (s), 1344 (s). $[\text{Cp}(\text{dppe})\text{Ru}(\text{MeCN})]\text{PF}_6$ (21a): ^1H NMR δ 7.72–7.24 (m, aryl), 4.70 (s, C_5H_5), 2.49 (s, CH_2), 2.34 (s, CH_2), 1.43 (t, $^5J_{\text{HP}} = 1.32$ Hz, MeCN). $[\text{Cp}(\text{dppe})\text{Ru}(\text{C}_5\text{H}_5\text{N})]\text{PF}_6$ (21b): ^1H NMR δ 8.59–8.54 (m, aryl), 7.82–7.07 (m, aryl), 4.63 (s, C_5H_5), 2.88 (s, CH_2), 2.79 (s, CH_2). $[\text{Cp}(\text{CO})_2\text{Ru}(\text{MeCN})]\text{PF}_6$ (25): ^1H NMR δ 5.56 (s, C_5H_5), 2.44 (s, MeCN). $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{MeCN})]\text{PF}_6$ (26a): ^1H NMR δ 7.59–7.21 (m, aryl), 5.13 (s, C_5H_5), 1.98 (d, $^5J_{\text{HP}} = 1.31$ Hz, MeCN); IR 1993 (s), 844 (s). $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\text{Me}_2\text{CO})]\text{PF}_6$ (26b): ^1H NMR δ 7.60–7.45 (m, aryl), 7.40–7.33 (m, aryl), 5.12 (s, C_5H_5), 2.09 (s, Me_2CO). $[\text{Cp}^*(\text{CO})_2\text{Ru}(\text{MeCN})]\text{PF}_6$ (27): ^1H NMR δ 2.46 (s, MeCN), 1.97 (s, C_5Me_5); IR 2063 (s), 2014 (s), 844 (s). $[\text{Cp}(\text{CO})_2\text{Fe}(\text{MeCN})]\text{PF}_6$ (28): ^1H NMR δ 5.36 (s, C_5H_5), 2.35 (s, MeCN). $[\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Cl})\text{Ru}(\text{MeCN})]\text{PF}_6$ (29a): ^1H NMR δ 7.53 (m, aryl), 7.32 (m, aryl), 6.81 (ddd, $J = 11.9$, 7.68, 1.48 Hz, aryl ortho to Cl), 5.09 (s, C_5H_5), 2.00 (d, $^5J_{\text{HP}} = 1.1$ Hz, MeCN). $[\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Br})\text{Ru}(\text{MeCN})]\text{PF}_6$ (29b): ^1H NMR δ 7.84–7.55 (m, aryl), 7.60–7.23 (m, aryl), 6.86–6.75 (m, aryl ortho to Br), 5.11 (s, C_5H_5), 2.03 (s, MeCN). $[\text{Cp}(\text{CO})(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}o\text{-Cl})\text{Ru}(\text{Ime})]\text{PF}_6$ (30a): ^1H NMR δ 7.96–7.92 (m, aryl), 7.74–7.46 (m, aryl), 7.43–7.22 (m, aryl),

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6.81–6.72 (m, aryl ortho to Cl), 5.21 (s, C₅H₅), 2.49 (s, MeI). [Cp(CO)(Ph₂PC₆H₄-o-Cl)Ru(p-I-tolyl)]PF₆ (**30b**): ¹H NMR δ 7.96–7.92 (m, aryl), 7.75–7.46 (m, aryl), 7.34–7.25 (m, aryl), 6.74 (m, aryl ortho to Cl), 5.14 (s, C₅H₅), 2.37 (s, Ar-Me).

X-ray Diffraction Study of 10b. Data collection parameters for [(C₅H₅)Ru(CO)(PPh₃)(IC₆H₄-p-CH₃)]PF₆ are given in Table I. The general methods used are published.⁵⁰ The compound crystallized in thin plates. The structure was solved by using the Patterson method, which gave the positions of the I and Ru atoms. A difference Fourier synthesis showed the PF₆⁻ ion, and two peaks of intensity equal to that of the PF₆⁻ P atom in the range 2.3–2.7 Å from the Ru atom, indicating a disorder problem. To obtain sufficient data to handle the increased number of parameters, a larger plate was selected, and a new data set collected. The coordinates of the Cp group and phenyl groups were located in subsequent difference Fourier syntheses, but it became clear that a 4:1 disorder of the iodine of the iodotoluene and the CO was present. After refinement with 80% and 20% occupancy of the two iodine positions and 80% occupancy of the major CO and tolyl positions, difference Fourier synthesis yielded the locations of the remaining 20% occupancy tolyl carbon atoms, although the C(28) and C(30) locations were common to both major and minor tolyls (see Figure 2). Isotropic refinement of all atoms at this stage yielded an *R* = 0.12. ψ -scan data indicated that the irregularly shaped plate had a minimum transmission of 45.2% and a maximum of 99.81%. A DIFABS⁵¹ empirical absorption correction was applied, and isotropic refinement yielded *R* = 0.092. Anisotropic refinement of the 80% iodine atom and all non-hydrogen atoms that were not disordered yielded *R* = 0.065. Difference Fourier synthesis yielded a plausible candidate for the 20% carbonyl carbon atom in the vicinity of the 80% iodine atom, but the oxygen atom could not be located. The 20% carbon atom and a calculated position for the 20% oxygen atom were included at fixed positions in subsequent refinements. Hydrogen atoms with thermal parameters of 1.3 times that of the atom to which they were attached were included in calculated positions for the Cp and phosphine phenyl groups in subsequent full-matrix least-squares refinement. Neutral-atom scattering factors were calculated by standard procedures.^{52a} Anomalous dispersion corrections were applied to all atoms.^{52b,53}

Calculations were performed on a VAX-station 2000 computer using SDP-Plus Software developed by Enraf-Nonius and B. A. Frenz & Associates. Positional and thermal parameters, bond distances and bond angles are given in Tables II–IV. Tables of

calculated hydrogen positions and structure factor tables are provided in the supplementary material (see the paragraph at the end of the paper).

Alkylation of Enamine by 9a. To a cooled (0 °C) solution of MeI complex **9a** (100 mg, 0.117 mmol) in CH₂Cl₂ (15 mL) was added 1-(*N*-pyrrolidinyl)cyclohexene (0.37 mL, 2.35 mmol, 20 equiv, Aldrich Chemical Co., distilled at 69–71 °C and 0.5 mmHg before use). After warming to room temperature (1 h), the reaction mixture was hydrolyzed with acetate buffer (15 mL, 0.2 M, pH 4) for 1 h, and the organic layer separated, washed with dilute HCl, NaHCO₃, and brine, dried over Na₂SO₄, filtered, and evaporated. The residue was dissolved in hexanes, filtered through a short column of silica to remove the ruthenium complex, and analyzed by GC (Varian Model 3700, with a 50-m SE 30 methylsilicone capillary column, using a 4270 integrator). The program used was 100 °C for 4 min and then 10 °C/min for 9 min. The retention times (minutes) were compared for experimental and authentic samples: cyclohexanone, 5.83; 2-methylcyclohexanone, 6.66. Alkylation by complex **10a** was performed by an identical procedure.

NMR Experiments. These were performed by dissolving the organometallic complex in CD₂Cl₂ (0.5 mL) under nitrogen, followed by addition of reagent (either as a solid or by microliter syringe), capping under N₂, sealing with Parafilm, and measuring the spectrum at 90 or 250 MHz. No other unusual precautions were taken to exclude air. In all cases, identity of products was confirmed by comparison with authentic samples.

Kinetics. Rate constants were determined by integrating at timed intervals of Cp resonances of halocarbon complex and acetonitrile complex, plotting of ln ([MeI complex + MeCN complex]/[MeI complex]) vs time, and determining the least-squares slope of the resulting straight line. Data were taken for 5 half-lives, with at least eight data points within the first half-life. Correlation coefficients of >0.999 were obtained. Since the substitutions proceeded cleanly, with no other Cp-containing products, we assumed that [MeI complex]_{initial} = [MeI complex + MeCN complex]_t. The reported rate constant is the average of seven runs, using varying amounts of MeCN (5–40 equiv); the reported uncertainty is the standard deviation.

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Supplementary Material Available: Tables of calculated hydrogen positions, thermal parameters, and general temperature factor expressions (3 pages); structure factor tables (30 pages). Ordering information is given on any current masthead page.

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