CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Nucleophilic Properties of Cyclopentadienyl(triphenylphosphine)carbonyliridium

BY A. J. OLIVER AND W. A. G. GRAHAM*

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The compound $C_5H_5IrP(C_6H_5)_3(CO)$ (1) has been prepared by the reaction of $[P(C_6H_5)_3]_2Ir(CO)Cl$ with sodium cyclopentadienide. Some oxidative addition reactions of 1 have been studied and indicate that this iridium compound is a relatively strong base. Treatment of 1 with halogens and alkyl halides affords $[C_5H_5IrP(C_6H_5)_3(CO)R]^+X^-$ (R = X = Cl, Br, I; R = CH_3, C_2H_5, C_6H_{13}, $CH_2C_6H_5$, C_3F_7 and X = I). Acids protonate complex 1 although only $[C_5H_5IrP(C_6H_5)_3(CO)H]^+$-$[B(C_6H_5)_4]^-$ could be isolated. The Lewis acids $ZnBr_2$, $HgCl_2$, and $TlCl_3$ afford adducts such as $C_5H_5IrP(C_6H_5)_3(CO)\cdot HgCl_2$.

Introduction

Many oxidative addition reactions on d^8 organo transition metal systems have been described and these have been reviewed.[1] Little work has been carried out on the cyclopentadienyl derivatives of the heavier transition metals. Recent work in this laboratory has expanded the known reactions of cyclopentadienyldicarbonylrhodium[2] and its phosphine[3,4] derivatives. However, no work has been reported on similar iridium systems. Although $C_5H_5Ir(CO)_2$ (2) can be prepared in good yield by the method of Fischer and Brenner,[5] we have found a less tedious procedure to form the closely related compound $C_5H_5IrP(C_6H_5)_3(CO)$ (1). The latter compound could be expected to give more stable Ir(III) derivatives than the dicarbonyl (2) by analogy with similar rhodium complexes.[3]

The strong resemblance of $C_5H_5Co(CO)_2$ and $Fe(CO)_5$ has often been noted[6,7] and thus the phosphine-substituted cyclopentadienyldicarbonyl compounds of rhodium and iridium might usefully be compared with the phosphine-substituted pentacarbonyls of ruthenium and osmium, *e.g.*, $Ru(CO)_3[P(C_6H_5)_3]_2$. The oxidative addition reactions of the latter systems have been well studied by Collman and Roper.[8-10] Osmium compounds were found to give stable ionic derivatives, *e.g.*, $\{OsBr(CO)_3[P(C_6H_5)_3]_2\}^+Br^-$, as intermediates in the formation of the neutral dihalide.[9] No such ionic intermediates could be isolated for the analogous ruthenium systems.[8] This was attributed to the heavier transition metal having more strongly bound carbonyl groups.[9] In comparison, $C_5H_5RhP(CH_3)_2C_6H_5(CO)$ reacts with halogens to give unstable ionic intermediates which could be isolated only with difficulty.[3] It might be expected therefore that comparable iridium complexes would give stable ionic derivatives, and this has been borne out by the work reported here.

Discussion

Cyclopentadienyl(triphenylphosphine)carbonyliridium (1) has been reported to form by the reaction of $C_5H_5Ir(CO)_2$ (2) with triphenylphosphine but was poorly characterized in the essentially kinetic study.[11] This method could be expected efficiently to produce 1; however a very lengthy procedure is necessary to obtain high yields of $Ir(CO)_3Cl$ which is required as an intermediate.[5] Thus the method adopted was that of treating the well-known and easily prepared compound $[(C_6H_5)_3P]_2Ir(CO)Cl$[12] with sodium cyclopentadienide. The reaction requires the displacement of a phosphine ligand by the π-electron system. This is similar to the recently reported preparation of $C_5H_5Co[P(C_6H_5)_3]_2$[13] from $[(C_6H_5)_3P]_3CoN_2H$ and cyclopentadiene. The derivative $C_5H_5RhP(C_6H_5)_3(CO)$ may likewise be formed by the reaction of sodium cyclopentadienide with $[(C_6H_5)_3P]_2Rh(CO)Cl$.[14] The latter is reported to be produced in high yield from $RhCl_3$ *via* Wilkinson's compound $[(C_6H_5)_3P]_3RhCl$.[15] It is doubtful if this method has any advantage compared to the reported procedure from cyclopentadienyldicarbonylrhodium and triphenylphosphine.[4,11] The reactions were not carried out in tetrahydrofuran, in which the sodium cyclopentadienide was prepared, for compound 1 was found to decompose slowly in this solvent.

Iodine readily reacts with solutions of 1 without evolution of carbon monoxide to form an ionic derivative 3. Bromine and chlorine react similarly but the product with chlorine decomposes slowly in the solid state at room temperature; the other ionic halides are stable. This indicates the high stability of these derivatives compared to other ionic halide intermediates[8,9] and also confirms the very basic nature of compound 1. The reactions with bromine and iodine require equimolar ratios or a slight excess of 1 to forestall the formation of the complex anions I_3^- and Br_3^-. The ionic nature of 3 was confirmed by the immediate

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* To whom correspondence should be addressed.

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[14] This type of reaction is even more general, for we have similarly prepared $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$ from $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$: A. J. Oliver and W. A. G. Graham, to be submitted for publication.

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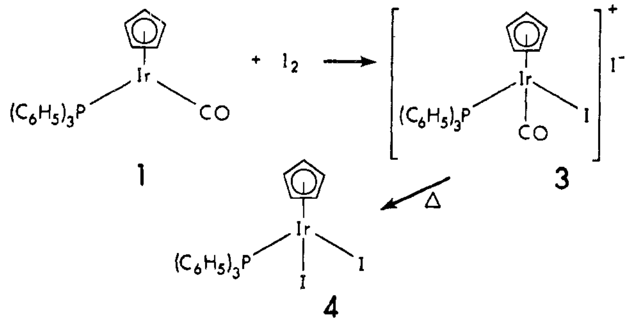
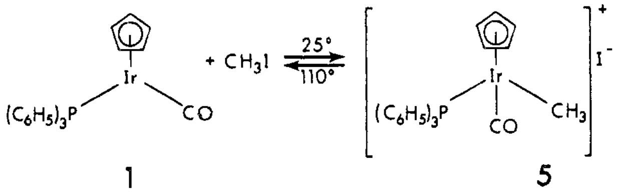
formation of a precipitate on reaction with a solution of sodium tetraphenylboron in methanol. In less polar solvents these ionic dihalides were almost insoluble.



On refluxing a suspension of **3** in toluene, carbon monoxide was evolved with the formation of a neutral diiodide **4** and some decomposition. The analogous chloride and bromide reacted similarly. The closely related compound $C_5(CH_3)_5IrP(C_6H_5)_3Cl_2$ has been prepared by treatment of $[C_5(CH_3)_5IrCl_2]_2$ with triphenylphosphine.[16]

The reaction of methyl iodide with the iridium complex **1** also yields an ionic product $[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot 0.5CH_2Cl_2$ (**5**). The presence of solvent in the crystals was confirmed by analysis and nmr spectroscopy. A limited number of other alkyl halides undergo this reaction, for which a kinetic study[4] has been made. Some steric restriction seems to apply although this is not as severe as in analogous rhodium reactions.[3,4] There can be little dependence on chain length, since *n*-hexyl iodide yields a stable product. Under the same conditions, infrared spectroscopy gives no evidence for the required product with isopropyl iodide; the reaction thus seems limited to primary halides. Typical of nucleophilic attack on alkyl halides,[17] the rate of reaction is in the order I > Br > Cl, and a product is formed with ease from the activated benzyl iodide. These ionic alkyliridium complexes tend to form oils in their preparation but solids result using the solvent mixtures dichloromethane–diethyl ether or dichloromethane–benzene rather than dichloromethane–hexane. In some cases, however, the latter solvent mixture affords larger crystals. The presence of dichloromethane in the crystals appeared independent of the three possible mixtures used for recrystallization and even high vacuum did not remove this solvent. It remains unclear why dichloromethane is held strongly in the crystal lattice of most alkyl halide derivatives but is not retained by the derivatives of benzyl iodide or perfluoropropyl iodide or the ionic dihalides.



The reaction of methyl iodide with a similar rhodium system was found[3] to give a neutral acyl compound $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)I$, presumably *via* an ionic intermediate analogous to complex **5**. Use of heat to encourage the nucleophilic attack of iodide ion on $C_5H_5IrP(C_6H_5)_3(CO)CH_3^+$ might also be expected to give an acyl compound; however, refluxing in toluene was found to give a high yield of **1**. It seems reasonable that an equilibrium between compounds **1** and **5** is displaced by removal of methyl iodide into the gas phase and this results in the re-forming of **1**.

The nucleophilic character of **1** is evident from the reactions already mentioned and is very clearly shown in its reactions with acids. The protonation of d^8 complexes by strong acids is well known.[1,10,18] The compound **1** is shown by a shift in the carbonyl stretching frequency to 2063 cm^{-1} to be protonated by most moderately strong acids. Silicotungstic acid, as would be expected,[19] gives an immediate precipitate on reaction with **1** in acetone solution. Derivatives with the oxidizing acids perchloric and sulfuric rapidly decompose, and those with halogen acids dissociate in solution. A pure product could be obtained, however, using hydrogen bromide and quickly treating the protonated compound with sodium tetraphenylboron.

Lewis acids were similarly found to form adducts with **1**. Boron and aluminum trichlorides afford products which could not be isolated in a pure state, but adducts were characterized with zinc bromide, mercuric chloride, and thallic chloride. In forming these adducts it is necessary that exactly equimolar ratios be used, as purification of the products is very difficult. Kemmitt and coworkers[20,21] have shown that a number of d^8 compounds can form adducts with mercuric chloride, and of particular interest is the related iridium adduct $C_5H_5Ir(C_8H_{12})\cdot HgCl_2$.[21a] Adducts with zinc bromide and thallic chloride are unusual since very few such complexes have been formed between these metals and any transition metal.[22]

Infrared Spectra.—The compound **1** exhibits a single carbonyl absorption at the same frequency as that of an authentic sample of $C_5H_5IrP(C_6H_5)_3(CO)$ prepared from $C_5H_5Ir(CO)_2$ and $(C_6H_5)_3P$. This is at a frequency (Table I) below that of the rhodium analog as seems to be usual for the carbonyls of third-row transition metals compared to second row.[5,11,23] This has been attributed to the lanthanide contraction in the group VI hexacarbonyls[23] and such an explanation should be equally valid for group VIII carbonyls.

The formation of ionic derivatives of **1** and conse-

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TABLE I

PHYSICAL PROPERTIES AND INFRARED SPECTRAL DATA

Compound	Mp, °C	Color	% yield	Carbonyl str freq	
				Solvent	ν_{CO}, cm^{-1}
$C_5H_5IrP(C_6H_5)_3(CO)$	160	Orange	60	C_6H_{12}	1944
				CH_2Cl_2	1926
$[C_5H_5IrP(C_6H_5)_3(CO)Cl]^+Cl^-$		Pale yellow	86	CH_2Cl_2	2088
$C_5H_5IrP(C_6H_5)_3Cl_2$	290	Yellow	26		
$[C_5H_5IrP(C_6H_5)_3(CO)Br]^+Br^-$	140	Yellow	93	CH_2Cl_2	2085
$C_5H_5IrP(C_6H_5)_3Br_2$	275	Orange	31		
$[C_5H_5IrP(C_6H_5)_3(CO)I]^+I^-$	110	Orange	85	CH_2Cl_2	2079
$C_5H_5IrP(C_6H_5)_3I_2$	290	Red	41		
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Cl^-\cdot 0.5CH_2Cl_2$	170	White	77	CH_2Cl_2	2049
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Br^-\cdot 0.5CH_2Cl_2$	180	White	84	CH_2Cl_2	2049
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot 0.5CH_2Cl_2$	180	White	89	CH_2Cl_2	2050
$[C_5H_5IrP(C_6H_5)_3(CO)C_2H_5]^+I^-\cdot 0.5CH_2Cl_2$	160	White	51	CH_2Cl_2	2044
$[C_5H_5IrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-\cdot 0.5CH_2Cl_2$	120	White	47	CH_2Cl_2	2043
$[C_5H_5IrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	180	White	90	CH_2Cl_2	2045
$[C_5H_5IrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	185	Yellow	61	CH_2Cl_2	2086
$[C_5H_5IrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$	155	White	85	CH_2Cl_2	2063
$C_5H_5IrP(C_6H_5)_3(CO)\cdot ZnBr_2$	220	Pale yellow	85	CH_2Cl_2	2005
				$(CH_3)_2CO$	1928
				Nujol mull	2000
$C_5H_5IrP(C_6H_5)_3(CO)\cdot HgCl_2$	260	Pale yellow	90	CH_2Cl_2	2024
				$(CH_3)_2CO$	2020
				Nujol mull	2017
$C_5H_5IrP(C_6H_5)_3(CO)\cdot TlCl_3$	160	Pale yellow	89	CH_2Cl_2	2050
				$(CH_3)_2CO$	2047
				Nujol mull	2062 m
					2045 m

TABLE II

^{1}H NMR SPECTRAL DATA[a]

Compound	Solvent	$\tau_{C_6H_5}$	$\tau_{C_5H_5}$	τ_R[b]	$J_{P-C_5H_5}$[c]	J_{PR}
$C_5H_5IrP(C_6H_5)_3(CO)$	CCl_4	2.68	5.00		0.6	
$C_5H_5IrP(C_6H_5)_3Cl_2$	$CDCl_3$	2.51	4.60		1.5	
$C_5H_5IrP(C_6H_5)_3Br_2$	$CDCl_3$	2.57	4.62		1.4	
$C_5H_5IrP(C_6H_5)_3I_2$	$CDCl_3$	2.57	4.58		1.5	
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Cl^-\cdot 0.5CH_2Cl_2$[d]	$CDCl_3$	2.43	3.95	8.87	1.1	5.1
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Br^-\cdot 0.5CH_2Cl_2$[d]	$CDCl_3$	2.42	3.95	8.85	1.2	5.1
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot 0.5CH_2Cl_2$[d]	$CDCl_3$	2.43	3.98	8.84	1.2	5.0
$[C_5H_5IrP(C_6H_5)_3(CO)C_2H_5]^+I^-\cdot 0.5CH_2Cl_2$[d]	$CDCl_3$	2.40	3.98	8.47 (4)[e]	1.1	
				7.07 (1)[e]		
$[C_5H_5IrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-\cdot 0.5CH_2Cl_2$[d]	$CDCl_3$	2.40	4.00	8.87	1.1	
$[C_5H_5IrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	$CDCl_3$	2.36	4.17	5.84 (1)[e]	1.1	
				6.90 (1)[e]		
$[C_5H_5IrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	$CDCl_3$	2.37	3.73		1.0	
$[C_5H_5IrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$[f]	$(CD_3)_2CO$	2.44		24.42		25

[a] Measured at 60 Mc at 40°. [b] The symbol R refers to the alkyl group or proton directly attached to iridium. [c] Recorded in cps. [d] These derivatives exhibited one resonance at τ 4.70 ($\pm$0.02), integrating to one proton, attributable to dichloromethane. [e] Refers to center of unresolved resonances and the number in parentheses corresponds to the number of protons by integration. [f] The spectrum of this compound was recorded at 100 Mc.

quent increase in formal oxidation state and effective electronegativity of iridium cause the usual increase in the carbonyl stretching frequencies.[24] The extent of this increase is affected by the electron-withdrawing ability of the added substituent on the metal; the change is observed to be in the order Cl > Br > I > H > CH_3 > R, in accordance with expectations.

The adducts with $ZnBr_2$, $HgCl_2$, and $TlCl_3$ also show increases in carbonyl stretching frequencies depending on the acidity of these halides; Lewis acids can be expected to remove charge from iridium although there is no formal increase in oxidation state of iridium. The spectra of the adducts were taken in acetone and in Nujol mulls, as well as in dichloromethane so that comparisons could be made with such derivatives as $C_5H_5Rh(CO)_2\cdot HgCl_2$[21a] and $C_5H_5Co(CO)_2\cdot HgCl_2$.[20] The latter derivatives were found to dissociate in acetone, whereas this is not so for $C_5H_5IrP(C_6H_5)_3(CO)\cdot HgCl_2$. This may be attributed to the higher basicity of **1**, although a complex of **1** with the weaker Lewis acid, $ZnBr_2$, does dissociate in acetone.

^{1}H Nmr Spectra.—At least two sets of resonances were observed in each spectrum (Table II) and these can be attributed to the phenyl protons of the phosphorous ligand and the cyclopentadienyl protons. The phenyl resonances show typical complex structures and thus for each compound only the chemical shift of the most intense line is listed in Table II.

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[24] Compare with the addition products of $[(C_6H_5)_3P]_2Ir(CO)Cl$: L. Vaska, *Accounts. Chem. Res.*, **1**, 335 (1968).

TABLE III
ANALYTICAL DATA

	% calcd				% found			
	C	H	X[a]	P	C	H	X[a]	P
$C_5H_5IrP(C_6H_5)_3(CO)$	52.64	3.68			53.09	3.94		
$[C_5H_5IrP(C_6H_5)_3(CO)Cl]^+Cl^-$	46.60	3.26			46.90	3.31		
$C_5H_5IrP(C_6H_5)_3Cl_2$	46.78	3.41			46.65	3.45		
$[C_5H_5IrP(C_6H_5)_3(CO)Br]^+Br^-$	40.75	2.85	22.59	4.38	40.70	2.80	21.56	4.14
$C_5H_5IrP(C_6H_5)_3Br_2$	40.66	2.97			41.33	2.98		
$[C_5H_5IrP(C_6H_5)_3(CO)I]^+I^-$	35.97	2.52	31.67	3.86	35.90	2.94	31.42	3.66
$C_5H_5IrP(C_6H_5)_3I_2$	35.72	2.61	32.81	4.00	35.76	2.66	33.04	3.88
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Cl^-\cdot 0.5CH_2Cl_2$	47.81	3.78			48.02	3.63		
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Br^-\cdot 0.5CH_2Cl_2$[b]	44.71	3.53	11.67	4.52	44.89	3.71	11.57	4.39
$[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot 0.5CH_2Cl_2$	41.84	3.30			41.59	3.60		
$[C_5H_5IrP(C_6H_5)_3(CO)C_2H_5]^+I^-\cdot 0.5CH_2Cl_2$[c]	42.66	3.51	17.01	4.15	42.65	3.14	17.45	4.14
$[C_5H_5IrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-\cdot 0.5CH_2Cl_2$	45.66	4.27			44.88	4.44		
$[C_5H_5IrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	48.63	3.55	16.57	4.05	48.28	3.67	17.01	4.05
$[C_5H_5IrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	38.44	2.39			38.28	2.51		
$[C_5H_5IrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$	66.43	4.76		3.57	66.74	4.85		3.03
$C_5H_5IrP(C_6H_5)_3(CO)\cdot ZnBr_2$	37.30	2.61			37.55	2.39		
$C_5H_5IrP(C_6H_5)_3(CO)\cdot HgCl_2$	35.19	2.46	3.78	8.66	35.25	2.67	3.78	8.56
$C_5H_5IrP(C_6H_5)_3(CO)\cdot TlCl_3$	33.58	2.35			33.92	2.66		

[a] The symbol X refers to halogen and if two different halogens are present it refers to the halogen of higher atomic number. [b] Cl analysis: calcd, 5.18; found, 5.10. [c] Cl analysis: calcd, 4.75; found, 4.91.

Spectral data were obtained for most compounds. However, the ionic dihalides and the neutral Lewis acid adducts were not measured since they were insufficiently soluble in deuteriochloroform or carbon tetrachloride.

As expected, phosphorus caused the cyclopentadienyl resonances to appear as doublets, and the size of this coupling was similar to that in related rhodium compounds.[2]

The unique iridium proton in the compound $[C_5H_5IrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$ was confirmed by a broad doublet at high field; the doublet is clearly due to phosphorus coupling, and the broad nature of these peaks is probably caused by coupling to the five cyclopentadienyl protons.[25] The chemical shift and coupling constant of the single proton were in agreement with those of other phosphorus-substituted iridium hydrides.[26-28]

For the methyliridium complexes $[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+X^-$, the resonances are independent of X as would be predicted for such ionic compounds. The couplings of phosphorus to the cyclopentadienyl and methyl protons are consistent with those in $[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$, confirming the tentative assignments made for the latter compound.[3] The ethyl, hexyl, and benzyl derivatives of **1** give complex resonances for the alkyl group; in particular the α-methylene group (and possibly a β-methylene group) would be expected to exhibit an AB pattern due to the asymmetry around iridium, and further splitting is likely from coupling to phosphorus and β protons. The resonances of each compound were found to integrate correctly.

Experimental Section

All reactions were carried out under a nitrogen atmosphere and solid products were handled with minimum exposure to air. Hexane, benzene, and toluene were dried over sodium or 9.5% sodium–lead alloy, tetrahydrofuran was distilled from calcium hydride, and dichloromethane was dried over anhydrous magnesium sulfate. Diethyl ether (anhydrous) and other solvents and reagents were used as obtained from commercial sources. Alkyl iodides were purified before use by distillation from sodium thiosulfate. The starting materials $[(C_6H_5)_3P]_2Ir(CO)Cl$[12] and $[(C_6H_5)_3P]_3RhCl$[15] were prepared by literature methods.

Microanalyses (Table III) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of this department. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127 A recorder using gaseous CO and DBr for calibration purposes. Nmr measurements were made on Varian A56/60A and HA100 instruments.

Preparation of $C_5H_5IrP(C_6H_5)_3(CO)$.—A 1 *M* solution of sodium cyclopentadienide in tetrahydrofuran (20 ml) was evaporated to dryness. Benzene (100 ml) and $[(C_6H_5)_3P]_2Ir(CO)Cl$ (3.5 g, 5 mmol) were added and the mixture was refluxed for 6 hr. After cooling and filtering through a short column of Florisil the filtrate was concentrated to 5 ml. Addition of hexane (25 ml) and cooling to −15° yielded bright orange crystals of product (1.64 g, 3 mmol, 60%).

Preparation of $C_5H_5RhP(C_6H_5)_3(CO)$.—Tris(triphenylphosphine)rhodium chloride (1.0 g, 1.08 mmol) was suspended in benzene (25 ml) and carbon monoxide bubbled through the mixture for 1 hr. After this time the solid and solution had become pale yellow, indicating the formation of $[(C_6H_5)_3P]_2Rh(CO)Cl$. This product was allowed to react in benzene solution with excess sodium cyclopentadienide (6 ml of 1 *M* solution in tetrahydrofuran). Using the work-up procedure of the analogous iridium system, orange crystals of the required product (0.24 g, 0.51 mmol, 48%) were obtained, mp 153–155°, lit.[11] mp 153°. *Anal.* Calcd for $C_{24}H_{20}OPRh$: C, 62.90; H, 4.40. Found: C, 63.34; H, 4.22.

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)Cl]^+Cl^-$.—The compound $C_5H_5IrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) was dissolved in toluene (10 ml) and cooled to liquid nitrogen temperature and chlorine (0.09 g, 1.27 mmol) was distilled in. The mixture was allowed to warm to −78° and excess chlorine was removed under reduced pressure. Addition of pentane (10 ml) and warming to −30° yielded a light yellow microcrystalline powder. This was collected and washed twice with 10-ml portions of pentane, keeping

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the temperature close to −30°. After drying under high vacuum the yield was 0.34 g (0.55 mmol, 86%).

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)Br]^+Br^-$.—A solution of bromine (0.10 g, 0.64 mmol) in dichloromethane (10 ml) was added to a stirred solution of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) in dichloromethane (10 ml). After 10 min, hexane (20 ml) was added and the mixture was cooled to 0°. The small yellow crystals of product which formed were collected, washed with pentane (5 ml), and dried (yield 0.42 g, 93%).

A similar procedure using iodine in place of bromine was used to prepare $[C_5H_5IrP(C_6H_5)_3(CO)I]^+I^-$ in 85% yield.

Preparation of $C_5H_5IrP(C_6H_5)_3Cl_2$.—The ionic derivative $[C_5H_5IrP(C_6H_5)_3(CO)Cl]^+Cl^-$ (0.20 g, 0.32 mmol) was refluxed in toluene (20 ml) for 3 days. After filtering off some black decomposition product, the filtrate was cooled to −15° to afford yellow crystals of the required product (0.05 g, 0.08 mmol).

Using this procedure, the neutral complexes of $C_5H_5IrP(C_6H_5)_3Br_2$ and $C_5H_5IrP(C_6H_5)_3I_2$ were prepared from the corresponding ionic halides with reaction times of 3 days and 12 hr, respectively.

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Cl^- \cdot 0.5CH_2Cl_2$.—Methyl chloride (2 ml) was distilled into a Carius tube in which had been placed a sample of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.30 g, 0.55 mmol). After sealing and allowing the mixture to stand at room temperature for 5 days, excess methyl chloride was removed under reduced pressure. The solid residue was taken up in dichloromethane (3 ml) and this solution was added slowly to 30 ml of stirred diethyl ether. The resulting white precipitate was collected and recrystallized from dichloromethane–diethyl ether to give silvery white crystals (0.27 g, 0.42 mmol).

Methyl bromide was treated similarly for a period of 3 days with subsequent recrystallization from dichloromethane–hexane to give $[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+Br^- \cdot 0.5CH_2Cl_2$.

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)CH_3]^+I^- \cdot 0.5CH_2Cl_2$.—A sample of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.55 g, 1.0 mmol) was dissolved in dichloromethane (10 ml) and methyl iodide (1.0 g, 7.0 mmol) was added. The mixture was stirred for 15 min and hexane (40 ml) was added. A white crystalline precipitate was formed which was recrystallized from dichloromethane–hexane (yield 0.61 g, 89%).

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)C_2H_5]^+I^- \cdot 0.5CH_2Cl_2$.—Ethyl iodide (2.0 ml, 3.9 g, 25 mmol) was added to a solution of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.55 g, 1.0 mmol) in dichloromethane (10 ml). The mixture was allowed to stand for 48 hr and was evaporated to dryness. The residue was recrystallized from dichloromethane–benzene to give silvery white crystals. Subsequent recrystallization from dichloromethane–hexane afforded the analytically pure compound (0.38 g, 0.51 mmol, 51%).

Benzyl iodide was allowed to react in similar fashion for a period of 12 hr to yield $[C_5H_5IrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$.

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)C_6H_{13}]^+I^- \cdot 0.5CH_2Cl_2$.—Dichloromethane (5 ml) was used to dissolve $C_5H_5IrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) and *n*-hexyl iodide (1.0 ml, 1.44 g, 6.8 mmol) was added. After 1 week, solvent and excess halide were removed under reduced pressure. The remaining solid was recrystallized three times from dichloromethane–diethyl ether to afford the required product (0.24 g, 0.30 mmol).

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)C_3F_7]^+I^-$.—The compound $C_5H_5IrP(C_6H_5)_3(CO)$ (0.30 g, 0.55 mmol) was dissolved in dichloromethane (5 ml), the solution was cooled to −70°, and perfluoropropyl iodide (3.0 g, 10.1 mmol) was added. The mixture was allowed to attain room temperature over a period of 2 hr and hexane (10 ml) was added. The solid produced was collected and recrystallized from dichloromethane–hexane to yield yellow crystals (0.28 g, 0.33 mmol, 61%).

Preparation of $[C_5H_5IrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$.—A sample of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) was dissolved in dichloromethane (10 ml), and, after cooling to −70°, hydrogen bromide was passed through the solution until the yellow color had completely disappeared. Addition of pentane (30 ml) and warming to room temperature produced small white crystals which were collected, washed with two 10-ml portions of pentane, and dried. Part of this product (0.17 g) was dissolved in methanol (10 ml) and a solution of sodium tetraphenylboron (0.17 g, 0.50 mmol) in methanol (10 ml) was immediately added. The solution was stirred for 10 min and the white precipitate which had formed was collected. After washing with two 5-ml portions of methanol and 5 ml of pentane and drying, the yield of product was 0.20 g, 0.23 mmol.

Preparation of $C_5H_5IrP(C_6H_5)_3(CO) \cdot HgCl_2$.—Mercuric chloride (0.174 g, 0.639 mmol) was dissolved in a 1:2 methyl ethyl ketone–benzene mixture (10 ml) and a solution of $C_5H_5IrP(C_6H_5)_3(CO)$ (0.350 g, 0.639 mmol) in the same solvent (5 ml) was added quickly with vigorous stirring. The resultant pale yellow precipitate was collected, washed with acetone (10 ml), and dried (yield 0.473 g, 0.578 mmol).

Reactions with zinc bromide and thallic chloride were carried out using the procedure outlined above; however in the former case, the final washing was done with the methyl ethyl ketone–benzene mixture, not acetone. Thus the adducts $C_5H_5IrP(C_6H_5)_3(CO) \cdot ZnBr_2$ and $C_5H_5IrP(C_6H_5)_3(CO) \cdot TlCl_3$ were produced.

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