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## New Cationic Complexes of Iridium(I), Iridium(III), and Rhodium(III)

H. C. CLARK\* and K. J. REIMER

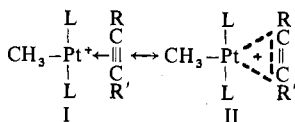
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The syntheses of two new series of cationic Ir(III) and Rh(III) complexes are described: namely, [IrCl(Me)CO-(PMePh<sub>2</sub>)<sub>2</sub>L]PF<sub>6</sub>, where L = CO, carbene, nitrile, or imino ether, and [MCl<sub>2</sub>L(PMe<sub>2</sub>Ph)<sub>3</sub>]PF<sub>6</sub>, where M = Ir or Rh and L = H<sub>2</sub>O, pyridine, carbene, etc. Their spectroscopic parameters and stereochemistries are described. Two new iridium(I)-acetylene cations have been prepared. Attempts to prepare the Rh(III) analogs of the above methyliridium(III) cations led to cationic acylrhodium species. The applicability of the metal-induced carbonium ion model to account for carbene complex formation from iridium(III)- and rhodium(III)-acetylene complexes is considered.

### Introduction

Much of the recent research in this laboratory has dealt with the reactions of organoplatinum cations with unsaturated species such as acetylenes, olefins, isocyanides, and nitriles. It has been found that the course of some of these reactions can be interpreted in terms of a platinum-induced carbonium ion model.<sup>1</sup> Reactivity characteristic of carbonium ions, II, such as intramolecular rearrangement and/or nucleophilic addition is thus observed.



Clearly, this reactivity is directly related to the bonding in these particular compounds and other reactions may occur with different metal complexes.

We have now attempted to apply the concept of metal-induced carbonium ions to complexes of other metals to determine if a system could be designed which would undergo reactions analogous to those of the organoplatinum cations.

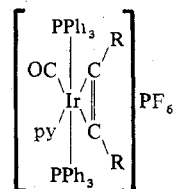
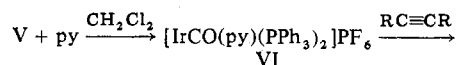
### Results and Discussion

**A. Reactions of Rhodium(I) and Iridium(I) Complexes.** A large number of cationic complexes of rhodium(I) and iridium(I) are known.<sup>2-14</sup> Since removal with a silver salt in solution of the chloride ligand in MClCO(PPh<sub>3</sub>)<sub>2</sub>, III (M = Rh, Ir),<sup>7</sup> gives [M(CO)(solvent)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, IV, which is isoelectronic with [Pt(Me)(solvent)L<sub>2</sub>]<sup>+</sup>, it was of interest to investigate reactions of such cations with acetylenes. However, no products could be isolated from the reaction of methanol or acetone solutions of IV with a variety of di- or mono-substituted acetylenes. Displacement of coordinated acetylenes in the presence of a large excess of oxygen donors (such as

methanol or acetone) was observed for the methylplatinum(II) cations and it is possible that a similar "solvation" effect was operative in these present reactions.

Although III did react with silver hexafluorophosphate in dichloromethane, the reaction was always incomplete unless a small amount of acetone was added to the reaction mixture. In the absence of other donors (such as pyridine) the addition of pentane gave crystals of [MCO(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>, V. This is a convenient starting material for a large number of compounds, [MCO(L)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>, but no complexes could be isolated from reactions with acetylenes. The addition of acetylenes to dichloromethane solutions of V resulted in intensely colored (red or orange) solutions from which only the unreacted acetone cation could sometimes be recovered. A reaction between ethylene and the iridium-acetone cation afforded a product which appeared analogous to the previously reported<sup>15</sup> complex [IrCO(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>+</sup>.

However, 1:1 adducts were isolated with electrophilic acetylenes if 1 equiv of pyridine was introduced into the reaction mixture before the acetylene addition (eq 1). If the



VII (R = CF<sub>3</sub>, CO<sub>2</sub>CH<sub>3</sub>)

order of addition was reversed, no compound could be isolated from the reaction. Presumably the pyridine discourages al-

Table I. Infrared Data (cm<sup>-1</sup>) for Some Acetylene Complexes of Rhodium and Iridium<sup>a</sup>

Complex <sup>b</sup>	$\nu(\text{C}\equiv\text{O})$ (s, sp)	$\nu(\text{CO}_2\text{CH}_3)$ (m, br)	$\nu(\text{C}\equiv\text{C})$ (m, br)	Ref
[IrCO(py)(CF <sub>3</sub> C≡CCF <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]Z	2030		1768	This work
[IrCO(py)(dma)(PPh <sub>3</sub> ) <sub>2</sub> ]Z	2000	1728, 1698	1785	This work
[Ir(CO) <sub>2</sub> (dma)(PPh <sub>3</sub> ) <sub>2</sub> ]Y	2091, 2049	1708	1814	10
[Ir(CO) <sub>2</sub> (dma)(PMePh <sub>2</sub> ) <sub>2</sub> ]Y	2086, 2038	1704	1808	10
[Ir(CO) <sub>2</sub> (dma)(PEt <sub>3</sub> ) <sub>2</sub> ]Y	2088, 2044	1697	1791	10
[IrClCO(dma)(PPh <sub>3</sub> ) <sub>2</sub> ]	1980	1725, 1680	1770	16

<sup>a</sup> Spectra measured as Nujol mulls. <sup>b</sup> Z<sup>-</sup> = PF<sub>6</sub><sup>-</sup>; Y<sup>-</sup> = BPh<sub>4</sub><sup>-</sup>; dma = CH<sub>3</sub>OCC≡CCOCH<sub>3</sub>.

Table II. Analytical and Physical Data for Cationic Methyliridium(III) Complexes

Complex <sup>a</sup>	M ≡	Mp, °C	% C		% H	
			Found	Calcd	Found	Calcd
M-CO		170-173	41.08	41.26	3.38	3.46
M-CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O		128-130	43.35	43.37	3.97	3.98
M-C(OCH <sub>3</sub> )CH <sub>3</sub>		160-165	43.50	43.39	4.23	4.11
M-NCC <sub>6</sub> F <sub>5</sub>		>60 <sup>d</sup>	41.99	41.66	3.14	2.90
M- <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>		193-195	43.17	43.60	3.41	3.45
M- <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>		152-153	46.25	46.33	3.70	3.89
M- <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>		192-194	45.51	45.55	3.78	3.82
M-NCC <sub>6</sub> H <sub>4</sub> CN-M <sup>b</sup>		>115 <sup>d</sup>	43.96	43.67	3.16	3.55
M-NCC <sub>6</sub> F <sub>4</sub> CN-M		190-192	41.86	41.95	2.84	3.19
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub>		124-126	41.29	41.53	3.11	3.19
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub>		169-170	41.82	42.11	3.11	3.34
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> O)C=NH-M		193-195	41.47	41.43	3.46	3.37
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> CH <sub>2</sub> O)C=NH-M		>130 <sup>d</sup>	42.24	42.44	3.88	3.66

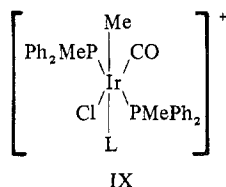
<sup>a</sup> All complexes are white unless otherwise stated. <sup>b</sup> Pale yellow. <sup>c</sup> All complexes melt with decomposition. <sup>d</sup> Indicates complex decomposes without melting.

ternative reactions either by sterically preventing attack on the coordinated acetylene or, more likely, by blocking one of the coordination sites, thus preventing the formation of intermediates with more than one coordinated acetylene.

The value of  $\nu(\text{C}\equiv\text{C})$  for the dimethyl acetylenedicarboxylate (dma) complex, VII, is lower than the frequencies reported<sup>10</sup> for the compounds [Ir(CO)<sub>2</sub>(dma)(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and approaches the value observed<sup>16</sup> in the spectrum of the neutral compound IrClCO(dma)(PPh<sub>3</sub>)<sub>2</sub> (Table I). Such low values have been interpreted in terms of a bonding description involving considerable metalocyclopropene character. This would preclude reaction by the carbonium ion mechanism. These observations emphasize the importance of the energy of the d orbitals and the electron density on the metal, for even though the complex has a formal positive charge, the metal may still act as a strong nucleophile toward acetylenes.

These data suggested that higher valent, more electrophilic complexes such as those of rhodium(III) and iridium(III) might more successfully duplicate the reactions of the methylplatinum cations.

**B. Methyliridium(III) Complexes.** The iodide ligand in IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub>, VIII, is labile due to the high trans influence of the methyl group<sup>17</sup> and reaction with silver hexafluorophosphate in a polar donor solvent (such as methanol or acetone) caused the immediate precipitation of silver iodide. After centrifugation, the addition of neutral ligands to the resulting clear solutions resulted in the formation of a variety of cationic complexes, IX. The analytical and physical data



for these new complexes are given in Table II. Attempts to isolate the solvated complexes (i.e., IX with L = acetone or

methanol) gave only yellow oils which on attempted crystallization gave extensive decomposition.

The <sup>1</sup>H NMR spectra (Table III) of the phosphine methyl protons show 1:2:1 triplets for all of these new complexes, indicative of large <sup>31</sup>P-<sup>31</sup>P coupling, characteristic of trans phosphines.<sup>18-20</sup> The iridium methyl group gives a triplet in all cases due to coupling with the two equivalent <sup>31</sup>P nuclei.

More importantly, these spectra show clearly that only one isomer is present, although theoretically three isomeric forms of IX are possible. This is supported by vibrational spectroscopic data (Table IV) which show that the introduction of L has very little effect on any of the absorption frequencies characteristic of the parent compound. The most significant difference is a small shift of the band at 300 cm<sup>-1</sup> (assigned<sup>19</sup> to  $\nu(\text{Ir}-\text{Cl})$  in VIII) to higher frequencies. However, for all the compounds, this band lies in the 310-320-cm<sup>-1</sup> range. Such a narrow and essentially constant range is consistent with the shown stereochemistry for IX with Cl always trans to CO.<sup>17</sup>

When acetylene is bubbled through a methanol solution containing the solvated cation, prepared from VIII and silver hexafluorophosphate, the methylmethoxycarbene complex, X, with L = C(OMe)Me is obtained. The carbene ligand is identified<sup>21</sup> in the <sup>1</sup>H NMR by the presence of two singlets at  $\delta(\text{OCH}_3)$  4.10 and  $\delta(\text{CH}_3)$  1.50 ppm (each equivalent to three protons). Bands at ca. 1300 cm<sup>-1</sup> have been assigned to  $\nu(\text{C}-\text{O})$  for a number of alkoxycarbene complexes<sup>21</sup> but the presence of other ligand absorptions in this region of the infrared spectra precludes any definite assignment for the carbenes obtained in this study.

The mechanism of formation of the carbene is presumably analogous to that proposed<sup>1,22</sup> for the methylplatinum compounds: specifically, initial coordination of the acetylene to iridium to give a metal-induced carbonium ion, XI, followed by H<sup>-</sup> migration and nucleophilic attack by methanol as in (2). The synthesis of this compound was accompanied by extensive polymerization in contrast to the "cleaner" reaction observed between acetylene and the analogous methyliridium cation containing dimethylphenylphosphine ligands.<sup>23</sup> Since

Table III. <sup>1</sup>H NMR<sup>a</sup> Data for Cationic Methyliridium(III) Complexes

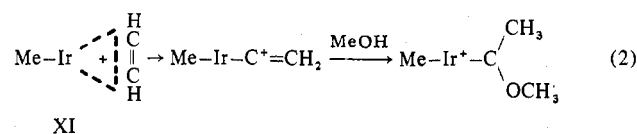
Complex $\left( M \equiv \left[ \begin{array}{c} \text{Ph}_2\text{MeP} \\   \\ \text{Me} \\   \\ \text{Ir} \\   \\ \text{Cl} \\   \\ \text{PMePh}_2 \end{array} \right] \text{PF}_6 \right)$	Phosphine methyls <sup>b</sup>		Iridium methyl <sup>b</sup>		Other resonances <sup>d</sup>
	$\delta(\text{CH}_3)$	$J^*c$	$\delta(\text{CH}_3)$	$J(\text{P-H})$	
M-CO	2.34	8.5	0.82	8.0	
M-CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O	2.32	9.0	0.63	7.0	$\delta(\text{OCH}_2\text{CH}_2)$ 0.93 qt, $\delta(\text{OCH}_2)$ 4.91 t, $\delta(\text{CCH}_2)$ 1.85 t
M-C(OCH <sub>3</sub> )CH <sub>3</sub>	2.10	8.2	0.60	7.0	$\delta(\text{OCH}_3)$ 4.10 s, $\delta(\text{CH}_3)$ 1.50 s
M-NCC <sub>6</sub> F <sub>5</sub>	2.32	7.0	0.84	6.0	
M-NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	2.36	10.0	0.86	6.0	
M-NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	2.34	10.0	0.82	6.0	$\delta(\text{CH}_3)$ 2.46 s
M-NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	2.34	9.0	0.81	6.0	$\delta(\text{OCH}_3)$ 3.94 s
M-NCC <sub>6</sub> H <sub>4</sub> -M	2.35	9.5	0.83	6.0	
M-NCC <sub>6</sub> F <sub>4</sub> -M	2.32	8.0	0.84	6.0	
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub>	2.22	8.0	0.76	6.0	$\delta(\text{OCH}_3)$ 3.66 s, $\delta(\text{NH})$ 8.66s
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub>	2.14	8.0	0.73	6.0	$\delta(\text{OCH}_2)$ 3.85 q, $\delta(\text{OCH}_2\text{CH}_3)$ 0.93 t, $\delta(\text{NH})$ 8.50 s
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> O)C=NH-M	2.22	8.0	0.70	6.0	$\delta(\text{OCH}_3)$ 3.70 s, $\delta(\text{NH})$ 8.82 s
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> CH <sub>2</sub> O)C=NH-M	2.22	8.3	0.76	6.0	$\delta(\text{OCH}_2)$ 4.04 q, $\delta(\text{OCH}_2\text{CH}_3)$ 0.92 t, $\delta(\text{NH})$ 8.71 s

<sup>a</sup> Chemical shifts ( $\delta$ ) in ppm downfield (positive) from TMS, measured at 100 MHz in dichloromethane-*d*<sub>2</sub> solution. Coupling constants are given in hertz. Phenyl resonances are omitted. <sup>b</sup> Resonance appears as a triplet. <sup>c</sup>  $J^* = {}^2J(\text{P-H}) + {}^4J(\text{P-H})$ : R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964). <sup>d</sup> Abbreviations: s, singlet; t, triplet; q, quartet; qt, quintet.

Table IV. Vibrational Spectroscopic Data (cm<sup>-1</sup>) for Cationic Methyliridium(III) Complexes<sup>a</sup>

Complex $\left( M \equiv \left[ \begin{array}{c} \text{Ph}_2\text{MeP} \\   \\ \text{Me} \\   \\ \text{Ir} \\   \\ \text{Cl} \\   \\ \text{PMePh}_2 \end{array} \right] \text{PF}_6 \right)$	$\nu(\text{CO})^b$	$\nu(\text{C}\equiv\text{N})$	$\Delta\nu(\text{C}\equiv\text{N})^c$	$\nu(\text{C}=\text{N})^b$	$\nu(\text{IrCl})^d$	Others
	M-CO	2128, 2187				320
M-CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O	2056				315	
M-C(OCH <sub>3</sub> )CH <sub>3</sub>	2054				315	
M-NCC <sub>6</sub> F <sub>5</sub>	2063	2280	35	313		1654 <sup>b</sup>
M-NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	2067	2288	60	317		
M-NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	2063	2278	46	315		
M-NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	2061	2277	64	317		
M-NCC <sub>6</sub> H <sub>4</sub> CN-M	2066	<i>f</i>		317		
M-NCC <sub>6</sub> F <sub>4</sub> CN-M	2067	2291	55	313		
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub>	2056			1642	310	1658, <sup>b</sup> 3298 <sup>e</sup>
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub>	2055			1633	310	1656, <sup>b</sup> 3315 <sup>e</sup>
M-NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> O)C=NH-M	2056			1640	310	3316 <sup>e</sup>
M-NH=C(OCH <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> (CH <sub>3</sub> CH <sub>2</sub> O)C=NH-M	2057			1635	315	3300 <sup>e</sup>

<sup>a</sup> Infrared measurements except for  $\nu(\text{C}\equiv\text{N})$  which was observed in the Raman spectra. <sup>b</sup> Measured in dichloromethane solution. <sup>c</sup>  $\nu(\text{C}\equiv\text{N})_{\text{complex}} - \nu(\text{C}\equiv\text{N})_{\text{free ligand}}$ . <sup>d</sup> Nujol mulls; bands are weak. <sup>e</sup>  $\nu(\text{NH})$ , measured as Nujol mull. <sup>f</sup> Not observed in infrared spectrum; sample decomposes in Raman experiment.



XI

PMePh<sub>2</sub> is a poorer donor than PMe<sub>2</sub>Ph,<sup>24</sup> this would enhance the carbonium ion reactivity by making the cation more electrophilic, consistent with the observed polymerization. Similar effects have been noted in the reactions of [Pt(R)-(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>+</sup> where R = CF<sub>3</sub> instead of Me.<sup>22,25</sup>

Polymerization may be avoided by using stoichiometric quantities of the reactants. This is conveniently accomplished by using 3-butyne-1-ol (HC≡CCH<sub>2</sub>CH<sub>2</sub>OH) as a carbene precursor, thus giving the analog of X with L = :CCH<sub>2</sub>C-H<sub>2</sub>CH<sub>2</sub>O. The <sup>1</sup>H spectrum of the carbene cation supports the cyclic nature of the carbene; the  $\alpha$ -alkoxy (OCH<sub>2</sub>) and  $\alpha$ -carbene (CCH<sub>2</sub>) protons appear as triplets at  $\delta$  4.91 and 1.85, respectively, and  $\beta$ -alkoxy protons (OCCH<sub>2</sub>) as a quintet at  $\delta$  0.93.<sup>21,26</sup>

No complex was obtained when a methanol solution of the cation was allowed to react with PhC≡CH, nor were reactions

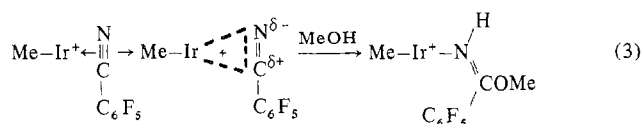
observed with disubstituted acetylenes.

A number of nitrile complexes have also been obtained (Tables II-IV). They are characterized by an absorption due to  $\nu(\text{C}\equiv\text{N})$  which is weak in the infrared but very strong in the Raman spectra. In all cases, the band appeared at higher frequency than that for the free ligand indicative of  $\sigma$  bonding through nitrogen.<sup>27,28</sup> Molecular orbital studies have attributed this increase primarily to an increased C-N force constant with coupling between  $\nu(\text{C}\equiv\text{N})$  and  $\nu(\text{M}-\text{C})$  of secondary importance.<sup>28</sup> Back-donation from the metal reduces the value of  $\Delta\nu(\text{C}\equiv\text{N})$  (defined as  $\nu(\text{C}\equiv\text{N})_{\text{complex}} - \nu(\text{C}\equiv\text{N})_{\text{free ligand}}$ ) and negative values have been found for cases where back-donation is large.<sup>29</sup> Negative values of  $\Delta\nu(\text{C}\equiv\text{N})$  are also observed in instances where the nitrile is bonded to the metal by the  $\pi$  electrons but complexes of this type are rare<sup>30</sup> and some are known to rearrange to the N-bonded form.<sup>31,32</sup>

For the series of complexes *trans*-[Pt(Me)(PMe<sub>2</sub>Ph)<sub>2</sub>(*p*-NCC<sub>6</sub>H<sub>4</sub>X)]<sup>+</sup> a correlation was observed between  $\nu(\text{C}\equiv\text{N})$  and the electron-withdrawing ability of the aromatic substituent.<sup>30</sup> As the electron-withdrawing ability increased (OCH<sub>3</sub> < CH<sub>3</sub> < NO<sub>2</sub>), the value of  $\Delta\nu(\text{C}\equiv\text{N})$  decreased, reflecting less ligand  $\rightarrow$  metal charge transfer and/or more

back-bonding from the platinum. For the present compounds there is no apparent correlation between the aromatic substituent and  $\Delta\nu(\text{C}\equiv\text{N})$ . It is also interesting that the values of  $\nu(\text{C}=\text{O})$  for these complexes are essentially identical. Since the iridium is six-coordinate in contrast to the four-coordination of the platinum compounds, it is probably less sensitive to small changes on one of the ligands.

Although reaction with pentafluorobenzonitrile in acetone gave  $[\text{IrCl}(\text{Me})\text{CO}(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph}_2)_2]\text{PF}_6$ , imino ether complexes  $\{\text{IrCl}(\text{Me})\text{CO}[\text{NH}=\text{C}(\text{OR})\text{C}_6\text{F}_5](\text{PMe}_2\text{Ph}_2)_2\}\text{PF}_6$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$ ) were obtained when the reaction was conducted in methanol or ethanol at room temperature. Perfluoroarylnitriles also react with methylplatinum cations in alcohols to give imino ether complexes. A similar mechanism<sup>30</sup> is probably operative involving the formation of a  $\pi$ -nitrile complex which is activated to nucleophilic attack at the nitrile carbon as in (3). The analogy to the metal-induced carbonium ion is obvious.



This proposed mechanism again gains credence from the fact that the N-bonded nitrile complexes could not be converted to imino ethers even in refluxing methanol. The formation of imino ethers is again limited to perfluoroarylnitriles as for the methylplatinum(II) cations; reactions with *p*-NCC<sub>6</sub>H<sub>4</sub>X ligands in methanol showed no evidence of imino ether formation. This presumably reflects differences in energies of the ligand orbitals favoring formation of a  $\pi$ -bonded intermediate for the perfluoroarylnitriles.

Bis(imino ether) complexes were obtained from the reaction with 2,3,5,6-tetrafluoroterephthalonitrile (NCC<sub>6</sub>F<sub>4</sub>CN) in methanol or ethanol. The imino ether complexes are characterized in the <sup>1</sup>H NMR spectra by the expected resonances due to the methoxy and ethoxy groups as well as a broadened singlet at  $\delta$  ca. 9.0 ppm due to the NH absorption. The infrared spectra show broad bands at ca. 3300 cm<sup>-1</sup> due to  $\nu(\text{N}-\text{H})$ . For the bis(imino ether) complexes, bands at 1640 and 1635 cm<sup>-1</sup> are assigned to  $\nu(\text{C}=\text{N})$  for the methoxy and ethoxy compounds, respectively. No bands are observed between 1600 and 1700 cm<sup>-1</sup> for the dinitrile derivatives of NCC<sub>6</sub>F<sub>4</sub>CN. Assignment of the C=N stretching frequency for the mono(imino ether) complexes  $\{\text{IrCl}(\text{Me})\text{CO}[\text{NH}=\text{C}(\text{OR})\text{C}_6\text{F}_5](\text{PMe}_2\text{Ph}_2)_2\}\text{PF}_6$  is more difficult. Two bands (1658 and 1642 cm<sup>-1</sup> for  $\text{R} = \text{CH}_3$ ; 1656 and 1633 cm<sup>-1</sup> for  $\text{R} = \text{CH}_2\text{CH}_3$ ) are observed in the region 1600–1700 cm<sup>-1</sup> in both the infrared and the Raman spectra. One of these may be attributed to a ligand vibration since a single band between 1600 and 1700 cm<sup>-1</sup> is found in the infrared spectra of C<sub>6</sub>F<sub>5</sub>CN (1655 cm<sup>-1</sup>) and  $[\text{IrCl}(\text{Me})\text{CO}(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph}_2)_2]\text{PF}_6$  (1654 cm<sup>-1</sup>). Reinvestigation of the infrared spectra of the platinum complexes  $[\text{Pt}(\text{Me})(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph}_2)_2]\text{PF}_6$  and  $\text{Pt}(\text{Me})[\text{NH}=\text{C}(\text{OMe})\text{C}_6\text{F}_5](\text{PMe}_2\text{Ph}_2)_2\text{BF}_4$  showed similar features, i.e., a band at 1656 cm<sup>-1</sup> for the former and two bands at 1665 and 1645 cm<sup>-1</sup> for the latter. These bands also appeared in the Raman spectra.

If it is assumed that the C=N stretching frequency is more sensitive to the nature of the alkoxy group than is the ligand vibration,  $\nu(\text{C}=\text{N})$  may be assigned to the lower frequency band for the iridium complexes. This assignment is supported by the similar frequencies of these bands and those attributed to  $\nu(\text{C}=\text{N})$  in the bis(imino ether) complexes.

The above results give support to the generality of the carbonium ion mechanism for carbene formation from terminal acetylenes. The failure to obtain complexes with disubstituted acetylenes could be due to steric effects and does not preclude

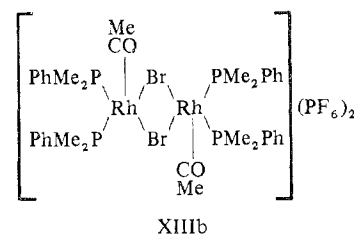
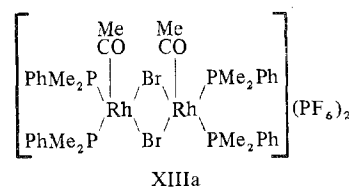
their transitory existence in solution. The extensive polymerization observed in the presence of excess acetylene is similar to that observed in reactions of  $[\text{Pt}(\text{CF}_3)(\text{PMe}_2\text{Ph}_2)_2]^+$ <sup>22,25</sup> as well as Pt(IV) cations. It is notable that no simple complexes of unsaturated hydrocarbons with CF<sub>3</sub>Pt<sup>III</sup> or Pt<sup>IV</sup> cations have been isolated although carbene complexes have been obtained from reactions with HC≡CCH<sub>2</sub>CH<sub>2</sub>O-H.<sup>22,33</sup>

It would therefore appear that the methyliridium(III) system has greater carbonium ion reactivity than that of the methylplatinum(II) cations and undergoes reactions comparable to those of the trifluoromethylplatinum(II) and organo-platinum(IV) cations. This could also account for the formation of a bis(imino ether) complex from the reaction with NCC<sub>6</sub>F<sub>4</sub>CN in ethanol. The corresponding reaction with the methylplatinum(II) complex gave a product which contained one imino ether and one  $\pi$ -bonded nitrile.<sup>30</sup> This was attributed to steric effects but other factors would appear to be involved in light of the present results.

**C. Methylrhodium(III) Cations.** To prepare the related methylrhodium(III) cations, carbonylchlorobis(diphenylmethylphosphine)iodomethylrhodium, RhClI(Me)CO-(PMe<sub>2</sub>Ph)<sub>2</sub>, would be the analogous starting material. Not only has this compound not been reported but attempts to prepare it by oxidative addition of methyl iodide to *trans*-RhClCO(PMe<sub>2</sub>Ph)<sub>2</sub> were unsuccessful. On replacing the phosphine, however, with dimethylphenylphosphine, smooth oxidative addition of MeX to *trans*-RhClCO(PMe<sub>2</sub>Ph)<sub>2</sub> occurs.<sup>34</sup> By this route we were able to prepare RhClI(Me)CO-(PMe<sub>2</sub>Ph)<sub>2</sub>, although only as a mixture of isomers resulting from *cis* and *trans* addition. Accordingly, because of its greater stability and because of its ready availability as a pure isomer we have used RhBr<sub>2</sub>(Me)CO(PMe<sub>2</sub>Ph)<sub>2</sub>, XII, to prepare cationic rhodium(III) species.

The addition of silver hexafluorophosphate to a methanol solution of XII gave an immediate precipitate of silver bromide. Filtration and concentration of the filtrate induced the formation of yellow crystals. The infrared spectrum did not show any bands in the C=O stretching region but showed, instead, two new bands at 1654 and 1679 cm<sup>-1</sup> (Table V) characteristic of absorptions due to acyl carbonyls.<sup>34,35</sup>

Consistent with acyl formation was the complete absence in the PMR spectrum of any high-field resonances due to a rhodium methyl group and the appearance of a sharp singlet at  $\delta$  2.84 ppm which is assigned to the COMe absorption. The phosphine methyl resonance appeared as a doublet. Such a pattern is associated with *cis* phosphines where <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) is small.<sup>18</sup> Moreover, the presence of only one doublet indicates the phosphines are equivalent which suggests a dimeric structure, XIIIa and/or XIIIb. Analytical and molecular



weight data (Table V) are consistent with this formulation.

It was anticipated that XIII would be especially reactive to the addition of another ligand. However, no appreciable

Table V. Analytical and Spectroscopic Data for Acylrhodium Complexes<sup>a</sup>

	A	B		C
		CH <sub>2</sub> Cl <sub>2</sub> solvate	CHCl <sub>3</sub> solvate <sup>c</sup>	
Mp, b °C	140-142	149-150	149-150	155-158
Analytical data				
% C calcd	33.41	44.86	43.42	41.87
% C found	33.42	44.96	43.55	42.10
% H calcd	3.89	3.57	3.36	4.14
% H found	4.19	4.34	4.16	4.29
NMR parameters <sup>d</sup>				
δ(P-CH <sub>3</sub> )	1.69 d	0.98 2.16		1.46 t 1.62 t
J(P-H) <sup>e</sup>	11.2	10.0 10.0		6.9 7.4
J(Rh-H)		2.2 2.2		
δ(COMe)	2.84	2.06		2.91
ν(C=O), <sup>f</sup> cm <sup>-1</sup>	1654 m 1679 s	1721 s, sp		1636 s, br

<sup>a</sup> A = [RhBr(COMe)(PMe<sub>2</sub>Ph)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>; mol wt found 1400; calcd 1294. B = [RhBr(COMe)(PMe<sub>2</sub>Ph)(diphos)]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>. C = [RhBr(COMe)(PMe<sub>2</sub>Ph)<sub>2</sub>(bipy)]PF<sub>6</sub>. <sup>b</sup> All complexes melt with decomposition. <sup>c</sup> Mol wt found 1840; calcd 1814. <sup>d</sup> Chemical shifts are reported in ppm downfield (positive) from TMS and were measured at 100 MHz in dichloromethane-*d*<sub>2</sub>; phenyl resonances are omitted; d = doublet, t = triplet. <sup>e</sup> Coupling constants are given in Hz; J(P-H) is given by separation of outer peaks for triplets (i.e., <sup>2</sup>J(P-H) + <sup>4</sup>J(P-H)) and the two peak positions for the doublets. <sup>f</sup> Measured in dichloromethane solution.

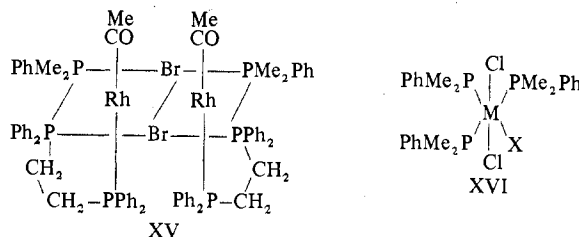
yield of any product was obtained from the reaction of XII, AgPF<sub>6</sub>, and py. Reactions with bidentate ligands such as bipy and diphos were more successful, however, and were conducted by the addition of the appropriate ligand either to a filtered methanol solution obtained from the reaction of RhBr<sub>2</sub>(Me)CO(PMe<sub>2</sub>Ph)<sub>2</sub> and AgPF<sub>6</sub> or to samples of XIII dissolved in dichloromethane. The products so obtained were usually identical by either method.

Although the product obtained from the reaction with bipy could not be recrystallized, evaporation of the solvent and drying of the residue under high vacuum afforded an analytically pure sample of [RhBr(COMe)(bipy)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub>, XIV. The infrared spectrum of this compound showed a broad, strong acyl carbonyl absorption at 1636 cm<sup>-1</sup> as well as other bands characteristic of bipy, PMe<sub>2</sub>Ph, and PF<sub>6</sub><sup>-</sup>. The proton NMR spectrum indicated the presence of two isomers. Thus, the major component of XIV gave a doublet of triplets as expected for the phosphine methyl resonances of the mutually trans phosphines. A strong singlet of appropriate corresponding relative intensity at δ 2.91 ppm is assigned to the COMe absorption. In addition to these peaks there was evidence for doublet resonances in the phosphine methyl region but these were partially obscured by the triplets. This could indicate the presence of a second isomer with cis phosphines, although its concentration was less than 5% of the product.

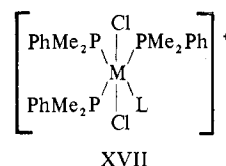
In contrast, the addition of diphos to a solution of [RhBr(COMe)(PMe<sub>2</sub>Ph)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> gave an intensely yellow solution from which the characteristic odor of PMe<sub>2</sub>Ph could be immediately detected. Analytical and molecular weight data indicated a dimeric product, [RhBr(COMe)(diphos)(PMe<sub>2</sub>Ph)]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>, which is assigned the configuration XV. The infrared spectrum, in addition to the other expected ligand absorptions, has a strong sharp band at 1721 cm<sup>-1</sup> which is assigned to the acyl carbonyl absorption. The proton NMR spectrum showed a sharp singlet at δ 2.06 ppm (COMe) and a complex multiplet between δ 2.5 and 3.5 ppm due to the A<sub>2</sub>A'<sub>2</sub>XX' spin system of the chelating phosphine. The phosphine methyl resonance pattern appeared essentially as two well-separated doublets with J(P-H) = 10.0 Hz but each peak showed further coupling to rhodium (I = 1/2, 100% abundant) with J(Rh-H) = 2.3 Hz. This inequivalence of the methyl groups, P(Me)(Me')Ph, is consistent with the proposed

structure. Samples recrystallized from dichloromethane-hexane or chloroform-hexane always occluded 1 equiv of CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, respectively.

The isolation of different products for these reactions with bidentate ligands probably reflects the considerable steric constraints imposed by the very bulky diphos ligand. Molecular models show that there would be great steric interaction in a compound such as [RhBr(COMe)(diphos)(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>+</sup> but that this may be relieved by loss of a phosphine ligand. Dimerization does not appear to be sterically inhibited.



**D. Cationic Dichloro Complexes of Rhodium(III) and Iridium(III).** The chloride in the position trans to the phosphine ligand in *mer*-trichlorotrakis(dimethylphenylphosphine)rhodium, XVI (M = Rh, X = Cl), has been found to be more labile than the other two.<sup>36</sup> Consequently, treatment with alkali metal salts readily gives complexes of the type RhYCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (Y = Br, I, N<sub>3</sub>, NCS, NO<sub>2</sub>). The analogous iridium complex, XVI (M = Ir, X = Cl), shows similar reactions but the formation of complexes of the type *mer*-IrY<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> occurs less readily than for the rhodium system.<sup>37</sup> The cations [IrCl<sub>2</sub>(L)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> have been obtained by the addition of the appropriate ligand to alcohol solutions of the nitrate complex XVI (M = Ir, X = NO<sub>3</sub>) in a reaction believed<sup>37</sup> to occur via a solvolysis step whereby the nitrate group is replaced first by a molecule of solvent followed by nucleophilic attack by the ligand. If the reaction is carried out at room temperature, all of the products are of configuration XVII.



Similar reactions have not been reported for the rhodium complexes but would be expected to occur readily and allow a comparison of the reactivities of analogous rhodium(III) and iridium(III) cations.

We found that the reaction of *mer*-RhCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> with silver hexafluorophosphate in acetone or methanol solution resulted in the immediate precipitation of silver chloride to give solutions of the cation [RhCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup>, XVIII. The addition of a ligand such as pyridine, carbon monoxide, or dimethylphenylphosphine afforded the corresponding cations [RhCl<sub>2</sub>(L)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup>, XIX. In the absence of an added ligand the cation acquires a water molecule (reactions were conducted in air and no precautions were taken to dry the solvents in these reactions) to give the analogous aquo complex (XVII, L = H<sub>2</sub>O). A similar result was found for the reaction of *mer*-IrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> with silver hexafluorophosphate which gave the previously unreported compound [IrCl<sub>2</sub>(H<sub>2</sub>O)(PMe<sub>2</sub>Ph)<sub>3</sub>]PF<sub>6</sub>.

Reactions of methanol solutions of the cation XVIII or its iridium analog with pentafluorobenzonitrile or 2,3,5,6-tetrafluoroterephthalonitrile did not give imino ether complexes but rather the nitrile derivatives [MCl<sub>2</sub>(NCC<sub>6</sub>F<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and {[MCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub>(NCC<sub>6</sub>F<sub>4</sub>CN)}<sup>+</sup> (M = Rh, Ir).

If acetylene was bubbled through methanol solutions of [MCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> (M = Rh, Ir) there was no evidence of reaction (not even polymerization) and after work-up the aquo

Table VI. Analytical and Physical Data for Cationic Complexes of Rhodium(III) and Iridium(III),  $[\text{MCl}_2(\text{L})(\text{PMe}_2\text{Ph})_3]\text{PF}_6$ 

Complex <sup>a</sup>		Mp, <sup>b</sup> °C	% C		% H	
M	L		Calcd	Found	Calcd	Found
Rh	H <sub>2</sub> O	120–121	38.37	38.43	4.69	4.74
Rh	py	180–182	42.88	42.97	4.72	4.78
Rh	CO	>110	39.44	39.37	4.37	4.01
Rh	PMe <sub>2</sub> Ph	150–151	44.11	44.00	5.09	5.47
Rh	NCC <sub>6</sub> F <sub>5</sub>	159–161	40.20	40.36	3.59	3.62
Rh	$\frac{1}{2}\text{NCC}_6\text{F}_4\text{CN}$	172–174	40.36	40.48	3.99	4.20
Rh	$\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$	148–150	41.87	41.87	4.89	4.78
Ir	NCC <sub>6</sub> F <sub>5</sub>	194–195	36.66	36.58	3.28	3.26
Ir	H <sub>2</sub> O	147–148	34.30	34.44	4.20	4.36
Ir	$\frac{1}{2}\text{NCC}_6\text{F}_4\text{CN}$	222–225	35.45	36.52	3.61	3.44
Ir	$\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$	198–200	37.68	37.90	4.40	4.65

<sup>a</sup> The rhodium complexes were orange and the iridium compounds yellow. <sup>b</sup> All complexes melt with decomposition.

complexes  $[\text{MCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3]^+$  were obtained. Similar results were observed if the cations were stirred under an atmosphere of  $\text{HC}\equiv\text{CH}$  for several days. The reaction of a methanol solution of  $[\text{RhCl}_2(\text{PMe}_2\text{Ph})_3]^+$  in a vessel pressurized with acetylene (7 psi) resulted in the formation of organic tars but no methylmethoxycarbene complex could be isolated. However the reaction of both the rhodium and iridium cations  $[\text{MCl}_2(\text{PMe}_2\text{Ph})_3]^+$  with 3-butyne-1-ol in acetone gave the corresponding cyclic carbene complexes,  $[\text{MCl}_2(\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})(\text{PMe}_2\text{Ph})_3]^+$  (M = Rh, Ir).

The analytical and physical data for the complexes are presented in Table VI.

The <sup>1</sup>H NMR spectrum of  $[\text{RhCl}_2(\text{py})(\text{PMe}_2\text{Ph})_3]\text{PF}_6$  showed a 1:2:1 triplet and a 1:1 doublet (relative intensities 2:1) for the phosphine methyl resonances (Table VII). This is similar to that observed for the analogous iridium complex indicating that the product has configuration XVII. Most of the complexes showed a similar pattern, but often the chemical shift difference of the doublet and triplet was small and the resonances overlapped. However, comparison of the 60- and 100-MHz spectra usually allowed the assignment of the peak positions and coupling constants. The peak corresponding to

Table VII. <sup>1</sup>H NMR<sup>a</sup> and Vibrational Spectroscopic Data for Cationic Complexes of Rhodium(III) and Iridium(III),  $[\text{MCl}_2(\text{L})(\text{PMe}_2\text{Ph})_3]\text{PF}_6$ 

Complex		Phosphine methyls		Other NMR resonances	Infrared bands, <sup>f</sup> cm <sup>-1</sup>
M	L	$\delta(\text{CH}_3)$	Coupling constants <sup>b</sup>		
Rh	H <sub>2</sub> O	1.69 t 1.64 d	5.8 3.7	$\delta(\text{OH}_2)$ 2.50 s	$\nu(\text{H}_2\text{O})$ 3580 m, br, 3480 m, br, 1590 w
Rh	py	1.88 d 1.42 t	11.8 8.0		
Rh	CO				$\nu(\text{CO})$ 2120 s
Rh	PMe <sub>2</sub> Ph	1.64 br, s			
Rh	NCC <sub>6</sub> F <sub>5</sub>	1.75 t 1.71 d <sup>e</sup>	6.0 5.0		$\nu(\text{C}\equiv\text{N})$ 2300 w
Rh	$\frac{1}{2}\text{NCC}_6\text{F}_4\text{CN}$	1.58 br, s			
Rh	$\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$	1.75 d 1.61 t	9.2 7.6	$\delta(\text{OCH}_2)$ 3.78 t, $\delta(\text{CCH}_2)$ 3.17 t, $\delta(\text{OCH}_2\text{CH}_2)$ 0.93 q	
Ir	H <sub>2</sub> O	1.65 d 1.58 t	6.0 3.0	$\delta(\text{OH}_2)$ 2.86 s	$\nu(\text{H}_2\text{O})$ 3550 m, br, 3450 m, br, 1590 w
Ir	NCC <sub>6</sub> F <sub>5</sub>	1.86 d 1.71 t	11.0 7.0		$\nu(\text{C}\equiv\text{N})$ 2300 w
Ir	$\frac{1}{2}\text{NCC}_6\text{F}_4\text{CN}$	d			
Ir	$\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$	1.79 d 1.59 t	9.6 7.5	$\delta(\text{OCH}_2)$ 3.98 t, $\delta(\text{CCH}_2)$ 2.84 t, $\delta(\text{OCH}_2\text{CH}_2)$ 1.06 q	

<sup>a</sup> Measured at 100 MHz in dichloromethane-d<sub>2</sub> solution; chemical shifts are reported in ppm downfield from TMS; coupling constants are given in hertz. Key: t, triplet; d, doublet; s, singlet; br, broad; q, quartet; phenyl resonances are omitted. <sup>b</sup> Values quoted are separations of outer peaks for the triplets, i.e., <sup>2</sup>J(P-H) + <sup>4</sup>J(P-H),<sup>18</sup> and the two peaks for the doublets. <sup>c</sup> Complex unstable in solution. <sup>d</sup> Complex too insoluble for measurement. <sup>e</sup> Position of doublet not certain due to overlap of resonances. <sup>f</sup> Measured as Nujol mulls in the infrared spectrum.

the phosphine methyl protons of  $[\text{RhCl}_2(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  appeared as a single, broad resonance with poorly resolved fine structure. A similar pattern was observed in the spectra of the analogous iridium complex<sup>37</sup> and the rhodium(I) cation  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$ .<sup>2,4</sup> Consistent with the assignment of configuration XVII to the present compounds is the absence of any bands in the region 262–290 cm<sup>-1</sup> indicative of  $\nu(\text{M}-\text{Cl})$  of a chloride trans to a phosphine ligand.<sup>17,36–38</sup> Overlap with other ligand vibrations prevented the unequivocal assignment of vibrations involving the two trans chlorines but these occurred at slightly higher frequency (ca. 330 cm<sup>-1</sup>) than for the starting materials.

The values of  $\nu(\text{CO})$  for the rhodium (2120 cm<sup>-1</sup>) and iridium (2105 cm<sup>-1</sup>) compounds are very high indicating little back-donation from the metal. Similarly, high values were found for  $\nu(\text{C}\equiv\text{N})$ , which appeared as a weak band in the infrared spectrum for two of the nitrile complexes.

### Experimental Section

Standard laboratory techniques were used for handling the rhodium(III) and iridium(III) compounds most of which are quite air stable. Rhodium(I) and iridium(I) compounds were handled under nitrogen.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. Solid-state spectra (4000–450 cm<sup>-1</sup>) were obtained as Nujol mulls between KBr plates or as KBr pellets. For examination of the region 500–200 cm<sup>-1</sup> Nujol mulls were smeared on polyethylene strips and the instrument was purged with dry air to remove water vapor. Such spectra are accurate to ca.  $\pm 2$  cm<sup>-1</sup>. Solution spectra were obtained in dichloromethane solution using 0.1-mm matched KBr solution cells and are accurate to  $\pm 5$  cm<sup>-1</sup>. In all cases calibration was accomplished using the 1602-cm<sup>-1</sup> peak of polystyrene.

Raman spectra were obtained from crystalline samples using a Cary 82 laser Raman spectrometer. The 5146-Å line of the argon laser was employed as the exciting line and reported frequencies are accurate to  $\pm 2$  cm<sup>-1</sup>.

<sup>1</sup>H NMR spectra were run on a Varian Associates HA-100 spectrometer at 100 MHz with tetramethylsilane as an internal reference-lock signal.

Molecular weights were determined by osmometry in chloroform solution.

Melting points were obtained in air using a Thomas-Hoover

"Unimelt" capillary melting point apparatus and are uncorrected.

Analyses were performed by Alfred Bernhardt, Elbach über Engelskirchen, West Germany; Spang Microanalytical Laboratory, Ann Arbor, Mich.; or Chemalytics Inc., Tempe, Ariz.

The following chemicals were obtained commercially and were sufficiently pure for immediate use: RhCl<sub>3</sub>·3H<sub>2</sub>O and IrCl<sub>3</sub>·3H<sub>2</sub>O from Alfa Inorganics and Johnson, Matthey, and Mallory; silver hexafluorophosphate from Cationics Inc.; *p*-toluinitrile, *p*-terephthalonitrile, *p*-methoxybenzonitrile, and *p*-nitrobenzonitrile from Eastman Kodak Co.; pentafluorobenzonitrile from Peninsular ChemResearch Inc.; 2,3,5,6-tetrafluoroterephthalonitrile from Pierce Chemicals; acetylene and propyne from Matheson Ltd.; phenylacetylene and 3-butyn-1-ol from Aldrich Chemical Co. Ltd. Triphenylphosphine, dimethylphenylphosphine, and methylidiphenylphosphine were purchased from Maybridge Chemical Co. or prepared by established methods.<sup>39</sup>

Since many of the new compounds were prepared by similar methods, only illustrative examples will be given.

**Preparation of Starting Materials.** The following compounds were prepared by standard literature procedures: IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub>,<sup>19</sup> *mer*-IrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>,<sup>38</sup> *mer*-RhCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>,<sup>36</sup> RhBr<sub>2</sub>(Me)CO(PMe<sub>2</sub>Ph)<sub>2</sub>,<sup>34</sup> RhClCO(PPh<sub>3</sub>)<sub>2</sub>,<sup>40</sup> and IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>.<sup>41</sup>

The synthesis of *trans*-RhClCO(PMe<sub>2</sub>Ph)<sub>2</sub> followed the literature procedure<sup>42</sup> but with some minor, but significant, modifications. It was found that better yields (as high as 70% in contrast to the reported value of 34%) could be obtained by refluxing the solution for a longer time (5 hr instead of 3 hr) with vigorous stirring. Additional amounts of product could always be obtained by concentrating and cooling the mother liquor after the initial crop of crystals had been filtered off. It is essential to recrystallize the crude product from methanol as it is always contaminated with another unidentified rhodium-carbonyl compound.

The preparation of *trans*-RhClCO(PMePh<sub>2</sub>)<sub>2</sub> from [RhCl(CO)<sub>2</sub>]<sub>2</sub> has been described.<sup>43</sup> Although this procedure gives good yields, an alternative synthesis starting with the cyclooctene complex RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub> was devised. The major attraction of this method is that the latter compound is more conveniently obtained<sup>44</sup> than di- $\mu$ -chloro-tetracarbonyl dirhodium.<sup>45</sup>

*trans*-Carbonylchlorobis(methylidiphenylphosphine)rhodium, RhClCO(PMePh<sub>2</sub>)<sub>2</sub>, was prepared as follows. To a suspension of RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub> (1.50 g, 4.18 mmol) in degassed toluene (25 ml) was added PMePh<sub>2</sub> (2.70 g, 13.5 mmol). The cyclooctene complex immediately dissolved to give a deep red solution which was refluxed under nitrogen for 1 hr. It was then cooled to ca. 60° and carbon monoxide was bubbled through the solution, with stirring, for 30 min. The bubbler was then removed, the reaction mixture was cooled to room temperature, and hexane (25 ml) was added. Yellow crystals formed immediately, and after cooling to -20° overnight, the product was filtered, washed with hexane, and dried in vacuo. The yield was 1.7 g (72%) and no purification was required.

**Reactions of Rhodium(I) and Iridium(I) Compounds.** (a) **Preparation of the Acetone Complexes [MCO(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>.** (i) **M = Ir.** To a suspension of IrClCO(PPh<sub>3</sub>)<sub>2</sub> (0.5 g, 0.64 mmol) in dichloromethane (25 ml) was added a solution of AgPF<sub>6</sub> (0.162 g, 0.64 mmol) in acetone (~1 ml). A precipitate of silver chloride was immediately formed. The reaction mixture was stirred for 10 min and filtered and the solvent was removed under reduced pressure (the product could be obtained by direct addition of pentane to the filtrate but crystallization was facilitated if the excess acetone was removed first). The residue was redissolved in a minimum of dichloromethane and pentane was added slowly with scratching until crystallization was induced. Subsequent cooling to -15° completed crystallization. The mother liquor was sucked away and the product was washed twice with pentane. Drying under vacuum gave 0.57 g (55%) of large yellow crystals of [IrCO(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>, mp >150° dec. Anal. Calcd for IrC<sub>41</sub>H<sub>38</sub>Cl<sub>2</sub>F<sub>6</sub>P<sub>3</sub>O<sub>2</sub>: C, 47.69; H, 3.68. Found: C, 47.58; H, 3.80. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), downfield (positive) from TMS in ppm:  $\delta$  1.78 (6 H, acetone), 5.34 (2 H, CH<sub>2</sub>Cl<sub>2</sub>), 7.54 (30 H, Ph). Infrared spectrum (cm<sup>-1</sup>):  $\nu$ (C=O) 1630 (m, br) and  $\nu$ (C=O) 1970 (s) (Nujol mull).

(ii) **M = Rh.** This complex was prepared as in (i), from RhClCO(PPh<sub>3</sub>)<sub>2</sub> (0.854 g, 1.23 mmol) and AgPF<sub>6</sub> (0.313 g, 1.23 mmol) in dichloromethane-acetone (20 ml:1 ml) giving 1.0 g (85%) of [RhCO(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>, mp 170–175°, dec pt >150°. Anal. Calcd for RhC<sub>40</sub>H<sub>36</sub>F<sub>6</sub>P<sub>3</sub>O<sub>2</sub>: C, 55.8; H, 4.2. Found: C, 55.53; H,

4.13. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), downfield (positive) from TMS:  $\delta$  1.75 (6 H, acetone), 7.50 (30 H, Ph). Infrared spectrum (cm<sup>-1</sup>):  $\nu$ (C=O) 1656 (m) and  $\nu$ (C=O) 2013 (vs) (Nujol mull).

(b) **Preparation of the Acetylene Complexes [IrCO(py)(RC $\equiv$ CR)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>.** (i) **R = COOCH<sub>3</sub>.** The acetone complex [IrCO(acetone)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> (0.100 g, 0.096 mmol) was dissolved in dichloromethane (5 ml), and pyridine (7.5  $\mu$ l, 0.096 mmol) was added. The reaction mixture was stirred for 5 min and then dimethyl acetylenedicarboxylate (15  $\mu$ l, 0.130 mmol) was added. The solution turned deeper yellow on addition. The addition of ether and cooling induced the formation of pale yellow crystals which were recrystallized from dichloromethane-ether; yield 0.08 g (78%). The complex decomposed at 159° without melting. Anal. Calcd for IrC<sub>48</sub>H<sub>41</sub>F<sub>6</sub>NP<sub>3</sub>O<sub>5</sub>: C, 51.91; H, 3.69. Found: C, 51.83; H, 3.84.

(ii) **R = CF<sub>3</sub>.** This complex was prepared as described above by stirring a solution of the acetone cation (0.150 g, 0.145 mmol) and pyridine (11.2  $\mu$ l, 0.145 mmol) in dichloromethane (5 ml) under an atmosphere of CF<sub>3</sub>C $\equiv$ CCF<sub>3</sub> for 4 hr; yield 0.125 g (75%), dec pt >150°. Anal. Calcd for IrC<sub>46</sub>H<sub>35</sub>F<sub>12</sub>NP<sub>3</sub>O: C, 49.60; H, 3.48. Found: C, 49.44; H, 3.21.

**Preparation of the Complexes [IrCl(Me)CO(L)(PMePh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub>.**

(a) **Organonitrile or Carbon Monoxide Compounds.** (i) **L = CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN.** To a suspension of IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub> (0.15 g, 0.188 mmol) in methanol (10 ml) was added AgPF<sub>6</sub> (0.048 g, 0.188 mmol) in 2 ml of methanol. Yellow silver iodide was precipitated immediately. After 15 min of stirring the silver iodide was separated by centrifugation to give a clear colorless supernatant liquid. The latter was decanted into a 25-ml round-bottomed flask and a solution of *p*-methoxybenzonitrile (0.025 g, 0.188 mmol) in 2 ml of methanol was added. The solution was stirred for 15 min and the methanol was then evaporated under reduced pressure. The residue was dissolved in dichloromethane and filtered through a short (1 in.) Florisil column to remove traces of silver salts. The slow addition of ether induced crystallization and this process was completed by cooling first to 5° and then to -20°. The product was filtered, washed with ether, and dried in vacuo to give white crystals of [IrCl(Me)CO(NCC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(PMePh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> (0.134 g, 75% yield).

The other nitrile complexes were prepared analogously; the dinitrile compounds were also obtained in this manner except that 0.5 equiv of the ligand was used, and for the reaction with 2,3,5,6-tetrafluorophthalonitrile (*p*-NCC<sub>6</sub>F<sub>4</sub>CN), acetone was used as a solvent to prevent imino ether formation. Yields were found to be greater than 70% in all cases.

(ii) **L = CO.** Silver hexafluorophosphate (0.048 g, 0.188 mmol) in methanol (2 ml) was added to a suspension of IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub> (0.150 g, 0.188 mmol) in methanol (5 ml). The mixture was stirred for 15 min and the silver iodide was removed by centrifugation. Carbon monoxide was bubbled through the clear solution and after several minutes crystals began to separate. The mixture was evaporated to dryness and white crystals of [IrCl(Me)(CO)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> (0.110 g, 70% yield) were obtained upon recrystallization from dichloromethane-ether.

(b) **Imino Ether Complexes.** A solution of the solvated iridium cation in methanol (10 ml) was prepared from the reaction of IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub> (0.150 g, 0.188 mmol) and AgPF<sub>6</sub> (0.048 g, 0.188 mmol) as described above. To this was added solid 2,3,5,6-tetrafluoroterephthalonitrile (0.019 g, 0.094 mmol) and the mixture was stirred overnight during which time a white precipitate had formed. Evaporation of the methanol and recrystallization from dichloromethane-ether gave [IrCl(Me)CO(PMePh<sub>2</sub>)<sub>2</sub>][NH=C(OCH<sub>3</sub>)C<sub>6</sub>F<sub>4</sub>(CH<sub>3</sub>O)C=NH]IrCl(Me)CO(PMePh<sub>2</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (0.107 g, 69% yield).

The other imino ether complexes were obtained in a similar manner by reaction with the appropriate ligand and alcohol.

(c) **Carbene Complexes.** (i) **L = CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O.** To a colorless acetone solution (10 ml) of the solvated iridium cation obtained from the standard reaction of IrClI(Me)CO(PMePh<sub>2</sub>)<sub>2</sub> (0.300 g, 0.376 mmol) and AgPF<sub>6</sub> (0.096 g, 0.376 mmol) was added 3-butyn-1-ol (0.019  $\mu$ l, ca. 0.4 mmol). The solution turned slightly yellow and after 15 min of stirring the acetone was evaporated under reduced pressure to give a pale yellow oil. This was dissolved in dichloromethane and filtered through a Florisil column. The slow addition of ether gave cream-colored needles of [IrCl(Me)(CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)CO(PMePh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> (0.202 g, 61% yield).

(ii) **L = C(OCH<sub>3</sub>)CH<sub>3</sub>.** This complex was prepared as in (i) by



passing a stream of acetylene through a methanolic solution of the solvated iridium cation for 5 min. The resulting solution was very yellow due to the presence of organic tars and required several filtrations through Florisil to remove enough of this material to isolate uncontaminated crystals of the product. Yields were variable but always in excess of 40%.

**Reactions of Dibromocarbonylbis(dimethylphenylphosphine)-methylrhodium,  $\text{RhBr}_2(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$ .** (a) **Preparation of  $[\text{RhBr}(\text{COCH}_3)(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$ .** Silver hexafluorophosphate (0.065 g, 0.258 mmol) in methanol (2 ml) was added to a suspension of  $\text{RhBr}_2(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$  (0.150 g, 0.258 mmol) in methanol (10 ml) in a nitrogen-filled Schlenk tube. A precipitate of silver bromide was immediately formed. The reaction mixture was stirred for 15 min and then filtered under nitrogen. The yellow filtrate was concentrated to ca. 5 ml and yellow crystals separated. They were filtered off in air and recrystallized from dichloromethane-hexane to give 0.085 g (51%) of product.

(b) **Preparation of  $[\text{RhBr}(\text{COCH}_3)(\text{bipy})(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$ .** To a suspension of  $\text{RhBr}_2(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$  (0.200 g, 0.344 mmol) in methanol (10 ml) was added a solution of  $\text{AgPF}_6$  (0.087 g, 0.344 mmol) in methanol. After being stirred for 15 min under nitrogen the solution was filtered into a Schlenk tube containing 2,2'-bipyridyl (0.054 g, 0.344 mmol). The clear yellow solution was stirred for 30 min and then evaporated to dryness. The resulting oil was dissolved in dichloromethane and filtered through a short Florisil column. All attempts to crystallize the product from dichloromethane or chloroform by the addition of hexane or ether were unsuccessful. However, by evaporation of a dichloromethane solution a pale yellow powder was obtained. This was washed several times with ether to remove any traces of ligand and then thoroughly dried in vacuo to give 0.221 g (80%) of product.

(c) **Preparation of  $[\text{RhBr}(\text{COCH}_3)(\text{PMe}_2\text{Ph})(\text{diphos})_2](\text{PF}_6)_2$ .** Silver hexafluorophosphate (0.065 g, 0.258 mmol) and  $\text{RhBr}_2(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$  (0.150 g, 0.258 mmol) were allowed to react as in (b) and the mixture was filtered. A suspension of 1,2-bis(dimethylphosphino)ethane (0.103 g, 0.258 mmol) in methanol (5 ml) was added to the filtrate; the reaction mixture was stirred for 30 min and then evaporated to dryness. The residue was dissolved in dichloromethane and filtered through Florisil. The slow addition of hexane induced crystallization and on cooling large yellow crystals separated. They were filtered off, washed several times with hexane, and dried under vacuum to give 0.184 g (70%) of product.

**Preparation of the Complexes  $[\text{MCl}_2\text{L}(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$  ( $\text{M} = \text{Rh}$ ,  $\text{Ir}$ ;  $\text{L} = \text{Neutral Ligand}$ ).** (a)  $\text{L} = \text{C}_6\text{F}_5\text{CN}$ . To a suspension of *mer*- $\text{RhCl}_3(\text{PMe}_2\text{Ph})_3$  (0.150 g, 0.241 mmol) in methanol (10 ml) was added  $\text{AgPF}_6$  (0.061 g, 0.241 mmol) in methanol (2 ml). Silver chloride immediately precipitated and after 15 min of stirring this was removed by centrifugation. Pentafluorobenzonitrile (0.046 g, 0.241 mmol) was added to the clear orange solution and the reaction mixture was stirred for 15 min. It was then stripped to dryness and the residue was dissolved in dichloromethane. The product was crystallized by the slow addition of ether, to give 0.167 g (70%) of orange  $[\text{RhCl}_2(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ .

The other complexes of this type were obtained similarly. However the carbon monoxide complex was particularly labile with respect to loss of CO and had to be crystallized under an atmosphere of the ligand. The iridium starting material is less soluble in methanol than the rhodium compound. Accordingly, larger volumes of solvent (ca. 25 ml/150 mg of compound) and longer treatment with silver hexafluorophosphate were used to ensure complete reaction. For  $\text{L} = \text{H}_2\text{O}$  the reaction was conducted as described above but no ligand was added to the centrifuged solution of the cation.

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**Registry No.**  $[\text{IrCO}(\text{py})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2](\text{PF}_6)_2$ , 55493-50-0;  $[\text{IrCO}(\text{py})(\text{dma})(\text{PPh}_3)_2](\text{PF}_6)_2$ , 55493-52-2;  $\text{M}-\text{CO}$ , 55493-54-4;  $\text{M}-\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}$ , 40903-25-1;  $\text{M}-\text{C}(\text{OCH}_3)\text{CH}_3$ , 55530-08-0;  $\text{M}-\text{NCC}_6\text{F}_5$ , 55493-11-3;  $\text{M}-p\text{-NCC}_6\text{H}_4\text{NO}_2$ , 55493-13-5;  $\text{M}-p\text{-NCC}_6\text{H}_4\text{CH}_3$ , 55493-15-7;  $\text{M}-p\text{-NCC}_6\text{H}_4\text{OCH}_3$ , 55493-17-9;

$\text{M}-\text{NCC}_6\text{H}_4\text{CN}-\text{M}$ , 55493-19-1;  $\text{M}-\text{NCC}_6\text{F}_4\text{CN}-\text{M}$ , 55493-21-5;  $\text{M}-\text{NH}=\text{C}(\text{OCH}_3)\text{C}_6\text{F}_5$ , 55493-23-7;  $\text{M}-\text{NH}=\text{C}(\text{OCH}_2\text{CH}_3)\text{C}_6\text{F}_5$ , 55493-25-9;  $\text{M}-\text{NH}=\text{C}(\text{OCH}_3)\text{C}_6\text{F}_4(\text{CH}_3\text{O})\text{C}=\text{NH}-\text{M}$ , 55493-27-1;  $\text{M}-\text{NH}=\text{C}(\text{OCH}_2\text{CH}_3)\text{C}_6\text{F}_4(\text{CH}_3\text{CH}_2\text{O})\text{C}=\text{NH}-\text{M}$ , 55493-29-3;  $[\text{RhBr}(\text{COMe})(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$ , 55493-31-7;  $[\text{RhBr}(\text{COMe})(\text{PMe}_2\text{Ph})(\text{diphos})_2](\text{PF}_6)_2$ , 55493-33-9;  $[\text{RhBr}(\text{COMe})(\text{PMe}_2\text{Ph})(\text{bipy})](\text{PF}_6)_2$ , 55493-35-1;  $[\text{RhCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55493-37-3;  $[\text{RhCl}_2(\text{py})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55493-39-5;  $[\text{RhCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55492-97-2;  $[\text{RhCl}_2(\text{PMe}_2\text{Ph})_4](\text{PF}_6)_2$ , 55528-67-1;  $[\text{RhCl}_2(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55492-99-4;  $\{[\text{RhCl}_2(\text{PMe}_2\text{Ph})_3]_2(\text{NCC}_6\text{F}_4\text{CN})\}(\text{PF}_6)_2$ , 55493-01-1;

$[\text{RhCl}_2(\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55530-04-6;  $[\text{IrCl}_2(\text{NCC}_6\text{F}_5)(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55493-03-3;  $[\text{IrCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55493-05-5;  $\{[\text{IrCl}_2(\text{PMe}_2\text{Ph})_3]_2(\text{NCC}_6\text{F}_4\text{CN})\}(\text{PF}_6)_2$ , 55493-07-7;

$[\text{IrCl}_2(\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{PF}_6)_2$ , 55530-06-8; *trans*- $\text{RhClCO}(\text{PMe}_2\text{Ph})_2$ , 17966-81-3; *trans*- $\text{RhClCO}(\text{PMe}_2\text{Ph})_2$ , 19552-34-2;  $\text{IrClCO}(\text{PPh}_3)_2$ , 14871-41-1;  $\text{AgPF}_6$ , 26042-63-7;  $\text{RhClCO}(\text{PPh}_3)_2$ , 13938-94-8;  $[\text{IrCO}(\text{acetone})(\text{PPh}_3)_2](\text{PF}_6)_2$ , 55493-09-9;  $\text{RhBr}_2(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$ , 55528-68-2; *mer*- $\text{RhCl}_3(\text{PMe}_2\text{Ph})_3$ , 14882-42-9; *mer*- $\text{IrCl}_3(\text{PMe}_2\text{Ph})_3$ , 15664-86-5;  $\text{IrCl}(\text{Me})\text{CO}(\text{PMe}_2\text{Ph})_2$ , 55528-69-3;  $\text{RhCl}(\text{C}_8\text{H}_{14})_2$ , 12112-71-9; 3-butyn-1-ol, 927-74-2.

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