HYDRIDE COMPLEXES OF RUTHENIUM, RHODIUM, AND IRIDIUM

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I. Introduction

Transition metal hydride chemistry is a rather recent area of development in inorganic and organometallic chemistry. In 1931, Hieber (*156*) discovered the first well-defined, although unstable, transition metal hydrides, $H_2Fe(CO)_4$ and $HCo(CO)_4$, but it was not until 1955 that the first stable hydride, $HRe(C_5H_5)_2$, was prepared by Wilkinson and Birmingham (*326*). The field has expanded tremendously since that time, and one can now find a number of review articles on transition metal hydride complexes, most of them written prior to 1972 (*55*, *123*, *130*, *131*, *183*). A recent article (*276*) reviews the chemistry of hydride complexes of nickel, palladium, and platinum. The purpose of this article is to review the literature of the hydride complexes of the three catalytically important metals ruthenium, rhodium, and iridium. The synthesis, characterization, and chemical and physical properties of the hydride complexes are presented first, and each of the three metals is then discussed individually in separate sections. The comprehensive tables presented in the individual sections listing all the known hydride complexes of each metal are probably the most useful aspect of this review and include the important data and references for each complex. The literature coverage is through December 1974.

Although transition metal–hydride complexes have an interesting chemistry of their own, the greatest interest in hydrides comes from their importance in homogeneous catalysis. A large number of transition metal complexes have been demonstrated to catalyze homogeneously a wide variety of organic transformations, and the hydride ligand ranks second only to phosphorus donor ligands in importance of having a crucial role in catalysis. Hydride complexes are known to be intimately involved in catalyzed hydrogenations, deuterations, olefin isomerizations, hydroformylations, and hydrosilations, and also have been shown to be important in some olefin oligomerization and polymerization reactions. Although the catalytic properties of selected complexes is described in this review, the detailed mechanisms of the individual catalytic reactions are not presented. However, several excellent articles reviewing homogeneous catalysis and the role of metal hydrides have appeared in recent years (*77*, *78*, *82*, *124*, *188*, *239*, *298*, *312*).

II. Synthesis of Transition Metal–Hydride Complexes

Green and Jones (*131*) have proposed five general categories for the synthesis of hydride complexes. These include direct hydrogenation, reduction of metal halide complexes, hydride transfer and reverse carbonylation, hydrolysis of alkali metal salts of complex carbonyls, and protonation. We have adopted their classification and present general examples below.

The syntheses of specific hydride complexes are presented in the tables in Sections V, VI, and VII. Because the success of a preparation often depends on careful control of the reaction conditions, reference to the original papers is suggested. Reagent and solvent purification, concentration, temperature, order of addition of reagents, etc., may greatly alter the nature of the final product.

A. Reactions with Molecular Hydrogen

Hydride complexes can be synthesized from the direct combination of metal, ligand, and hydrogen at increased temperatures and pressures (*131*). However, a more convenient route is the replacement of coordinated ligands by elemental hydrogen. For example, Knoth (*193*) has shown that coordinated N_2 is easily and reversibly displaced by H_2 in $[H_2Ru(N_2)(PPh_3)_3]$ to yield the tetrahydride, $[H_4Ru(PPh_3)_3]$:

$$[H_2Ru(N_2)(PPh_3)_3] + H_2 \longrightarrow [H_4Ru(PPh_3)_3] + N_2 \qquad (1)$$

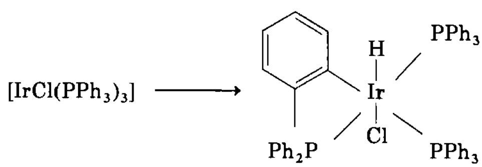
Hydride complexes can also be formed by addition of H_2 to coordinatively unsaturated metal complexes. The reversible addition of H_2 to complexes of iridium was first shown by Vaska and Rhodes (*321*):

$$\textit{trans}\text{-}[IrCl(CO)(PPh_3)_2] + H_2 \longrightarrow [H_2IrCl(CO)(PPh_3)_2] \qquad (2)$$

Many unsaturated complexes have since been shown to undergo addition of H_2 and four- or five-coordinate d^8 complexes have been the most studied (*69*, *143*). Formally, addition of H_2 results in an oxidation of the metal center and such addition is often termed oxidative addition. Such terminology should be used carefully, however, since it is unclear exactly how much electron density is located on the metal center in hydride complexes.

A key factor as to whether a metal will undergo oxidative addition is the basicity of the metal center. Basicity increases (*a*) going down a column in the periodic table, (*b*) with metals in lower oxidation states, and (*c*) with electron-donating ligands present (*297*). These three factors increase the electron density around the metal, and oxidative addition may be viewed as a removal of some electron density from a basic metal center. The tendency for oxidative addition to occur decreases in the order Ru(0) > Ir(I) > Rh(I), and reactivity is enhanced by ligands that favor higher oxidation states (PPh_3 > CO).

A special case of oxidative addition is ortho-metalation which is insertion of the central metal into an aryl *o*-carbon–hydrogen bond in a complexed ligand to form a metal–*o*-carbon linkage. The displaced hydrogen can be transferred to the metal as a hydride or eliminated as H^+ or H_2 (*1*). Chlorotris(triphenylphosphine)iridium(I), for example, readily ortho-metalates in benzene solution (*19*):



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B. Reduction of Metal–Halide Complexes

A very common and useful route for the formation of hydride complexes is the reduction of a metal halide with reducing agents such as $NaBH_4$, $LiAlH_4$, or hydrazine (*119*). For example, $\{H_2Ru[P(OR)_3]_4\}$ complexes can be readily synthesized by treatment of $RuCl_3$ with $NaBH_4$ in the presence of $P(OR)_3$ (*119*):

$$RuCl_3 + P(OR)_3 + NaBH_4 \longrightarrow \{H_2Ru[P(OR)_3]_4\} \qquad (4)$$

Occasionally incorporation of the BH_4^- anion into the final product occurs (*161*) as follows:

$$[Ru_5Cl_{12}]^{2-} + NaBH_4 + PPh_3 \longrightarrow [HRu(PPh_3)_2(BH_4)] \qquad (5)$$

C. Hydride Transfer from Solvent

In many synthetic reactions, no external hydrogen source is required and hydrogen is abstracted from the solvent during the course of the reaction. With ethanol the formation of hydride complexes from metal halides is believed to occur by the displacement of the halogen from the metal by ethoxide ion, followed by transfer of a hydrogen from the ethyl group. Vaska and DiLuzio (*320*) have shown, using CH_3CD_2OH, that the hydride hydrogen originated on the ethyl α-carbon:

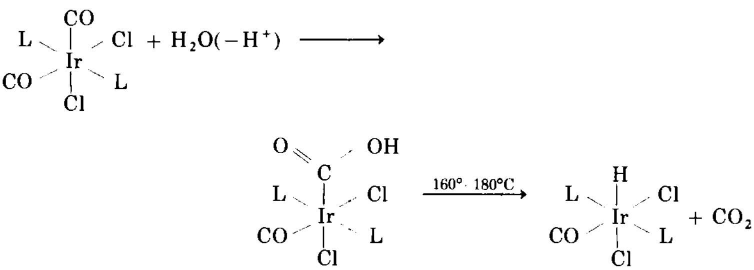
$$CH_3CH_2OH + OH^- + [IrCl_3(PEt_2Ph)_3] \longrightarrow [HIrCl_2(PEt_2Ph)_3] + H_2O + CH_3CHO + Cl^- \quad (6)$$

The reaction of $[Ru_2Cl_3(PR_3)_6]Cl$ with KOH in ethanol results in abstraction of both H and CO by ruthenium (*55*):

$$[Ru_2Cl_3(PR_3)_6]Cl + CH_3CH_2OH + KOH \longrightarrow 2[HRuCl(CO)(PR_3)_3] + 2CH_4 + 2KCl + 2H_2O \quad (7)$$

D. Hydrolysis of Metal Carbonyl Cations

The hydrolysis of metal carbonyl cations often results in the formation of hydridometal complexes (*106*). Deeming and Shaw (*84*), for example, have shown that treatment of an iridium cation with water produces a carboxy derivative, which on pyrolysis gives a hydridometal complex:



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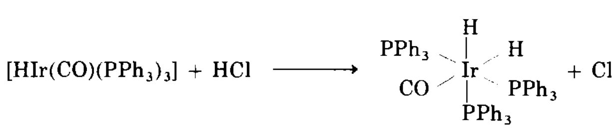
E. Protonation

Addition of H^+ to a coordinatively unsaturated metal complex can produce a metal hydride. Vaska (*315*), for example, reported that protonation of $[HIr(CO)(PPh_3)_3]$ gives $[H_2Ir(CO)(PPh_3)_3]^+$:



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The reaction of concentrated H_2SO_4 with polynuclear ruthenium carbonyls now appears to be a general method for producing cationic hydridometal carbonyl complexes (*85*):

$$[HRu_3(CO)_{10}SEt] + H_2SO_4 \longrightarrow [H_2Ru_3(CO)_{10}SEt]_2SO_4 \qquad (10)$$

F. Other Methods

New methods for the synthesis of hydride complexes will certainly be developed. One very promising pathway, especially for the synthesis of organometallic hydrides, is the metal atom cocondensation reaction. Skell and co-workers (*313*) have shown, for example, that Mo and W vapors condense with cyclopentadiene to give bis(cyclopentadienyl)dihydridometal derivatives:

$$M + 2C_5H_6 \longrightarrow [(C_5H_5)_2MH_2] \qquad (M = Mo, W) \qquad (11)$$

This synthetic technique has not yet been employed for the synthesis of hydride complexes of Ru, Rh, or Ir, but it clearly is a promising research area.

III. Chemical Properties and Chemical Reactions of Transition Metal–Hydride Complexes

A. Stability

The hydride complexes of ruthenium, rhodium, and iridium have relatively high thermal, oxidative, and hydrolytic stability, especially when compared to hydrides of the early transition metals. The M—H bond in complexes of these three metals is usually quite covalent in nature and consequently shows considerable resistance to hydrolysis by water. Many of the hydride complexes of these metals that contain phosphine ligands are air-sensitive, giving oxidation of the phosphine to phosphine oxide. The isolatable, thermally stable hydride complexes generally have either a 16- or an 18-electron configuration.

Many hydride complexes have the central metal in a low-oxidation state and consequently have ligands that can stabilize these states. The most stable hydride complexes contain strong π-accepting ligands, such as cyanides or tertiary phosphines (*131*). In a homologous series, the thermal stability appears to increase with increasing atomic number of the metal.

B. Trans Effect

Hydrogen bound to a transition metal is very effective in causing labilization of the trans ligand in substitution reactions (*257*). The hydride's high trans influence arises from its ability to direct a large portion of the s character in the σ bonds toward itself, and this weakens the remaining σ bonds, especially the one trans to the hydride.

Powell and Shaw (*257*) find that in the complexes, $HIrX_2L_3$, the L ligand trans to the hydride exchanges rapidly with other ligands present in solution, whereas exchange of the other L ligands occurs slowly or not at all. In another study, Douglas and Shaw (*94*) have determined the relative affinity of L in the following substitution reaction:

$$\underset{\text{(I)}}{[HRuCl(CO)(PR_2Ph)_3]} + L \longrightarrow [HRuCl(CO)(PR_2Ph)_2L] \qquad (12)$$

The phosphine ligand trans to the hydride in compound I was substituted in each case, and the order of increasing affinity of L is

$$AsEt_2Ph < AsMe_2Ph < PBu_2{}^nPh \simeq PPr_2{}^nPh \simeq PEt_2Ph$$
$$< PEt_3 < P(OEt)_3 \simeq PMe_2Ph < P(OMe)_2Ph$$

The ordering from arsines to phosphines to phosphites results primarily because phosphines are better σ-donors than phosphites, and phosphites are better π-acceptors.

In crystal structures, the bond length of the ligand trans to hydride has been shown to be longer than the bond length of the same ligand trans to itself. For example, the crystal structure (*76*) of the complex $[RhH(NH_3)_5](ClO_4)_2$ reveals an octahedral geometry about Rh. Four of the Rh—N bond lengths are 2.079 Å, whereas the NH_3 trans to the hydride has an Rh—N bond length of 2.244 Å. The trans influence also has significant effects on spectroscopic data. In infrared spectroscopy, a ligand trans to hydride will have a lower stretching frequency than it would if it were trans to a less trans-directing ligand.

C. Chemical Reactions

1. Reactions with Halocarbons, Hydrogen Halides, and Halides

Many hydrides react with the halocarbon solvents to yield metal halide derivatives. For example, $[H_2Ru(PPh_3)_4]$ reacts with $CHCl_3$ to give $[HRuCl(PPh_3)_3]$ (*116*):

$$[H_2Ru(PPh_3)_4] + CHCl_3 \longrightarrow [HRuCl(PPh_3)_3] + PPh_3 + CH_2Cl_2 \qquad (13)$$

The order of increasing reactivity is $CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$ (*119*).

Many hydrides also react with hydrogen halides resulting in elimination of H_2 and a metal halide complex (*120*):

$$[HRuCl(CO)_2(PPr_2{}^nBu^t)_2] + HCl \longrightarrow [RuCl_2(CO)_2(PPr_2{}^nBu^t)_2] + H_2 \quad (14)$$

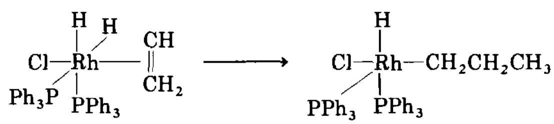
Halogens often react with hydrides to produce a metal halide and hydrogen halide (*131*):

$$[HRhBr_2(AsMePh_2)_3] + Br_2 \longrightarrow [RhBr_3(AsMePh_2)_3] + HBr \quad (15)$$

This reaction is often quantitative and has been used to determine the number of hydrogens in hydride complexes (*131*), although there is now evidence that in some hydride complexes not all the hydrogens can be replaced by halogen (*223*).

2. *Hydride Transfer to a Coordinated Ligand*

The transfer of hydride to another ligand in a complex is one of the key reaction steps in many catalytic cycles. In the hydrogenation of olefins, for example, hydride (or hydrogen) transfer to a coordinated olefin gives an intermediate alkyl complex:



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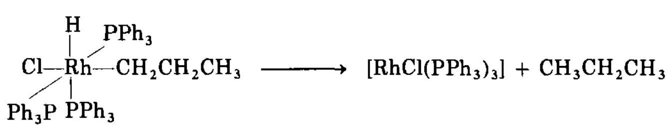
After addition of PPh_3, the reaction is followed by a second hydride transfer resulting in elimination of the alkane product:



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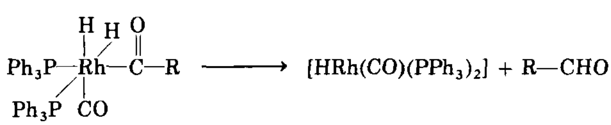
Similar reactions occur during the homogeneously catalyzed isomerization of olefins, and transfer of hydrogen to a intermediate acyl complex is the final step in the catalytic hydroformylation of olefins:



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3. *Elimination of Hydrogen*

Elimination of molecular hydrogen occurs from many coordinatively saturated complexes containing cis-hydride ligands. For example, $[H_2IrCl(CO)(PPh_3)_2]$ readily loses hydrogen if heated under an inert gas purge or when stirred under vacuum (*319*):

$$[H_2IrCl(CO)(PPh_3)_2] \xrightarrow[N_2]{\text{heat}} [IrCl(CO)(PPh_3)_2] + H_2 \tag{19}$$

Many stable dihydrides that will not lose H_2 under thermal conditions are known, but several recent reports (*117, 98, 118*) have shown that elimination of molecular hydrogen can often be induced by irradiation with light. Green and co-workers (*98*), for example, have shown that irradiation of $[(C_5H_5)_2WH_2]$ results in elimination of H_2 and formation of very reactive tungstenocene:

$$[(C_5H_5)_2WH_2] \xrightarrow{h\nu} [(C_5H_5)_2W] + H_2 \tag{20}$$

In our laboratory, we have discovered that elimination of hydrogen from the stable iridium hydrides $[H_2IrCl(PPh_3)_3]$ and *mer-* and *fac-* $[H_3Ir(PPh_3)_3]$ can be induced with either UV irradiation or with sunlight (*118*), e.g.,

$$[H_2IrCl(PPh_3)_3] \underset{H_2}{\overset{h\nu, \Phi = 0.6}{\rightleftharpoons}} [IrCl(PPh_3)_3] + H_2 \tag{21}$$

Since the reaction expressed in Eq. (21) is reversible, the $[H_2IrCl(PPh_3)_3]$—$[IrCl(PPh_3)_3]$ couple is a good model system for storage of hydrogen and for storage of energy. The photoinduced elimination of hydrogen from the iridium hydrides has been shown to proceed in a concerted fashion since irradiation of a mixture of $[H_2IrCl(PPh_3)_3]$ and $[D_2IrCl(PPh_3)_3]$ gives only H_2 and D_2.

IV. Physical Properties and Methods of Characterization

Transition metal–hydride complexes are generally colorless, white, or yellow and contain a discrete metal–hydrogen bond. In this respect, they differ from interstitial hydrides that contain no discrete ionic or molecular units and are frequently nonstoichiometric in nature. The following techniques have been employed for the characterization of hydride complexes.

A. Elemental Analysis, Dipole Moments, and Mass Spectrometry

Although elemental analysis is generally useful in determining the overall composition of a complex, the determination of hydride is analytically difficult, because of the small contribution to the total hydrogen content of the molecule.

As in many complexes, dipole moment measurements may enable the differentiation of geometrical isomers of hydride complexes. Chatt and co-workers (*59*, *57*), for example, measured the dipole moments of a series of iridium complexes and obtained the results listed in Table I. The α-isomer has hydride trans to Cl, and the β-isomer has hydride trans to CO or L. Because of the small size of the hydride ligand, unpredictable distortions of the molecule from regular symmetry may cause some uncertainty in interpretation of dipole moment data.

Because of the limited volatility of most hydride complexes, mass spectrometry is used mostly with carbonyl hydrides. From the fragmentation pattern of a complex, one can generally ascertain if a hydride ligand is bridging or terminally positioned. For example, the mass spectrum of $[HRu_3SR(CO)_{10}]$ (R = Et, Bu) shows successive loss of ten carbonyl groups (*79*). No loss of hydride was detected and this led the authors to suggest that the hydride occupies a bridging position.

TABLE I

Dipole Moments of Some $[HIrL_5]$ Complexes

Complex	μ_0
α-$[HIrCl_2(CO)(PEt_2Ph)_2]$	5.1
β-$[HIrCl_2(CO)(PEt_2Ph)_2]$	1.2
α-$[HIrCl_2(PEt_2Ph)_3]$	7.95
β-$[HIrCl_2(PEt_2Ph)_3]$	2.65

B. X-Ray and Neutron Diffraction

Originally, the hydride ligand was thought to be buried in the *d* orbitals of the metal. However, in 1963, the first X-ray diffraction study on a rhodium hydride was performed (*206*), and the actual metal–hydride bond length in $[HRh(CO)(PPh_3)_3]$ was determined by difference Fourier to be 1.60 ± 0.12 Å. In most crystal structures, however, the hydride is not definitely located owing to the small amount of electron density associated with the ligand. The hydride ligand does occupy an accepted coordination position, and assumptions of the hydride position can be made using the geometry of the remaining ligands, the trans effect, and bond lengths of the other ligands.

C. Nuclear Magnetic Resonance

The two most fruitful techniques for characterization of hydride complexes are NMR spectroscopy and IR spectroscopy. In the NMR, hydride resonances generally occur in the range 12–60 τ, and this high field shift has been attributed to paramagnetic shielding by the valence *d* electrons of the metal (*225*). Where comparisons of homologous compounds are possible, it appears that the high field shift of M—H is largest for first-row transition metals. Second- and third-row metal complexes show shifts approximately 25% less than the first row.

The magnitude of NMR coupling constants and the splitting pattern often provides valuable evidence for the configuration of various geometrical isomers. The coupling constant $J_{P,H}$ for a phosphine ligand trans to hydride is between 80–160 Hz, whereas a phosphine ligand cis to a hydride gives a value between 10–40 Hz. The difference has been attributed to an increased *s* character of the metal-hydride bond in the trans isomer (*131*). Further stereochemical evidence can be obtained by using phosphine ligands containing alkyl substituents such as dimethylphenylphosphine. The methyl proton resonance is a triplet if two such ligands are trans to one another due to coupling of the trans-phosphines. A doublet appears if the ligands are cis (*132*).

Reddy and Goluda (*262*) have prepared a series of complexes $[IrHX_2L_3]$ and have shown that two isomeric forms are present. In one the hydride is trans to halide, and in the other, the hydride is trans to an arsine ligand. The former exhibits a higher field shift, and the authors conclude that the τ value of the hydridic hydrogen appears to depend on the M—H bond length and the *d*-electron density of the metal.

Although NMR is very valuable for characterizing hydride complexes, failure to observe a hydride resonance due to limited solubility of the complex or because the signal is too weak does not exclude the existence of a hydride. As can be seen in the tables of hydrides (see Tables V–VII, Sections V–VII), no signals have been reported for a number of hydride complexes.

D. Infrared Spectroscopy

Just as with NMR measurements, IR spectroscopy may be used to verify the existence of a hydride and to elucidate structural information. Metal–hydride stretching frequencies generally occur in the

1650–2250 cm^{-1} range. The deuteride analogs show the expected shift to lower frequencies by a factor of about 1.40. Bridging hydrides possess a vibrational frequency in the range 1000–1200 cm^{-1} (*131*).

Jenkins and Shaw (*176*) have used Ir—Cl stretching modes as a further aid in structure determination for chlorohydride complexes. The ν_{Ir-Cl} is very sensitive to the nature of the trans-ligand. For chloride trans to chloride, the Ir—Cl stretching frequency lies between 303–320 cm^{-1}. For a phosphine or arsine trans to chloride, ν_{Ir-Cl} varies between 262–278 cm^{-1}. Finally, for a hydride trans to Cl, the stretching frequency lies in the range 246–249 cm^{-1}. These data are summarized in Table II.

TABLE II

IRIDIUM CHLORIDE STRETCHING FREQUENCY AS A FUNCTION OF THE LIGAND TRANS TO CHLORIDE

Trans Ligand	ν_{Ir-Cl} (cm^{-1})
H	246–249
PR_3, AsR_3	262–278
Cl	303–320

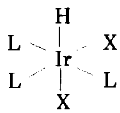
For octahedral dihydrido complexes with cis-hydrides, ν_{M-H} generally ranges from 1850 to 2050 cm^{-1}. As a rule, ν_{M-H} decreases with increasing π-bonding character of the ligand trans to hydride as the greater the trans influence of this ligand, the weaker the M—H bond. The range of ν_{M-H} for various trans-ligands in iridium hydride complexes is given in Table III.

TABLE III

IRIDIUM HYDRIDE STRETCHING FREQUENCY AS A FUNCTION OF THE LIGAND TRANS TO HYDRIDE

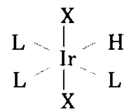
Trans Ligand	ν_{M-H} (cm^{-1})
H	1650–1750
CO, PR_3	2000–2100
Cl, Br, I	2200–2250
Bridging hydride	1000–1200

Reddy and Leelamani [263] have prepared complexes of the formula $[HIrX_2L_3]$, which exist in the α- and β-isomeric forms (II and III). The ν_{M-H} values of the α-compounds are higher by 10–14 cm^{-1} in chloroform as compared to benzene due to the increased solvent polarity. The ν_{M-H} values of the β-compounds show no solvent dependence. The sensitivity of ν_{M-H} of the α-isomers as a function of solvent may be caused by the preferential solvation of the halogen trans to the hydride in the polar solvent.



α

(II)



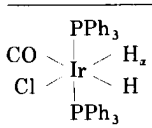
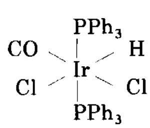
β

(III)

Structural information from IR data may also be elucidated for hydridocarbonyl complexes. Vaska (*316*) has demonstrated that a resonance interaction between the vibrational states of metal–hydride and carbonyl stretching motions in certain complexes of rhodium and iridium can aid in deducing structures. This interaction occurs with hydride and carbonyl trans to each other. By comparing the hydrido and deutero forms of the same complex, one observes a shift in the ν_{CO}, if the carbonyl and hydride were originally trans; no shift occurs if CO and H were originally cis. Data for two iridium complexes are given in Table IV.

TABLE IV

INFRARED DATA FOR $[H_2IrCl(CO)(PPh_3)_2]$ AND $[HIrCl_2(CO)(PPh_3)_2]$ AND THEIR DEUTERATED ANALOGS

Complex	ν_{M-H} (cm^{-1})	ν_{CO}	ν_{CO} (deuterated)	ν_{M-D}
	2196α 2100β	— 1982	— 2003	1575α 1497β
	2240	2027	2027	1608

As with NMR, the absence of a vibrational band does not exclude the existence of a hydride. Some bands may be too weak to be observed.

V. Hydride Complexes of Ruthenium

The following three sections discuss hydride complexes of ruthenium, rhodium, and iridium, respectively. Each section contains a comprehensive table summarizing the data on individual hydrides, and some interesting chemistry of representative complexes is presented in the text of each section. Monohydrides are discussed before polyhydrides, and in each of these divisions complexes with the least number of ligands appear first followed by complexes with increasing number of ligands.

Table V, presented at the end of this section, summarizes data on hydride complexes of ruthenium.

A. [$HRuL_4$]

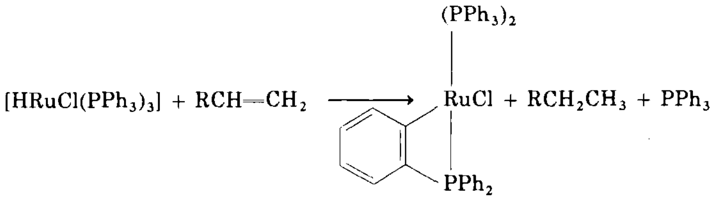
1. [*HRu(NO)*L_3]

Wilson and Osborn (*327*) prepared a series of ruthenium hydridonitrosyl complexes, [$HRu(NO)L_3$] [L = PPh_3, PPh_2Me, PPh_2Pr^i, $PPh_2(C_6H_{11})$], which, with the exception of the PPh_2Me complex, exhibit catalytic activity in the isomerization of hex-1-ene and the hydrogenation of sytrene. The PPh_2Me complex, unlike the catalytically active complexes, may have the hydride and nitrosyl ligands cis instead of trans, and the cis configuration may render the complex catalytically inactive.

2. [$HRuCl(PPh_3)_3$]

This complex is the most active hydrogenation catalyst known, hydrogenating terminal olefins at 25°C and 1 atm H_2 pressure (*142*). Di- and trisubstituted olefins, however, are hydrogenated only very slowly (*198*). The complex's high selectivity in hydrogenating terminal olefins is attributed to steric hindrance in the formation of an alkyl intermediate. In the catalytic cycle this alkyl complex is thought to undergo oxidative addition of H_2, followed by reductive elimination of the alkane product.

Stoichiometric hydrogenation of olefins by [$HRuCl(PPh_3)_3$] in the absence of H_2 results in the formation of an ortho-metalated complex (*172*):



(22)

The ortho-metalated complex was characterized by IR absorptions at 720 (σ_{C-H}) and 1510 cm^{-1} ($\nu_{C=C}$).

The crystal structure (*300*) of $[HRuCl(PPh_3)_3]$ shows a highly distorted trigonal-bipyramidal arrangement about the metal center. Two PPh_3 ligands occupy axial positions, whereas the third PPh_3 ligand, Cl, and hydride form the equatorial plane. A phenyl α-hydrogen is almost in the equatorial plane at a distance of 2.85 Å from the ruthenium atom, and this hydrogen is believed to block the sixth coordination site of the metal.

B. $[HRuL_5]$

1. $[HRu(PPh_3)_3]^+$

The reaction of $[HRu(MeCO_2)(PPh_3)_3]$ with MeOH and HBF_4 produces the tris(triphenylphosphine) complex, $[HRu(PPh_3)_3]BR_4$ (*216*). A crystal structure of this complex shows one triphenylphosphine ligand π-bonded to the metal through one phenyl group. The remaining two triphenylphosphine ligands bond in a normal fashion via the phosphorus nucleii. The Ru—H bond length has been approximated to be 1.7 Å.

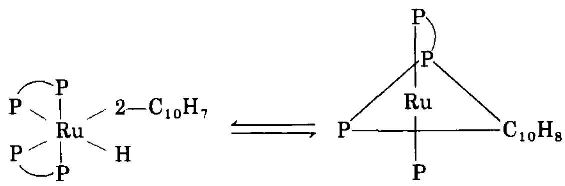
2. $[HRu(naphthyl)(dmpe)_2]$

Complex $[HRu(naphthyl)(dmpe)_2]$ is prepared by the following reaction (*56*):

$$NaC_{10}H_8 + trans\text{-}[RuCl_2(dmpe)_2] \longrightarrow cis\text{-}[HRu(naphthyl)(dmpe)_2] \qquad (23)$$

The crystal structure [134] of the complex shows that the Ru atom is approximately octahedrally coordinated, and the hydride is cis to the

σ-bonded naphthyl group. In solution, the equilibrium

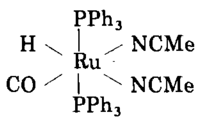


(24)

is established (*56*).

3. [HRuCl(CO)L$_3$]

Lupin and Shaw (*215*) have reported that [HRuCl(CO)L$_3$] (L = PPhPr$_2$^{n}, PPhBu$_2$^{n}, AsPhMe$_2$) reacts with HCl to give [RuCl$_2$(CO)L$_3$] and H$_2$. The triphenylphosphine complex, [HRuCl(CO)(PPh$_3$)$_3$], is reported (*25*) to have a higher activity toward the isomerization of pent-1-ene to pent-2-ene than [HRuCl(PPh$_3$)$_3$]. [HRuCl(CO)(PPh$_3$)$_3$] reacts with AgClO$_4$ and MeCN to form [HRu(CO)(MeCN)$_2$(PPh$_3$)$_2$] (IV), a versatile synthetic intermediate, since the two acetonitriles are of very different lability (*53*).



(IV)

4. [HRu(RCO$_2$)(PPh$_3$)$_3$]

Many hydride and low-oxidation state triphenylphosphine derivatives of d^6, d^8, and d^{10} platinum metal ions react with carboxylic acids to produce carboxylate complexes (*189*). Many of these complexes act as homogeneous hydrogenation catalysts. Complex [HRu(CF$_3$CO$_2$)(PPh$_3$)$_3$] hydrogenates alk-1-enes twice as fast as [HRh(CO)(PPh$_3$)$_3$], but only one-tenth as fast as [HRuCl(PPh$_3$)$_3$] (*275*). The low rates of hydrogenation of cyclic alkenes and the complete lack of hydrogenation of nonterminal alkenes is attributed to steric difficulty in hydride transfer to coordinated alkene.

Crystal structures (*135*) of complexes [HRu(HCO$_2$)(PPh$_3$)$_3$] and [HRu(MeCO$_2$)(PPh$_3$)$_3$] both show a distorted octahedral arrangement about the Ru atoms. The formate and acetate groups are bidentate and weakly held with 1 oxygen atom trans to the hydride. The ability of carboxylates to shift from bidentate to unidentate coordination is believed to be important in the catalytic cycles for these complexes.

The formate complex reacts as follows with various ligands to produce a polyhydride and CO_2 (*199, 202*):

$$[HRu(HCO_2)(PPh_3)_3] + PPh_3 \longrightarrow [H_2Ru(PPh_3)_4] + CO_2 \tag{25}$$

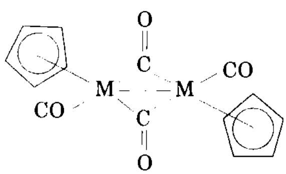
$$[HRu(HCO_2)(PPh_3)_3] + N_2 \longrightarrow [H_2Ru(N_2)(PPh_3)_3] + CO_2 \tag{26}$$

$$[HRu(HCO_2)(PPh_3)_3] + H_2 \longrightarrow [H_4Ru(PPh_3)_3] + CO_2 \tag{27}$$

5. $[HRu(CO)_2(\pi\text{-}C_5H_5)]$

Complex $[Ru_3(CO)_{12}]$ and cyclopentadiene react in the absence of O_2 to produce quantitatively $[HRu(CO)_2(\pi\text{-}C_5H_5)]$ (*30*). The same reaction in air produces a dimer with bridging carbonyl ligands and a metal–metal bond (*166*):

$$[Ru_3(CO)_{12}] + (\pi\text{-}C_5H_5)^- \xrightarrow{O_2}$$



(28)

C. $[HRu_2L_9]$

$\{HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]\}$

Complex $\{HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]\}$, a dinuclear ruthenium hydride, is obtained by heating $[Ru_3(CO)_9(P(OPh)_3)_3]$ in Decalin (*41*). Crystal structure analysis (*41*) indicates the presence of two ortho-metalated aryl groups. Two carbonyls are coordinated to 1 ruthenium, whereas 1 carbonyl and an ortho-metalated phosphite group are bound to the second ruthenium. The second ortho-metalated phosphite and the diphenylphosphonate ligand, $[OP(OPh)_2]$, are bound to both metal atoms.

D. $[HRu_2L_{10}]$

$[HRu_2(CO)_6(C_{10}H_9O)]$

Benzylidene acetone and $[(1,5\text{-cyclooctadiene})Ru(CO)_3]$ reacted to yield orange crystals of $[HRu_2(CO)_6(C_{10}H_9O)]$ (*91*). Crytsal structure analysis (*91*) indicates that the bonding of the $C_{10}H_9O$ group is unique, attaching to 1 ruthenium by 2 carbons in a π-olefinic manner, and to the other ruthenium by a carbon–metal σ-bond and an oxygen–metal dative σ-bond. Three carbonyl groups bond to each Ru, and the hydride is believed to bridge the 2 ruthenium atoms. The formation of this complex illustrates the ability of ruthenium carbonyls to abstract hydrides from olefins.

E. $[HRu_3L_{11}]$

$[HRu_3(CO)_{10}SR]$

Air-stable hydridothiol complexes, $[HRu_3(CO)_{10}SR]$ (R = Et, Bu^n), are obtained from the reaction of $[Ru_3(CO)_{12}]$ and HSR (*79*). The complexes are volatile, as are many ruthenium carbonyl complexes, and mass spectrometry indicates the loss of ten successive carbonyl groups. No loss of hydride was detected, and this observation together with NMR data suggest that the hydride is bridging.

F. $[HRu_3L_{12}]$

1. $[HRu_3(CO)_9(C_{13}H_9)]$

Treatment of $[Ru_3(CO)_{12}]$ with phenyllithium in H_3PO_4 produces the cluster $[HRu_3(CO)_9(C_{13}H_9)]$ (*250*). Mass spectrometry, NMR, and X-ray crystal structure data (*250*) indicate that the hydride is probably bridging 2 ruthenium atoms. The diphenylcarbene group, $C_{13}H_9$, is coordinated to all 3 metal atoms. Three terminal carbonyl groups are also coordinated to each ruthenium.

2. $[HRu_3(CO)_{12}]^+$

Knight and Mays (*191*) have shown that protonation of $[Ru_3(CO)_{12}]$ with concentrated H_2SO_4 produces the cation $[HRu_3(CO)_{12}]^+$. The complex is air-stable but deprotonates slowly in solution.

G. $[H_2RuL_3]$

$[H_2Ru(PPh_3)_3]$

Air-sensitive dihydridotris(triphenylphosphine)ruthenium(II) is prepared by the reaction of $[RuCl_2(PPh_3)_3]$ with H_2 and triethylamine (*97*). The complex reacts as follows at room temperature in the solid state with gaseous, small molecules:

$$[H_2Ru(PPh_3)_3] + CO \longrightarrow [H_2Ru(CO)(PPh_3)_3] \tag{29}$$

$$[H_2Ru(PPh_3)_3] + N_2 \longrightarrow [H_2Ru(N_2)(PPh_3)_3] \tag{30}$$

$$[H_2Ru(PPh_3)_3] + ClNO \longrightarrow [RuCl_3(NO)(PPh_3)_2] \tag{31}$$

Recent work has shown that this dihydride should probably be reformulated as the tetrahydrido species, $[H_4Ru(PPh_3)_3]$ (*145*, *193*).

H. $[H_2RuL_4]$

1. $[H_2Ru(PPh_3)_4]$

Levison and Robinson (*210*) prepared $[H_2Ru(PPh_3)_4]$ by treating $RuCl_3$ with excess PPh_3 and $NaBH_4$ in ethanol. If a benzene solution of the hydride is treated with excess D_2, then 24 or 25 hydrogens/mole of complex are exchanged, suggesting interaction of all ortho-hydrogens with the ruthenium (*171*).

2. $[H_2Ru(PF_3)_4]$

Thermally stable $[H_2Ru(PF_3)_4]$ has been prepared by Kruck and Prasch (*204*). In aqueous solution the complex behaves as a weak acid, similar to $[HCo(CO)_4]$, and IR and NMR studies suggest that the hydrides are cis.

3. $\{H_2Ru[PPh(OEt)_2]_4\}$

This six-coordinate dihydride has been examined by X-ray analysis by Guggenberger (*135*). The RuP_4 framework tends to approximate a flattened equatorial tetrahedron. The complex exhibits fluxional behavior in solution (*135*), and this has been interpreted in terms of a "tetrahedral tunneling mechanism."

4. $[H_2Ru(N_2)(PPh_3)_3]$

Reaction of $[HRuCl(PPh_3)_3]$ with Et_3Al under N_2 produces the dinitrogen complex, $[H_2Ru(N_2)(PPh_3)_3]$ (*193*). Treatment of the complex with HCl produces $[RuCl_2(PPh_3)_3]$, dinitrogen, and molecular hydrogen.

This dinitrogen complex has also been obtained by the technique of reverse osmosis (*129*) in which a solution of the complex is forced against a selectively permeable membrane under pressure. Uncoordinated triphenylphosphine and solvent diffuse through, but the metal species is retained. The technique provides a means for the removal of nonvolatile dissociated ligands from solutions of organometallic complexes. If the osmosis is carried out under nitrogen, complex $[H_2Ru(N_2)(PPh_3)_3]$ is isolated. (*129*):

$$H_2Ru(PPh_3)_4 \xrightarrow{N_2} H_2Ru(N_2)(PPh_3)_3 + PPh_3 \qquad (32)$$

Other dinitrogen complexes have also been prepared using this technique (*129*). Unfortunately, the membrane used in this work does not appear to be available to other investigators.

I. $[H_2Ru_3L_{12}]$

$[H_2Ru_3(CO)_9X]$

Air-sensitive complexes of the formula, $[H_2Ru_3(CO)_9X]$ (X = S, Se, Te) are obtained from the reaction of $[Ru_3(CO)_{12}]$ with XO_3^- (*282*). Mass spectrometry and NMR data suggests a bridging hydride. Magnetic measurements (*282*) of $[H_2Ru_3(CO)_9S]$ indicate the complex is paramagnetic and contains 2 unpaired electrons. Treatment of the complexes with concentrated H_2SO_4 produces the trihydride cation, $[H_3Ru_3(CO)_9X]^+$ (*85*).

J. $[H_2FeRu_3L_{13}]$

$[H_2FeRu_3(CO)_{13}]$

The reaction of $[Ru_3(CO)_{12}]$ with $[Fe(CO)_5]$ in water produces the mixed metal species, $[H_2FeRu_3(CO)_{13}]$ (*122*). The complex contains a tetrahedral cluster of metal atoms, with three terminal CO groups bonding to each Ru, and two CO groups bonding to Fe. There are also two iron–carbonyl–ruthenium bridges, and NMR data and X-ray crystal structure data suggest that the hydrides bridge two ruthenium–ruthenium bonds (*122*).

K. $[H_2Ru_4L_{13}]$

$[H_2Ru_4(CO)_{13}]$

Lewis *et al.* (*180*) prepared the cluster complex, α-$[H_2Ru_4(CO)_{13}]$, by the reaction of di-*n*-butyl ether with $[Ru_3(CO)_{12}]$. The crystal structure (*338*) of the complex shows eleven CO groups terminally bonded and two carbonyls bridging Ru—Ru bonds. Two long Ru—Ru bond distances and four shorter Ru—Ru bond lengths are observed, implying that the hydrides bridge the two long Ru—Ru bonds.

If $Ru_3(CO)_{12}$ is treated with KOH, MeOH, and H_2O, complex β-$[H_2Ru_4(CO)_{13}]$ is formed (*181*). The β-complex is also believed to contain bridging hydride ligands, consistent with mass spectral and NMR data.

L. $[H_2Ru_6L_{18}]$

$[H_2Ru_6(CO)_{18}]$

Churchill and Wormald (*63*) have obtained the crystal structure of the purple, air-stable complex, $[H_2Ru_6(CO)_{18}]$. The 6 Ru atoms define an octahedron, and each Ru contains three terminally bonded carbonyl ligands. The symmetrical enlargement of two opposite faces of each Ru_6 cluster implies triply bridging hydride ligands in mutually trans positions.

M. $[H_4RuL_3]$

$[H_4Ru(PPh_3)_3]$

The white, air-sensitive complex, $[H_4Ru(PPh_3)_3]$, decomposes when placed in halogenated solvents (*145*). The complex reacts with a number of small molecules with displacement of molecular hydrogen and often phosphine (*97*) as follows:

$$[H_4Ru(PPh_3)_3] + N_2 \longrightarrow [H_2Ru(N_2)(PPh_3)_3] + H_2 \tag{33}$$

$$[H_4Ru(PPh_3)_3] + CO \longrightarrow [H_2Ru(CO)(PPh_3)_3] + H_2 \tag{34}$$

$$[H_4Ru(PPh_3)_3] + NO \longrightarrow [Ru(NO)_2(PPh_3)_2] + H_2 + PPh_3 \tag{35}$$

$$[H_4Ru(PPh_3)_3] + SO_2 \longrightarrow [Ru(SO_2)_2(PPh_3)_2] + H_2 + PPh_3 \tag{36}$$

N. $[H_4Ru_4L_{12}]$

$[H_4Ru_4(CO)_{12}]$

A yellow, air-stable cluster complex, $[H_4Ru_4(CO)_{12}]$ is prepared in high yields by heating an octane solution of $[Ru_3(CO)_{12}]$ under hydrogen (*184*, *197*). Nuclear magnetic resonance and mass spectrometry data suggest that the hydrides are bridging. Substitution of one to four carbonyl ligands occurs when the complex is treated with tributylphosphine, triphenylphosphine, and trimethylphosphite (*253*). The resulting complexes show good solubility in most organic solvents and good thermal stability even in the presence of air. Complex $H_4Ru_4(CO)_{12}$ also reacts with ethylene to produce a ruthenium ethylidyne complex, $H_3Ru_3(CO)_9CCH_3$ (*50*).

The original report (*181*) that $[H_4Ru_4(CO)_{12}]$ exists in α- and β-forms has recently been shown to be incorrect (*253*, *197*) as the α-form is a mixture of $[H_4Ru_4(CO)_{12}]$ and $[Ru_3(CO)_{12}]$.

TABLE V

SURVEY OF HYDRIDE COMPLEXES: RUTHENIUM

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRu(\pi\text{-}C_6H_6)$	—	—	—	—	—	Possible active catalytic species	(*157*)
$HRu(NO)(PPh_3)_3$	$Ru(NO)Cl_3L_2 + KOH{\cdot}EtOH + L$	br	—	16.6	1970	—	(*327*)
$HRu(NO)(PPh_2Me)_3$	—	br	—	15.0	1900	—	(*327*)
$HRu(NO)(PPh_2i\text{-}Pr)_3$	—	br	—	17.2	1990, 1975	—	(*327*)
$HRu(NO)[PPh_2(C_6H_{11})]$	—	br	—	17.4	1985, 1960	—	(*327*)
$HRuCl(PPh_3)_3$	$(PPh_3)_3RuX_2 + Et_3N + H_2$	p	> 150 (dec)	27.75[e]	2020	Solid decomposes after several hours of exposure to air	(*287, 172, 25, 300, 141, 173*)
$HRuCl[P(OPh)_3]_3$	—	w	—	16.8	—	—	(*194*)
$HRuBr(PPh_3)_3$	—	p	238	27.11[e]	2025[f]	Solutions air-sensitive	(*142*)
$HRuCl(CO)(Pcy_3)_2$	$RuCl_3{\cdot}3H_2O + Pcy_3$	y	—	34.6[e]	2030/1905	Air-sensitive	(*327, 236, 182*)
$HRu(PPh_3)_2(BH_4)$	$Ru_5Cl_{12}^{2-} + NaBH_4 + PPh_3$	y–br	—	19	1928	—	(*161*)
$[HRu(PPh_3)_3]PF_6$	$HRu(CO_2Me)(PPh_3)_3 \xrightarrow[\text{MeOH HX}]{\text{heat}}$	w	200	18.75	2020	—	(*279*)
$[HRu(PPh_3)_3]BF_4$	—	w	120	18.75	2020	Crystal structure	(*216, 279*)
$[HRu(PPh_3)_4]PF_6$	$H_2Ru(PPh_3)_4 + (Ph_3PCPh_3)PF_6$	r	136	18.02	2020	—	(*279*)

$\{HRu[P(OEt)_2Ph]_5\}PF_6$	$[HRu(PPh_3)_4]^+ + L$	w	227	18.90	1900	—	*(279)*
$\{HRu[P(OMe)_2Ph]_5\}PF_6$	—	w	221	18.85	1908	Air-stable	*(279, 74)*
$[HRu(HPPh_2)_5]BF_4$	—	w	251	17.95	1972	—	*(279)*
$[HRu(HPPh_2)_5]PF_6$	$HRuCl(PPh_3)_3 + HPPh_2$	w	255	17.89	1961	Air-stable; soluble—acetone; insoluble—alcohols	*(280)*
$HRuCl(HPPh_2)_4$	$H_2Ru(HPPh_2)_4$ + alkali metal salt	w	230	27.70	1970	Air-stable	*(281)*
$HRuBr(HPPh_2)_4$	—	w	240	26.49	1985	—	*(281)*
$HRuI(HPPh_2)_4$	—	w	241	24.08	1987	—	*(281)*
$HRuSCN(HPPh_2)_4$	—	w	190	26.23	1956	—	*(281)*
$HRu(SnCl_3)(HPPh_2)_4$	—	w	235	20.15	1972	—	*(281)*
$HRuCl[P(OPh)_3]_4$	$HRuCl(PPh_3)_3 + P(OPh)_3$	w	—	16.8	1930	Air-stable	*(195)*
$[HRu(CO)(depe)_2]BPh_4$	$HRuCl(depe)_2 + L + NaBPh_4$	c	—	19.4[g]	—	—	*(16)*
$[HRu(p\text{-}MeO{-}C_6H_4{-}NC)(depe)_2]BPh_4$	—	c	—	20.5[g]	—	—	*(16)*
$[HRu(MeNC)(depe)_2]BPh_4$	—	c	—	21.2[g]	—	—	*(16)*
$[HRu\{P(OMe)_3\}(depe)_2]BPh_4$	—	c	—	21.3[g]	—	—	*(16)*
$[HRu\{P(OPh)_3\}(depe)_2]BPh_4$	—	c	—	21.5[g]	—	—	*(16)*
$[HRu(N_2)(depe)_2]BPh_4$	—	c	—	25.8[g]	—	—	*(16)*
$[HRu(PhCN)(depe)_2]BPh_4$	—	c	—	28.5[g]	—	—	*(16)*
cis-$HRu(C_6H_5)(dmpe)_2$	Na^+L^- + *trans*-$RuCl_2(dmpe)_2$	c	136	—	1806	$u = 5.3$[h]	*(56)*
cis-$HRu(2\text{-}C_{10}H_7)(dmpe)_2$	—	c	182	17.6, 19.8	1802	$u = 6.0$[h]	*(56, 134)*
cis-HRu(anthryl)$(dmpe)_2$	—	c	185	—	1802	$u = 6.35$[h]	*(56)*
cis-HRu(phenanthryl)$(dmpe)_2$	—	c	202	—	1796	—	*(56)*
cis-$HRu(C_{10}H_{16}O)(dmpe)_2$	—	c	180	—	1802	—	*(56)*
trans-$HRuCl(depe)_2$	—	c	174	32.3[i]	1938[j]	$u = 4.9$[h]	*(131)*

(Continued)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
trans-$HRuBr(depe)_2$	—	y	188 (dec)	31.5[i]	1945[j]	$u = 5.65$[h]	(*131*)
trans-$HRuI(depe)_2$	—	y	212 (dec)	29.8[i]	1948[j]	$u = 5.8$[h]	(*131*)
trans-$HRuSCN(depe)_2$	—	c	245 (dec)	—	1919[j]	—	(*131*)
trans-$HRuCN(depe)_2$	—	c	—	—	1803[j]	—	(*131*)
trans-$HRuCl(dmpe)_2$	—	c	217 (dec)	—	1891[j]	$u = 4.8$[h]	(*131*)
trans-$HRuBr(dmpe)_2$	—	y	215 (dec)	—	1895[j]	—	(*131*)
trans-$HRuI(dmpe)_2$	—	y	322 (dec)	—	1898[j]	—	(*131*)
trans-$HRu(SCN)(dmpe)_2$	—	c	240 (dec)	—	1870[k]	—	(*131*)
trans-$HRu(CN)(dmpe)_2$	—	y	230 (dec)	—	1754[k]	—	(*131*)
trans-$HRu(NO_2)(dmpe)_2$	—	y	240 (dec)	—	1858[k]	—	(*131*)
trans-$HRuCl[o\text{-}C_6H_4(PEt_2)_2]_2$	—	y	250 (dec)	—	1978[k]	$u = 4.45$[h]	(*131*)
trans-$HRuI[o\text{-}C_6H_4(PEt_2)_2]_2$	—	br	278 (dec)	—	1976[k]	—	(*131*)
trans-$HRuCl[CH_2(PPh_2)_2]_2 \cdot \frac{1}{2}C_6H_6$	—	y	283 (dec)	—	1978	$u = 4.95$[h]	(*131*)
trans-$HRuCl[o\text{-}C_6H_4(AsMe_2)_2]_2$	—	c	190 (dec)	—	1804[j]	—	(*131*)
cis-$HRuMe(dppe)_2$	—	c	247 (dec)	18.9[k]	1884[k]	$u = 3.25$[h]	(*131*)
trans-$HRuMe(dppe)_2$	—	c	290 (dec)	18.4[k]	1868[k]	$u = 2.95$[h]	(*131*)
cis-$HRuEt(dppe)_2$	—	c	289 (dec)	—	1873[k]	$u = 3.25$[h]	(*131*)
cis-$HRuPr^n(dppe)_2 \cdot C_6H_6$	—	c	278 (dec)	—	1867[k]	$u = 3.15$[h]	(*131*)
$HRu(p\text{-tolyl})(dmpe)_2$	—	c	146 (dec)	—	1766	—	(*131*)
trans-$HRuPh(dmpe)_2$	—	c	159 (dec)	23.3[k]	1757	$u = 3.90$[h]	(*131*)
$[HRu(CO)(HPPh_2)_4]BF_4$	$HRuCl(CO)(PPh_3)_3$ + $(HPPh_2)/NH_4BF_4$	w	—	16.79	1971	—	(*210*)
$HRuCl(CO)(PPh_3)_3$	$RuCl_3$ + PPh_3/H_2CO + 2-methoxyethanol	y	139	—	2010/1920, 1900	—	(*25*, *210*, *293*)

$HRuCl(CO)(PPhEt_2)_3$	$[Ru_2X_3L_6]^+$ + KOH + EtOH	w	99	17.1[k]	1880/1910[j]	$u = 3.2$[h]	*(58)*
$HRuBr(CO)(PPhEt_2)_3$	—	w	110	17.65[k]	1914[k]	$u = 3.3$[h]	*(58)*
$HRuI(CO)(PPhEt_2)_3$	—	w	141 (dec)	—	1920[k]	$u = 3.8$[h]	*(58)*
$HRuCl(CO)(PPhPr^n_2)_3$	$RuX_2(CO)L_3 + KOH/H_2O$	c	131	17.5[i]	1869/1898	—	*(215)*
$HRuBr(CO)(PPhPr^n_2)_3$	—	c	126	17.8[i]	1866/1908	—	*(215)*
$HRuI(CO)(PPhPr^n_2)_3$	—	y	118	18.5[i]	1880/1908	—	*(215)*
$HRuBr(CO)(PPhBu^n_2)_3$	—	w	—	17.9[i]	1901(ν_{CO})	—	*(215)*
$HRuI(CO)(PPhBu^n_2)_3$	—	w	—	18.4[i]	—	—	*(215)*
$HRuCl(CO)(AsPhMe_2)_3$	—	cr	91	18.2[i]	1908(ν_{CO})	—	*(215)*
$HRuCl(CO)(PPhBu^n_2)_3$	$HRuCl(CO)(PR_2Ph)_3 + L$	w	—	17.10[k]	—	—	*(94)*
$HRuCl(CO)(PPhEt_2)_2(PPhMe_2)$	—	w	108	16.82[k]	1864/1906[j]	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2(PPhMe_2)$	—	w	110	16.80[k]	1874/1906[j]	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2(PPhEt_2)$	—	w	—	17.14[k]	—	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2(PEt_3)$	—	w	—	16.90[k]	—	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2[PPh(OMe)_2]$	—	w	—	16.18[k]	—	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2[P(OEt)_3]$	—	w	—	16.20[k]	—	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2(AsPhMe_2)$	—	w	—	18.46[k]	—	—	*(94)*
$HRuCl(CO)(PPhPr^n_2)_2(AsPhEt_2)$	—	w	—	18.56[k]	—	—	*(94)*
$HRuCl(CO)(PPhBu^n_2)_2(PPhMe_2)$	—	w	110	16.72[k]	1874/1905[j]	—	*(94)*
$HRuCl(CO)(PPhBu^n_2)_2(AsPhMe_2)$	—	w	—	18.29[k]	—	—	*(94)*
$HRuCl(CO)(PPhMe_2)_3$	—	—	—	16.6[k]	—	—	*(27)*
$HRuBr(CO)(PPhMe_2)_3$	—	—	—	17.0[k]	—	—	*(27)*
$HRuI(CO)(PPhMe_2)_3$	—	—	—	17.7[k]	—	—	*(27)*
$[HRu(MeCN)_2(PPh_3)_3]PF_6$	$[HRu(PPh_3)_4]^+ + RCN$	y	195	23.70	1964	—	*(279)*
$[HRu(MeCN)_2(PPh_3)_3]BF_4$	—	y	207	23.64	1960	—	*(279)*
$[HRu(Pr^nCN)_2(PPh_3)_3]PF_6$	—	y	205	23.74	1964	—	*(279)*
$[HRu(Pr^iCN)_2(PPh_3)_3]PF_6$	—	y	205	23.62	1968	—	*(279)*

(Continued)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[HRu(PhCN)_2(PPh_3)_3]PF_6$	—	y	200	22.55	1972	—	(*279*)
$[HRu(MeC_6H_4CN)_2(PPh_3)_3]PF_6$	—	y	201	22.66	1968	—	(*279*)
$[HRu(MeOC_6H_4CN)_2(PPh_3)_3]PF_6$	—	y	205	22.78	1959	—	(*279*)
$[HRu(ClC_6H_4CN)_2(PPh_3)_3]PF_6$	—	y	199	22.43	1970	—	(*279*)
$[HRu(cod)\{N(CH_3)_2NH_2\}_3]BPh_4$	$[codRuCl_2]_x$ + MeOH, BPh_4^- substituted hydrazines	—	—	12.87	2000	Air-sensitive	(*164*)
$[HRu(cod)\{N(CH_3)_2NH_2\}_3]BPh_4$	—	—	—	14.0	2050	—	(*164*)
$[HRu(cod)(N_2H_4)_3]BPh_4$	—	—	—	15.3	2000	—	(*164*)
$[HRu(cod)(py)_3]BPh_4$	—	—	—	13.0	2062	—	(*164*)
$[HRu(cod)(picoline)_3]BPh_4$	—	—	—	12.87	2070	—	(*164*)
$HRu(HCO_2)(PPh_3)_3$	$(PPh_3)_3RuH_2 + CO_2$	o	75	—	2010	Crystal structure	(*275, 136, 202, 199, 273*)
$HRu(MeCO_2)(PPh_3)_3$	$RuCl_2(PPh_3)_3 + H_2 + RCO_2Na$	y	222	29.89[g]	2012	Reasonably stable in air	(*275, 301*)
$HRu(CH_2ClCO_2)(PPh_3)_3$	—	y	—	28.98[g]	1991	—	(*273*)
$HRu(CF_3CO_2)(PPh_3)_3$	—	y	—	29.70[g]	2030	Extremely sensitive to O_2 in solution	(*275, 214*)
$HRu(EtCO_2)(PPh_3)_3$	—	y	230	28.68[g]	2020	—	(*275*)
$HRu(Pr^nCO_2)(PPh_3)_3$	—	y	—	29.78[g]	1976	—	(*275*)
$HRu(Pr^iCO_2)(PPh_3)_3$	—	y	—	28.88[g]	2008	—	(*275*)
$HRu(Me_3C{\cdot}CO_2)(PPh_3)_3$	—	y	—	29.11[g]	2018	—	(*275*)

$HRu(PhCO_2)(PPh_3)_3$	—	y	217	27.86[k]	1989	—	(*275, 273*)
$HRu[o\text{-}(OH)C_6H_4{\cdot}CO_2](PPh_3)_3$	—	y	—	28.75[g]	2010, 1982	—	(*275*)
$HRu(o\text{-}MeC_6H_4{\cdot}CO_2)(PPh_3)_3$	—	y	219	—	2004, 1999	—	(*273*)
$HRu(p\text{-}MeC_6H_4{\cdot}CO_2)(PPh_3)_3$	—	y	222	28.7[g]	1979	—	(*273*)
$HRu(p\text{-}MeO{\cdot}C_6H_4{\cdot}CO_2)(PPh_3)_3$	—	y	220	28.6[g]	1981	—	(*273*)
$HRu(p\text{-}ClC_6H_4{\cdot}CO_2)(PPh_3)_3$	—	y	223	—	2018, 1950	—	(*273*)
$HRu(p\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2)(PPh_3)_3$	—	br	196	28.7[g]	2028	—	(*273*)
$HRu(MeCO_2)(CO)(PPh_3)_2$	$HRu(HCO_2)(PPh_3)_3$ + HOCOR + 2-methoxyethanol	w	181	26.45	2000/1928	Air-sensitive	(*273*)
$HRu(EtCO_2)(CO)(PPh_3)_2$	—	w	180	26.3	1994/1923	—	(*273*)
$HRu(p\text{-}MeC_6H_4CO_2)(CO)(PPh_3)_2$	—	w	202	26.3	2026/1929	—	(*273*)
$HRu(p\text{-}MeOC_6H_4CO_2)(CO)(PPh_3)_2$	—	w	199	26.3	2008/1922 2026/1935	—	(*273*)
$HRu(PhCO_2)(CO)(PPh_3)_2$	—	—	—	26.35	2003, 1988/ 1924	—	(*273*)
$HRu(dpt)(CO)(PPh_3)_2$	—	o	—	22.33	1917(ν_{CO})	Air-stable	(*272*)
$HRuCl(C_7H_8)(PPh_3)_2$	$HRuCl(PPh_3)_3$ + L	br	136	18.92[l]	2080	—	(*142*)
$HRuCl(bipy)(PPh_3)_2$	—	r	160	22.25[g]	1930	—	(*142*)
$HRuCl(CO)_2(PPh_3)_2$	$HRuCl(PPh_3)_2$ + CO	w	—	14.5	2042, 1995 (ν_{CO})	Air-stable	(*174, 175*)
$HRuBr(CO)_2(PPh_3)_2$	—	y	—	15.3	2030, 1980 (ν_{CO})	—	(*175*)
$HRuCl(CO)_2(PPr_2{}^nBu^t)_2$	$Ru(CO)_2Cl_2(PPr_2{}^nBu^t)_2$ + KOH/2-methoxyethanol	w	—	15.29[g]	2033, 1957, 1937	—	(*120*)
$HRuCl(CO)(CNR)(PPh_3)_2$	$HRuCl(CO)(PPh_3)_3$ + RNC + $AgClO_4$	c	—	15.5[g]	1935, 1922 (ν_{CO})	—	(*60*)
$HRu(OClO_3)(CO)(CNR)(PPh_3)_2$	—	c	—	15.4[g]	1947 (ν_{CO})	—	(*60*)
cis-$[HRu(CO)_2(CNR)(PPh_3)_2]ClO_4$	—	c	—	16.0[g]	2085, 2045 (ν_{CO})	—	(*60*)

(*Continued*)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
trans-$[HRu(CO)_2(CNR)(PPh_3)_2]ClO_4$	—	c	—	17.3[g]	2122, 2045 (ν_{CO})	—	*(60)*
$[HRu(CO)(CNR)(PPh_3)_2]ClO_4$	—	c	—	18.3[g]	1990(ν_{CO})	—	*(60)*
$HRuI(CO)(CNR)(PPh_3)_2$	—	—	120	15.6[g]	1987(ν_{CO})	—	*(61)*
$[HRu(CO)(MeCN)_2(PPh_3)_2]ClO_4$	—	—	—	—	—	—	*(53)*
$HRu(\pi\text{-}C_5H_5)(PPh_3)_2$	$(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ + $LiAlH_4$	y	135 (dec)	21.73[m]	1950	Air, thermally stable	*(30)*
$HRu(\pi\text{-}C_5H_5)(CO)_2$	$Ru_3(CO)_{12}$ + $\pi\text{-}C_5H_5^-$	c	—	—	—	Air-sensitive; air produces carbonyl-bridged dimer	*(166)*
$HRu(Me_3Si)(CO)_3(PPh_3)$	$(Me_3M)Ru(CO)_3(PPh_3)I$ + $NaBH_4$	y	90	16.88	2068, 1009, 1991	Air-sensitive	*(11)*
$HRu(Me_3Sn)(CO)_3(PPh_3)$	—	y	—	17.24	2061, 2009, 1989	—	*(11)*
$HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$	$Ru_3(CO)_9[P(OPh)_3]_3$ + Decalin (heat)	w	—	20.8	—	Crystal structure; metalated aryl groups	*(41)*
$HRu_2(CO)_6(C_{10}H_4O)$	Benzylidene acetone + $(1,5\text{-cod})Ru(CO)_3$	o	—	22.6	—	Crystal structure; slow thermal decomposition	*(91)*
$HRu_3(CO)_{11}^-$	$Ru_3(CO)_{12}$ + $Mn(CO)_5^-$	r	—	22.9	2072, 2011, 1983, 1949,[n]	—	*(192)*

					1898, 1730 (ν_{CO})		
$HRu_3SEt(CO)_{10}$	$HSR + Ru_3(CO)_{12}$	o	110	25.40[g]	2105, 2064, 2056, 2026,[o] 2012, 2008, 1994 (ν_{CO})	Air-stable; volatile	(*79*)
$HRu_3SBu^n(CO)_{10}$	—	o	69	25.42[g]	2105, 2064, 2056, 2025,[o] 2012, 2007, 1994 (ν_{CO})	—	(*79*)
$HRu_3(CO)_9(C_6H_5CC_6H_4)$	$LiPh + Ru_3(CO)_{12} + H_3PO_4$	r	139	30.2[m]	2097, 2071, 2041, 2032,[o] 2018, 2006, 1990 (ν_{CO})	Crystal structure	(*250*)
$HRu_3(CO)_9(C_8H_{11})$	$H_2Ru_4(CO)_{13}$ + 1,5-cod	y–o	—	30.6[g]	2093, 2063, 2039, 2022,[o] 2016, 2003, 1994, 1985, 1979 (ν_{CO})	Mass spec.	(*51*)

(*Continued*)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^1H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRu_3(CO)_{10}NHPh$	$Ru_3(CO)_{12} + C_6H_5NO_2$	r	—	23.3[p]	2101, 2065, 2051, 2026,[q] 2011, 2003, 1982 (ν_{CO})	Mass spec.	*(283)*
$HRu_3(CO)_9C_4H_3Ph_2$	$Ru_3(CO)_{12} + L$	y	—	31.0[p]	2097, 2072, 2044, 2030, 2016,[r] 2004, 1999, 1983, 1962 (ν_{CO})	—	*(112)*
$HRu_3(CO)_9C_6H_9$	—	y	—	30.6[p]	2094, 2066, 2042, 2025,[r] 2020, 2005, 1998, 1984 (ν_{CO})	Crystal structure	*(112, 101)*
$HRu_3(CO)_9C_5H_7$	—	y	—	31.3[p]	2097, 2069, 2043,[r] 2026, 2015, 2004, 1996, 1963	—	*(112)*

$HRu_3(CO)_9C_4H_5$	—	y	—	31.3[p]	2098, 2071, 2046, 2028, 2017,[r] 2009, 1999, 1984, 1966	—	*(112)*
$[HRu_3(CO)_{12}]PF_6$	$H_2SO_4 + Ru_3(CO)_{12}$	y	—	28.6[s]	2129, 2102, 2081,[t] 2068, 2030	Air-stable; deprotonates in solution	*(191)*
$HRu_3(CO)_9(C_{12}H_{15})$	$Ru_3(CO)_{12}$ + cyclododeca-1,5,9-triene	y	138 (dec)	30.24	2096, 2070, 2045, 2027,[o] 2015, 2007, 1995, 1973 (ν_{CO})	Crystal structure	*(42, 75)*
$HRu_3(CO)_9(C_{12}H_{17})$	—	o	150 (dec)	—	2087, 2058, 2033, 2017, 2009,[o] 2002, 1994, 1990, 1982, 1972 (ν_{CO})	Mass spec.	*(42)*

(Continued)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRu_3(CO)_7(C_{24}H_{34})$	—	y–br	194 (dec)	32.83	2054, 2018, 1998, 1977, 1965 (ν_{CO})[o]	—	(*42*)
$HRu_3(CO)_6(C_{12}H_{15})[P(OMe)_3]_3$	$HRu_3(CO)_9(C_{12}H_{15}) + L$	o	190 (dec)	30.01	2036, 2012, 1976, 1964, 1921 (ν_{CO})[o]	—	(*42*)
$HRu_3(CO)_7(C_{12}H_{15})[P(OMe)_3]_2$	—	y	145 (dec)	29.91	2057, 2018, 1983, 1965, 1957 (ν_{CO})[o]	—	(*42*)
$HRu_3(CO)_7(C_{12}H_{15})[P(OCH_2)_3CEt]_2$	—	y	190 (dec)	—	2077, 2040, 2023, 1995, 1978 (ν_{CO})[i]	—	(*42*)
$HRu_3(CO)_6(C_{12}H_{15})[P(OCH_2)_3CEt]_3$	—	y	135 (dec)	—	2050, 2018, 2010, 1970 (ν_{CO})[o]	—	(*42*)
$HRu_3(CO)_8(C_{12}H_{15})(PMe_2Ph)$	—	y	—	—	2074, 2053, 2035, 2016, 1989,[o]	—	(*42*)

					1980, 1966, 1956 (ν_{CO})		
$HRu_3(CO)_7(C_{12}H_{15})(PMe_2Ph)_2$	—	o	—	—	2040, 2004, 1965, 1954, 1944 (ν_{CO})[o]	—	(*42*)
$H_2Ru(PPh_3)_3$	$RuCl_2(PPh_3)_3 + H_2, Et_3N$	c	—	—	—	Extremely air-sensitive	(*97, 252*)
$H_2Ru(PPh_3)_4$	$RuCl_3 + PPh_3 + NaBH_4 + EtOH$	y	—	—	2080[q]	—	(*210, 171*)
cis-$H_2Ru(HPPh_2)_4$	$RuCl_2(HPPh_2)_4 +$ LiOMe/MeOH	y	150	18.47	1835	Air-stable; light-sensitive	(*281*)
$H_2Ru(PF_3)_4$	$PF_3 + H_2Cu + RuCl_3$	c	−76	18.5	1922, 1915	Volatile	(*204*)
cis-$H_2Ru(PPh_2Me)_4$	$[Ru_2(PPh_2Me)_6Cl_3]^+ + PPh_2Me + N_2H_4 + EtOH$	w	188	9.54[u]	1940, 1885[q]		(*89*)
$H_2Ru[PhP(OEt)_2]_4$	$RuCl_3 + P(OR)_3 + NaBH_4$	w	—	—	1895, 1950	Crystal structure	(*119, 135*)
$H_2Ru[P(OMe)_3]_4$	—	w	—	—	1850	—	(*119*)
$H_2Ru[P(OEt)_3]_4$	—	w	—	—	1880	—	(*119*)
$H_2Ru[P(O\text{-}i\text{-}C_3H_7)_3]_4$	—	—	—	—	1900	—	(*119*)
$H_2Ru[PPhMe_2]_4$	—	y	—	—	1850	—	(*119*)
cis-$H_2Ru(dmpe)_2$	—	c	82	18.6[v]	1806	$u = 3.15$[h]	(*56*)
trans-$H_2Ru(depe)_2$	—	c	147	—	1615	$u = 2.1$[h]	(*131*)
trans-$H_2Ru[o\text{-}C_6H_4(PEt_2)_2]_2$	—	y	276 (dec)	—	1617[k]	$u = 1.2$[h]	(*131*)
$H_2Ru(N_2)(PPh_3)_3$	$HRuCl(PPh_3)_3 + Et_3Al + N_2$	w	185	17–21, 22.8	1947, 1917	Air-sensitive	(*193, 129, 253*)

(Continued)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^1H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_2Ru(N_2)[(p\text{-}MeC_6H_4)_3P]_3$	—	w	—	18.1, 22.5	—	—	*(193)*
$H_2Ru(NH_3)[(p\text{-}MeC_6H_4)_3P]_3$	$H_2Ru(N_2)[(p\text{-}MeC_6H_4)_3P]_3 + NH_3$	y	—	19.75, 27.63	—	Air-sensitive	*(193)*
$H_2Ru(C_5H_{10})(PPh_3)_3$	$H_2Ru(N_2)(PPh_3)_3 + C_5H_{10}$	—	—	20	—	—	*(252)*
$H_2Ru(CO)(PPh_3)_3$	$NaBH_4/EtOH + N_2 + RuCl_2(PPh_3)_3$	o	147	—	2020	—	*(210, 142)*
cis-$H_2Ru(CO)(PPh_3)_3$	—	w	147	16.69, 18.67[g]	1960, 1900	—	*(210, 142, 323)*
$H_2Ru(CO)(PPh_2Me)_3$	$H_2Ru(PPh_2Me)_4 + CO$	w	170	6.80, 8.02[u]	1920 (ν_{CO})	—	*(89)*
$H_2Ru(PhCN)(PPh_3)_3$	$H_2Ru(N_2)(PPh_3)_3 + RCN$	o	—	18.6, 23.8	1918, 1895	—	*(193, 145)*
$H_2Ru(MeCN)(PPh_3)_3$	—	gr	—	—	1935, 1891	—	*(145)*
$H_2Ru(PPh_3)_3N_2B_{10}H_8S(CH_3)_2$	$H_2Ru(N_2)(PPh_3)_3 + N_2B_{10}H_8S(CH_3)_2$	—	—	15.2	—	—	*(193)*
$H_2Ru(CO)_2(PPh_3)_2$	$Ru(CO)_3(PPh_3)_2 + H_2$	w	—	16.90[v]	1873, 1823/ 2011, 1974[i]	Air-stable	*(209)*
$H_2Ru(CO)_2(PEt_3)_2$	—	w	—	18.48[w]	1996, 1953 (ν_{CO})	—	*(209)*
$H_2Ru(CO)_3(PPh_3)$	$Ru(CO)_5 + PPh_3 + H_2$	—	—	—	1908[f]/ 2089, 2080, 2061, 2021, 2010, 1987, 1955	—	*(328)*

$H_2Ru(CO)_4$	$Ru(CO)_4^{2-} + 2H^+$	w	−63	17.62[x]	1980/2082, 2074, 2070, 2066, 2018, 1980	Thermally unstable	(*73*)
$H_2Ru_3(CO)_9S$	$Ru_3(CO)_{12} + XO_3^-$	y	118	29.45	2120, 2084, 2062, 2050,[p] 2018, 2010 (ν_{CO})	Air-sensitive; paramagnetic	(*282*)
$H_2Ru_3(CO)_9Se$	—	o–y	110	29.55	2117, 2083, 2060, 2048,[p] 2016, 2009 (ν_{CO})	—	(*282*)
$H_2Ru_3(CO)_9Te$	—	y	135	29.70	2112, 2079, 2061, 2058,[p] 2047, 2014, 2011 (ν_{CO})	—	(*282*)
$H_2Ru_3(CO)_9NPh$	$Ru_3(CO)_{10}NPh + H_2$	y	130 (dec)	27.8[p]	2115, 2080, 2057, 2049,[q] 2013, 2000, 1989 (ν_{CO})	Mass spec.	(*283*)

(*Continued*)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_2Ru_3(CO)_9C_2Ph_2$	$Ru_3(CO)_{12} + C_2Ph_2$ + MeOH/KOH	y	110	28.9[m]	2107, 2081, 2058, 2043,[r] 2037, 2021, 2009, 1995 (ν_{CO})	—	*(113)*
$H_2Ru_3(CO)_9(C_8H_8)$	$Ru_3(CO)_{12}$ + bicyclo-[3,2,1]-2,6-octadiene	—	—	28.3	—	—	*(92)*
$H_2Ru_3(CO)_9C_8H_{12}$	α-$H_4Ru_4(CO)_{12}$ + 1,3-COD	y	—	28.06[g]	2105, 2076, 2054, 2040,[o] 2026, 2013, 2006, 1987 (ν_{CO})	—	*(113)*
$H_2Ru_3(CO)_9C_8H_{10}$	$Ru_3(CO)_{12}$ + 1,3-COD	y	—	27.9[l]	2104, 2076, 2053, 2044,[o] 2028, 2024, 2012, 2005, 1986 (ν_{CO})	—	*(113)*
$H_2Ru_3(CO)_{10}SEt$	$HRu_3(CO)_{10}SEt + H_2SO_4$	o–y	—	24.94, 29.39	—	Mass spec.	*(85)*

$H_2Re_2Ru(CO)_{12}$	—	y	—	—	2095, 2091, 2070, 2042, 2034,[j] 2009, 2001, 1987, 1978, 1956 (ν_{CO})	Mass spec.	(*192*)
$H_2Re_2Ru_2(CO)_{16}$	$Ru_3(CO)_{12}$ + $Re(CO)_5^-$ + H^+	y	—	—	—	—	(*192*)
$H_2FeRu_3(CO)_{13}$	$Ru_3(CO)_{12}$ + $Fe(CO)_5$	r	—	28.7[l]	—	Crystal structure	(*122*)
α-$H_2Ru_4(CO)_{13}$	$Ru_3(CO)_{12}$ + $NaBH_4$	r	—	28.6[k]	2078, 2068, 2056,[o] 2034, 2021, 2006, 1883 (ν_{CO})	Air-stable; crystal structure	(*180, 338*)
β-$H_2Ru_4(CO)_{13}$	KOH/MeOH + H_2O + $Ru_3(CO)_{12}$	r	—	19.1[g]	2083, 2068, 2056,[o] 2033, 2026, 2008, 1880 (ν_{CO})	Mass spec.; solid-stable	(*181*)
$H_2Ru_6(CO)_{18}$	$Mn(CO)_5^-$ + $Ru_3(CO)_{12}$ + H^+	p	—	—	2060, 2054, 2008 (ν_{CO})	Air-stable	(*63, 192, 64*)
$H_3Ru_3(CO)_9CCH_3$	α-$H_4Ru_4(CO)_{12}$ + C_2H_4	y	—	27.63[g]	—		(*50, 43*)

(*Continued*)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_4Ru(PPh_3)_3$	$RuCl_2(PPh_3)_3 + NaBH_4 + C_6H_6/MeOH$	w	—	17.1[k]	1950[q]	Very air-sensitive; decomposes in halogenated solvents	(*193, 145*)
α-$H_4Ru_4(CO)_{12}$	$Ru_3(CO)_{12} + H_2 +$ octane $+ CO$	y	—	28.0	2081, 2067, 2030,[o] 2024, 2009 (ν_{CO})	Air- and solution-stable	(*184, 284*)
$H_4Ru_4(CO)_{11}[P(C_4H_9)_3]$	$H_4Ru_4(CO)_{12} + L$	o–r	—	27.7[k]	2093, 2086, 2064, 2056, 2052, 2045,[o] 2032, 2024, 2007, 1988, 1973, 1968, 1958 (ν_{CO})	—	(*253*)
$H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$	—	r	—	26.5[l]	2052, 2045, 2014, 1996, 1977,[o]	—	(*253*)

					1951, 1932, 1924 (ν_{CO})		
$H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$	—	o	—	26.8[l]	1998, 1958, 1938, 1928 (ν_{CO})[o]	—	(*253*)
$H_4Ru_4(CO)_{11}(PPh_3)$	—	y–br	—	27.7[n]	2094, 2086, 2067, 2057, 2053, 2038,[o] 2032, 2027, 2015, 2008, 1998, 1994, 1966 (ν_{CO})	—	(*253*)
$H_4Ru_4(CO)_{10}(PPh_3)_2$	—	br–r	—	26.1, 26.9[n]	2082, 2077, 2058, 2050, 2033,[o] 2017, 2009, 2000, 1989, 1973, 1954 (ν_{CO})	—	(*253*)

(*Continued*)

TABLE V—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_4Ru_4(CO)_9(PPh_3)_3$	—	r	—	26.1, 27.1[h]	2068, 2024, 2003, 1993, 1993, 1987, 1963,[e] 1945, 1940 (ν_{CO})	—	(*253*)
$H_4Ru_4(CO)_8(PPh_3)_4$	—	r	—	25.65[h]	2016, 1984, 1952, 1930 (ν_{CO})[e]	—	(*253*)
$H_4Ru_4(CO)_{11}[P(OMe)_3]$	—	o	—	27.72[g]	2097, 2068, 2060, 2032,[e] 2030, 2017, 2008, 1974 (ν_{CO})	Air-stable	(*196*)
$H_4Ru_4(CO)_{10}[P(OMe)_3]_2$	—	o	—	27.61[g]	2080, 2059, 2039, 2023,[e] 2001, 1967 (ν_{CO})	—	(*196*)

$H_4Ru_4(CO)_9[P(OMe)_3]_3$	—	o	27.84[g]	2067, 2023, 2014, 1996,[o] 1985, 1976, 1962 (ν_{CO})	—	(*196*)
$H_4Ru_4(CO)_8[P(OMe)_3]_4$	—	o	27.83[g]	2025, 1970 (ν_{CO})[o]	—	(*196*)
$H_4Ru_4(CO)_9[P(OPh)_3]_3$	—	y	27.31[g]	2075, 2049 (ν_{CO})[o]	—	(*196*)

[a] The following abbreviations are used in complex formulas: Ph = phenyl; Me = methyl, Pr^i = isopropyl; OPh = phenoxy; OEt = ethoxy; OMe = methoxy; depe = 1,2-bisdiethylphosphinoethane; dmpe = 1,2-bisdimethylphosphinoethane; Et = ethyl; dppe = 1,2-bisdiphenylphosphinoethane; Pr^n = *n*-propyl; Bu^n = *n*-butyl; cod = cyclooctadiene; py = pyridine; dpt = 1,3-diphenyltriazenido; bipy = bipyridyl; Bu^t = *t*-butyl; cy = cyclohexyl.

[b] Colors: c = colorless; o = orange; w = white; gr = green; r = red; br = brown; p = purple; y = yellow; cr = cream.

[c] CH_2Cl_2 unless noted.

[d] Nujol unless noted.

[e] CD_2Cl_2.

[f] Hexachlorobutadiene.

[g] $CDCl_3$.

[h] Dipole moment.

[i] $CHCl_3$.

[j] Hexane.

[k] C_6H_6.

[l] C_6D_6.

[m] CS_2.

[n] THF.

[o] Cyclohexane.

[p] CCl_4.

[q] KBr.

[r] Heptane.

[s] CD_3COCD_3.

[t] $MeNO_2$.

[u] Upfield hexamethyldisiloxane.

[v] $[^2H_8]$THF.

[w] EtOH.

[x] Pentane.

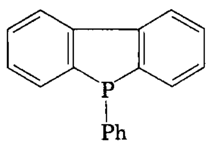
VI. Hydride Complexes of Rhodium

Table VI, presented at the end of this section, summarizes data on hydride complexes of rhodium.

A. $[HRhL_4]$

1. $[HRh(DBP)_4]$

An orange, air-stable dibenzophosphole complex, $[HRh(DBP)_4]$ [DBP = 5-phenyl-5*H*-dibenzophosphole (V)] has been obtained by treating $[RhCl_3(DBP)_3]$ with $NaBH_4$ (*44*). Oxygen-free solutions of the complex are effective in catalyzing the homogeneous hydrogenation of terminal olefins at 20°C and < 1 atm H_2 pressure (*44*). Addition of DBP to solutions of the complex during catalysis causes a decrease in the catalytic rate, suggesting that dissociation of DBP is an important step in the catalytic cycle. Internal monoenes, conjugated dienes, and acetylenic bonds are hydrogenated much slower than terminal olefins, and this specificity for terminal olefins is attributed mainly to steric factors.



(V)

2. $[HRh(PPh_3)_4]$

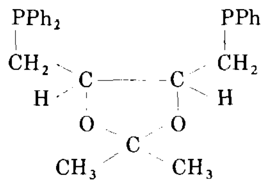
Hydridotetrakis(triphenylphosphine)rhodium(I) has been prepared by Levison and Robinson (*210*). Treatment of the complex with D_2 in benzene results in the exchange of 7–9 hydrogen atoms, suggesting that the ortho protons of the phenyl groups take part in the exchange reaction to a limited extent. Steric factors may hinder the participation of all of the ortho protons.

The crystal structure (*13*) of the complex shows a tetrahedral arrangement of the phosphorus atoms about rhodium, but the hydride is believed to lie on a threefold axis bridging one face of the tetrahedron.

3. $[HRh(diop)_2]$

Cullen, Fenster, and James (*80*) prepared $[HRh(diop)_2]$ [diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (VI)] by treating $RhCl_3$ with diop and formaldehyde in ethanolic KOH.

The yellow complex reacts with $HClO_4$ to give the dihydride species $[H_2Rh(diop)_2]^+$. Complex $[HRh(diop)_2]$ is an efficient catalyst for the hydrogenation of terminal olefins and unsaturated carboxylic acids.



(VI)

4. [HRh(CO)(TBA)$_3$]

Complex $[Rh_2(CO)_4Cl_2]$ reacts with tribenzylamine (TBA) and $NaBH_4$ to form the hydride $[HRh(CO)(TBA)_3]$ (*104*). In solution in the presence of O_2, the complex rapidly decomposes, but under an atmosphere of CO and H_2 it remains stable. The $[HRh(CO)(TBA)_3]$ catalyzes the hydroformylation of α-olefins into predominantly linear aldehydes at 25°C and 1 atm gas pressure.

5. [HRh(CO)(PPh$_3$)$_3$]

Compounds $RhCl_3$, H_2CO, $NaBH_4$, EtOH, and PPh_3 react to form carbonylhydridotris(triphenylphosphine)rhodium(I) (*210*). The complex reacts with allene and butadiene to give unstable complexes that decompose under N_2 or under vacuum (*38*),

$$[HRh(CO)(PPh_3)_3] \xrightarrow{\text{allene, EtOH}} [Rh(\pi\text{-allyl})(CO)(PPh_3)_2] \qquad (37)$$

but stable adducts of formula $[(RCH{=}CR)Rh(CO)(PPh_3)_2]$ (R = CO_2Me, CO_2Et, CO_2H, Ph) are obtained when the hydride reacts with alkynes (*236*).

The catalytic properties of $[HRh(CO)(PPh_3)_3]$ have been extensively studied (*39*, *158*, *303*, *304*). It is an efficient catalyst for the homogeneous hydrogenation of terminal olefins at 25°C and low H_2 pressure, but conjugated, internal, and cyclic olefins are not normally hydrogenated at atmospheric pressure (*245*). Excess PPh_3 decreases the catalytic rate, suggesting that loss of phosphine is important in the catalytic cycle, and the high selectivity of the complex for hydrogenating terminal olefins is attributed to steric factors caused by the bulky PPh_3 ligand (*245*).

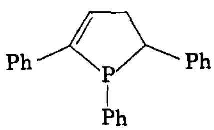
Hydrogenation, H–D exchange, and isomerization reactions are believed to proceed by way of alkene attack on the four-coordinate hydride, [$HRh(CO)(PPh_3)_2$], to give an alkyl complex (*334*). Under hydrogenation conditions, this alkyl complex is believed to add H_2 oxidatively to form the dihydride, with subsequent elimination of alkane product and regeneration of [$HRh(CO)(PPh_3)_2$].

Strohmeier and Csontos (*305*) have reported that the rate of catalytic hydrogenation of ethyl acrylate by [$HRh(CO)(PPh_3)_3$] decreases with time, but that weak UV irradiation can be used to reactivate the catalyst.

Crystal structure analysis (*206*) of [$HRh(CO)(PPh_3)_3$] shows the conformation of ligands around the Rh atom to be trigonal bipyramidal with 3P atoms in the equatorial plane, and H and CO at the apices. The Rh—H bond distance is 1.60 ± 0.12 Å.

6. [$HRhCl_2(TPP)_2$]

Holah *et al.* (*162*) prepared stable, yellow-brown [$HRhCl_2(TPP)_2$] [TPP = 1,2,5-triphenylphosphole (VII)]. In benzene solution and in the presence of triethylamine, [$HRhCl_2(TPP)_2$] is an extremely active catalyst for the hydrogenation of 1-hexene at 20°C and < 1 atm H_2 pressure (*162*). However, no catalytic activity occurs in the absence of the amine.



(VII)

7. [$HRhCl_2L_2$]

Treatment of $RhCl_3$ with excess *t*-butyl tertiary phosphines in alcohol results in formation of [$HRhCl_2L_2$] complexes (L = $PBu^tPr_2^n$, PBu_2^tMe, PBu_2^tEt, $PBu_2^tPr^n$) (*226*). The complexes in MeOH or EtOH solution in the presence of base abstract CO from solvent forming [$RhCl(CO)L_2$]. However, in propan-2-ol and in the presence of sodium isopropoxide, CO abstraction is slow, and [$HRhCl_2(PBu^tPr_2^n)_2$] will catalytically hydrogenate olefins and acetylenes at 20°C and 1 atm H_2 pressure (*226*). This complex is as reactive as Wilkinson's catalyst, [$RhCl(PPh_3)_3$].

8. [$HRhCl(PPh_3)_2SiR_3$]

[$RhCl(PPh_3)_3$] and $HSiR_3$ react to form [$HRhCl(PPh_3)_2SiR_3$] and PPh_3 (*148*). The stability of the phosphine complexes to thermal decomposition and to dissociation in solution varies widely [R = Cl, OEt (stable); R = alkyl or phenyl are completely dissociated in solution], and the differences are believed to be due to changes in the electronegativity of the silyl group (*148*).

Crystal structure analysis (*240*) of $[HRhCl(PPh_3)_2SiCl_3]$ shows the coordination about Rh to be a highly distorted trigonal bipyramid, with *trans*-phosphines at the apices and H, Cl^-, and $SiCl_3$ in the trigonal plane. The short Rh—Si bond length, 2.203 Å, is consistent with back donation of electrons from Rh to the silyl group. Alternatively, the coordination about Rh can be envisioned as a distorted octahedron, by including an ortho-hydrogen atom of a phenyl ring at the sixth coordination site. This hydrogen is located 2.79 Å from Rh and could possibly block off the sixth site, rendering the complex catalytically inactive for hydrosilation of olefins.

B. $[HRhL_5]$

1. $[HRh(NH_3)_5](ClO_4)_2$

The crystal structure (*76*) of hydridopentamminerhodium(III) indicates an octahedral coordination of ligands about Rh. Four Rh—N bond distances are 2.079 Å, the Rh—N bond trans to hydride is 2.244 Å, and the Rh—H bond length is 1.82 Å. The longer Rh—N bond length of the ligand trans to hydride illustrates the hydride's large trans effect.

2. $[HRh(CN)_5]^{3-}$

Originally postulated as $[HRh(CN)_4H_2O]^{2-}$, the complex has now been characterized as $[HRh(CN)_5]^{3-}$ by Jewsbury and Maher (*178*, *179*). Complex $K_3[HRh(CN)_5]$ is synthesized by reacting $[Rh(CO)_2Cl]_2$ with KCN in aqueous methanol.

C. $[HRh_2L_{10}]$

$[H\{Rh(C_5Me_5)\}_2Cl_3]$

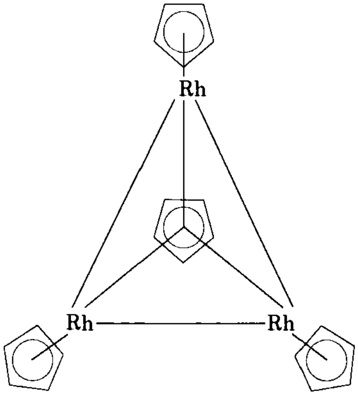
Treatment of $[\{Rh(C_5Me_5)\}_2Cl_4]$ with H_2 produces the dinuclear rhodium species $[H\{Rh(C_5Me_5)\}_2Cl_3]$ (*324*). The complex contains a bridging hydride ligand, indicated by the shift in ν_{M-H} from 1151 to 812 cm^{-1} upon deuteration. X-Ray crystal structure analysis (*62*) indicates that 1 Cl^- is also bridging the 2Rh atoms, and each Rh has a terminally coordinated Cl^-. The Rh—H bridging bond distance has been calculated to be 1.85 Å.

The hydride is soluble in many organic solvents and air-stable in the solid state. The complex is a powerful catalyst for the hydrogenation of olefins at 20°C and 1 atm H_2 pressure (*323*).

D. $[HRh_3L_{12}]$

$[HRh_3(C_5H_5)_4]$

Treatment of C_5H_5MgBr with an aqueous solution of $RhCl_3$ results in the formation of the air-stable hydride, $[HRh_3(C_5H_5)_4]$ (*107*). The Rh atoms are arranged in an almost equilateral triangle with three π-cyclopentadienyl groups, one coordinated to each Rh, displaced to one side of the triangle (VIII). The remaining C_5H_5 group lies parallel to the triangle on the opposite side of the other three ligands. It is postulated (*234*) that the hydride is near the center of the Rh triangle, giving an Rh—H bond distance of 1.57 Å.



(VIII)

E. $[H_2RhL_4]$

1. $H_2Rh\{(R)\text{-}PPhMe(PhCH_2)\}_2(solvent)_2]ClO_4$

Yamamoto *et al.* (*152*, *332*) report the use of optically active benzylmethylphenylphosphine as a chiral ligand in a cationic Rh complex, $[H_2Rh\{(R)\text{-}PPhMe(PhCH_2)\}_2S_2]^+$, to induce stereoselective addition of a hydrosilane to a variety of alkylphenyl ketones producing silyl ethers of alkylphenyl carbinols:

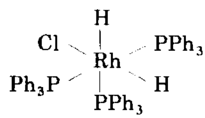
$$RCOPh + R'Me_2SiH \xrightarrow{[H_2RhL_2S_2]^+} RPh\overset{*}{C}HOSiMe_2R \tag{38}$$

2. $[H_2RhCl(PPh_3)_3]$

The proton-decoupled ^{31}P spectra of $RhCl(PPh_3)_3$ solutions under 100 psig of H_2 at $-25°C$ show complete conversion to the dihydride (*311*).

$$[RhCl(PPh_3)_3] + H_2 \rightleftharpoons [H_2RhCl(PPh_3)_3] \tag{39}$$

The spectral pattern and the hydride region ^1H NMR spectrum allow unambiguous assignment of the solution configuration as shown in structure IX (*311*). The complex undergoes slight dissociation of the PPh_3 group trans to the hydride. This dissociation opens a coordination site for reactant substrate, enabling the complex to enter the catalytic cycle.



(IX)

3. $[H_2RhCl\{PhP(CH_2CH_2CH_2PPh_2)_2\}]$

Treatment of [RhLCl] [L = $PhP(CH_2CH_2CH_2PPh_2)_2$] with H^+, EtOH, and Cl^- produces the hydride $[HRhCl_2L]$ (*243*). The complex reacts with H_2 to give the six-coordinate dihydride, $[H_2RhClL]$, which is air-stable and shows no tendency to lose H_2 in the solid state or in solution. The dissociative stability may account for the inactivity of the complex to function as a hydrogenation catalyst.

VII. Hydride Complexes of Iridium

Table VII, presented at the end of this section, summarizes data on hydride complexes of iridium.

A. $[HIrL_4]$

1. $[HIrCO(PPh_3)_3]$

The reaction of Vaska's complex, *trans*-$[IrClCO(PPh_3)_2]$, with $NaBH_4$ and excess PPh_3 results in the formation of $[HIrCO(PPh_3)_3]$ (*325*). This yellow complex catalyzes the homogeneous hydrogenation

TABLE VI

SURVEY OF HYDRIDE COMPLEXES: RHODIUM

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRh(PPh_3)_3$	$Rh(PPh_3)_3R$ H_2	o	150 (dec)	8.9[e]	2020[f]	Air-sensitive	(*186*, *89*, *168*, *169*)
$HRh(DBP)_4$	$RhCl_3(DBP)_3 + NaBH_4$	o	—	20.6[g]	2070	Air-stable	(*44*)
$HRh(PF_3)_4$	$RhCl_3 + PF_3 + H_2$	c	−40	130 lines	—	—	(*332*, *231*, *49*, *205*)
$HRh(PPh_3)_4$	$RhCl_3 + PPh_3 + NaBH_4 + EtOH$	o	168 (dec)	18.55[h]	2152	Air-sensitive	(*210*, *171*, *89*, *13*, *307*, *23*)
$HRh[P(OPh)_3]_4$	$HRhCO(PPh_3)_3 + P(OPh)_3 + EtOH$	w	—	—	—	Air-sensitive	(*211*)
$HRh(PPh_2Me)_4$	$RhCl(PPh_2Me)_3 + N_2H_4 + L$	y	174 (dec)	12.1[e]	2005[f]	—	(*89*)
$HRh[PPh(OEt)_2]_4$	$RhCl_3 + PPh(OEt)_2 + EtOH + NaBH_4$	y	173	—	2000	Air-sensitive	(*231*)
$HRh[P(OEt)_3]_4$	$RhCl_3 + P(OEt)_3 + EtOH + NaBH_4$	w	170	—	1940	Air-sensitive	(*231*)
$HRh(diop)_2$	$RhCl_3 + diop + H_2O + KOH + EtOH$	y	—	28.4[i]	—	—	(*80*, *278*)
$HRh(dppe)_2$	$HRh(PPh_3)_4 + dppe$	o	—	—	1907	Air-sensitive	(*254*)
$HRh(PPh_3)_3(AsPh_3)$	$HRh(PPh_3)_3 + AsPh_3$	y–o	—	—	2125, 2180	—	(*307*, *14*)
$HRh(PPh_3)(AsPh_3)_3$	$L + HRh(AsPh_3)_3$	y	168 (dec)	—	2140, 2118	—	(*307*)
$HRh(CO)(TBA)_3$	$Rh_2(CO)_4Cl_2 + TBA + NaBH_4$	y	—	—	2010/1970[j]	—	(*104*, *105*)
$HRh(CO)(PPh_3)_3$	$RhCl_3 + H_2CO + NaBH_4 + PPh_3 + EtOH$	y	166	19.2[i]	2030/1915	—	(*38*, *304*, *39*, *158*, *303*, *245*, *334*, *305*, *280*)

$HRh(CO)(PPh_2Me)_3$	$Rh(CO)ClL_2 + L +$ Na(propoxide) $+ H_2$	r–br	—	19.9[i]	1913/1969	—	(*133*)
$HRh(CO)(PPhEt_2)_3$	—	r	—	20.7[i]	1915/1970	—	(*133*)
$HRh(CO)(PEt_3)_3$	—	—	—	21.3[i]	1880/1952	—	(*133*)
$HRh(CO)(PBu^n_3)_3$	—	—	—	21.2[i]	1890/1960	—	(*133*)
$HRh(CO)[Ph_2PCH_2CH_2Si(OEt)_3]_2$	$RhCl(CO)L_2 + L + NaBH_4$	y	—	—	1990, 1915	—	(*3*)
$HRh(PF_3)(PPh_3)_3$	$HRh(PPh_3)_4 + PF_3$	y	—	19.98	2066	—	(*244*)
$HRh(PF_3)_2(PPh_3)_2$	$HRh(PPh_3)_4 + 2PF_3$	w	—	—	1986	—	(*244*)
$HRh(CO)_2(PPh_3)_2$	$HRh(CO)(PPh_3)_3 + CO$	y	—	19.1[i]	2038/1980, 1938[k]	Air-sensitive	(*100*)
$HRhCl_2(PBu^t_2Me)_2$	$RhCl_3 + L + EtOH$	r	170 (dec)	41.40	1938	—	(*225, 226*)
$HRhCl_2(PBu^t_2Et)_2$	—	r	157 (dec)	41.10	1940	—	(*225, 226*)
$HRhCl_2(PBu^tPr^n_2)_2$	—	r	122 (dec)	41.37	1945	—	(*225, 226*)
$HRhCl_2(PBu^t_2Pr^n)_2$	—	k	175 (dec)	41.15	1936	—	(*225, 226*)
$HRhBr_2(PBu^tPr^n_2)_2$	$HRhCl_2L_2 + LiBr$	r	161 (dec)	41.10	1946	—	(*225*)
$HRhBr_2(PBu^t_2Me)_2$	—	r	150 (dec)	41.10	1938	—	(*225*)
$HRhI_2(PBu^tPr^n_2)_2$	—	—	—	40.40	—	—	(*225*)
$HRhCl_2(TPP)_2$	$RhCl_3$ + TPP + EtOH	y–br	224 (dec)	—	1990	—	(*162*)
$HRhCl_2(SbPh_3)_2$	—	r–br	—	28.3	2014	—	(*217*)
$HRhCl(SH)(PPh_3)_2$	$RhCl(PPh_3)_3 + HY$	y	116 (dec)	—	2160	—	(*299*)
$HRhCl(SC_6H_4Me)(PPh_3)_2$	—	y	—	26.5	2119	—	(*299*)
$HRh(SO_2)(CO)(PPh_3)_2$	$HRh(CO)(PPh_3)_3 + SO_2$	o–y	—	—	2050(ν_{CO})	—	(*212*)
$HRhCl(PPh_3)_2(GeMe_3)$	$RhX(PPh_3)_3 + HMR_3$	y	90 (dec)	—	2080, 2035[f]	—	(*126*)
$HRhCl(PPh_3)_2(GeEt_3)$	—	y	117 (dec)	—	2107, 2062[f]	—	(*126*)
$HRhCl(AsPh_3)_2(GeMe_3)$	—	g	90 (dec)	—	2057, 2025[f]	—	(*126*)
$HRhCl(AsPh_3)_2(GeEt_3)$	—	g	118 (dec)	—	2114, 2042[f]	—	(*126*)
$HRhCl(PPh_3)_2(GeCl_3)$	—	o	148 (dec)	—	2123, 2098[f]	—	(*126*)
$HRhCl(cod)(GeCl_3)$	—	o	—	—	2000[f]	—	(*126*)

(*Continued*)

TABLE VI—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRhCl(PPh_3)_2(SiCl_3)$	—	y	168 (dec)	24.30	2040[f]	—	(*148, 240, 54*)
$HRhCl(PPh_3)_2(SiCl_2Me)$	—	y	143 (dec)	24.45	2050[f]	—	(*148, 54*)
$HRhCl(PPh_3)_2(SiCl_2Et)$	—	y	158 (dec)	23.2	2130[f]	—	(*148*)
$HRhCl(PPh_3)_2(SiClMe_2)$	—	y	123 (dec)	24.8	2060[f]	—	(*148*)
$HRhCl(PPh_3)_2(SiClEt_2)$	—	y	142 (dec)	—	2110[f]	—	(*148*)
$HRhCl(PPh_3)_2(SiMe_3)$	—	y	92 (dec)	—	2055[f]	—	(*148, 54*)
$HRhCl(PPh_3)_2(SiEt_3)$	—	y	103 (dec)	—	2020[f]	—	(*148, 246*)
$HRhCl(PPh_3)_2(SiPh_3)$	—	y	133 (dec)	—	2140[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiCl_3)$	—	o–y	165 (dec)	23.40	2120[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiCl_2Me)$	—	y	147 (dec)	—	2045[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiCl_2Et)$	—	y	155 (dec)	23.1	2130[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiClMe_2)$	—	y	128 (dec)	23.8	2050[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiClEt_2)$	—	y	143 (dec)	—	2130[f]	—	(*148*)
$HRhBr(PPh_3)_2(SiEt_3)$	—	y	108 (dec)	—	2070[f]	—	(*148*)
$HRhI(PPh_3)_2(SiCl_3)$	—	o	163 (dec)	—	2050[f]	—	(*148*)
$HRhCl(PPh_3)_2[Si(OEt)_3]$	—	y	127 (dec)	24.85	2060[f]	—	(*148*)
$HRhBr(PPh_3)_2[Si(OEt)_3]$	—	gr–y	122 (dec)	23.70	2080[f]	—	(*148*)
$HRhI(PPh_3)_2[Si(OEt)_3]$	—	y	125 (dec)	21.70	2060[f]	—	(*148*)
$HRhCl(AsPh_3)_2[Si(OEt)_3]$	—	y	142 (dec)	26.3	2065[f]	—	(*148*)
$HRhCl(SbPh_3)_2[Si(OEt)_3]$	—	gr	152 (dec)	21.3	2080[f]	—	(*148*)
$HRhCl(AsPh_3)_2(SiCl_3)$	—	y	178 (dec)	—	2080[f]	—	(*148*)
$HRhCl(SbPh_3)_2(SiCl_3)$	—	o–y	183 (dec)	—	2080[f]	—	(*148*)
$[HRhCl\ trien]^+$	—	—	—	28.5	2081	—	(*131*)

$[HRhClPPh(CH_2CH_2CH_2\text{-}PPh_2)_2]^+BF_4\cdot EtOH$	$LRhCl + H^+ + EtOH + HBF_4$	y	—	—	2175	Air-stable	(*243*)
$[HRhClPPh(CH_2CH_2CH_2\text{-}PPh_2)_2]^+PF_6\cdot EtOH$	—	y	—	—	2162	Air-stable	(*243*)
3,3-$(PPh_3)_2$—3-H—3,1,2-$RhC_2B_9H_{11}$	$Rh(PPh)_3{}^+ + MeOH + (CH_3)_3NH^+L^-$	y	—	18.4[l]	2120, 2080	—	(*251, 159*)
2,2-$(PPh_3)_2$—2-H—2,1,7-$RhC_2B_9H_{11}$	—	y	—	21.1[l]	2110, 2070	—	(*251, 159*)
$HRh[P(OMe)_3]_5(PF_6)_2$	$[RhL_5]PF_6 + CH_2Cl_2 + PF_6$	—	—	—	1968	—	(*271*)
$[HRh(NH_3)_5](ClO_4)_2$	—	w	—	—	—	Air-stable; crystal structure	(*76*)
$[HRh(NH_3)_5]SO_4$	$RhCl_3 + NH_3 + EtOH + SO_4{}^{2-}$	w	—	27.1	2079	—	(*249*)
$[HRh(CN)_5]^{3-}$	—	—	—	21.33	2108, 1952	—	(*178, 179*)
$[HRhCl\{PPh_2(OMe)\}_4]\text{-}(CF_3COO)_2H$	$[RhCl(CO)_2]_2 + PPh_2(OMe) + CF_3COOH$	y	110	—	2100	—	(*203*)
$[HRhCl\{PPh_2(OMe)\}_4]PF_6$	—	c	110	—	2100	—	(*203*)
trans-$[HRhBr\{P(OMe)_3\}_4]BPh_4$	$[RhL_5]^+ + HX$	w	129	23.5[m]	2072[c]	—	(*138*)
trans-$[HRhI\{P(OMe)_3\}_4]\text{-}BPh_4$	—	w	133	21.8[m]	2051[c]	—	(*138*)
trans-$[HRhCl(C_5H_5N)_4]^+$	—	—	—	28.6[n]	—	—	(*27*)
trans-$[HRhBr(dmpe)_2]^+$	$Rh(dmpe)_2{}^+ + HX$	—	—	—	2030	—	(*47*)
trans-$[HRhCl(dmpe)_2]^+$	—	w	183	—	2050	—	(*47*)
trans-$[HRhCl(dppe)_2]^+$	$RhCl_2(2\text{-Me—allyl}) + H_2 + EtOH$	w–y	—	25.85[m]	2048	—	(*258*)
trans-$[HRhCl(vdiphos)_2]\text{-}[Rh(CO)_2Cl_2]$	$RhX_3 + EtOH + CO + L$	y	—	26.0	2079/2070, 1996[c]	—	(*218*)

(*Continued*)

TABLE VI—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
trans-$[HRhBr(vdiphos)_2]$-$[Rh(CO)_2Br_2]$	—	y	—	24.9	2060, 1993(ν_{CO})[c]	—	(*218*)
trans-$[HRhCl(vdiars)_2]$-$[Rh(CO)_2Cl_2]$	—	y	—	29.3	2066, 1992(ν_{CO})[c]	—	(*218*)
trans-$[HRhCl(vdiars)_2]Cl$	—	—	—	28.4[m]	—	—	(*27*)
trans-$[HRhBr(vdiars)_2]$-$[Rh(CO)_2Br_2]$	—	y	—	27.9	2604, 1992(ν_{CO})[c]	—	(*218*)
trans-$[HRhBr(vdiars)_2]Br$	—	—	—	27.0[m]	—	—	(*27*)
trans-$[HRhCl(vdiphos)_2]Cl$	$[RhL_2]^+$ + HCl	—	—	25.9	2075[c]	—	(*218*)
trans-$[HRhCl(diars)_2]PF_6$	—	—	—	—	2000	—	(*218*)
trans-$[HRhCl(en)_2]^+$	—	—	—	31	2100–2093	—	(*131*)
trans-$[HRhI(en)_2]^+$	—	—	—	30.2	2140	—	(*131*)
trans-$[HRhNH_3(en)_2]$-$(ClO_4)_2$	$[HRh(NH_3)_5]^{2+}$ + en + $NaClO_4$	c	—	27.8	2056	—	(*310*)
cis-$[HRhNH_3(en)_2](ClO_4)_2$	—	—	—	26.3	2025	—	(*310*)
trans-$[HRhH_2O(en)_2]$-$(ClO_4)_2$	$[HRhNH_3(en)_2]^{2+}$ + H_2O + H^+	—	—	32.2	—	—	(*310*)
cis-$[HRhH_2O(en)_2](ClO_4)_2$	—	c	—	32.6	2135	—	(*310*)
trans-$[HRhNH_3(pn)_2]$-$(ClO_4)_2$	$[HRh(NH_3)_5]^{2+}$ + pn + $NaClO_4$	c	—	27.4	2060	—	(*310*)
cis-$[HRhNH_3(pn)_2](ClO_4)_2$	—	—	—	26.3	—	—	(*310*)
trans-$[HRhH_2O(pn)_2]$-$(ClO_4)_2$	—	—	—	31.7	—	—	(*310*)
cis-$[HRhH_2O(pn)_2](ClO_4)_2$	—	—	—	32.3	—	—	(*310*)
$[HRh(NH_3)_4(H_2O)]SO_4$	—	—	—	32.0	2146	—	(*310*)
$[HRh(OH)(en)_2]^+$	$[RhCl_2(en)_2]^+ \xrightarrow[\text{reduction}]{\text{electrochemical}}$	w	—	30.6	2058	—	(*121*)

$[HRhCl(dpda)_2]^+$	$[Rh(dpda)]^+ + HCl$	cr	—	25.3	2220	—	*(260)*
$HRhCl_2PPh(CH_2CH_2CH_2PPh_2)_2$	$[HRhClL]^+ + Cl^-$	y	—	—	2193	—	*(243)*
$[HRh(PPh_3)_2(CNBu^t)_3](PF_6)_2$	$Rh(PPh_3)_2(CNR)_3 + HPF_6$	w	—	Not resolved	—	—	*(81)*
β-$HRhCl_2(PMe_3)_3$	$RhCl(PR_3)_3 + HCl$	y	210	—	1960[o]	—	*(170)*
α-$HRhCl_2(PPhMe_2)_3$	—	y–o	160	—	2105[o]	—	*(170)*
β-$HRhCl_2(PPhMe_2)_3$	—	y	215	—	1980[o]	—	*(170)*
α-$HRhCl_2(PPh_2Et)_3$	—	y	210	—	2120[o]	—	*(170, 277)*
β-$HRhCl_2(PPh_2Et)_3$	—	y	180	—	1982[o]	—	*(170)*
$HRhCl_2(PPr_3^i)_2CO$	—	y–o	—	—	2119/2037[o]	—	*(170)*
α-$HRhCl_2(PEt_3)_3$	—	—	—	—	2090[g, m]	—	*(170)*
β-$HRhCl_2(PEt_3)_3$	—	—	—	—	1980[o]	—	*(170)*
α-$HRhCl_2(PPh_3)_3$	—	y	160 (dec)	—	2220[o]	—	*(170)*
β-$HRhCl_2(PPh_3)_3$	—	y	100 (dec)	—	2120[o]	—	*(170, 33)*
α-$HRhCl_2(PPhEt_2)_3$	—	y	140 (dec)	—	2115[o]	—	*(170)*
α-$HRhBr_2(PPh_2Et)_3$	$RhX_3 + PPh_2Et + EtOH$	y	—	—	2110	—	*(277)*
β-$HRhBr_2(PPh_2Et)_3$	—	y	—	—	1964	—	*(277)*
α-$HRhI_2(PPh_2Et)_3$	—	y	—	—	2100	—	*(277)*
β-$HRhI_2(PPh_2Et)_3$	—	y	—	—	1960	—	*(277)*
$HRhCl_2(PPh_2Bu^n)_3$	$RhCl_3 + L + EtOH$	y	140 (dec)	—	2090[c]	—	*(90)*
$HRhCl_2(AsPh_2Pr^n)_3$	—	y	145	—	2107	—	*(262)*
$HRhBr_2(AsPh_2Pr^n)_3$	—	o–y	141	—	2107	—	*(262)*
$HRhI_2(AsPh_2Pr^n)_3$	—	br	127	—	2090	—	*(262)*
$HRhCl_2(AsPh_2Me)_3$	—	y	172	—	2077	—	*(131)*
$HRhBr_2(AsPh_2Me)_3$	—	o–y	175	—	2073	—	*(131)*
$HRhI_2(AsPh_2Me)_3$	—	o–br	164	—	2058	—	*(131)*
$HRhCl_2(AsPh_3)_2\cdot\frac{1}{2}CH_2Cl_2$	—	y	—	25.9	2069[c]	—	*(217)*

(Continued)

TABLE VI—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HRhCl_2(PPh_3)_2 \cdot \frac{1}{2}CH_2Cl_2$	—	y	—	26.1[m]	2105	—	(*12*)
$HRhCl_2(PBu^tPr_2^n)_2$-MeNC	$HRhCl_2L_2 + L'$	o	124	20.86	2083	—	(*225*)
$HRhCl_2(PBu^tPr_2^n)_2$-MeCN	—	o	99	33.60	—	—	(*225*)
$HRhCl_2(PBu^tPr_2^n)_2py$	—	o	122	28.90	2188	—	(*225*)
$HRhCl_2(PBu^tPr_2^n)_2$-$(P(OMe)_3)$	—	o	85	—	2088	—	(*225*)
$HRhCl_2(CO)(phen)$	$RhCl_2(CO)_2^- + L - L +$ EtOH	r–br	—	—	2117/2075, 2052[f]	—	(*190*)
$HRhCl_2(CO)(bipy)$	—	r	—	—	2115/2080, 2060[f]	—	(*190*)
$HRhBr_2(CO)(phen)$	—	br	—	—	2110/2075, 2045[f]	—	(*190*)
$HRhBr_2(CO)(bipy)$	—	br	—	—	2115/2080, 2060[f]	—	(*190*)
$HRhBr_2(CO)(AsPh_3)_2$	$RhX(CO)L_2 + HX$	y–o	176	—	2080/2048	—	(*264*)
$HRhBr_2(CO)(AsPh_2Me)_2$	—	y–o	126	—	2085/2062	—	(*264*)
$HRhBr_2(CO)(AsPh_2Et)_2$	—	y–o	130	—	2060/2040	—	(*264*)
$HRhBr_2(CO)(PPh_3)_2$	—	y	160	—	2107/2049	—	(*21*)
$HRhCl_2(CO)(PPh_3)_2$	—	y	—	—	2122/2049	—	(*12*)
$HRhCl_2(CO)(AsPh_3)_2$	—	y	—	—	2087/2067[p]	—	(*155*)
$HRhCl_2(CO)(SbPh_3)_2$	—	—	—	—	2035/2062[p]	—	(*155*)
$HRhBrCl(PF_3)(PPh_3)_2$	$RhX(PF_3)(PPh_3)_2 + HX$	o	—	—	2092	—	(*18*)
$HRhCl_2(PF_3)(PPh_3)_2$	—	y	—	—	2098	—	(*18*)

$HRhCl(CO)(PPh_3)_2SiCl_3$	$HRhCl(PPh_3)_2SiCl_3 + CO$	—	—	—	2110/2050, 1969	—	(*148*)
$HRhCl(PPh_3)_2SiCl_3 \cdot \frac{1}{2}CH_2Cl_2$	$RhCl(PPh_3)_3 + HSiR_3 + CH_2Cl_2$	y	—	24.3[m]	2116	—	(*54*)
$HRhCl(PPh_3)_2SiCl_2Me \cdot \frac{1}{2}CH_2Cl_2$	—	y	—	24.4[m]	2048	—	(*54*)
$HRhCl(PPh_3)_2SiMe_3 \cdot \frac{1}{2}CH_2Cl_2$	—	y	—	—	2107, 2065	Decomposes rapidly	(*54*)
$HRhCl(CO)(PEt_3)_2SiCl_3$	$RhCl(CO)L_2 + HSiR_3$	y–w	—	—	2069/2037	—	(*54*)
$HRhCl(CO)(PEt_3)_2\text{-}SiCl_2Me$	—	y–w	—	—	2063/2041	—	(*54*)
$HRhCl(CF_2CF_2H)(CO)\text{-}(PPh_3)_2$	$RhL(CO)(PPh_3)_2 + HCl$	—	25 (dec)	22.6	2155/2090	—	(*335*)
$HRhCl(CN)(HCN)(PPh_3)_2$	$RhCl(PPh_3)_3 + HCN$	y	189	19.65[m]	2163	—	(*299*)
$[HRh(C_5H_5)(PPh_3)_2]BF_4$	$Rh(C_5H_5)(C_2H_4)_2 + L + HBF_4$	y	—	20.4	2045	Air-sensitive	(*285*)
$HRh(CO)(C_5H_5)SiPh_3$	$Rh(C_5H_5)(CO)_2 + SiR_3 + C_6H_6$	w	95 (dec)	21.1[q]	$2024(\nu_{CO})$[r]	—	(*247*)
$HRh(CO)(C_5H_5)\text{-}Si(CH_2Ph)_3$	—	w	64 (dec)	—	2023, 2020, $2008(\nu_{CO})$[r]	—	(*247*)
$H[Rh(C_5Me_5)]_2Cl_3$	$[Rh(C_5Me_5)]_2X_4 + H_2$	p	>155 (dec)	21.54	1151	Bridging hydride	(*323, 324, 65*)
$[H\{Rh(C_5Me_5)\}_2\text{-}(CF_3CO_2)](CF_3CO_2)$	—	r	—	20.28	—	—	(*323*)
$[H\{Rh(C_5Me_5)\}_2\text{-}(CF_3CO_2)_2]\text{-}[H(CF_3CO_2)_2]$	—	o	—	18.22	—	—	(*323*)
$[H\{Rh(C_5Me_5)\}_2\text{-}(CH_3CO_2)_2]\text{-}[H(CH_3CO_2)_2]H_2O$	—	o	—	19.05	—	—	(*323*)

(*Continued*)

TABLE VI—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[H\{Rh(C_5Me_5)\}_2(CF_3CO_2)_2]PF_6$	—	o	—	18.24	—	—	*(323)*
$[H\{Rh(C_5Me_5)\}_2(CH_3CO_2)_2]PF_6$	—	o–r	—	19.07	—	—	*(323)*
$HRhIr(C_5Me_5)_2Cl_3$	$H\{Rh(C_5Me_5)\}_2Cl_3$ + $H\{Ir(C_5Me_5)\}_2Cl_3$	—	—	22.97	—	—	*(323)*
$HRh_3(C_5H_5)_4$	$C_5H_5MgBr + H_2O + RhCl_3$	br–bl	>200	22.47[s]	—	Crystal structure; air-stable	*(107, 234)*
cis-$[H_2Rh\ trien]^+$	—	—	—	27.1	—	—	*(131)*
cis-$H_2Rh(CN)(PPh_3)_2$	$Rh(CN)(PPh_3)_3 + H_2$	y	—	—	2090, 1940	—	*(103)*
cis-$H_2RhCl(PBu_3^t)_2$	$HRhCl_2L_2 + H_2 + Et_3N$	r	178	35.50	2220, 2200	—	*(225, 226)*
cis-$H_2RhCl(PBu_2^tMe)_2$	—	o	160	32.30	2212, 2137	—	*(225)*
$H_2RhCl[P(C_6H_{11})_3]_2$	$RhCl[P(C_6H_{11})_3]_2C_2H_4 + H_2$	y	—	—	2165, 2120	—	*(110)*
cis-$[H_2Rh(PPhMe_2)_4]^+$	$[Rh(diene)L_2] + H_2 + L$	w	—	20.29	2010	—	*(286)*
cis-$[H_2Rh(PMe_3)_4]^+$	—	cr	—	20.70	1965	—	*(286)*
cis-$[H_2Rh(PPh_3)_4]^+$	—	—	—	—	—	—	*(286)*
cis-$[H_2Rh(AsPhMe_2)_4]^+$	—	w	—	22.31	1995, 1975	—	*(286)*
$[H_2Rh(PPhEt_2)_4]ClO_4$	$[Rhbipy(cod)]ClO_4$ + $H_2 + PR_3$	w	—	—	2016	—	*(203)*
$[H_2Rh(PEt_3)_4]ClO_4$	—	w	—	—	—	—	*(203)*
$[H_2Rh(PPr_3^n)_4]ClO_4$	—	w	—	—	—	—	*(203)*
$[H_2Rh(PPr_3^n)_4]ClO_4$	—	w	—	—	—	—	*(203)*
cis-$[H_2Rh\{P(OMe)_3\}_4]BPh_4$	$[RhL_4]BPh_4 + H_2$	w	80	—	1976[e]	—	*(138)*
cis-$[H_2Rh(PBu_3^n)_4]BPh_4$	—	w	79	21.4[m]	2020[e]	—	*(162)*

cis-$[H_2Rh\{P(OPh)_3\}_4]BPh_4$	—	—	—	—	1989[c]	—	(*162*)
cis-$[H_2Rh(PPh_3)_2(NCCH_3)_2]^+$	$RhC_7H_8(PPh_3)_2 + H_2 + CH_3CN$	—	—	27.4	—	—	(*292*)
$[H_2Rh(PPh_3)_2(bipy)]ClO_4$	$[Rh(bipy)(cod)]ClO_4 + PPh_3 + H_2$	w	—	25.7	2120, 2050	—	(*23, 203*)
$[H_2Rh(PPh_3)_2(AsPhMe_2)_2]^+$	$[Rh(diene)L_2]^+ + L + H_2$	y	—	21.80	2045, 2130	—	(*286*)
cis-$[H_2Rh(dmpe)_2]^+$	$[Rh(dmpe)_2]^+ + H_2$	w	—	—	1900, 1870	Readily loses H_2	(*47*)
$[H_2Rh(diars)_2]BPh_4$	—	y	—	21.9	1950, 1940[c]	—	(*218*)
$[H_2Rh\{(R)\text{-}PPhMe(PhCH_2)\}_2S_2]ClO_4$	—	—	—	—	—	—	(*332, 152*)
$H_2Rh(dtt)(PPh_3)_2$	—	r	—	27.35	2080, 2056, 2036	—	(*272*)
$H_2RhCl(PPh_3)_2CDCl_3$	$RhX(PPh_3)_3 + H_2 + S$	y	—	28.2, 21.5, 18.8[m]	2078, 2013	—	(*339, 24*)
$H_2RhCl(PPh_3)_2C_6H_6$	—	w	—	26.5, 20.4, 17.8[m]	2066, 2051	—	(*339*)
$H_2RhCl(PPh_3)_2C_5H_5N$	—	w	—	28.6, 27.7[m]	2143, 2075	—	(*339*)
$H_2RhCl(PPh_3)_2CH_2Cl_2$	—	y	—	—	2099, 2065	—	(*339*)
$H_2RhCl(PPh_3)_2MeCO_2Et$	—	w	—	28.2, 21.5[m]	2075, 2088	—	(*339*)
$H_2RhCl(PPh_3)_2MeNCHO$	—	w	—	28.2, 21.5[m]	2137, 2081	—	(*339*)
$H_2RhBr(PPh_3)_2CDCl_3$	—	w	—	28.2, 21.5, 18.8[m]	—	—	(*339*)
$H_2RhBr(PPh_3)_2C_6H_6$	—	w	—	26.5, 20.4, 17.8[m]	—	—	(*339*)
$H_2RhBr(PPh_3)_2C_5H_5N$	—	w	—	29.2, 28.4[m]	2144, 2099	—	(*339*)
$H_2RhBr(PPh_3)_2(PPh_3)_2\text{-}CH_2Cl_2$	—	w	—	—	2103, 2068	—	(*339*)
$H_2RhI(PPh_3)_2CDCl_3$	—	w	—	26.2, 23.1, 20.5[m]	—	—	(*339*)

(Continued)

TABLE VI—*Continued*

Complex[a]	Preparation	Color[b]	Mp (°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_2RhCl(AsPh_3)_2C_6H_6$	$RhClL_3 + H_2 + S$	—	—	28.3, 22.1[i]	2042, 2022	—	(*217*)
$H_2RhCl(AsPh_3)_2CHCl_3$	—	—	—	29.0, 22.1[g]	2078, 2033	—	(*217*)
$H_2RhCl(AsPh_3)_2CH_2Cl_2$	—	y	—	29.1, 22.1[c]	2051, 2030[c]	—	(*217*)
$H_2RhCl(SbPh_3)_2CHCl_3$	—	—	—	27.9, 19.9[g]	2078, 2002	—	(*217*)
$H_2RhCl(SbPh_3)_2C_6H_6$	—	—	—	30.1, 20.1[i]	—	—	(*217*)
cis-$H_2RhCl(PPh_3)_3$	—	y	110	—	2082, 2012	—	(*230, 311, 277, 144*)
cis-$H_2RhCl(PPh_2Et)_3$	—	y	90	27.7, 19.4	2115, 2059, 1915	—	(*277*)
$H_2RhCl(PPhBu^tMe)_3$	—	c	103	—	2101, 2066	—	(*225*)
$H_2Rh(PPh_3)_3(BH_3CN)$	$RhCl(PPh_3)_3$ + EtOH + $NaBH_3CN$	y	—	—	2060, 2048	—	(*161*)
$H_2Rh(PPh_3)_2N_3Ph_2$	$Rh(PPh_3)_2N_3Ph_2 + H_2$	y	174	28.4	—	—	(*43*)
$H_2Rh_2(CO_2)(PPh_3)_6$	$HRh(PPh_3)_4 + CO_2$	o	—	—	—	Hydride based on chemical reactions	(*202*)
$[H_2\{Rh(C_5Me_5)\}_2(CF_3CO_2)]PF_6$	$[Rh(C_5Me_5)]_2X_4 + H_2$	r	—	21.30	—	—	(*323*)

$[H_2\{Rh(C_5Me_5\}_2$-$(CH_3CO_2)]PF_6$	—	r	—	21.78	—	—	(*323*)
$H_3Rh(PPh_3)_2$	$RhCl(PPh_3)_3$ + EtOH + $NaBH_4$	—	—	—	—	—	(*101*)
$[H_2RhCl(PPh_3)_2]_2$	—	—	—	27.4[m]	—	—	(*339*)
$[H_2RhBr(PPh_3)_2]_2$	—	—	—	29.1[m]	—	—	(*339*)
$[H_2RhN_3Ph_2]_2C_8H_{14}$	$Ph_2N_3RhC_8H_{12} + H_2$	bl	177	29[j]	—	—	(*43*)
$[H_2RhN_3Ph_2]_3C_8H_{12}$	$Ph_2N_3RhC_8H_{12} + H_2$	bl	201	26.9[j]	—	—	(*43*)

[a] Complex abbreviations are the same as in Table V plus the following: DBP = 5-phenyl-5*H*-bibenzophosphole; diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; TBA = tribenzylamine; TPP = 1,2,5-triphenylphosphole; triene = triethylenetetramine; pn = 1,2-diaminopropane; α = H trans Cl; β = Cl trans to Cl; phen = 1,10-phenanthroline; dpda = *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline; vdiphos = *cis*-1,2-bis(diphenylphosphino)ethylene; vdiars = *cis*-1,2-bis(diphenylarsino)ethylene; diars = *o*-phenylene bis(dimethylarsine).

[b] Colors: o = orange; y = yellow; c = colorless; w = white; br = brown; bl = black; g = green; gr = gray; r = red; k = khaki; cr = cream; p = purple.

[c] CH_2Cl_2 unless noted.

[d] Nujol unless noted.

[e] Upfield hexamethyldisiloxane.

[f] KBr.

[g] $CHCl_3$.

[h] THF.

[i] C_6H_6.

[j] Toluene.

[k] Hexane.

[l] CD_2Cl_2.

[m] $CDCl_3$.

[n] EtOH.

[o] CsI.

[p] LiF.

[q] CCl_4.

[r] Cyclohexane.

[s] C_6D_6

of olefins at 25°C and 1 atm H_2 pressure (*304*). Catalysis is inhibited by a large excess of PPh_3, and studies of ethylene hydrogenation suggest that [$HIrCO(PPh_3)_2$] is the catalytically active species (*45*).

The complex reacts as follows with various ligands, eliminating PPh_3 and often CO (*325*):

$$[HIrCO(PPh_3)_3] + CO \longrightarrow [HIr(CO)_2(PPh_3)_2] + PPh_3 \quad (40)$$

$$[HIrCO(PPh_3)_3] + P(OPh)_3 \longrightarrow [HIr(CO)(P(OPh)_3)_3] + 3PPh_3 \quad (41)$$

Complex [$HIrCO(PPh_3)_3$] is believed to be trigonal bipyramidal with the hydride trans to CO (*316*). A resonance interaction between the vibrational states of metal–hydrogen and carbonyl stretching motions occurs with hydride and carbonyl trans to each other. Comparison of the hydride and deuteride forms of the same complex aid in structure determination, because the carbonyl stretching frequency generally shifts to higher energy in the deuteride complex. The [$HIrCO(PPh_3)_3$] possesses a CO stretch at 1921 cm^{-1} that shifts to 1939 cm^{-1} upon deuteration (*316*).

2. [$HIrNO(PPh_3)_3$]ClO_4

Reed and Roper (*267*) have prepared nitrosyl hydride complexes by reacting [$IrNO(PPh_3)_3$] with a noncomplexing acid, such as $HClO_4$. Green, brown, and black isomers, all of formula [$HIrNO(PPh_3)_3$]ClO_4, have been isolated. Crystal structure analysis (*235*) of the black isomer indicates a distorted trigonal-bipyramidal arrangement of ligands about Ir. The three PPh_3 ligands occupy positions in the equatorial plane, whereas hydride and nitrosyl coordinate at the apical positions. The Ir—N—O bond angle approximates 175°, suggesting the linear attachment of NO^+ (*235*).

A crystal structure analysis of the brown isomer was performed (*67*), and the geometry is also a distorted trigonal bipyramid. However, the equatorial plane contains one PPh_3, nitrosyl, and presumably the hydride. The remaining two PPh_3 ligands occupy apical positions. The nitrosyl again bonds as NO^+ in a linear fashion.

Treatment of complex [$HIrNO(PPh_3)_3$]BF_4 with oxygen produces [$Ir(OH)NO(PPh_3)_2$] BF_4 and triphenylphosphine oxide (*268*). It is believed that the unusual conversion of hydride to hydroxide proceeds via a dioxygen adduct that is unstable with respect to oxygen atom transfer to hydride and triphenylphosphine.

3. *[HIrCO(FUMN)(PPh₃)₂]*

The geometry of [HIrCO(FUMN)(PPh_3)$_2$] (FUMN = fumaronitrile), an olefin–metal hydride complex, is trigonal bipyramidal about Ir (*241*). The olefin and phosphine ligands are in the equatorial plane, and the hydride and carbonyl occupy apical positions. The Ir—H bond length is estimated to be 1.60 Å, giving a nonbonded contact distance between the hydride and an olefin carbon of 2.6 Å.

4. *[$HIrCl_2(PBu_2{}^tR)_2$]*

The reaction of [$IrCl_6$]$^{2-}$ with excess $PBu_2{}^tR$ in isopropanol yields stable purple crystals of the five-coordinate hydride, [$HIrCl_2(PBu_2{}^tR)_2$] (R = Me, Et, Pr^n) (*227*). The proton NMR spectra of the complexes all show a signal close to 60τ for the hydride resonance, which is the highest upfield signal found for hydrides. It is believed that steric effects inhibit the coordination of a third phosphine ligand, although molecules such as CO, MeCN, pyridine, and dimethyl sulfide add to give six-coordinate complexes of formula [$HIrCl_2(PBu_2{}^tR)_2L$] (*294*).

5. *[$HIr(CO)_2(PPh_3)_2$]*

Treatment of [$IrClCO(PPh_3)_2$] with $NaBH_4$ and CO yields the dicarbonyl complex, [$HIr(CO)_2(PPh_3)_2$] (*336*). Crystal structure analysis (*66*) indicates a distorted trigonal-bipyramidal arrangement of ligands about Ir. A phosphine and hydride occupy apical positions, and the Ir—H bond distance is 1.7 Å. In solution, a doubling of bands in the infrared occurs, suggesting that fluctional isomers are in the thermal equilibrium. The intensities of the bands are both solvent and temperature-dependent. Heating the complex with H_2 produces the trihydride [$H_3IrCO(PPh_3)_2$], whereas heating with phosphine produces [$HIrCO(PPh_3)_3$](*336*).

B. [$HIrL_5$]

1. *[$HIrX_2\{P(OR)_3\}_3$]*

Treatment of [$HIrX_2(C_8H_{12})$]$_2$ (X = Cl, Br, I) with 6 *M* equivalents of $P(OR)_3$ (R = Ph, *p*-MePh, *m*-MePh, *o*-MePh, *p*-ClPh) produces methanol-soluble products and methanol-insoluble products (*1*). The methanol-insoluble compounds are white air-stable solids of formula [$HIrX_2\{P(OR)_3\}_3$], and IR evidence indicates that hydride is trans to halogen. The methanol-soluble products formed from the initial reaction are metal, ortho-carbon bonded, Ir(III) hydride derivatives, $[HIrX\{P(OR)_2(OC_6H_4)\}\{P(OR)_3\}_2]$.

2. $[HIrX_2L_3]$

Heating an ethanol solution of *fac*-$[IrCl_3(PPr_2{}^nPh)_3]$ results in formation of the hydride complex, $[HIrCl_2(PPr_2{}^nPh)_3]$, with hydride trans to phosphine (*35*). Irradiation of this complex with a daylight fluorescent tube results in isomerization giving the isomer with hydride trans to chloride (*36*). The analogous triethylphosphine complex undergoes a similar isomerization in the absence of light (*36*).

3. $[HIrXYCO(PPh_3)_2]$

Vaska (*317*) has performed studies on the mode of addition of gaseous hydrogen halides to *trans*-$[IrYCO(PPh_3)_2]$ (Y = Cl, Br, I). The high ν_{Ir-H} values and the absence of vibrational interaction suggest that hydride is trans to Y. The ν_{Ir-H} is insensitive to the addenda X of HX, but the values do vary with the halogen Y of the starting complex, thus suggesting cis addition of HX. A later study by Blake and Kubota (*32*) confirm that the addition is cis in a solvent such as benzene. However, with CH_2Cl_2, C_6H_6—MeOH, and C_6H_6—CH_3CN mixtures of cis and trans isomers are obtained. This result is in agreement with the ability of polar solvents to solvate ions and permit trans addition of HX.

C. $[HIrL_9]$

$[H\{Ir(C_5Me_5)\}_2Cl_3]$

Treatment of $[\{Ir(C_5Me_5)\}_2Cl_4]$ with hydrogen leads to the dinuclear iridium species, $[H\{Ir(C_5Me_5)\}_2Cl_3]$ (*324*). This red air-stable hydride contains a bridging hydride ligand, evidenced by the ν_{Ir-H} at 1151 cm^{-1} shifting to 812 cm^{-1} upon deuteration. This hydride is an efficient catalyst for the homogeneous hydrogenation of olefins at 1 atm H_2 pressure and 24°C.

D. $[H_2IrL_4]$

$[H_2IrCl(PPh_3)_3]$

This white air-stable hydride complex is easily prepared by heating $Na_2[IrCl_6]$ with PPh_3 in ethyleneglycol (*314*). Infrared analysis (*314*) and NMR analysis (*309*) indicate that the complex is meridional with *cis*-hydrides.

Although, in contrast to $[H_2IrCl(CO)(PPh_3)_2]$, the complex does not eliminate molecular hydrogen thermally, loss of hydrogen to generate $[IrCl(PPh_3)_3]$ can easily be achieved by irradiation with either sunlight, fluorescent room light, or UV light (*118*):

$$[H_2IrCl(PPh_3)_3] \xrightarrow[\Phi_{254} = 0.56]{h\nu} H_2 + [IrCl(PPh_3)_3] \qquad (42)$$

E. $[H_3IrL_3]$

$[H_3Ir(PPh_3)_3]$

Treatment of $[IrCl_6]^{2-}$ with $NaBH_4$ and PPh_3 in 2-methoxy ethanol gives facial and meridional isomers of the trihydride $[H_3Ir(PPh_3)_3]$ (*210*). Kolomnikov *et al.* (*200*) have reported the reduction of CO_2 by hydrogen in methanol containing $[H_3Ir(PPh_3)_3]$. Work-up of the products gives the methyl ester of formic acid:

$$CO_2 + H_2 + CH_3OH \xrightarrow{[H_3Ir(PPh_3)_3]} HCOOCH_3 + H_2O \qquad (43)$$

Although neither isomer of $[H_3Ir(PPh_3)_3]$ eliminates molecular hydrogen thermally, loss of hydrogen can be induced by UV irradiation (*118*).

F. $[H_5IrL_2]$

$[H_5Ir(PR_3)_2]$

Treatment of $[IrCl_3L_3]$ with $LiBH_4$ produces the pentahydride complexes $[H_5IrL_2]$ (L = PEt_2Ph, PEt_3, PMe_3) (*223*). The complexes were originally postulated as trihydrides, but more recent work indicates this earlier conclusion to be incorrect (*59*). Treatment of the complexes with HCl produces 3 moles of H_2/ Ir atom, with the remaining residue being an uncharacterized hydride. The ^{31}P NMR spectra of $[H_5Ir(PEt_3)_2]$, with decoupling of the ethyl protons, is a sextet due to coupling with five equivalent hydridic hydrogens. Other hydrides, originally postulated as $[H_3IrL_2]$, may also be pentahydrides instead of trihydrides.

TABLE VII

SURVEY OF HYDRIDE COMPLEXES: IRIDIUM

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIr(CO)(PPh_3)_2$	$H_3Ir(PPh_3)_2 + CO$	y	132	—	2040, 1980, 1920	—	(*218, 340*)
$HIr(pyS)_2(PPh_3)$	$HIr(CO)(PPh_3)_3 + pySH$	y	175 (dec)	31.2[e]	2143	—	(*40*)
$HIr[P(OPh)_3]_4$	$H_3Ir(PPh_3)_3 + P(OPh)_3$	w	127	23.0[f]	2055[f]	—	(*125*)
$HIr(PF_3)_4$	$IrCl_3 + PF_3 + H_2 + Cu$	c	−39	21.93	—	Air-stable	(*205*)
$HIr(CO)_4$	$Ir_4(CO)_{12} + CO + H_2$	—	—	—	2055, 2031, 1999	Unstable	(*329, 330*)
$HIr(dppe)_2$	$[Ir(dppe)_2]Cl \xrightarrow[\text{reduction}]{\text{electrochemical}}$	o–r	—	—	2015	—	(*254*)
$HIr(CO)(PPh_3)_3$	$IrCl_6{}^{2-} + PPh_3 + NaBH_4 + H_2CO$	y	185 (dec)	20.3[g]	2120/1915	Catalyst	(*210, 304, 325, 45, 26, 322, 34, 163, 306*)
$HIr(CS)(PPh_3)_3$	$IrCl(CS)(PPh_3)_2 + NaBH_4/EtOH$	o	—	23.0	2000	—	(*337*)
$HIr(CO)[P(OPh)_3]_3$	$HIr(P(OPh)_3)_4 + CO$	w	175	19.5[f]	2000[f]/1980	—	(*125, 213*)
$[HIr(NO)(PPh_3)_3]ClO_4$, BF_4, or PF_6	$Ir(NO)(PPh_3)_3 + HY$	g	177	—	2070	—	(*267*)
$[HIr(NO)(PPh_3)_3]ClO_4$, BF_4, or PF_6	—	br	152	—	2130	Crystal structure	(*267, 67*)
$[HIr(NO)(PPh_3)_3]ClO_4$	—	bl	158	—	2150	Crystal structure	(*267, 235*)
$[HIr(NO)(AsPh_3)_3]ClO_4$	—	g	103	—	—	—	(*269*)
$HIrCl(NO)(PPh_3)_2$	$[HIr(NO)L_3]^+ + LiX$	r	184	—	2080	—	(*267, 268*)
$HIrBr(NO)(PPh_3)_2$	—	br	176	—	2080	—	(*267*)

$HIrI(NO)(PPh_3)_2$	—	br	169	—	2080	—	(*267*)
$HIrClCN(COD)$	$[IrCl(C_8H_{12})]_2 + HCN$	y	—	24.1	2140	—	(*289*)
$HIrCO(fumn)(PPh_3)_2$	$HIrCO(PPh_3)_3$ + fumn	c	—	—	—	Crystal structure	(*241*)
$HIrCl_2(PBu_2{}^tMe)_2$	$IrCl_6{}^{2-} + PBu_2{}^tR$ + isopropanol	p	195	60.5[g]	2000[g]	Stable	(*227, 228*)
$HIrCl_2(PBu_2{}^tEt)_2$	—	p	171	59.6[g]	2012[g]	—	(*227, 228*)
$HIrCl_2(PBu_2{}^tPr^n)_2$	—	p	192	60.0[g]	2016[g]	—	(*227, 294, 228*)
$HIrCl_2(PPh_3)_2$	$H_3Ir(PPh_3)_2 + HCl$	y	162	—	2245	Catalyst	(*5, 201*)
$HIrI_2(PPh_3)_2$	$H_3Ir(PPh_3)_3 + I_2$	y	220	—	2270	—	(*219*)
$HIr(CO)_2(PPhEt_2)_2$	$H_5Ir(PPhEt_2)_2 + CO$	c	59	—	2041[g]/1965, 1908	—	(*223*)
$HIr(CO)_2(PPh_3)_2$	$[Ir(CO)_3(PPh_3)]^- +$ HOAc + PPh_3	y	135	20.97	2029/1970, 1915	Crystal structure	(*38, 336, 66, 70*)
$HIr(CO)_2(AsPh_3)_2$	$IrCl(CO)L_2 + NaBH_4/CO$	y	—	22.30	2080/1970, 1925	Very air-sensitive	(*336*)
$HIr(CO)_2(PPh_2Et)_2$	—	w	—	21.58	2083/1962, 1915	Solutions	(*336*)
$HIr(CO)_2[P(C_6H_4F)_3]_2$	—	gr–w	—	20.58[i]	2075/1989, 1928	—	(*336*)
$HIr(pyS)_2(PPh_3)_2$	$HIr(pyS)_2(PPh_3) + PPh_3$	y	—	31.5[e]	2151	—	(*40*)
$HIr(NO)_2(PPh_3)_2$	$Ir(CO)(PPh_3)_2(NCO)$-$(NO_3)_2 + CHCl_3/EtOH$	y	—	—	2274, 2259	—	(*52*)
$HIr(CO)_3(PPh_3)$	$Ir_2(CO)_6L_2 + CO/H_2$	—	—	—	2046, 1982, 1948	Stable with CO/H_2	(*331, 220*)
$HIr(CO)_3P(p\text{-}MeC_6H_4)_3$	—	—	—	—	2043, 1979, 1946	—	(*331*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIr(CO)_3PEt_3$	—	—	—	—	2035, 1973, 1938	—	(*331*)
$HIr(CO)_3PPr_3^i$	—	—	—	—	2040, 1970, 1934	—	(*331*)
$HIr(CO)_3PBu_3^n$	—	—	—	—	2039, 1972, 1937	—	(*331*)
$HIr(CO)_3PPr_3^n$	—	—	—	—	2041, 1973, 1940	—	(*331*)
$HIr(CO)(SO_2)(PPh_3)_2$	$HIr(CO)(PPh_3)_3 + SO_2$	gr	—	—	1965/2065	—	(*212*)
$HIr[PPh(OMe)_2]_5^+$	$IrCl(CO)(PPh_3)_2 + L + NaBH_4$	c	—	22.0[j]	2080	—	(*74*)
$[HIr(C_5H_{10}NH)_4Cl]ClO_4$	$C_5H_{10}NH + IrCl_6^{2-} + EtOH + ClO_4^-$	y	—	39.2[k]	2198[f]	Stable	(*27, 28*)
$[HIr(C_5H_{10}NH)_4Br]ClO_4$	$C_5H_{10}NH + IrCl_6^{2-} + EtOH + NaX$	y	200 (dec)	39.0[k]	2194[f]	—	(*27, 28*)
$[HIr(C_5H_{10}NH)_4I]ClO_4$	—	y	200 (dec)	37.9[k]	2184[f]	—	(*27, 28*)
$[HIr(C_5H_{10}NH)_4I]I$	—	y	156 (dec)	38.4[k]	2186[f]	—	(*27, 28*)
$[HIr(C_5H_{10}NH)_4Br]Br$	—	y	190 (dec)	38.8[k]	2193[f]	—	(*27, 28*)
$[HIr(C_5H_{10}NH)_4NCO]NCO$	$HIrCl(C_5H_{10}NH)_4 + KX$	y	176 (dec)	26.05[l]	2230, 2170, 2160[h]	—	(*29*)
$[HIr(C_5H_{10}NH)_4NCS]NCS$	—	y	194 (dec)	25.79, 25.89[l]	2200, 2080, 2050[h]	—	(*29*)
$[HIr(C_5H_{10}NH)_4NCSe]NCSe$	—	y–w	180 (dec)	25.95[l]	2200, 2080, 2050[h]	—	(*29*)
trans-$[HIrCl\{PPh(OMe)_2\}_4]^+$	$[IrHCl_2(C_8H_{12})]_2 + L$	c	—	28.1[j]	2200	—	(*74*)
trans-$[HIrCl\{PPh_2(OMe)\}_4]^+$	—	c	—	27.65[m]	2210	—	(*74*)

trans-$[HIrCl\{PPh(OEt)_2\}_4]^+$	—	c	—	28.4[m]	2200	—	(*74*)
trans-$[HIrCl\{PPh_2(OEt)\}_4]^+$	—	c	—	27.93[m]	2200	—	(*74*)
cis-$[HIrCl\{PPh(OEt)_2\}_4]^+$	—	c	—	20.8[m]	2085	—	(*74*)
trans-$[HIrCl(AsPhMe_2)_4]PF_6$	$[IrCl(C_8H_{12})]_2$ + $AsPhMe_2$ + EtOH	w	209	31.2[m]	—	—	(*139*)
$[HIrClP(o\text{-}Ph_2PC_6H_4)_3]BPh_4$	$[HIrCl_2(C_8H_{12})]_2$ + L	c	180 (dec)	19.02	2100	—	(*187*, *242*)
$[HIrBrP(o\text{-}Ph_2PC_6H_4)_3]BPh_4$	—	c	233 (dec)	19.45	—	—	(*187*, *242*)
$[HIrClAs(o\text{-}Ph_2AsC_6H_4)_3]BPh_4$	—	c	190 (dec)	—	2080	—	(*187*, *242*)
$[HIrCl(PPh_2C_6H_4NMe_2)_2]PF_6$	$[IrCl(C_8H_{14})_2]_2$ + L + NH_4PF_6	c	148	32.0	2240	—	(*260*)
cis-$[HIr(PH_2)(dppe)_2]Cl$	$[Ir(dppe)_2]Cl$ + PH_3	cr	198 (dec)	21.7[m]	2114	—	(*288*)
trans-$[HIr(PH_2)(dmpe)_2]BPh_4$	$[Ir(dmpe)_2]Cl$ + PH_3 + BPh_4	w	185 (dec)	23.23[m]	1960	—	(*288*)
$[HIrCl\ bipy(C_8H_{12})]PF_6$	$[Ir(chel)(L—L)]^+$ + HX	w	—	—	—	—	(*232*)
$[HIrCl\ phen(C_8H_{12})]PF_6$	—	w	—	—	—	—	(*232*)
$[HIrCl\ bipy(C_8H_{12})]ClO_4$	—	w	—	—	2241	—	(*232*)
$[HIrBr\ bipy(C_8H_{12})]ClO_4$	—	w	—	—	2226	—	(*232*)
$[HIrI\ bipy(C_8H_{12})]ClO_4$	—	cr	—	—	2207	—	(*232*)
$[HIrCl\ phen(NBD)]PF_6$	—	cr	—	—	—	—	(*232*)
$[HIrI\ bipy(NBD)]ClO_4$	—	g	—	—	2127	—	(*232*)
$[HIrPEt_3phen(C_8H_{12})](ClO_4)_2$	—	w	—	—	—	—	(*232*)
$HIrCl(dpt)(PPh_3)_2$	$HIrCl_2(PPh_3)_3$ + dpt	r	—	33.53[g]	2160	Air-stable	(*272*)
$[HIr(MeNC)(dppe)_2]^+$	$[Ir(MeNC)(dppe)_2]^+$ + HCl	—	—	20.7	—	Hydroscopic	(*17*)
$[HIrCl(dp)_2]Cl$, ClO_4, BPh_4	$[Ir(dp)_2]^+$ + HX	w	245 (dec)	—	2218	—	(*93*)
$[HIrBr(dp)_2]Cl$, ClO_4, BPh_4	—	w	245 (dec)	—	2208	—	(*93*)
$[HIrI(dp)_2]Cl$, ClO_4, BPh_4	—	w–cr	216 (dec)	—	2187	—	(*93*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[HIrCl(dppe)_2]Cl$	—	w	270 (dec)	—	2216	—	*(318)*
$[HIrBr(dppe)_2]Cl$	—	w	272 (dec)	—	2209	—	*(318)*
trans-$[HIrCl(dmpe)_2]BPh_4$	—	w	225	32.2	2162	—	*(167)*
trans-$[HIr(EtCO_2)(dmpe)_2]BPh_4$	$[Ir(CO)(dmpe)_2]Cl$ + EtOH + BPh_4^-	w	184	25.56	1935	—	*(167)*
trans-$[HIr(MeCO_2)(dmpe)_2]BPh_4$	—	w	180	25.50	1960	—	*(167)*
trans-$[HIr(CO)(dmpe)_2](BPh_4)_2$	—	w	237	22.09	2135	—	*(167)*
$HIrCl_2[P(OPh)_3]_3$	$[HIrX_2(C_8H_{12})]_2 + P(OR)_3$	w	—	27.55[e]	2180	—	*(315)*
$HIrBr_2[P(OPh)_3]_3$	—	w	—	26.50[e]	2165	—	*(1)*
$HIrI_2[P(OPh)_3]_3$	—	w	—	25.25[e]	2145	—	*(1)*
$HIrCl_2[P(O$-*p*-tolyl$)_3]_3$	—	w	—	26.45[e]	2190	—	*(1)*
$HIrBr_2[P(O$-*p*-tolyl$)_3]_3$	—	w	—	25.95[e]	2180	—	*(1)*
$HIrI_2[P(O$-*p*-tolyl$)_3]_3$	—	w	—	24.70[e]	2165	—	*(1)*
$HIrCl_2[P(O$-*m*-tolyl$)_3]_3$	—	w	—	26.50[e]	2200	—	*(1)*
$HIrBr_2[P(O$-*m*-tolyl$)_3]_3$	—	w	—	26.00[e]	2180	—	*(1)*
$HIrI_2[P(O$-*m*-tolyl$)_3]_3$	—	w	—	25.00[e]	2160	—	*(1)*
$HIrCl_2[P(O$-*o*-tolyl$)_3]_3$	—	w	—	26.30[e]	2205	—	*(1)*
$HIrBr_2[P(O$-*o*-tolyl$)_3]_3$	—	w	—	25.60[e]	2200	—	*(1)*
$HIrI_2[P(O$-*o*-tolyl$)_3]_3$	—	w	—	—	2180	—	*(1)*
$HIrCl_2[P(O$-*p*-$ClC_6H_4)_3]_3$	—	w	—	27.00[e]	2200	—	*(1)*
$HIrBr_2[P(O$-*p*-$ClC_6H_4)_3]_3$	—	w	—	26.20[e]	2170	—	*(1)*
$HIrI_2[P(O$-*p*-$ClC_6H_4)_3]_3$	—	w	—	24.90[e]	2160	—	*(1)*
$HIrCl_2[PMe_2(1\text{-naphthyl})]_3$	$[IrHCl_2C_8H_{12}]_2$ + L	cr	195 (dec)	30.9	2270	—	*(95)*
α-$HIrCl_2(PPh_3)_3$	IrX_3L_3 + EtOH	y	—	29.2	2228	—	*(210, 19, 309)*

β-$HIrCl_2(PPh_3)_3$	—	y	256 (dec)	22.4, 25.3[f]	2193	—	(*210, 19, 309*)
$HIrCl_2(PPhPr^n_2)_3$	—	c	170	31.5[g]	2188[g]	—	(*35*)
$HIrCl_2(PPhBu^n_2)_3$	—	c	143	31.0[g]	2189[g]	—	(*35*)
$HIrCl_2(AsPh_3)_3$	$IrCl(MPh_3)_3$ + HCl	y	240 (dec)	29.9[g]	2170	—	(*19*)
$HIrCl_2(SbPh_3)_3$	—	y	201 (dec)	32.7[m]	2152	—	(*19*)
$HIrCl_2[P(p\text{-}FC_6H_4)_3]_3$	—	y	—	27.2[g]	2208	—	(*19*)
$HIrCl_2[P(p\text{-}MeOC_6H_4)_3]_3$	—	y	—	28.7[g]	2206	—	(*19*)
$HIrCl_2[P(p\text{-}MeC_6H_4)_3]_3$	—	y	—	—	2208	—	(*19*)
$HIrBr_2(PPh_3)_3$	—	—	—	23.6	—	—	(*131*)
$HIrI_2(PPh_3)_3$	—	y	220	—	2270	—	(*131*)
$HIrBr_2(AsPh_3)_3$	—	—	244 (dec)	—	2188	—	(*131*)
$HIrBr_2(SbPh_3)_3$	—	—	—	—	—	—	(*131*)
α-$HIrCl_2(AsPh_2Me)_3$	$IrCl_6^{3-}$ + L + EtOH	—	—	31.93[m]	2178[g]	—	(*263*)
β-$HIrCl_2(AsPh_2Me)_3$	—	—	—	25.27[m]	2126[g]	—	(*263*)
α-$HIrCl_2(AsPh_2Et)_3$	—	c	194	31.62[m]	2180[g]	—	(*263*)
β-$HIrCl_2(AsPh_2Et)_3$	—	y	175	25.23[m]	2110[g]	Crystal structure	(*259*)
α-$HIrBr_2(AsPh_2Me)_3$	$IrCl_6^{3-}$ + L + EtOH + HX	y	—	—	2180[g]	—	(*263*)
β-$HIrBr_2(AsPh_2Me)_3$	—	—	—	25.75[m]	2130[g]	—	(*263*)
α-$HIrBr_2(AsPh_2Et)_3$	—	y	196	30.72[m]	2180[g]	—	(*263*)
β-$HIrBr_2(AsPh_2Et)_3$	—	o	201	25.95[m]	2110[g]	—	(*263*)
α-$HIrI_2(AsPh_2Me)_3$	—	y	—	—	2166[b]	—	(*263*)
β-$HIrI_2(AsPh_2Et)_3$	—	o	174	—	2168[g]	—	(*263*)
α-$HIrCl_2(PEt_3)_3$	IrX_3L_3 + KOH/MeOH	w	99	31.6[g]	2213	$u = 8.0$[n]	(*176, 59, 68*)
β-$HIrCl_2(PEt_3)_3$	—	y	83	22.55[g]	2112	$u = 2.5$[n]	(*176, 59*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
β-$HIrCl_2(PPr_3^n)_3$	—	y	70	—	2167, 2045	—	(*176, 59*)
α-$HIrCl_2(PPhMe_2)_3$	—	c	178	30.6[g]	2212, 2183, 2167	—	(*176, 177*)
β-$HIrCl_2(PPhMe_2)_3$	—	y	163 (dec)	21.6[g]	2070	—	(*176, 177*)
α-$HIrCl_2(PPhEt_2)_3$	—	w	170	31.2[g]	2232, 2201	—	(*176, 59*)
β-$HIrCl_2(PPhEt_2)_3$	—	y	118	22.55[g]	2061, 2031	—	(*176, 59*)
β-$HIrCl_2(PEt_2$*p*-$MeOC_6H_4)_3$	—	y	140	—	2015	—	(*59*)
β-$HIrCl_2(PPhPr_2^n)_3$	—	y	147	—	2035	—	(*176*)
β-$HIrCl_2(AsEt_3)_3$	—	y	72	25.2[g]	2110	—	(*176, 59*)
α-$HIrCl_2(AsPhEt_2)_3$	—	y	153	—	2208	—	(*59*)
β-$HIrCl_2(AsPhEt_2)_3$	—	y	110	25.55[g]	2099	—	(*59*)
α-$HIrBr_2(PEt_3)_3$	—	w	98	—	2213	—	(*59*)
β-$HIrBr_2(PEt_3)_3$	—	o	93	23.6[g]	2141	—	(*59*)
α-$HIrBr_2(PPhEt_2)_3$	—	w	182	30.4[g]	2227, 2193	$u = 8.3$[n]	(*176, 59*)
β-$HIrBr_2(PPhEt_2)_3$	—	o	121	—	2041	$u = 2.05$[n]	(*176, 59*)
β-$HIrI_2(PEt_3)_3$	—	cr	139	—	2222	$u = 8.65$[n]	(*59*)
α-$HIrI_2(PPhEt_2)_3$	—	y	185	29.3[g]	2220[g]	—	(*176, 59, 177*)
α-$HIrI_2(PPhMe_2)_3$	—	y	151 (dec)	28.8[f]	2204, 2168	—	(*176, 177*)
α-$HIrCl_2(PPh_2Me)_3$	—	w	183	—	2251	—	(*4*)
β-$HIrCl_2(PPh_2Me)_3$	—	y	186	22.5	2060	—	(*4*)
α-$HIrCl_2(PPh_2Et)_3$	—	w	178	—	2210	—	(*4*)
β-$HIrCl_2(PPh_2Et)_3$	—	y	172	21.9[e]	2050	—	(*4*)
α-$HIrBr_2(PPh_2Me)_3$	—	w	220	—	2250	—	(*4*)

β-$HIrBr_2(PPh_2Me)_3$	—	y	240	—	2151	—	(*4*)
α-$HIrBr_2(PPh_2Et)_3$	—	w	220	—	2210	—	(*4*)
β-$HIrI_2(PPh_2Et)_3$	—	o	195	—	2050	—	(*4*)
α-$HIrCl_2(AsPh_2Pr^n)_3$	—	w	194	32.08^m	2220	—	(*262*)
β-$HIrCl_2(AsPh_2Pr^n)_3$	—	y	186	25.46^m	2140	—	(*262*)
α-$HIrBr_2(AsPh_2Pr^n)_3$	—	y	203	31.29^m	2227	—	(*262*)
β-$HIrBr_2(AsPh_2Pr^n)_3$	—	o	199	25.83^m	2120	—	(*262*)
α-$HIrI_2(AsPh_2Pr^n)_3$	—	br	188	—	2220	—	(*262*)
α-$HIrCl_2(Me_2SO)_3$	$[IrCl_4(Me_2SO)_2]^-$ + Me_2SO + propanol	y	160	28.8^m	2180	—	(*252, 137, 153*)
β-$HIrCl_2(Me_2SO)_3$	—	y	184	35.3^m	2190	—	(*252, 137, 153*)
$HIrCl_2(PEt_3)_2(PPhMe_2)$	$HIrX_2L_3$ + L′	y	108	22.40^g	2051, 2040	—	(*257*)
$HIrBr_2(PEt_3)_2(PPhMe_2)$	—	o–y	118	23.02^g	2060, 2050	—	(*257*)
$HIrCl_2(PPhEt_2)_2(PPhMe_2)$	—	y	135	22.27^g	2038, 2022	—	(*257*)
$HIrCl_2(AsEt_3)_2(PPhMe_2)$	—	y	99	21.48^g	2011, 2005	—	(*257*)
$HIrCl(C_5Me_5)(PPh_3)$	$Ir(C_5Me_5)Cl_2(PPh_3)$ + EtOH + OH^-	y	223	23.3^g	2090	Air-stable	(*238*)
$HIr(BH_3CN)_2(PPh_3)_3$	$HIrCl_2(PPh_3)_3$ + EtOH + $NaBH_3CN$	w	—	—	2135	—	(*161*)
$HIrCl_2(PPh_3)_2CH_3OH$	$IrN_2Cl(PPh_3)_2$ + HCl + L	—	—	—	2271	—	(*31*)
$HIrCl_2(PPh_3)_2AsPh_3$	—	—	—	—	2232	—	(*31*)
$HIrCl_2(PPh_3)_2As(p\text{-tolyl})_3$	—	—	—	—	2218	—	(*31*)
$HIrCl_2(PPh_3)_2m\text{-}NH_2—C_6H_4NO_2$	—	—	—	—	2223	—	(*31*)
$HIrCl_2(PPh_3)_2NCPh$	—	—	—	—	2213	—	(*31*)
$HIrCl_2(PPh_3)_2p\text{-}NC—C_6H_4Cl$	—	—	—	—	2194	—	(*31*)
$HIrCl_2(PPh_3)_2p\text{-}NC—C_6H_4NO_2$	—	—	—	—	2193	—	(*31*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^1H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIrCl_2(PPh_3)_2$*p*-NC—C_6H_4Me	—	—	—	—	2191	—	(*31*)
$HIrCl_2(PPh_3)_2P$(*p*-tolyl)$_3$	—	—	—	—	2190	—	(*31*)
$HIrCl_2(PPh_3)_2C_5H_5N$	—	y	—	—	2183	—	(*31*)
$HIrCl_2(PPh_3)_2SbPh_3$	—	—	—	—	2180	—	(*31*)
$HIrCl_2(PPh_3)_2SEt_2$	—	—	—	—	2178	—	(*31*)
$HIrCl_2(PPh_3)_2NH_2CH_2Ph$	—	—	—	—	2156	—	(*31*)
$HIrCl_2(PPh_3)_2NCC_5H_5N$	—	—	—	—	2150	—	(*31*)
$HIrCl_2(PPh_3)_2PPh_2Me$	—	—	—	—	2125	—	(*31*)
$HIrCl_2(PPh_3)_2P(OPh)_3$	—	—	—	—	2120	—	(*31*)
$HIrCl_2(PPh_3)_2PPhMe_2$	—	—	—	—	2102	—	(*31*)
$HIrCl_2(PBu_2{}^tMe)_2CO$	$HIrCl_2L_2 + L'$	y	125	18.36[g]	2179/2020[f]	—	(*294*)
$HIrCl_2(PBu_2{}^tMe)_2MeNC$	—	y	128 (dec)	21.75[g]	—	—	(*294*)
$HIrCl_2(PBu_2{}^tMe)_2py$	—	y	142	33.8[g]	2315[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tMe)_2$4-Mepy	—	y	128 (dec)	33.8[g]	2304[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tMe)_2P(OMe)_3$	—	y	106 (dec)	21.55[g]	2198[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tEt)_2CO$	—	y	219	18.3[g]	2208/2015[f]	—	(*294*)
$HIrCl_2(PBu_2{}^tEt)_2MeNC$	—	y	162	21.8[g]	2165	—	(*294*)
$HIrCl_2(PBu_2{}^tEt)_2MeCN$	—	y	186 (dec)	33.5[g]	2294[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tPr^n)_2CO$	—	y	220	18.4[g]	2200/2020[f]	—	(*294*)
$HIrCl(PBu_2{}^tPr^n)_2MeNC$	—	y	174	21.85[g]	2160[f]	—	(*294*)
$HIrCl_2(PBu_2{}^tEt)[P(OMe)_3]_2$	$HIrCl_2L_2L' + L'$	y	102 (dec)	21.4[g]	2123[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tPr^n)[P(OMe)_3]_2$	—	y	105 (dec)	21.4[g]	2119[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tPr^n)$(4-Mepy)$_2$	—	y	135	35.6[g]	2273, 2237[g]	—	(*294*)
$HIrCl_2(PBu_2{}^tPr^n)(py)_2$	—	y	198	35.53[g]	2336[g]	—	(*294*)

$HIrCl_2(COD)PPh_3$	$(COD)IrXL + HX$	y	154	22.95[m]	2242	—	(149, 150)
$HIrBr_2(COD)PPh_3$	—	y	176	22.57[m]	2257	—	(149, 150)
$HIrI_2(COD)PPh_3$	—	y	158	21.97[m]	2227	—	(149)
$HIr(CN)_2(COD)PPh_3$	—	y	>300	24.97[m]	2215	—	(149)
$HIrCl_2(COD)PPh_2Me$	—	y	168	23.24[m]	2227	—	(149)
$HIrBr_2(COD)PPh_2Me$	—	y	188	22.90[m]	2243	—	(149)
$HIrCl_2(COD)AsPh_3$	—	y	164	22.70[m]	2228	—	(149)
$HIrBr_2(COD)AsPh_3$	—	y	182	22.47[m]	2232	—	(149)
$HIrCl_2(COD)Me_3PS$	—	cr	155	22.06[g]	2210	—	(2)
$HIrCl_2(COD)Me_2PhPS$	—	cr	—	—	2210	—	(2)
$HIrI_2CO(PPh_3)_2$	$[IrI_5CO]^{2-} + PPh_3 +$ EtOH	y	155	—	2180/2040	—	(219)
$HIrCl_2CO(PPh_3)_2$	$IrCl_6{}^{2-} + PPh_3 +$ H_2CO	w	315 (dec)	—	2230/2020	—	(210, 155, 6, 15)
$HIrCl_2CO(PBu^tMe_2)_2$	$IrCl_6{}^{2-} + PR_3 + CO +$ EtOH	w	220 (dec)	25.98[g]	2208/2028[f]	—	(295)
$HIrCl_2CO(PBu^tEt_2)_2$	—	w	160 (dec)	26.24[g]	2227/2020[f]	—	(295)
$HIrCl_2CO(PBu^tBu_2{}^n)_2$	—	w	81	26.36[g]	2222/2020[f]	—	(295)
$HIrCl_2CO(PBu_2{}^tMe)_2$	—	w	210	26.46[g]	2249/2008[g]	—	(295)
$HIrCl_2CO(PBu_2{}^tEt)_2$	—	w	218 (dec)	26.26[g]	2278/2012[g]	—	(295)
$HIrCl_2CO(PBu_2{}^tPr^n)_2$	—	w	223 (dec)	26.26[g]	2283/2008[g]	—	(295)
$HIrCl_2CO(PBu^tPr_2{}^n)_2$	—	w	181	25.75[g]	2222/2016[g]	—	(295)
$HIrBr_2CO(PBu^tMe_2)_2$	—	w	275 (dec)	25.5[g]	2198/2028[f]	—	(295)
$HIrBr_2CO(PBu^tEt_2)_2$	—	w	216 (dec)	25.75[g]	2232/2028[f]	—	(295)
$HIrBr_2CO(PBu^tPr_2{}^n)_2$	—	w	163	25.78[g]	2222/2016[g]	—	(295)
$HIrBr_2CO(PBu^tBu_2{}^n)_2$	—	w	134	25.78[g]	2227/2024[f]	—	(295)
$HIrCl_2CO(Pcy_3)_2$	$IrCl(CO)L_2 + HX$	w	—	—	2276/2015	—	(237)
$HIrCl_2CO(PPh_2Me)_2$	—	c	—	—	2225/2050[h]	—	(71)

(Continued)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIrBr_2CO(PPh_2Me)_2$	—	w	—	—	2210/2045[h]	—	(*71*)
$HIrCl_2CO(SbPh_3)_2$	$CH_3OCOIr(CO)L_3$ + HCl	y	163 (dec)		2157/2016[h]	—	(*155*)
$HIrCl_2CO(AsPh_3)_2$	—	y	249	—	2200/2024[h]	—	(*155*)
$HIrCl_2CO(PPhMe_2)_2$	$IrCl_6^{2-}$ + CO + L + EtOH	w	149 (dec)	25.7[g]	2189/2028	—	(*86*)
$HIrCl_2CO(PPhMe_2)_2$	—	y	138	18.7[g]	2110/2009	—	(*86*)
$HIrBr_2CO(PPhMe_2)_2$	—	w	161 (dec)	25.3[g]	2183/2031	—	(*86*)
$HIrCl_2CO(AsPhMe_2)_2$	—	w	132	26.1[g]	2179/2024	—	(*86*)
$HIrCl_2CO(PEt_3)_2$	—	w	93	19.2	2188/2012	—	(*86*, *289*)
$HIrCl_2CO(PMe_3)_2$	—	w	150 (dec)	26.6	2177/2124	—	(*86*)
$HIrCl_2CO(PPhEt_2)_2$	$IrCl_3CO(PPhEt_2)_2$ + KOH/EtOH	y	110	19.0[g]	2008/2109, 2101	—	(*54*)
$HIrCl_2CO(PPhEt_2)_2$	$IrX_3(PPhEt_2)_3$ + CO + EtOH	c	123 (dec)	26.05[g]	2237/2032, 1987	—	(*54*)
$HIrBr_2CO(PPhEt_2)_2$	—	c	140 (dec)	—	2232/2035	—	(*54*)
$HIrCl_2CO[PMe_2(o\text{-}MeOC_6H_4)]_2$	$IrClCOL_2$ + HCl	w	180 (dec)	27.14[m]	2188/2039, 2020[f]	—	(*233*)
$HIrCl_2CO[PMe_2(p\text{-}MeOC_6H_4)]_2$	—	w	116	26.7[m]	2180/2040, 1990[g]	—	(*233*)
α-$HIrCl_2CO(AsPh_2Me)_2$	$IrCl_6^{3-}$ + CO + L + HX	w	160	26.42[m]	2195/2038	—	(*265*)
α-$HIrCl_2CO(AsPh_2Et)_2$	—	w	150	26.64[m]	2200/2020	—	(*265*)
α-$HIrBr_2CO(AsPh_2Me)_2$	—	w	155	25.75[m]	2185/2035	—	(*265*)
α-$HIrBr_2CO(AsPh_2Et)_2$	—	w	169	26.20[m]	2185/2030	—	(*265*)
α-$HIrI_2CO(AsPh_2Me)_2$	—	cr	173	24.05[m]	2203/2050	—	(*265*)
α-$HIrI_2CO(AsPh_2Et)_2$	—	cr	157	24.40[m]	2187/2052	—	(*265*)

β-$HIrCl_2CO(AsPh_2Me)_2$	$HIrX_2L_3 + CO$	y	135	18.31[m]	2017/2115	—	*(265)*
β-$HIrCl_2CO(AsPh_2Et)_2$	—	y	146	18.35[m]	1993/2093	—	*(265)*
β-$HIrBr_2CO(AsPh_2Me)_2$	—	y	141	19.15[m]	2011/2106	—	*(265)*
β-$HIrBr_2CO(AsPh_2Et)_2$	—	y	155	19.30[m]	2000/2100	—	*(265)*
β-$HIrCl_2CO(AsPh_2Pr^n)_2$	—	y	181	18.33[m]	2000/2102	—	*(262)*
β-$HIrBr_2CO(AsPh_2Pr^n)_2$	—	y	172	19.25[m]	2000/2100	—	*(262)*
α-$HIrCl_2CO(AsPh_2Pr^n)_2$	$IrCl_6^{3-} + CO + L + HX$	w	174	26.66[m]	2195/2027	—	*(262)*
α-$HIrBr_2CO(AsPh_2Pr^n)_2$	—	w	184	25.87[m]	2192/2027	—	*(262)*
α-$HIrI_2CO(AsPh_2Pr^n)_2$	—	cr	167	24.38[m]	2167/2033	—	*(262)*
α-$HIrCl_2CO[As(cy)_3]_2$	—	w	>280	27.32[m]	2179/2012	—	*(266)*
α-$HIrBr_2CO[As(cy)_3]_2$	—	w	>280	26.60[m]	2180/2010	—	*(266)*
$HIrBr_2CO(PPh_3)_2$	$HIrX_2(PPh_3)_2 + L'$	y	244 (dec)	—	2220/2020	—	*(5)*
$HIrBr_2NH_3(PPh_3)_2$	—	y–o	166	—	2120	—	*(5)*
$HIrBr_2(C_5H_5N)(PPh_3)_2$	—	y	201	—	2250	—	*(5)*
$HIrBr_2SbPh_3(PPh_3)_2$	—	y	182	—	2190	—	*(5)*
$HIrCl_2NH_3(PPh_3)_2$	—	y	148	—	2120	—	*(5)*
$HIrCl_2CH_3CN(PPh_3)_2$	—	y	187	—	2220	—	*(5)*
$HIrCl(\sigma$-$C_6Cl_5)CO(PPh_3)_2$	$IrClCO(PR_3)_2 + RLi +$ HCl	cr	238	—	2236/2015	—	*(261)*
$HIrCl(\sigma$-$C_6F_5)CO(PPh_3)_2$	—	w	147	—	2234/2041	—	*(261, 22)*
$HIrBr(C_6F_5)CO(PPh_3)_2$	—	w	—	—	2225/2041	—	*(21, 22)*
$HIrCl(C_6H_5)CO(PPh_3)_2$	—	w	274	—	2246/2041	—	*(21)*
$HIrCl(C_6F_5)CO(PPh_2Me)_2$	—	w	191	—	2226/2034	—	*(21)*
$HFIrClCO(PPh_3)_2$	$IrXCO(PPh_3)_2 + HX$	w	—	—	2240/2024	—	*(317)*
$HFIrBrCO(PPh_3)_2$	—	w	—	—	2230/2024	—	*(317)*
$HFIrICO(PPh_3)_2$	—	w	—	—	2200/2023	—	*(317)*
$HBrIrICO(PPh_3)_2$	—	w	—	—	2203/2023	—	*(317)*

(Continued)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HBrIrClCO(PPh_3)_2$	—	w	—	—	2239/2044	—	(*317, 32*)
$HIIrClCO(PPh_3)_2$	—	w	—	—	2240/2044	—	(*32*)
$HBrIrClCO(PPh_2Me)_2$	—	w	—	—	2218/2043	—	(*32*)
$HBrIrClCO[P(p\text{-}MeC_6H_4)_3]_2$	—	w	—	—	2220/2042	—	(*32*)
$HBrIrClCO(AsPh_3)_2$	—	w	—	—	2200/2043	—	(*317, 32*)
$HClIrBrCO(PPh_3)_2$	—	w	—	—	2226/2045	—	(*32*)
$HClIrBrCO(PPh_2Me)_2$	—	w	—	—	2208/2043	—	(*317, 32*)
$HClIrICO(PPh_3)_2$	—	w	—	—	2190/2046	—	(*32*)
$HClIrNCS(CO)(PPh_3)_2$	—	w	—	—	2237/2047	—	(*32*)
$HClIrNCO(CO)(PPh_3)_2$	—	w	—	—	2236/2045	—	(*32*)
$HClIrN_3(CO)(PPh_3)_2$	—	w	—	—	2238/2044	—	(*32*)
$HIrClCO(CN)(PPh_3)_2$	$IrClCO(PPh_3)_2$ + HX	c	275	19.4[m]	2145/2020	—	(*299*)
$HIrClCO(CF_3CO_2)(PPh_3)_2$	—	c	—	29.5[m]	2235/2034	—	(*299*)
$HIrClCO(ClO_4)(PPh_3)_2$	—	c	230	—	2231/2019	—	(*299*)
$HIrCO(CF_3CO_2)_2(PPh_3)_2$	—	w	210 (dec)	28.1[m]	2245/2040	—	(*299*)
$HIrClCO(SH)(PPh_3)_2$	$IrXCO(PPh_3)_2$ + RSH	y	245	26.6[m]	2225/2010	Unstable	(*299, 289, 165*)
$HIrClCO(SC_6H_4Me)(PPh_3)_2$	—	y	260	26.3[m]	2258/2022	—	(*299, 289*)
$HIrClCO(SC_6H_3SHMe)(PPh_3)_2$	—	y	—	25.4[m]	2222/2042	—	(*299*)
$HIrClCO(SPr^i)(PPh_3)_2$	—	y	—	—	2250/2040	—	(*165, 111*)
$HIrClCO(SPh)(PPh_3)_2$	—	y	236	26.6[m]	2263/2029	—	(*289, 165, 111*)
$HIrClCO(SEt)(PPh_3)_2$	—	y	—	—	2240/2045	—	(*111*)
$HIrClCO(SBu^n)(PPh_3)_2$	—	y	—	—	2240/2045	—	(*111*)

$HIrClCO(Scy)(PPh_3)_2$	—	y	—	—	2260/2045	—	(111)
$HIrClCO(SC_6H_4NO_2)(PPh_3)_2$	—	y	188	26.5[m]	2249/2056	—	(289)
$HIrClCO(SC_6H_4Br)(PPh_3)_2$	—	y	244	26.6[m]	2260/2031	—	(289)
$HIrClCO(SC_6H_4Cl)(PPh_3)_2$	—	y	246	26.5[m]	2212/2033	—	(289)
$HIrClCO(SC_6H_4F)(PPh_3)_2$	—	y	235	26.6[m]	2260/2038	—	(289)
$HIrClCO(SC_6H_4OMe)(PPh_3)_2$	—	y	227	26.6[m]	2268/2023	—	(289)
$HIrBrCO(SC_6H_4NO_2)(PPh_3)_2$	—	y	—	25.04[m]	2241/2058	—	(115)
$HIrBrCO(SC_6H_4Br)(PPh_3)_2$	—	y	—	25.33[m]	2233/2045	—	(115)
$HIrBrCO(SC_6H_4Cl)(PPh_3)_2$	—	y	—	25.21[m]	2206/2033	—	(115)
$HIrBrCO(SC_6H_4F)(PPh_3)_2$	—	y	—	25.38[m]	2265/2037	—	(115)
$HIrBrCO(SPh)(PPh_3)_2$	—	y	—	25.51[m]	2253/2031	—	(115)
$HIrBrCO(SC_6H_4Me)(PPh_3)_2$	—	y	—	25.40[m]	2258/2030	—	(115)
$HIrBrCO(SC_6H_4OMe)(PPh_3)_2$	—	y	—	25.34[m]	2258/2027	—	(115)
$HIrICO(SC_6H_4NO_2)(PPh_3)_2$	—	y	—	23.04[m]	2214/2056	—	(115)
$HIrICO(SC_6H_4Br)(PPh_3)_2$	—	y	—	23.25[m]	2217/2043	—	(115)
$HIrICO(SC_6H_4Cl)(PPh_3)_2$	—	y	—	23.28[m]	2213/2045	—	(115)
$HIrICO(SC_6H_4F)(PPh_3)_2$	—	y	—	23.33[m]	2236/2037	—	(115)
$HIrICO(SPh)(PPh_3)_2$	—	y	—	23.33[m]	2226/2027	—	(115)
$HIrICO(SC_6H_4Me)(PPh_3)_2$	—	y	—	23.31[m]	2211/2042	—	(115)
$HIrICO(SC_6H_4OMe)(PPh_3)_2$	—	y	—	23.37[m]	2208/2043	—	(115)
$HIrClCO(SeH)(PPh_3)_2$	$IrClCO(PPh_3)_2 + RSeH$	y	160(dec)	—	2250/2018[h]	Air-sensitive	(165)
$HIrClCO(SePr^n)(PPh_3)_2$	—	y	240(dec)	16.63[m]	2220/2020[h]	—	(165)
$HIrClCO(SeBu^n)(PPh_3)_2$	—	y	235(dec)	16.62[m]	2236/2038[h]	—	(165)
$HIrClCO(SePh)(PPh_3)_2$	—	y	—	16.63[m]	2230/2021[h]	—	(165)
$HIrClCO(SeC_6H_4Me)(PPh_3)_2$	—	y	235(dec)	19.52[g]	2242/2028	—	(185)
$[HIrCN(CO)(PPh_3)_3]ClO_4$	$IrCN(CO)(PPh_3)_2$ + $EtOH + HClO_4$	c	—	—	2150, 2140/ 2055	—	(270)

(Continued)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[HIrClCO(PPhMe_2)_3]BPh_4$	$IrCOL_4 + HX$	w	152	19.2	2066/2047	—	(*87*)
$[HIrBrCO(PPhMe_2)_3]BPh_4$	—	w	130	19.74	2068/2047	—	(*87*)
$[HIrClCO(PPhMe_2)_2AsPhMe_2]BPh_4$	—	w	136	20.7	2099/2047	—	(*87*)
$[HIrClCO(AsPhMe_2)_3]BPh_4$	$HIrCl_2COL_2 + L +$ $MeOH + BPh_4^-$	w	—	—	2125/2039	—	(*140*)
$HIrClCO(PPh_3)_2(GeH_3)$	$IrClCO(PPh_3)_2 + R_3GeH$	w	—	—	2225, 2120/ 1970	—	(*96*)
$HIrClCO(PPh_3)_2(GeH_2Cl)$	—	w	—	27.14, 17.77[g]	2200, 2100/ 1990	—	(*96*)
$HIrClCO(PPh_3)_2(GeH_2Br)$	—	w	—	27.10[g]	2200, 2011/ 1997	—	(*96*)
$HIrClCO(PPh_3)_2(GeH_2I)$	—	w	—	26.97[g]	2100/2020	—	(*96*)
$HIrClCO(PPh_3)_2(GeH_5)$	—	w	—	27.6[g]	2200/1970	—	(*96*)
$HIrClCO(PPh_3)(GePh_3)$	—	w	157	18.50[e]	2083/1968[h]	—	(*96*)
$HIrClCO(PPh_3)_2(SiH_3)$	$IrXCO(PPh_3)_2 + R_3SiH$	w	—	—	2130/1980	—	(*96*)
$HIrClCO(PPh_3)_2(SiH_2Cl)$	—	w	—	—	2180, 2040/ 1995, 1980	—	(*96*)
$HIrClCO(PPh_3)_2(SiH_2Br)$	—	w	—	—	2180/1990	—	(*96*)
$HIrClCO(PPh_3)_2(SiH_2I)$	—	w	—	—	2170, 2040/ 1990, 1980	—	(*96*)
$HIrClCO(PPh_3)_2(SiHMeCl)$	—	w	—	—	2020/1975	—	(*96*)
$HIrBrCO(PPh_3)_2(SiH_2Cl)$	—	w	—	—	2165, 2030/ 1993, 1978	—	(*96*)
$HIrClCO(PPh_3)_2(SiMe_2Cl)$	—	w	—	—	2110/2002, 1995	—	(*151*)

$HIrClCO(PPh_3)_2Si(OEt)_3$	—	w	—	—	2085, 2077/ 1972, 1965	—	(*151*)
$HIrClCO(PPh_3)_2(SiMeCl_2)$	—	w	—	—	2118, 2100/ 1989, 1981	—	(*151*)
$HIrClCO(PPh_3)_2(SiCl_3)$	—	w	—	—	2105, 2100/ 1998, 1988	—	(*151*)
$HIrClCO(PPh_3)_2(SiF_3)$	—	w	—	—	2103, 2085/ 1990, 1975	—	(*151*)
$HIrBrCO(PPh_3)_2(SiMe_2Cl)$	—	w	—	—	2110/2001, 1995	—	(*151*)
$HIrBrCO(PPh_3)_2Si(OEt)_3$	—	w	—	—	2077/1970	—	(*151*)
$HIrBrCO(PPh_3)_2(SiMeCl_2)$	—	w	—	—	2119, 2103/ 1989, 1983	—	(*151*)
$HIrBrCO(PPh_3)_2(SiCl_3)$	—	w	—	—	2092/1986	—	(*151*)
$HIrBrCO(PPh_3)_2(SiF_3)$	—	w	—	—	2107/2002, 1996	—	(*151*)
$HIrCO(PPh_3)_2(C_6F_5)(SiCl_3)$	—	w	325	—	2244, 2212/ 2047, 2035	—	(*21*)
$HIrCl(PPh_3)_3(SnCl_3)$	$IrCl_6^{2-} + SnCl_2 +$ L + EtOH	o–y	132	24.7, 30.3, 31.4	2155[f]	—	(*309*)
$HIrClCO(PPh_3)_2(SnCl_3)$	$IrClCO(PPh_3)_2 +$ $SnCl_2 + Me_2CO$	y	155	19.9	2148/2053[f]	—	(*309*)
$HIrClCO(PPh_3)_2(SnMe_3)$—II	$IrXCO(PPh_3)_2 + R_3SnH$	y	—	18.8[g]	2080/1963[h]	—	(*207*)
$HIrClCO(PPh_3)_2(SnMe_3)$—I	—	w	—	—	2093/1998[h]	—	(*207*)
$HIrClCO(PPh_3)_2(SnEt_3)$—II	—	y	—	20.4[g]	2067/1955	—	(*207*)
$HIrClCO(PPh_3)_2(SnPh_3)$—I	—	w	—	—	2138/1998	—	(*207*)
$HIrClCO(PPh_2Me)_2(SnMe_3)$—I	—	w	—	—	2065/1980	—	(*207*)
$HIrClCO(PPh_2Me)_2(SnPh_3)$—I	—	w	—	15.3[g]	2073/2005[h]	—	(*207*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIrClCO(PPhEt_2)_2(SnPh_3)$—I, II,	—	w	—	—	2082, 2047/ 2002, 1990	—	(*207*)
$HIrBrCO(PPh_3)_2(SnMe_3)$—II	—	—	—	—	2080/1963[h]	—	(*207*)
$HIrBrCO(PPh_3)_2(SnPh_3)$—I	—	w	—	—	2138/1998	—	(*207*)
$HIrICO(PPh_3)_2(SnPh_3)$—I	—	y	—	—	2140/1997	—	(*207*)
$HIrCO(PPh_3)_2$(fumn)	$HIrCOL_3$ + olefin	w	232	—	2115/1995[c]	—	(*108*)
$HIrCO(AsPh_3)_2$(fumn)	—	w	190	—	2094/1982[c]	—	(*108*)
$HIrCO(PPh_3)_2$(CINN)	—	w	145	—	2108/1974[c]	—	(*108*)
$HIrCO(PPh_3)_2$(BMN)	—	w	135	—	2116/1992[c]	—	(*108*)
$HIrCO(PPh_3)_2$(FUMA)	—	w	192	—	2123/1992[o]	—	(*108*)
$HIrCO(PPh_3)_2$(DFUM)	—	y	—	—	2105/1979[o]	—	(*108*)
$[HIr(CNBu^t)_3(PPh_3)_2](PF_6)_2$	$Ir(CNR)_3(PPh_3)_2 + HPF_6$	w	—	20.90[p]	—	—	(*81*)
$[HIr\{CN(p\text{-}MeC_6H_4)\}_3(PPh_3)_2](PF_6)_2$	—	w	—	27.04[p]	—	—	(*81*)
$[HIr\{CN(p\text{-}ClC_6H_4)\}_3(PPh_3)_2](PF_6)_2$	—	w	—	19.71[p]	—	—	(*81*)
$HIrCl(PPh_3)_2[P(O)(OMe)_2][P(OH)(OMe)_2]$	$[IrCl(C_8H_{14})_2]_2 + MPh_3 + (CH_3O)_2P(O)H$	—	—	19.49[m]	2180	—	(*20*)
$HIrCl(AsPh_3)_2[P(O)(OH)_2][P(OH)_3]$	—	—	—	31.26[m]	2200	—	(*20*)
$HIrClCO(PPh_3)_2(MeCO_2)$	$HIrCl(PPh_3)_2(RCO_2)$ + L	w	235 (dec)	—	2135	—	(*302*)
$HIrClCO(PPh_3)_2(EtCO_2)$	—	w	228 (dec)	—	2115	—	(*302*)
$HIrClCO(PPh_3)_2(PhCO_2)$	—	w	260 (dec)	—	2145	—	(*302*)
$HIrClCO(PPh_3)_2(HCO_2)$	—	w	235 (dec)	—	2145	—	(*302*)
$HIrClCO(PPh_3)_2(Pr^nCO_2)$	—	w	—	—	2145	—	(*302*)
$HIrClCO(PPh_3)_2(MeCHClCO_2)$	—	w	—	—	2120, 2105	—	(*302*)
$HIrCl(PPh_3)_2(C_5H_5N)(MeCO_2)$	—	—	157 (dec)	—	2254	—	(*302*)

$HIrCl(PPh_3)_2(C_5H_5N)(EtCO_2)$	—	—	150 (dec)	—	2269	—	(*302*)
$HIrCl(PPh_3)_2(PhCN)(Pr^nCO_2)$	—	—	—	—	2238	—	(*302*)
$HIrCl(PPh_3)_2PPhMe_2(PhCO_2)$	—	—	151 (dec)	—	2242	—	(*302*)
$HIrCl(PPh_3)_2(p\text{-}MeC_6H_4NC)(MeCO_2)$	—	—	—	—	2180	—	(*302*)
$HIrCl(PPh_3)_2(C_5H_5N)(PhCO_2)$	—	—	—	—	2256	—	(*302*)
$HIrCl(PPh_3)_2(PhCN)(MeCO_2)$	—	—	—	—	2201	—	(*302*)
$HIrCl(PPh_3)_2(MeCO_2)$	$IrCl(PPh_3)_2N_2$ + RCOOH	y	187 (dec)	—	2304	—	(*302*)
$HIrCl(PPh_3)_2(EtCO_2)$	—	y	—	—	2293	—	(*302*)
$HIrCl(PPh_3)_2(Pr^nCO_2)$	—	y	169 (dec)	—	2293	—	(*302*)
$HIrCl(PPh_3)_2(PhCO_2)$	—	y	156 (dec)	—	2242	—	(*302*)
$HIrCl(PPh_3)_2(HCO_2)$	—	y	161 (dec)	—	2304	—	(*302*)
$HIrCl(PPh_3)_2(CF_3CO_2)$	—	y	136 (dec)	—	2221	—	(*302*)
$HIrCl(PPh_3)_2(C_2F_5CO_2)$	—	y	—	24.3, 26.3, 28.2, 29.8[m]	2232	—	(*299*)
$HIrCO(PPh_3)_2[(CF_3)_2CS]$	$HIrCO(PPh_3)_3 + (CF_3)_2CS$	w	145	20.51[m]	2173/2014	—	(*72*)
$[HIr(C_5H_5)CO(PPh_3)_3]BPh_4$	$C_5H_5IrCO(PPh_3)_3$ + HBr + BPh_4^-	w	155	—	2442/2063	—	(*248*)
$[HIr(C_5H_5)(PPh_3)_2]I$	$C_5H_5Ir(PPh_3)I_2 + PPh_3$ + isopropanol	c	194	24.4	2150	—	(*333*)
$[HIr(C_5H_5)CO(PPh_3)]PF_6$	$C_5H_5IrCO(PPh_3)$ + MeOH + $NOPF_6$	y	85	—	2142/2050	—	(*102*)
$[HIr(C_5H_5)CO(PPh_3)]BPh_4$	—	w	80	—	2140/2048	—	(*102*)
$[HIrClCO(PPh_3)_2\{CN(Me)C(Me)CHS\}]BF_4$	$[IrCO\{CN(Me)C(Me)CHS\}(PPh_3)_2]^+$ + HX	w	200 (dec)	25.5[m]	2251/2050	—	(*109*)
$[HIrBrCO(PPh_3)_2\{CN(Me)C(Me)CHS\}]BF_4$	—	w	190 (dec)	24.59[m]	2279/2063	—	(*109*)
$HIrCl[C_2B_{10}H_{10}PMe_2](C_2B_{10}H_{11}PMe_2)_2$	$[Ir(C_8H_{14})_2Cl]_2$ + L	w	—	30.9	2230	—	(*160*)
$HIrOMe[P(OPh)_2\text{—}(OC_6H_4)][P(OPh)_3]_2$	$HIrX_2(C_8H_{12})]_2 + P(OR)_3$	—	—	18.66[e]	2070	—	(*1*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$HIrCl[P(OPh)_2—(OC_6H_4)][P(OPh)_3]_2$	—	—	—	19.32[e]	2080	—	(*1*)
$HIrCl[P(OPh)_2—(OC_6H_4)][P(OPh)_3]_2$	—	—	—	19.82[e]	2070	—	(*1*)
$HIrCl[P(O\text{-}p\text{-tolyl})_2—(O\text{-}p\text{-}C_6H_4Me)]\text{-}[P(O\text{-}p\text{-tolyl})_3]_2$	—	—	—	19.38[e]	2070	—	(*1*)
$HIrBr[P(O\text{-}p\text{-tolyl})_2—(O\text{-}p\text{-}C_6H_4Me)]\text{-}[P(O\text{-}p\text{-tolyl})_3]_2$	—	—	—	1981[e]	2080	—	(*1*)
$HIrI[P(O\text{-}p\text{-tolyl})_2—(O\text{-}p\text{-}C_6H_4Me)]\text{-}[P(O\text{-}p\text{-tolyl})_3]_2$	—	—	—	20.64[e]	—	—	(*1*)
$HIrCl[P(O\text{-}m\text{-tolyl})_2—(O\text{-}m\text{-}C_6H_4Me)]\text{-}[P(O\text{-}m\text{-tolyl})_3]_2$	—	—	—	—	2080	—	(*1*)
$HIrBr[P(O\text{-}m\text{-tolyl})_2—(O\text{-}m\text{-}C_6H_4Me)]\text{-}[P(O\text{-}m\text{-tolyl})_3]_2$	—	—	—	19.77[e]	2070	—	(*1*)
$HIrCl[P(O\text{-}o\text{-tolyl})_2—(O\text{-}o\text{-}C_6H_4Me)]\text{-}[P(O\text{-}o\text{-tolyl})_3]_2$	—	—	—	19.52[e]	2090	—	(*1*)
$HIrBr[P(O\text{-}o\text{-tolyl})_2—(O\text{-}o\text{-}C_6H_4Me)]\text{-}[P(O\text{-}o\text{-tolyl})_3]_2$	—	—	—	19.98[e]	2090	—	(*1*)
$HIrCl[P(O\text{-}p\text{-}PhCl)_2—(O\text{-}p\text{-}C_6H_4Cl)]\text{-}[P(O\text{-}p\text{-}PhCl)_3]_2$	—	—	—	19.80[e]	2080	—	(*1*)
$HIrBr[P(O\text{-}p\text{-}PhCl)_2—(O\text{-}p\text{-}C_6H_4Cl)]\text{-}[P(O\text{-}p\text{-}PhCl)_3]_2$	—	—	—	—	2070	—	(*1*)
$HIrCl[PPh_2C_6H_4](PPh_3)_2$	$IrCl(PPh_3)_3$	c	—	—	2190	—	(*1*)
$HIrCl_2(PPhMe_2)_3HgCl_2$	$HIrX_2L_3 + HgX_2$	c	285	—	2219	—	(*37*)
$HIrI_2(PPhMe_2)_3HgCl_2$	—	y	108	—	2183	—	(*37*)
$HIrCl_2(PPhEt_2)_3HgCl_2$	—	w	135	—	2275	—	(*37*)
$HIrBr_2(PPhEt_2)_3HgCl_2$	—	cr	152	—	2215	—	(*37*)
$[HIrBrPPh_3P(o\text{-}C_6H_4PPh_2)_3]BPh_4$	$HIrBr_2(PPh_3)_3 + L$	y	—	27.2	—	—	(*83*)

$[H\{Ir(C_5Me_5)\}_2(OH)(MeCO_2)]PF_6$	$[Ir(C_5Me_5)X_2]_2 + H_2$	o	30	20.28	—	—	(*323*)
$[H\{Ir(C_5Me_5)\}_2(OH)(CF_3CO_2)]CF_3CO_2$	—	o	159	20.26	—	—	(*323*)
$[H\{Ir(C_5Me_5)\}_2Cl_3]$	—	r	—	23.55[g]	1155	Air-stable	(*323, 324*)
$[H\{Ir(C_5Me_5)\}_2(CF_3CO_2)_2]CF_3CO_2H$	—	y	169	20.46	—	—	(*323*)
$[H\{Ir(C_5Me_5)\}_2(MeCO_2)_2]CH_3CO_2H$	—	y	—	21.47	—	—	(*323*)
$[H\{Ir(C_5Me_5)\}_2(CF_3CO_2)_2]PF_6$	—	y	227	20.42	—	—	(*323*)
$[H\{Ir(C_5Me_5)\}_2(MeCO_2)_2]PF_6$	—	y	—	21.65	—	—	(*323*)
$[HIr_4(CO)_{11}]^-$	$Ir_4(CO)_{12} + K_2CO_3 +$ MeOH + CO	y	—	5.5	2065, 2015, 1965, 1800[q]	—	(*221*)
$[H_2Ir(PPh_3)_2]ClO_4$	$H_3Ir(PPh_3)_2 + HClO_4$	w	152	—	2315, 2280	—	(*219*)
$[H_2Ir(PPh_2Me)_3]ClO_4$	$H_3IrL_3 + HClO_4$	w	149	—	2293, 2147	—	(*4*)
$[H_2Ir(PPh_3)_3]ClO_4$	—	w	139	—	2249, 2140	—	(*131*)
$[H_2Ir(AsPh_3)_3]ClO_4$	—	w	120 (dec)	—	2222, 2141	—	(*131*)
$H_2IrCN(PPh_3)_2$	—	—	231	—	2180, 2090	—	(*131*)
$[H_2IrCO(PPh_3)_2]ClO_4$	$HIrCO(PPh_3)_2 + HClO_4$	y	103	—	2165/2085, 2050	—	(*219*)
$H_2IrCl(PPh_3)_2$	—	w	172	19.9, 22.3, 30.2	2162, 2112	—	(*309*)
$H_2IrI(PPh_3)_2$	$[H_2Ir(PPh_3)_2]ClO_4$ + NaI	—	167	—	2220	—	(*219*)
$[H_2Ir(PPh_3)_4]ClO_4$	—	w	207 (dec)	—	2250, 2225	—	(*131*)
trans-$[H_2Ir\{PPh(OMe)_2\}_4]BPh_4$	$[IrL_5]^+ + H_2$	c	—	19.33[m]	1805	—	(*74*)
trans-$[H_2Ir(PPh_2OMe)_4]BPh_4$	—	c	—	19.3[m]	—	—	(*74*)
cis-$[H_2Ir\{PPh(OMe)_2\}_4]BPh_4$	—	c	—	22.7[m]	—	—	(*74*)
cis-$[H_2Ir(PPh_2OMe)_4]BPh_4$	—	c	—	22.1[m]	—	—	(*74*)
cis-$[H_2Ir\{PPh(OEt)_2\}_4]BPh_4$	—	c	—	22.8[m]	—	—	(*74*)
cis-$[H_2Ir(PPh_2OEt)_4]BPh_4$	—	c	—	22.3[m]	—	—	(*74*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[H_2Ir\{P(OPh)_3\}_4]Cl$, Br, I, ClO_4, or NO_3	$HIr(P(OPh)_3)_4 + HX$	w	113	19.8[f]	2050[f]	—	*(125)*
cis-$[H_2Ir(PBu_3{}^n)_4]BPh_4$	$[IrClC_8H_{12}]_2 + PR_3 + EtOH + BPh_4{}^-$	w	160	23.3[m]	—	—	*(139)*
cis-$[H_2Ir(PPhEt_2)_4]BPh_4$	—	w	160	23.8[m]	—	—	*(139)*
cis-$[H_2Ir(dp)_2]Cl$, Br, I, ClO_4, or BPh_4	$[Ir(p\text{-}p)_2]Cl + H_2$	w	160	—	2080, 2060	—	*(93)*
cis-$[H_2Ir(dppe)_2]BPh_4$	—	w	220 (dec)	—	2091, 2080	—	*(318)*
$[H_2Ir(PPh_3)_2(dppe)]ClO_4$	—	—	182 (dec)	—	2150, 2100	—	*(131)*
$H_2Ir(dpt)(PPh_3)_2$	$H_3Ir(PPh_3)_3$ + dpt	r	—	31.89[g]	2164, 2140	Air-stable	*(272)*
$H_2Ir(PPh_3)_2(MeO)_2PS_2$	H_3IrL_3 + chelate	w	195 (dec)	30.0[m]	2210,2143	—	*(6)*
$H_2Ir(PPh_3)_2(EtO)_2PS_2$	—	w	188 (dec)	30.4[m]	2190, 2127	—	*(6)*
$H_2Ir(PPh_3)_2(p\text{-}ClPhO)_2PS_2$	—	w	199 (dec)	30.8[m]	2185, 2136	—	*(6)*
$H_2Ir(AsPh_3)_2(EtO)_2PS_2$	—	w	181 (dec)	24.4[m]	2115, 2085	—	*(6)*
$H_2Ir(PPh_3)_2Et_2PS_2$	—	w	185 (dec)	31.7[m]	2242, 2140	—	*(6)*
$H_2Ir(PPh_3)_2Ph_2PS_2$	—	w	183 (dec)	32.2[m]	2160, 2131	—	*(6)*
$H_2Ir(AsPh_3)_2Et_2PS_2$	—	w	176 (dec)	24.5[m]	2200, 2120	—	*(6)*
$H_2Ir(PPh_3)_2$acac	—	w	198	34.7[g]	2180, 2140	Air-stable	*(7)*
$H_2Ir(PPh_3)_2$tfac	—	y	198	35.7, 35.2[g]	2220, 2180	—	*(7)*
$H_2Ir(PPh_3)_2$hfac	—	o	213	36.2[g]	2220, 2180	—	*(7)*
$H_2Ir(AsPh_3)_2$acac	—	w	214	37.4[g]	2155, 2100	—	*(7)*
$H_2Ir(AsPh_3)_2$tfac	—	y	194	38.05[g]	2170, 2145	—	*(7)*
$H_2Ir(AsPh_3)_2$hfac	—	o	217	38.7[g]	2200, 2180	—	*(7)*
$H_2Ir(PPh_3)_2[S_2CN(Et)_2]$	$H_3IrL_2 + NaS_2CN(Et)_2$	y	193	29.5[m]	2125, 2085	Air-stable	*(8)*
$H_2Ir(AsPh_3)_2[S_2CN(Et)_2]$	—	y	198	31.0[m]	2085, 2045	—	*(8)*
$H_2Ir(PPh_3)_2[S_2CO(Et)_2]$	—	y	190	29.2[m]	2150, 2000	—	*(8)*

$H_2Ir(AsPh_3)_2[S_2CO(Et)_2]$	—	y	199	30.4[m]	2095, 2065	—	(8)
$[H_2Ir(PPh_3)_2(Me_2CO)_2]^+$	$[IrC_8H_{12}(PPh_3)_2]^+$ + $Me_2CO + H_2$	—	—	—	2260, 2230	Catalyst	(292)
$[H_2Ir(PPh_3)_2(py)_2]ClO_4$	—	—	224	—	2155, 2150	—	(131)
$[H_2Ir(CO)_2(PPh_3)_2]BPh_4$	$[Ir(CO)_3L_2]^+ + H_2$	y	—	19.8[m]	2169, 2151, 2083, 2041[f]	—	(62)
$[H_2Ir(CO)_2(AsPh_3)_2]BPh_4$	—	—	—	20.5[m]	2154, 2136, 2074, 2032[f]	—	(62)
$[H_2Ir(CO)_2(PPh_2Me)_2]BPh_4$	—	w	—	20.4[m]	2157, 2143, 2077, 2042[f]	—	(62)
$[H_2Ir(CO)_2(PPh_2Et)_2]BPh_4$	—	—	—	20.5[m]	2158, 2143, 2078, 2039[f]	—	(62)
$[H_2Ir(CO)_2(PPhEt_2)_2]BPh_4$	—	—	—	21.0[m]	2153, 2140, 2072, 2036[f]	—	(62)
$[H_2Ir(CO)_2(PEt_3)_2]BPh_4$	—	—	—	21.4[m]	2153, 2140, 2072, 2035[f]	—	(62)
$[H_2Ir(CO)_2\{P(C_6H_{11})_3\}_2]BPh_4$	—	—	—	21.5[m]	2144, 2068, 2027[f]	—	(62)
$[H_2Ir(CO)_2(PPr_3{}^i)_2]BPH_4$	—	—	—	21.8[m]	2172, 2150, 2070, 2030[f]	—	(62)
$[H_2Ir(CO)_2(PPh_2Bu^t)_2]BF_4$	—	w	149	—	2180, 2160/ 2082, 2060, 2050[c]	—	(255)

(Continued)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$[H_2Ir(CO)_2(PPh_3)_2]PF_6$	$HIr(CO)_2(PPh_3)_2 + H^+$	y	—	—	2180, 2155/ 2085, 2050[h]	—	(*70*)
$[H_2Ir(CO)CS\{P(C_6H_{11})_3\}_2]ClO_4$	$[Ir(CO)_2CS\{P(C_6H_{11})_3\}_2]^+ + H_2$	w	—	24.05, 19.95[m]	2151, 2143, 2129/2038	—	(*229*)
$H_2IrCl(PPh_3)_3$	$IrCl(MPh_3)_3 + H_2$	c	250	—	2215, 2110	Light-sensitive	(*19*)
$H_2IrCl(AsPh_3)_3$	—	c	—	—	2160, 2120	Light-sensitive	(*19*)
$H_2IrCl(SbPh_3)_3$	—	c	—	—	2090	Light-sensitive	(*19*)
$H_2IrI(PPh_3)_3$	$H_2IrCl(PPh_3)_3 + NaI$	w	226	—	2157[h]	Light-sensitive	(*127*)
$H_2IrI(PPh_3)_3$	—	cr	197	—	2222, 2083	—	(*127*)
cis-$H_2IrCl(PPhEt_2)_3$	$IrCl_3L_3 + KOH/EtOH$	w	132	31.5, 18.6[g]	2178, 2018	—	(*176, 59*)
cis-$H_2IrCl(PPhMe_2)_3$	—	c	122	32.0, 20.1[g]	2204, 2010	—	(*59, 177*)
cis-$H_2IrCl(AsPhEt_2)_3$	—	y	105	35.0, 24.3[g]	2159, 2061	—	(*59*)
cis-$H_2IrCl(PPh_2Me)_3$	—	w	206	20.09[m]	2191, 2059	—	(*4*)
cis-$H_2IrCl(PPh_2Et)_3$	—	w	166	21.5[e]	2225, 2100	—	(*4*)
cis-$H_2IrBr(PPhEt_2)_3$	$IrCl_3L_3 + KOH/EtOH + LiBr$	w	132	32.4, 21.8[g]	2179, 2020	—	(*176, 59, 177*)
cis-$H_2IrBr(PPh_2Me)_3$	—	w	206	—	2218, 2069	—	(*4*)
cis-$H_2IrI(PPhEt_2)_3$	$IrCl_3L_3 + KOH/EtOH + NaI$	w	120	—	2162, 2023	—	(*176, 59*)
$H_2IrBr(PPh_3)_3$	—	w	242(dec)	—	2240, 2090	—	(*131*)
$H_2IrBr(AsPh_3)_3$	—	—	234(dec)	—	2188	—	(*131*)
$[H_2IrNH_3(PPh_3)_3]ClO_4$	—	—	233(dec)	—	2152, 2148	—	(*131*)
$H_2IrNO_2(PPh_3)_3$	—	c	141	—	2180, 2130	—	(*131*)

$H_2IrCl(Me_2SO)_3$	$[IrCl_4(Me_2SO)_2]^- +$ Me_2SO + propanol + H_2O	w	164	29.5, 26.3[m]	2250, 2170	—	(*137*)
$H_2Ir(PPh_3)_3(MeCO_2)$	$H_3Ir(PPh_3)_3$ + RCOOH	c	150	33.6, 21.1[m]	2198, 2157	—	(*273*)
$H_2Ir(PPh_3)_3$(*p*-$MeC_6H_4CO_2$)	—	c	170	33.6, 20.52[m]	2178	—	(*273*)
$H_2Ir(PPh_3)_3$(*p*-$ClC_6H_4CO_2$)	—	c	151	33.75, 20.62[m]	2192	—	(*273*)
$H_2Ir(PPh_3)_3$(*p*-$NO_2C_6H_4CO_2$)	—	y	164	33.90, 20.61[m]	2176	—	(*273*)
$H_2Ir(PPh_3)_3(MeCO_2)$	—	w	167	—	2200, 2150	—	(*131*)
$H_2Ir(PPh_3)_3(OCOCOOH)$	—	w	184	—	2260, 2210	—	(*131*)
$H_2Ir(PPh_3)_3(OCOCH_2COOH)$	—	w	157	—	2180, 2160	—	(*131*)
$[H_2IrCO(PPh_3)_2\{\overline{CN(Me)C(Me)CHS}\}]BF_4$	$[IrCO(PPh_3)_2L]^+ + H_2$	w	170(dec)	22.69, 19.53[m]	2135, 2057/ 2011	—	(*109*)
cis-$[H_2Ir(PPh_3)_3NHNC_6H_4OMe]BPh_4$	$H_3Ir(PPh_3)_3$ + $[Ar{-}N{\equiv}N]^+$	y	132	28.9, 21.52[m]	2150	—	(*48*)
cis-$[H_2Ir(PPh_3)_3NHNC_6H_4OMe]BPh_4$	—	y	169	—	2210, 2120	—	(*48*)
cis-$[H_2Ir(PPh_3)_3NHNC_6H_4Me]BPh_4$	—	y	133	—	2130	—	(*48*)
cis-$[H_2Ir(PPh_3)_3NHNC_6H_4N(Me)_2]BPh_4$	—	y	75	—	2130	—	(*48*)
$[H_2IrCO(PPh_3)_3]ClO_4$	$HIrCO(PPh_3)_3 + HClO_4$	w	137	—	2155, 2118/ 2011	—	(*315, 219, 40, 146*)
cis-$[H_2IrCO(PPhMe_2)_3]BPh_4$	$[IrCOL_4]^+ + H_2$	w	117	22.8, 19.6	2088, 2047/ 1978	—	(*87*)
$[H_2IrCO(PPh_2Me)_3]BPh_4$	$[Ir(CO)_2L_3]^+ + H_2$	w	—	—	2115, 2085/ 2013[f]	—	(*62*)
$H_2IrCO(PPh_3)_2(C_2F_5CO_2)$	$HIrCO(PPh_3)_3$ + C_2F_5COOH	w	80	—	2148, 2100/ 2000	—	(*72*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_2IrClCO(PPh_3)_2$	$IrXCOL_2 + H_2$	y	315(dec)	28.4, 17.3	2222, 2098/ 2010[f]	—	(*309*)
$H_2IrBrCO(PPhEt_2)_2$	—	c	—	28.29, 18.73[g]	2196, 2100/ 1975	—	(*88*)
$HDIrBrCO(PPhEt_2)_2$	—	c	—	28.30, 18.75[g]	2188, 2090/ 2014, 1980	—	(*88*)
$H_2IrClCO(PPhMe_2)_2$	—	c	—	28.36, 17.58[g]	2169, 2067/ 1961	—	(*88*)
$H_2IrClCO(PEt_3)_2$	—	y	62	29.45, 18.27[e]	2193, 2081/ 1967[h]	—	(*127*)
$H_2IrICO(PEt_3)_2$	—	y–gr	114	27.50, 20.20[e]	2159, 2080/ 1975[h]	—	(*127*)
$H_2IrBrCO(PPh_3)_2$	—	cr	—	—	2232, 2073/ 2028[h]	—	(*127*)
$H_2IrICO(PPh_3)_2$	—	c	242	—	2092, 2045/ 1987[h]	—	(*127*)
cis-$H_2IrClCO(PBu^tMe_2)_2$	—	w	137	28.84, 18.98[g]	2183, 2066/ 1965[g]	—	(*296*)
cis-$H_2IrClCO(PBu^tEt_2)_2$	—	w	148(dec)	29.91, 18.54[g]	2186, 2083/ 1976[g]	—	(*296*)
cis-$H_2IrClCO(PBu^tPr_2^n)_2$	—	y	—	29.39, 18.16[g]	2182, 2085/ 1988[g]	—	(*296*)
cis-$H_2IrClCO(PBu^tBu_2^n)_2$	—	y	—	29.34, 18.22[g]	—	—	(*296*)
cis-$H_2IrBrCO(PBu^tMe_2)_2$	—	w	—	28.16, 18.74[g]	2186, 2070/ 1965[g]	—	(*296*)

cis-$H_2IrCO(PBu^tPr_2^n)_2$	—	y	—	28.72, 18.84[g]	2174, 2079/ 1968[g]	—	(*296*)
$H_2Ir(C_6F_5)CO(PPh_3)_2$	$Ir(C_6F_5)(CO)(PPh_3)_2$ + $NaBH_4$	w	169	—	2164/2024, 2004	—	(*21*)
$H_2IrCl(AsPh_3)_2$(*p*-totyl NC)	$H_3Ir(RNC)(AsPh_3)_2$ + HX + EtOH	w	173(dec)	19.6, 19.5	2185, 2140	Air-stable	(*9*)
$H_2IrBr(AsPh_3)_2$(*p*-tolyl NC)	—	y	185(dec)	20.11, 20.01	2185, 2140	—	(*9*)
$H_2IrI(AsPh_3)_2$(*p*-tolyl NC)	—	w	187(dec)	21.2, 21.1	2165, 2145	—	(*9*)
$H_2IrF(AsPh_3)_2$(*p*-tolyl NC)	—	y	143(dec)	19.68, 19.58	2150	—	(*9*)
$H_2IrN_3(AsPh_3)_2$(*p*-tolyl NC)	—	w	172(dec)	23.5, 19.8	2135, 2020	—	(*9*)
$H_2IrCO(PPh_3)_2(GeMe_3)$	$IrXCOL_2 + R_3GeH$	w	153	20.50, 19.50[e]	2123, 2071/ 1956[h]	Crystal	(*127*)
$H_2IrCO(PPh_3)_2(GeEt_3)$	—	c	148	20.86, 19.77[e]	2119, 2081/ 1953[h]	—	(*128*)
$H_2IrCO(PPhMe_2)_2(GeMe_3)$	—	y	—	—	2045, 2000, 1978, 1943	—	(*128*)
$H_2IrCO(PEt_3)_2(GeMe_3)$	—	y	—	21.80, 21.31[e]	2058, 1948, 1914[h]	—	(*128*)
$H_2IrCO(dppe)(GeEt_3)$	—	w	196	20.82, 20.04[e]	2070, 1951, 1902[h]	—	(*128*)
$H_2IrCO(PPh_3)_2(GeCl_3)$	—	w	184	—	2084, 2065, 2055[h]	—	(*128*)
$H_2IrCO(PPh_3)_2(SiMe_3)$	$HIrCO(PPh_3)_3 + R_3SiH$	—	—	20.39, 19.36[e]	2094, 2082/ 1978[g]	Stable	(*128, 147*)
$H_2IrCO(PPh_3)_2(SiCl_3)$	—	w	284	—	2148, 2128/ 2018	—	(*128, 147*)
$H_2IrCO(PPh_3)_2(SiCl_2Me)$	—	w	>300	—	2117/2010[h]	—	(*147*)
$H_2IrCO(PPh_3)_2Si(OEt)_3$	—	w	152	21.5, 20.2	2142, 2108/ 1995[h]	—	(*147*)

(*Continued*)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
$H_2IrCO(PPh_3)_2(SiPh_3)$	—	—	160(dec)	20.7, 19.5	2134, 2075/ 1963[h]	—	(*147*)
$H_2IrCO(PPh_3)_2(SiPhMe_2)$	—	—	—	21.0, 20.0	2080/1963[h]	—	(*147*)
$H_2IrCO(PPh_3)_2(SiHCl_2)$	—	w	—	20.6, 19.58	2100, 2080/ 1990	—	(*196*)
$H_2IrCO(PPh_3)_2(SnMe_3)$	$HIrCO(PPh_3)_2 + HSnMe_3$	w	146	21.04, 20.06[e]	2098, 2063/ 1974[r]	—	(*128*)
$H_2IrCO(PPh_3)_2(SnCl_3)$	$H_2IrClCOL_2 + SnCl_2$	y	191	22.5, 19.9	2112, 2104/ 2062[f]	—	(*309*)
$H_2Ir(PPh_3)_3(SnCl_3)$	$IrCl_6{}^{2-} + SnCl_2 +$ EtOH	w	206	24.7, 23.0, 21.3	2262, 2205[f]	—	(*309*)
$H_2Ir_2Cl_2(PPh_3)_2(COD)$	$IrClC_8H_{12}(PPh_3) + H_2$	y	195(dec)	35.88[m]	2230, 2210	Stable	(*114*)
$[HIrCl_2(COD)]_2$	$IrCl_3$ + COD + EtOH	y	198(dec)	—	2256	—	(*2, 308, 274*)
$[HIrBr_2(COD)]_2$	$IrBr_6{}^{2-}$ + HX + COD	cr	200(dec)	—	2239	—	(*274*)
$[HIrI_2(COD)]_2$	—	br	—	—	2188	—	(*274*)
$[HIrCl_2CO(PEt_3)]_2$	$IrCl_6{}^{3-}$ + HCl + L	c	170(dec)	—	2242/2058	—	(*54*)
$[HIrCl_2CO(PPh_3)]_2$	$[Ir(CO)_3PPh_3]^+ + HX + C_6H_6$	w	—	—	2250/2060	—	(*222*)
$[HIrBr_2CO(PPh_3)]_2$	—	w	—	—	2215/2040	—	(*222*)
$[HIrCl(PPh_3)_2SC_6H_4Br]_2$	$IrClL_3$ + ArSH	y	199(dec)	—	2231[f]	Air-stable	(*154*)
$[HIrCl(PPh_3)_2SC_6H_4F]_2$	—	y	223(dec)	—	2234, 2210[f]	—	(*154*)
$[HIrCl(PPh_3)_2SPh]_2$	—	y	172(dec)	—	2237[f]	—	(*154*)
$[HIrCl(PPh_3)_2SC_6H_4Me]_2$	—	y	187(dec)	—	2230[f]	—	(*154*)

$[HIrCl(PPh_3)_2SC_6H_4OMe]_2$	—	y	192(dec)	—	2222[f]	—	*(154)*
$[HIrCl(AsPh_3)_2SC_6H_4Br]_2$	—	y	197(dec)	—	2196[f]	—	*(154)*
$[HIrCl(AsPh_3)_2SC_6H_4F]_2$	—	y	175(dec)	21.36[m]	2203, 2192[f]	—	*(154)*
$[HIrCl(AsPh_3)_2SPh]_2$	—	y	176(dec)	21.36[m]	2202, 2184[f]	—	*(154)*
$[HIrCl(AsPh_3)_2SC_6H_4Me]_2$	—	y	172(dec)	21.37[m]	2194[f]	—	*(154)*
$[HIrCl(AsPh_3)_2SC_6H_4OMe]_2$	—	y	185(dec)	21.33[m]	2201, 2190[f]	—	*(154)*
$[H_2\{Ir(C_5Me_5)\}_2CF_3CO_2]PF_6$	$[Ir(C_5Me_5)X_2]_2 + H_2$	o–br	—	22.06	—	—	*(323)*
$[H_2\{Ir(C_5Me_5)\}_2CF_3CO_2]H(CF_3CO_2)_2$	—	r	145	22.67	—	—	*(323)*
$H_3Ir(PEt_3)_2$	$IrCl_3L_3 + LiAlH_4$	w	34	20.7[g]	1931	Could be H_5IrL_2	*(59)*
$H_3Ir(PPhEt_2)_2$	—	w	78(dec)	19.9[g]	1950	—	*(59)*
$H_3Ir(PPh_3)_2$	—	w	184(dec)	—	1948	—	*(219, 59)*
$H_3Ir(AsPh_3)_2$	—	w	143(dec)	—	1937	—	*(131)*
fac-$H_3Ir(PPhEt_2)_3$	$HIrCl_2L_3 + LiBH_4$	w	105	23.0[g]	2044, 2026, 2010	—	*(59)*
fac-$H_3Ir(PPh_3)_3$	—	w	223(dec)	22.1[g]	2106, 2094, 2083	—	*(340, 59)*
fac-$H_3Ir(AsPhEt_2)_3$	—	w	75	24.9[g]	2072, 2057, 2022	—	*(59)*
fac-$H_3Ir(PPhMe_2)_3$	—	w	—	21.7[g]	—	—	*(177)*
fac-$H_3Ir(PPh_2Me)_3$	—	w	115	21.5[e]	2074, 2040, 2021	—	*(4)*
fac-$H_3Ir(PPh_2Et)_3$	—	w	131	21.17[e]	2080, 2050	—	*(4)*
mer-$H_3Ir(PPhEt_2)_3$	$IrCl_3L_3 + LiAlH_4$	w	62	21.73[g]	2019, 1725	—	*(59)*
mer-$H_3Ir(PPh_3)_3$	—	w	225(dec)	—	2110, 1771, 1750	—	*(210, 59)*
mer-$H_3Ir(PPh_2Me)_3$	—	w	95	—	2030, 1740	—	*(4)*
mer-$H_3Ir(PPh_2Et)_3$	—	w	117	21.75[m]	2100, 1750	—	*(4)*
$H_3IrPPh[Ph_2PCH_2CH_2]_2$	$IrCl_3L + LiAlH_4$	w	—	—	2030,1975[h]	—	*(189)*

(Continued)

TABLE VII—*Continued*

Complex[a]	Preparation	Color[b]	Mp(°C)	^{1}H NMR[c] (τ)	IR[d] ν_{MH}/ν_{CO}	Comments	Ref.
fac-$H_3Ir(AsPh_3)_3$	—	w	210(dec)	—	2100	—	(*131*)
mer-$H_3Ir(AsPh_3)_3$	—	w	223(dec)	—	2109, 1715	—	(*131*)
$H_3Ir(PPhEt_2)_2PPh_3$	$H_5Ir(PPhEt_2)_2$ + L′	c	95	23.31, 21.25[g]	2049, 1751[g]	—	(*223, 224*)
$H_3Ir(PPhEt_2)_2P(OMe)_3$	—	c	—	22.57, 21.71[g]	2020, 1764[g]	—	(*223, 224*)
$H_3Ir(PPhEt_2)_2AsPhMe_2$	—	c	92	25.53, 21.81[g]	2088, 1727[g]	—	(*223, 224*)
$H_3Ir(PPhEt_2)_2SbPh_3$	—	c	123	24.95, 21.72[g]	2096, 2008, 1733[g]	—	(*223, 224*)
$H_3Ir(PPhEt_2)_2MeCN$	—	c	—	23.36, 21.50[g]	2016, 1739[g]	—	(*223, 224*)
$H_3Ir(PPhEt_2)_2SMe_2$	—	c	—	28.43, 20.89[g]	—	—	(*224*)
$H_3Ir(PPhEt_2)_2PPh(OMe)_2$	—	c	—	22.54, 21.34[g]	—	—	(*224*)
$H_3Ir(PEt_3)_2AsPhMe_2$	—	c	—	25.94, 22.42[g]	2092, 2000, 1721[g]	—	(*223, 224*)
$H_3Ir(PPh_3)_2py$	—	—	134	—	2120, 1700	—	(*59*)
$H_3Ir(AsPh_3)_2(CNEt)$	$H_3Ir(AsPh_3)_3$ + CNR	—	—	22.6, 21.6[e]	2130, 2090, 2075	—	(*10*)
$H_3Ir(AsPh_3)_2(CNC_6H_{11})$	—	—	—	22.62, 21.73	2128, 2120, 2080	—	(*10*)

$H_3Ir(AsPh_3)_2(CN\text{-}p\text{-tolyl})$	—	—	—	22.14, 20.88	2120, 2080, 2060	—	(*10*)
$H_3Ir(AsPh_3)_2(CN\text{-}p\text{-anisyl})$	—	—	—	22.21, 20.98	2120, 2075, 2060	—	(*10*)
$H_3IrCO(PPh_3)_2$	$IrClCO(PPh_3)_2 + LiAlH_4$	w	135	—	2080, 1785/ 1965	—	(*219, 46*)
$H_3IrCO(PBu_2{}^tPr^n)_2$	$HIrCl_2(PBu_2{}^tPr^n)_2 + CO$	y	—	22.39, 21.58[g]	—	—	(*294*)
$H_3IrCO(PPhEt_2)_2$	$H_5IrL_2 + CO$	—	—	21.58, 20.79[g]	—	—	(*224*)
$[H_3\{Ir(C_5Me_5)\}_2]CF_3CO_2$	$[Ir(C_5Me_5)X_2]_2 + H_2$	y	—	25.57	936	—	(*323*)
$[H_3\{Ir(C_5Me_5)\}_2]PF_6$	—	y	228(dec)	25.33[m]	—	—	(*323*)
$H_5Ir(PPhEt_2)_2$	$IrCl_3L_3 + LiBH_4$	w	—	20.02[g]	—	—	(*223*)
$H_5Ir(PEt_3)_2$	—	w	—	20.59[g]	—	—	(*223*)
$H_5Ir(PMe_3)_2$	—	w	—	19.73[g]	—	—	(*223*)
$H_5Ir(PBu_2{}^tPr^n)_2$	—	o	—	20.85[g]	—	—	(*294*)

[a] Ligand abbreviations are the same as in Tables V and VI with the following additions: α = H trans to X; β = H trans to L; I = H trans SnR_3; II = H trans to CO; fumn = fumaronitrile; phen = phenanthroline; COD = cyclooctadiene; dp = *cis*-vinylenebis(diphenylphosphine); 4-VCH = 4-vinylcyclohexene; cy = cyclohexyl; CINN = cinnamonitrile; BMN = benzylidenemalononitrile; FUMA = fumaric acid; DFUM = dimethylfumarate; acac = acetylacetonate; tfac = trifluoroacetylacetonate; hfac = hexafluoroacetylacetonate.

[b] Colors: g = green; p = purple; y = yellow; o = orange; r = red; br = brown; bl = black; w = white; cr = cream; c = colorless.

[c] CH_2Cl_2.

[d] Nujol.

[e] C_6D_6.

[f] $CHCl_3$.

[g] C_6H_6.

[h] KBr.

[i] Toluene.

[j] CD_2Cl_2.

[k] MeOH.

[l] $(CD_3)_2SO$.

[m] $CDCl_3$.

[n] Dipole moment.

[o] Hexachlorobutadiene.

[p] $(CD_3)_2CO$.

[q] THF.

[r] Cyclohexane.

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