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PLATINUM-GROUP METALS, COMPOUNDS

The platinum-group metals (qv) (PGMs) comprise the elements in the second and third row of Groups 8–10 (VIII) of the Periodic Table, ie, ruthenium, osmium, rhodium, iridium, palladium and platinum. These elements are kinetically inert relative to other transition-metal ions. However, the second-row elements ruthenium, rhodium, and palladium are more labile and more oxidizing in the higher oxidation states than are the third-row PGMs. All of these elements have several readily accessible stable oxidation states. The extreme case is that of Ru and Os, which exhibit oxidation states ranging from -2 and 0 to $+8$. The relative ease of conversion between oxidation states gives rise to a rich catalytic chemistry. The lower oxidation states of the PGMs tend to enable them to form complexes with soft ligands such as sulfur and phosphorus whereas higher oxidation states tend toward hard ligands such as oxygen and fluorine (see Coordination compounds). The platinum-group metals form binary compounds, coordination compounds, and organometallic compounds. The latter two classes have been the most active areas of research and development in the latter part of the twentieth century. Examples of important commercial applications include several homogenous catalytic processes and platinum chemotherapeutics (see Chemotherapeutics, anticancer). Additionally, substantial progress has been made in the areas such as catalytic enantioselective reduction and oxidation, and palladium-catalyzed carbon–carbon bond formation.

1. Economic Aspects

The annual market for PGM compounds is a relatively small ($<10\%$) but very important fraction of the overall PGM market. The total demand and average annual prices of the PGMs from 1984 to 1994 are summarized in Table 1. The high intrinsic cost of each PGM is the principal limitation on applications of these compounds. Two of the more important PGM-containing products are the platinum antitumor agents cisplatin and carboplatin, which produced $155 and $265 million in sales, respectively, for Bristol-Myers Squibb in 1994 (2). The worldwide market for cisplatin is even larger. Cisplatin has become a generic drug in most parts of the world. PGM catalysts, especially platinum, palladium, and rhodium, are used to produce commodity and fine chemicals and pharmaceuticals. Although large quantities of these catalysts are installed in production sites worldwide, annual demand for new PGMs is quite modest because spent catalysts are recycled (3) (see Catalysis; Catalysts, regeneration; Recycling). Ruthenium oxides employed in resistor plates for miniaturized electronic circuits account for 45% of the ruthenium demand; another 45% is required for the production of ruthenium-coated anodes for the chlor–alkali industry (3) (see Alkali and chlorine products; Metal anodes). Iridium and iridium–ruthenium coatings, an alternative to ruthenium-coated anodes in the chlor–alkali industry, account for 58% of the demand for iridium (3). Worldwide demand for osmium is very small. The metal is used primarily as a biological staining agent and oxidation catalyst (3).

Table 1. Total Demand and Prices of PGMs, 1984–1994[a]

	Total demand, t[b]			Price range, \$/kg[c]		
Metal	1984	1989	1994	1984	1989	1994
platinum	85.5	107.8	140.26	12,860–9,320	17,850–14,690	13,760–12,150
palladium	90.8	102.9	150.2	5,240–4,150	5,760–4,080	5,180–3,950
rhodium	6.8[d]	10.3	12.0	ca 28,940–11,090	53,860–40,190	31,510–19,600
ruthenium	6.2[d]	4.8	10.0	ca 6,430–ca 1,130	2,090–1,960	870–580
iridium		0.8	1.3	16,720–ca 9,970	10,130–9,650	2,250
osmium			0.2[e]	32,150–4,500		12,860

[a]Ref. 1.
[b]To convert metric tons to troy oz, multiply by 32,154.
[c]To convert \$/kg to \$/troy oz, multiply by 0.0311.
[d]Value is estimated.
[e]Data is for 1993.

2. Refining

PGMs are obtained from mined ores or from secondary sources such as industrial scrap and used catalysts. After initial processing to form concentrates, the PGMs are dissolved in acid under oxidizing conditions. Typically, chlorine is used (4). The overall efficiency and methods of final refining processes used to produce pure metals from solution streams have evolved considerably since the early 1980s. Historically PGMs were separated by selective precipitation of complex salts, followed by recrystallization and recycling of filtrates and washes. These processes were efficient neither in the degree of purification achieved nor in the amount of time that was required. Modern plants, such as the one opened by Johnson Matthey (Royston, Hertfordshire, U.K.) in 1983, employ solvent extraction methods to extract the individual metals (5). General principles and some details of these proprietary procedures have been published (4–7).

In sequential steps, each metal is selectively extracted from an aqueous solution into an immiscible organic solvent, from which it is then removed by reduction or back-extraction. The extractant forms a coordination compound, solvate, or ion pair with a solution species of the desired element. Thus, palladium may be extracted using oximes in the presence of organic amine, sulfur, phosphorus, or arsenic compounds which serve to accelerate the rate of formation of an extractable coordination compound (5). Extraction systems based on long-chain alkyl sulfides (8), hydroxy oximes (5), and 8-hydroxyquinolines (9) have also been reported. Provided that palladium and gold have been removed and iridium is present in the +3 oxidation state, platinum is removed by extraction of $[PtCl_6]^{2-}$ as an ion pair with tri-*n*-octyl amine (5). Ruthenium and osmium are removed by oxidation to their respective tetroxides and distilled, or extracted into carbon tetrachloride. Separation of the two oxides is based on the ability of RuO_4 to be reduced to Ru(IV) in the presence of OsO_4. Subsequent distillation separates the volatile OsO_4 from ruthenium (4). Alternatively, ruthenium is converted to a nitrosyl species, extracted with a tertiary amine, and eventually precipitated as ammonium hexachlororuthenate (6). Next, iridium is oxidized to Ir(IV), and $[IrCl_6]^{2-}$ is extracted in the same way as with platinum (5). Finally, rhodium is removed by conventional precipitation and isolated as impure rhodium sulfate (4–6). Rhodium may also be separated from iridium by extraction with a mono-*N*-substituted amide (10, 11). Compared to earlier precipitation–dissolution methods, the solvent extraction method offers the advantages of reduced processing time, improved safety owing to enclosure of allergenic platinum solutions, improved primary yields, and greater versatility.

3. Analysis

Gravimetric methods of analysis of PGM compounds have been largely superseded by spectroscopic methods, which are not only more versatile and selective, but require significantly less labor (12). The methods most often used are inductively coupled plasma-emission spectroscopy (icp-es), flame atomic absorption spectroscopy (faas), and graphite furnace atomic absorption spectroscopy (gfaas). For routine determinations where the PGM compound can be dissolved in aqueous or organic solution, icp-es is generally preferred to faas, because the former is freer from chemical interference caused by differences between the sample and standard matrix. The preferred method for trace level determinations is gfaas, which can also be used for solid samples and small (as little as 1 μL) samples (12) (see Trace and residue analysis). The analysis of noble metals by classical and spectroscopic methods as well as a variety of specialized spectroscopic methods has been reviewed (12–14).

4. Ruthenium Compounds

The most common oxidation states and the corresponding electronic configuration of ruthenium are +2 (d^6) and +3 (d^5). Compounds are usually octahedral. Compounds in oxidations states from -2 (d^{10}), and 0 (d^8) to +8 (d^0) have various coordination geometries. Important applications of ruthenium compounds include oxidation of organic compounds and use in dimensionally stable anodes (DSA).

4.1. Binary Compounds

The ruthenium fluorides are RuF_3 [51621-05-7], RuF_4 [71500-16-8], tetrameric $(RuF_5)_4$ [14521-18-7] (15), and RuF_6 [13693-087-8]. The chlorides of ruthenium are $RuCl_2$ [13465-51-5], an insoluble $RuCl_3$ [10049-08-8] which exists in an α- and β-form, ruthenium trichloride trihydrate [13815-94-6], $RuCl_3 3H_2O$, and $RuCl_4$ [13465-52-6]. Commercial $RuCl_3 3H_2O$ has a variable composition, consisting of a mixture of chloro, oxo, hydroxo, and often nitrosyl complexes. The overall ruthenium oxidation state is closer to +4 than +3. It is a water-soluble source of ruthenium, and is used widely as a starting material. Ruthenium forms bromides, $RuBr_2$ [59201-36-4] and $RuBr_3$ [14014-88-1], and an iodide, RuI_3 [13896-65-6].

The high valent ruthenium oxides are important because of their use as oxidizing agents in organic synthesis. Ruthenium(VIII) oxide [20427-56-9], RuO_4, the most important of these compounds, is most readily prepared by oxidation of RuO_2 using $NaIO_4$, followed by extraction into CCl_4 (16–19). Other methods of preparation have been reviewed (20, 21). Ruthenium also forms a dioxide [12036-10-1], RuO_2. The ruthenium chalcogens RuS_2 [12166-20-0], $RuSe_2$ [12166-21-1], and $RuTe_2$ [12166-22-2] have all been prepared by direct reaction of ruthenium and the elemental chalcogen (22). Ruthenium also forms numerous borides, silicides, phosphides, and arsenides (23, 24).

4.2. Coordination Compounds

Ruthenium forms a variety of complexes, particularly in oxidation states +2 and +3, with ammonia and amines. Some examples are $[Ru(NH_3)_6]^{2+}$ [19052-44-9], $[Ru(NH_3)_6]^{3+}$ [18943-33-4], and the mixed valent compounds $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ [26253-76-9], $[(NH_3)_3RuCl_3Ru(NH_3)_3]^{2+}$ [39003-96-8], and ruthenium red [32696-80-3], $[Ru_3O_2(NH_3)_{14}]^{6+}$. Deprotonation of $[Ru(NH_3)_6]^{3+}$ forms an amido complex $[Ru(NH_3)_5(NH_2)]^{2+}$ [35273-31-5] that reacts with 2,3-butandione to form a coordinated diimine, $[Ru(NH_3)_4\{CH_3C(NH)C(NH)CH_3\}]^{2+}$ [56370-80-0] (25, 26). Basic oxidation of $[Ru(NH_3)_6]^{3+}$ produces $[Ru(NH_3)_5NO]^{2+}$ [37874-79-6] (27), whereas $[Ru(en)_3]^{2+}$ [21393-86-2] can be oxidized to $[Ru(en)_2(diim)]^{2+}$ [36216-30-5] (28). Complexes of dinitrogen such as $[Ru(NH_3)_5N_2]^{2+}$ [19504-40-6] and $[Ru(NH_3)_5\text{-}N_2Ru(NH_3)_5]^{4+}$ [25754-89-6] are also known (see Nitrogen fixation). Examples of compounds containing heterocyclic amine ligands include $[Ru(bipy)_3]^{2+}$ [50525-27-4],

cis-[Ru(bipy)$_2$Cl$_2$] [19542-80-4], [Ru(terpy)(bipy)Cl]$^+$ [47690-83-5], and [RuCl(bipy)$_2$CO] [85719-81-9]. The complexes of [RuL$_3$]$^{2+}$ containing 2,2′-bipyridine, phenanthroline, and similar ligands are very stable, and the photochemistry and redox properties of this class have been the subject of intensive study (29). Ruthenium also forms complexes with nitriles, oximes, and Schiff bases. The base hydrolysis of the nitrile coordinated to Ru(NCC$_2$H$_5$)(NH$_3$)$^{3+}{}_5$ [58560-96-6] is accelerated by a factor of about 10^8 relative to the free ligand (30). Ruthenium forms macrocyclic complexes with porphyrins and phthalocyanines (31–35), and tetra and triaza macrocycles such as [RuCl$_2$(cyclam)]$^+$ [66652-53-7].

Nitric oxide has a high affinity for ruthenium, and its complexes have been reviewed (36–41). The RuNO group can occur in many coordination environments. Examples include [Ru(NO)(OH$_2$)$_2$Cl$_3$] [34416-98-3], [Ru(NO)(NH$_3$)$_5$]Cl$_3$ [37874-79-6], [Ru(NO)(S$_2$CN(C$_2$H$_5$)$_2$)$_3$] [51139-54-9], [RuCl(NO)(bipy)$_2$] [29102-12-3], [Ru(NO)Cl(P(C$_6$H$_5$)$_3$)$_2$] [38856-98-3], and the stable amido complex [Ru(NO)(NH$_3$)$_4$(NH$_2$)] [60133-06-4]. Nucleophilic attack on the coordinated NO is a characteristic reaction of the RuNO group, an example being the reaction of [RuCl(NO)(bipy)$_2$] and hydroxide to produce [RuCl(NO$_2$)(bipy$_2$)] [34398-51-1]. Ruthenium nitrosyls reduce the efficiency of nuclear fuel reprocessing because these compounds are extracted along with the uranium and plutonium, and away from other fission products, by trialkylphosphines, OPR$_3$ (42) (see Nuclear reactors, chemical reprocessing). Phosphines tend to stabilize oxidation states +0 and +2 of ruthenium, although other oxidation states are also accessible. Typical compounds include [Ru(P(C$_6$H$_5$)$_3$)$_3$(CO)(CN-*p*-C$_6$H$_4$CH$_3$)] [34830-25-6], [Ru(P(C$_6$H$_5$)$_3$)$_4$H$_2$] [19529-00-1], and one of the few known ruthenium(−2) complexes, [Ru(PF$_3$)$_4$]$^{2-}$ [26876-73-3].

Complexes of oxygen ligands include the hexaaqua ions of Ru(II) and Ru(III); ketoenolates, [Ru(acac)$_3$] [14284-93-6]; complexes of iminodiacids, [RuCl(Hedta)]$^-$ [129726-27-8]; and dicarboxylates such as [Ru(ox)$_3$]$^{3-}$ [25072-75-7]. Dinuclear and trinuclear monocarboxylates in which the metals are bridged by carboxylates, such as [Ru$_2$(OOCCH$_3$)$_4$]Cl [55598-01-1] and [Ru$_3$O(OOCCH$_3$)$_6$(OH$_2$)$_3$]OOCCH$_3$ [38998-79-7], have also been prepared. The high oxidation state complexes of ruthenium invariably contain oxo ligands. Their properties and chemistry have been reviewed (43–45). The dark green perruthenate anion [14333-21-2], [RuO$_4$]$^-$, is the only well-characterized compound of ruthenium(VII) and is most readily prepared by oxidation of RuCl$_3$ using KIO$_4$, followed by precipitation as the tetra-*i*-propylammonium salt (46). The ruthenate anion [14333-22-3], [RuO$_4$]$^{2-}$, can be prepared by oxidation of RuCl$_3$ by peroxydisulfate in KOH (47–49). This orange salt is stable in basic solution but disproportionates in neutral or acidic solution (50, 51). The O═Ru═O and Ru═O groups are also found in a number of coordination compounds, eg, [Ru(VI)O$_2$(bipy)$_2$] [84988-24-9] and [Ru(IV)O(bipy)$_2$py] [67202-43-1]. Ruthenium forms complexes with sulfur ligands including sulfoxides, which may be O- or S-bound (52), as in [RuCl$_2$(DMSO)$_4$] [11070-19-2], as well as thioethers, thioureas, dithiolenes, dithiophosphinates, thiolates, and thiocarbamates. Very few complexes with ligands of the higher chalcogenides selenium and tellurium have been reported. Ruthenium also forms complexes of silyl, germyl, and stannyl ligands (23, 29).

4.3. Organometallic Compounds

Ruthenium, predominately in the oxidation states 0 and +2, forms numerous mononuclear and polynuclear organometallic compounds. A few examples of compounds in both higher and lower oxidation states also exist. The chemistry of polynuclear ruthenium complexes is extensive and has been reviewed (53–59).

Numerous examples exist of complexes of carbon monoxide(qv), such as [Ru(CO)$_4$]$^{2-}$ [57398-60-4], [Ru(CO)$_5$] [16406-48-7], [Ru(CO)Cl$_3$]$^{2-}$ [66115-12-6], [Ru$_3$(CO)$_{12}$] [15243-33-1], and [Ru$_6$(CO)$_{18}$] [12277-77-9] (see Carbonyls); isocyanides, eg, [Ru(CNCH$_3$)$_6$]$^{2+}$ [49631-67-6]; carbenes, [Ru(CNCH$_3$)$_5${C(NHCH$_3$)$_2$}]$^{2+}$ [42566-55-2]; and carbynes (60). Ruthenium alkyls and acyls are less common; examples include [RuN(CH$_3$)$_4$]$^{1-}$ [102649-23-0] and [Ru(CO)$_2$(η^5-C$_5$H$_5$)(CO-*c*-C$_3$H$_5$)] [107769-65-3]. Ligands with π-systems form η^2–η^6 compounds of ruthenium. Examples include [Ru(CO)$_3$(1,5-cod)] [32874-17-2], [Ru(η^6-C$_7$H$_8$)(η^5-C$_7$H$_7$)]

[77357-78-9], and a large number of arene complexes such as $[Ru_2Cl_4(\eta^6\text{-}C_6H_6)_2]$ [51831-98-2]. Ruthenocene [1287-13-4], $[Ru(\eta^5\text{-}C_5H_5)_2]$, and its derivatives have chemistry similar to the ferrocenes.

4.4. Synthesis

The most important starting material for the synthesis of ruthenium compounds is the commercial trichloride trihydrate. Other useful starting materials include $[RuCl_5(OH_2)]^{2-}$ [3187-84-2], $[Ru_3O(OOCCH_3)_6(OH_2)_3]OOCCH_3$ [38998-79-7], and $[Ru_3(CO)_{12}]$ [15243-33-1].

4.5. Uses

4.5.1. Oxidation

The use of ruthenium oxo complexes as oxidants has been reviewed (44, 61). The most important of these is RuO_4, a very strong oxidant (60, 62) which reacts violently with common organic solvents such as ether and benzene (62). Ruthenium tetraoxide oxidizes alcohols to aldehydes (qv) and ketones (qv), aldehydes to acids, ethers to esters (qv) or lactones, tertiary amines to amides, and amides to imides. It generally cleaves olefins to aldehydes or ketones. It can oxidize aromatic rings and sterically hindered groups that are inert to other oxidants. Oxidations are frequently carried out catalytically in carbon tetrachloride or acetone, regenerating the RuO_4 with sodium hypochlorite or sodium metaperiodate. The perruthenate ion $[RuO_4]^-$, by contrast, is a much milder and more selective oxidant, able to oxidize alcohols to aldehydes and ketones in the presence of sensitive functional groups such as epoxides, silyl ethers, lactones, acetals, and allyl groups. This anion can be generated catalytically using *N*-methylmorpholine *N*-oxide (63). A variety of ruthenium complexes catalyze aerobic oxidation of alcohols (64). $[RuO_2(TPP)]$ [123051-66-1] catalyzes the aerobic epoxidation of olefins with retention of configuration (65).

4.5.2. Catalysis

Ruthenium complexes catalyze a wide range of reactions, including hydroformylation (66) (see Oxo process), carbonylation (67), water gas shift reaction (68), homogeneous hydrogenation (69), and transfer hydrogenation (64, 70). Other catalyzed reactions include addition of aromatic C–H bonds to olefins (71), homologation of carboxylic acids (72, 73), N-alkylation of amines by alcohols (64), N-alkyl migration of amines (74), disproportionation of aldehydes to esters (64), dehydrogenation of alcohols (75), reductive carbonylation of nitroaromatics to form carbamates (76), addition to carboxylic acids to terminal alkynes to form vinyl esters (77), photochemical reduction of carbon dioxide (qv) to formate (78, 79), and formation of ethylene glycol and other products from synthesis gas in melts (80, 81). A series of well-defined ruthenium carbene complexes capable of metathesizing both strained and unstrained olefins have been reported. These catalysts are tolerant to many functional groups and some are active in aqueous media (82). Enantioselective hydrogenations and transfer hydrogenations can be accomplished using chiral auxiliaries (71, 83). For example, hydrogenation of itanoic acid, an α, β,-unsaturated carboxylic acid, occurs with an enantioselectivity of 97% in the presence of the chiral ruthenium catalyst $[RuH_2((-)binap)_2]$ (70). Results are substrate- and catalyst-dependent.

4.5.3. Biology and Medicine

Biological and medicinal applications of ruthenium complexes have been reviewed (84, 85). The photochemical and electrochemical properties, and kinetic stability, of ruthenium complexes have led to use as probes for the structure of deoxyribonucleic acid (DNA) (86) and for the study of the electron-transfer process in proteins (qv) (87–89). Ruthenium complexes have been developed to cleave DNA (90). Ruthenium red is used as a histological stain. The compound $[Ru_2(\mu\text{-}O)(OOCH)_2(NH_3)_8]^{3+}$ [133399-54-9] has been reported to be a potent *in vitro* noncompetitive inhibitor of biological Ca^{2+} transport (91). Several compounds including *cis*-$[RuCl_2(DMSO)_4]$

[11070-19-2] and $[RuCl_4(im)_2]^+$ [103875-27-0] have been reported to have antitumor activity (85). However, efficacy in humans has not been demonstrated.

4.5.4. Miscellaneous

Ruthenium dioxide-based thick-film resistors have been used as secondary thermometers below 1 K (92). Ruthenium dioxide-coated anodes are the most widely used anode for chlorine production (93). Ruthenium(IV) oxide and other compounds are used in the electronics industry as resistor material in applications where thick-film technology is used to print electrical circuits (94) (see Electronic materials). Ruthenium electroplate has similar properties to those of rhodium, but is much less expensive. Electrolytes used for ruthenium electroplating (95) include $[Ru_2Cl_8(OH_2)_2N]^{3-}$ [55186-41-9], $Na_2[Ru(NO_2)_4(NO)OH]$ [13859-66-0], and $(NH_4)_2[RuCl_5(NO)]$ [13820-58-1]. Several photocatalytic cycles that generate H_2 or O_2 from water in the presence of a sacrificial reductant or oxidant employ a ruthenium complex, typically $[Ru(bipy)_3]^{2+}$, as the photon absorber (96, 97). A series of mixed binuclear ruthenium complexes having a variety of bridging ligands have been the subject of numerous studies into the nature of bimolecular electron-transfer reactions and have been extensively reviewed (99–102). The first example of this system, reported in 1969 (103), is the Creutz-Taube complex [35599-57-6], $[Ru_2(pyz)(NH_3)_{10}]^{5+}$.

5. Osmium Compounds

The most common oxidation states and the corresponding electronic configurations of osmium are +2 (d^6) and + (d^5), which are usually octahedral. Stable oxidation states that have various coordination geometries include −2 (d^{10}), and 0 (d^8), to +8 (d^0). The single most important application is OsO_4 oxidation of olefins to diols. Enantioselective oxidations have also been demonstrated.

5.1. Binary Compounds

Osmium forms four fluorides: OsF_4 [54120-05-7], OsF_5 [31576-40-6], OsF_6, and OsF_7 [16949-69-2]. Osmium hexafluoride [13768-38-2] is more stable than the other platinum-metal hexafluorides. Three chlorides, $OsCl_3$, $OsCl_4$ [10026-01-4], and $OsCl_5$ [71328-74-0]; two bromides, $OsBr_3$ [59201-51-3] and $OsBr_4$ [59201-52-4]; and three iodides, OsI [76758-38-8], OsI_2 [59201-57-9], and OsI_3 [59201-58-0], have been described. Osmium tetroxide [20816-12-0], OsO_4, is a volatile, toxic liquid and is obtained by oxidizing osmium-containing solutions using HNO_3, or by heating the finely divided metal in air (104). The tetroxide is reduced readily by organic matter. The other stable oxide is osmium dioxide [12036-02-1], OsO_2. Other binary chalcogenides include OsS_2 [12137-61-0], $OsSe_2$ [12310-19-9], and $OsTe_2$ [12165-67-2]. Osmium also forms borides, silicides, and phosphides (24).

5.2. Coordination Compounds

Osmium in oxidation states from +2 to +8 forms a wide range of complexes with nitrogen ligands. Amine complexes of osmium include $[Os(NH_3)_5(CO)]^{2+}$ [70528-08-4], $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ [83781-29-7], $[Os(NH_3)_6]^{3+}$ [48016-91-7],$[OsO_2(en)_2]^{2+}$ [61202-82-2], porphyrins [Os(TPP)CO] [104677-48-7] and $[Os(OEP)(O)_2]$ [59650-32-7], and the tetraamido complex $[OsO_2(o\text{-}(NH)_2C_6H_4)_2]$ [127472-00-8]. Schiff base and chelating amide complexes have also been prepared. Unlike ruthenium, Os(II) hexaammine is labile and as of this writing has not been isolated. Osmium(II) and (III) form many dinitrogen complexes, such as $[Os(NH_3)_5N_2]^{2+}$ [22840-90-0] and $[Os_2N_2(NH_3)_{10}]^{5+}$ [81988-68-3].

Like ruthenium, amines coordinated to osmium in higher oxidation states such as Os(IV) are readily deprotonated, as in $[Os(en)(NHCH_2CH_2NH_2)]^{2+}$ [111614-75-6]. This complex is subject to oxidative dehydrogenation to form an imine complex (105). An unusual Os(IV) hydride, $[OsH_2(en)_2]^{2+}$ [57345-94-5] has been isolated and

characterized. The complexes of aromatic heterocyclic amines such as pyridine, bipyridine, phenanthroline, and terpyridine are similar to those of ruthenium. Examples include $[Os(bipy)_3]^{2+}$ [23648-06-8], $[Os(bipy)_2acac]$ [47691-08-7], $[Os(terpy)_2]^{3+}$ [100815-62-1], $[Os_2(pyz)(NH_3)_{10}]^{5+}$ [85282-23-1], $[Os(OSO_2CF_3)_2(bipy)_2]$ [104474-97-7], $[OsCl_4(bipy)]$ [57288-05-8], and $[Os(phen)(OH)_2(O)_2]$ [69531-97-1]. The photochemistry and redox properties of $OsL_3^{2+/3+}$ complexes, where L = heteroaromatic chelating amines, have been investigated, although less thoroughly than the corresponding ruthenium complexes.

Osmium readily forms nitrosyl complexes such as $[OsCl_5(NO)]^{2-}$ [53796-27-3], $[Os(NO)(NH_3)_5]^{3+}$ [52720-70-4], and $[Os(P(C_6H_5)_3)_2(OH)(NO)_2]^+$ [47847-71-2]. Coordinated NO in $[Os(NO)(terpy)(bipy)]^{2+}$ [90219-19-5] is subject to nucleophilic attack analogous to this same effect on ruthenium complexes. A much more unusual reaction is protonation of the NO of $[OsCl(P(C_6H_5)_3)_2(NO)(CO)]$ [22186-54-5] to produce the complex $[OsCl_2(P(C_6H_5)_3)_2(HNO)(CO)]$ [31011-34-4], containing coordinated nitrous acid. Osmium forms a variety of imido and nitrido compounds, such as $[OsO_3(N\text{-}t\text{-}C_4H_9)]$ [50381-48-1], $[Os(N\text{-}tC_4H_9)_4]$ [129117-79-9], $[OsCl_5(N)]^{2-}$ [42718-64-9], $[OsCl_4(OH_2)(N)]^-$ [59187-86-9], $[OsCl_2(terpy)(N)]^+$ [127571-47-5], and $[Os_3(OH_2)_6(NH_3)_8(N)_2]^{6+}$ [76247-72-8].

Numerous phosphine and arsine complexes have been synthesized and characterized predominately with osmium in the +2, +3 or +4 oxidation states. Examples include $[OsCl_2(dppm)_2]$ [108341-10-2], $[OsCl_3(P(CH_3)_2(C_6H_5)_3]$ [20500-70-3], $[Os_2Cl_6(dppm)_2(O)]$ [87883-12-3], and $[Os(AsC_2H_5(C_6H_5)_2)_4H_2]$ [27498-19-7]. An example of an unusually low oxidation state is the Os(−2) complex $K_2[Os(PF_3)_4]$ [26876-74-4]. High coordination numbers and formal oxidation states are found in the phosphine hydrides, eg, $[Os(P(CH_3)(C_6H_5)_2)H_6]$ [25895-55-0] and $Os(P(C_2H_5)_2C_6H_5)_3H_4$ [24228-58-8].

The oxo ligand is the most common motif in osmium chemistry. By far the single most important complex is OsO_4 a much milder oxidizing agent than RuO_4. Many complexes containing the oxo or cis or trans dioxo group (O═Os═O) are known, including $[OsO_4(OH)_2]^{2-}$ [131725-28-5], *trans*-$[OsO_2(OH)_4]^{2-}$ [88993-76-4], $[OsO_2(OCH_3)_4]^{2-}$ [120169-51-9], and $[OsO_3N]^-$ [19662-38-5]. Osmium does not form a hexaaqua complex, although the aqua ligand is known in combination with other ligands such as $[Os(NH_3)_5(OH_2)]^{3+}$ [53222-99-4]. Other complexes include $[Os(acac)_3]$ [60133-05-3], $[Os(ox)Cl_4]^{2-}$ [74325-52-3], $[Os(cat)_3]$ [67799-34-2], and the bridging carboxylato complex $[Os_2Cl_2(O_2CCH_3)_4]$ [81519-41-7]. Relatively few osmium compounds having sulfur ligands have been characterized. Some complexes include sulfoxides, $[OsCl_3(DMSO)_3]$ [66009-49-2]; dithiocarbamates, $[Os(S_2CN(C_2H_5)_2)_3]$; thioureas, $[Os(SC(NH_2)_2)_6]^{3+}$ [12300-37-7]; thiocarbonyls, $Os(sacsac)_3$ [29966-35-6]; and macrocyclic thioethers, $[Os([9]aneS_3)_2]^{2+}$ [145312-30-7].

5.3. Organometallic Compounds

Osmium forms numerous mononuclear and polynuclear organometallic complexes, primarily in lower oxidation states. There are many complexes of carbon monoxide, such as $[Os(CO)_5]$ [16406-49-8], $[Os(CO)_4H_2]$ [22372-70-9], $[Os_3(CO)_{11}H_2]$ [56398-24-4], $[Os_6(CO)_{18}]$ [37216-50-5], $[Os_3(CO)_{10}(\mu\text{-}O{=}CCH_3)(H)]$ [65908-54-5], and to a lesser extent isonitriles such as *trans*-$[OsBr_2(CNCH_3)_4]$ [42608-08-2]. The most important carbon monoxide complex is the trinuclear complex $[Os_3(CO)_{12}]$ [15696-40-9], which is a starting material for many mononuclear and polynuclear complexes. Osmium forms alkyl, $[Os(CO)_4(CH_3)_2]$ [22639-01-6]; aryl, $[Os(2\text{-methylphenyl})_4]$ [101191-32-6]; acyl, *trans*-$[Os(dppe)_2(CHO)(CO)]^+$ [89411-52-9]; vinyl; carbene, $[OsCl(P(C_6H_5)_3)_2(NO)(=_2)]$ [86645-81-0]; and carbyne complexes, $[OsCl(P(C_6H_5)_3)_2(CO)(C_6H_5)]$ [75346-82-6]. Osmium is unusual in its tendency for *dihapto* binding of acyls and related ligands such as iminoacyl, and thioacyl complexes as in $[Os(\eta^2\text{-}CS(p\text{-}C_6H_4CH_3))(P(C_6H_5)_3)_2(O_2CCF_3(CO)]$ [68111-80-8].

Many unsaturated compounds form π-complexes with osmium including alkenes, $[Os(P(C_6H_5)_3)_2(CO)_2(\eta\text{-}C_2H_4)]$ [79725-76-1]; alkynes, $[Os(P(C_6H_5)_3)_2(NO)(CO)(\eta\text{-}C_2H_2)]^+$ [41529-78-6]; allyls, $[Os(NH_3)_5(\eta^3\text{-}C_3H_5)]^{3+}$ [131617-37-3]; dienes, $[Os(CO)_3(1,4\text{-}\eta\text{-}C_4H_6)]$ [75756-64-8]; cyclopentadienes, $[Os(C_5H_5)_2]$ [1273-81-0]; and arenes, $[Os_2Cl_3(\eta\text{-}C_6H_6)_2]^+$ [70317-01-0]. Other unusual complexes are the stable η^2-bound carbonyl, $[Os(NH_3)_5\{\eta^2\text{-}(C,O)\text{-acetone})\}]$ [105164-47-4], and benzene adducts, $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ [107202-74-4] and

$[Os(NH_3)_5(C_6H_6)Os(NH_3)_5]^{4+}$ [107202-75-5] (106, 107). The chemistry of osmium clusters is replete with examples of ligands engaged in intimate and unusual bonding modes with multiple metal centers.

5.4. Synthesis

The most important starting material for synthesis of osmium complexes is OsO_4. Other important complexes are disodium hexachloroosmium [1307-81-9], $Na_2[OsCl_6]$; $[Os(NH_3)_5(O_2SCF_3)]^{2+}$; and $[Os_3(CO)_{12}]$.

5.5. Uses

5.5.1. Oxidations

The use of osmium for oxidations has been reviewed (108, 109). The most important application is the oxidation of olefins to cis-diols using OsO_4. This reaction occurs via an osmate ester intermediate that is oxidatively or reductively cleaved to form the cis-diol. The reaction may be carried out stoichiometrically, but most often catalytic amounts are used in the presence of appropriate oxidants such as hydrogen peroxide(qv), ferricyanide, chloramine-T, chlorate, or *N*-methylmorpholine *N*-oxide. Osmium tetroxide can also oxidize alcohols to aldehydes, ketones, or carboxylic acids. Catalytic enantioselective dihydroxylation of achiral olefins by OsO_4 can be accomplished in the presence of chiral ligands (109–111). Enantiomeric excesses of 77% to >99.5% have been achieved using simple olefins in the presence of a chiral pthalazine ligand, an organic sulfonamide to accelerate the rate of osmate ester hydrolysis, and ferricyanide as the cooxidant (110).

Nitrogen-transfer reactions of osmium imido species lead to cis diamines or amino alcohols. Reaction of $OsO_2(N\text{-}t\text{-}C_4H_9)_2$ [63174-13-0] with olefins produces vicinal diamines after reductive cleavage. Catalytic oxyamination of olefins using chloramine-T or *N*-chlor-*N*-argenocarbamates yields vicinal hydroxy toluenesulfonamides (112) or carbamates (113), respectively, which may be deprotected to vicinal amino alcohols.

5.5.2. Miscellaneous

Aside from the oxidation chemistry described, only a few catalytic applications are reported, including hydrogenation of olefins (114, 115), α, β-unsaturated carbonyl compounds (116), and carbon monoxide (117); and the water gas shift reaction (118). This is so owing to the kinetic inertness of osmium complexes. A 1% by weight osmium tetroxide solution is used as a biological stain, particularly for preparation of samples for electron microscopy. In the presence of pyridine or other heterocyclic amines it is used as a selective reagent for single-stranded or open-form B-DNA (119) (see Nucleic acids). Osmium tetroxide has also been used as an indicator for unsaturated fats in animal tissue. Osmium tetroxide has seen limited if controversial use in the treatment of arthritis (120, 121).

6. Rhodium Compounds

The most common oxidation states and corresponding electronic configurations of rhodium are +1 (d^8), which is usually square planar although some five coordinate complexes are known, and +3 (d^6) which is usually octahedral. Dimeric rhodium carboxylates are +2 (d^7) complexes. Compounds in oxidation states −1 (d^{10}) to +6 (d^3) exist. Significant industrial applications include rhodium-catalyzed carbonylation of methanol to acetic acid and acetic anhydride, and hydroformylation of propene to *n*-butyraldehyde. Enantioselective catalytic reduction has also been demonstrated.

6.1. Binary Compounds

Four fluorides of rhodium can be prepared. These include the most stable, RhF_3 [60804-25-3]; RhF_4 [60617-65-4]; tetrameric $(RhF_5)_4$ [14521-17-6]; and very reactive RhF_6 [13693-07-7]. The trihalides $RhCI_3$ [10049-07-7], $RhBr_3$ [15608-29-4], and RhI_3 [15492-38-3] are the only other well-characterized halides. These are insoluble when anhydrous. The chloride and bromide form soluble hydrates, ie, $RhCl_3 \cdot 3H_2$ [13569-65-8] and $RhBr_3 \cdot 2H_2O$ [76758-40-2]. Rhodium forms two oxides, RhO_2 [12137-27-8] and Rh_2O_3 [12036-35-0]. The latter is used as a catalyst in the manufacture of HI. Rhodium(III) hydroxide [21656-02-0], $Rh(OH)_3$, has a variable water content and is likely a hydrated form of Rh_2O_3 (121). Rhodium forms a sulfide, Rh_2S_3 [12067-06-0], and a selenide, $RhSe_2$ [12038-76-5], as well as borides, silicides, phosphides, and arsenides (23, 24).

6.2. Coordination Compounds

A large number of Rh(III) ammine and amine complexes have been isolated, including $[Rh(NH_3)_6]^{3+}$ [16786-63-3], $[RhCl(NH_3)_5]^{2+}$ [15379-09-6], $[RhCl_2(en)_2]^+$ [29701-59-5], and *cis*-$[Rh(en)_2H_2]^+$ [108566-47-8]. These d^6 complexes are substitutionally and sterochemically inert, allowing resolution of optically active complexes such as $[Rh(en)_3]^{3+}$ [30983-68-7]. The high degree of kinetic inertness of Rh(III) is evident in the apparent anation of $[Rh(OH)_2(NH_3)_5]^{3+}$ [15337-79-8], which actually occurs by electrophilic attack of NO^+ on coordinated hydroxyl, followed by intramolecular isomerization of the initially formed O-bound nitrito to an N-bound nitrito ligand (122). The substitution chemistry of Rh(III) amine complexes has been extensively studied and reviewed (123). The redox stability of the +3 oxidation state, combined with photolability of many amine complexes, has resulted in considerable investigation of the photochemistry of these complexes (124). Rhodium compounds containing heterocyclic amine ligands are numerous. Examples include $[RhCl_2(py)_4]^+$ [14077-03-3], *mer*-$[RhCl_3(py)_3]^+$ [14267-66-4], and $[Rh(bipy)_3]^{3+}$ [47780-17-6]. The last complex has been employed as part of an aqueous photochemical cycle that produces H_2 by oxidation of an organic donor (96). Other complexes contain nitriles, eg, $[Rh(NCC_6H_5)(NH_3)_5]^{2+}$ [46343-55-9] and $[RhCl_3(NCCH_3)_3]$ [15747-79-2]; oximes, eg, $[Rh(OH_2)(DMG)_2CH_3]$ [26026-41-5]; Schiff bases, $[Rh(salen)O_2]$ [91067-88-8]; pyrazolylborates, $[RhCl_2(CH_3OH)\{HB(3,5\text{-dimethylpyrazolato})_3\}]$ [73117-95-0]; nitrito ligands, $[Rh(NO_2)(NH_3)_5]^{2+}$ [34412-13-0]; and nitrosyl ligands, $[Rh(P(C_6H_5)_3)_2(O_2CCF_3)_2(NO)]$ [87652-47-9]. Basic hydrolysis of coordinated nitriles is accelerated by six orders of magnitude relative to the free ligand. However, this is two orders of magnitude slower than hydrolysis catalyzed by ruthenium. Macrocyclic complexes of rhodium include $[Rh(cyclam)Cl_2]^+$ [38781-23-6]; porphyrins, [RhCl(TPP)(CO)] [42892-91-1]; and phthalocyanines, [Rh(Pc)] [37099-31-3]. Phosphine complexes of rhodium are a large class of compounds that are important catalytically. Phosphines stabilize a range of oxidation states from −1 to +3, but +1 and +3 are the most important. Some phosphine complexes of rhodium are Wilkinson's catalyst [14694-95-2], $[RhCl(P(C_6H_5)_3)_3]$; $[RhCl_2(P(C_6H_5)_3)_2]^+$ [132108-94-2]; $[RhCl(P(C_6H_5)_3)_2H_2]$ [12119-41-4]; $[Rh(diphos)_2]^+$ [65521-62-2]; and the cluster $[Rh_{55}Cl_{20}(P(t\text{-}C_4H_9)_3)_{12}]$ [104619-08-1]. A few arsine complexes, eg, $[Rh(diars)_2]^+$ [53450-80-9], that are similar to the corresponding phosphine complexes, are also known.

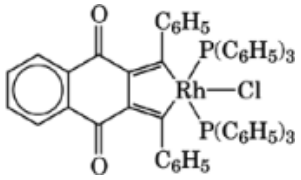
Rhodium complexes with oxygen ligands, not nearly as numerous as those with amine and phosphine complexes, do, however, exist. A variety of compounds are known, including $[Rh(ox)_3]^{3-}$ [18307-26-1], $[Rh(acac)_3]$ [14284-92-5], the hexaaqua ion $[Rh(OH_2)_6]^{3+}$ [16920-31-3], and Schiff base complexes. Soluble rhodium sulfate, $Rh_2(SO_4)_3xH_2O$, exists in a yellow form [15274-75-6], which probably contains $[Rh(H_2O)_6]^{3+}$, and a red form [15274-78-9], which contains coordinated sulfate (125). The structure of the soluble nitrate $[Rh(NO_3)_3 \cdot 2H_2O$ [10139-58-9] is also complex (126). Another class of rhodium compounds is the Rh(II) oxo-bridged dimers such as $[Rh_2(OOCCH_3)_4L_2]$, where L is an oxygen, nitrogen, carbon, sulfur, or phosphorus donor ligand. Examples are $[Rh_2(OOCCH_3)_4(OH_2)_2]$ [28410-96-0] and $[Rh_2(mhp)_4]$ [75310-08-6]. Complexes containing sulfur ligands include dithiocarbamates, $[Rh_2(S_2CN(C_2H_5)_2)_5]^+$ [15109-46-5]; dialkyldithiophosphonates, $[Rh(S_2P(OC_2H_5)_2)_3]$ [33991-54-7]; thioethers, $[RhCl_3(S(C_2H_5)_2)_3]$ [14784-72-6]; thiocyanates, $[Rh(SCN)_6]^{3-}$ [17731-24-7];

sulfoxides, $[RhCl_3(DMSO)_3]$ [56195-04-1]; thiocarbonyls, $[Rh(sacsac)_3]$ [26304-95-0]; and macrocyclic complexes, $[Rh((SCH_2CH_2)_3)_2]$ [116115-75-4]. A few complexes containing selenium ligands, eg, $[Rh(Se_2C_2(CN)_2)_3]$ [45229-91-2], have been prepared.

6.3. Organometallic Compounds

The predominant oxidation states of rhodium organometallics are +1 and +3. Rhodium forms a large number of mononuclear and polynuclear carbonyl complexes, including the complexes $[Rh(CO)_4]^-$ [44797-04-8], *trans*-$[RhI_4(CO)_2]^-$ [55634-00-9], $[Rh_2Cl_2(CO)_4]$ [14523-22-9], $[Rh_4(CO)_{12}]$ [19584-30-6], $[Rh_6(CO)_{16}]$ [28407-51-4], and the A-frame molecules, typified by $[Rh_2Cl_2(dppm)_2(CO)_2]$ [22427-58-3]. An unusual dinuclear porphyrin complex is $[Rh_2(CO)_4(TPP)]$ [88083-36-7], which contains two $Rh(CO)_2$ units, one on each side of the ring and each coordinated to two porphyrin nitrogens (127). Isocyanides react readily with many rhodium compounds to form complexes such as $[Rh(CN{-}t{-}C_4H_9)_4]^+$ [34195-61-4], $[Rh_2Cl_2(CN\text{-}t\text{-}C_4H_9)_4]$ [37017-32-6], and the bridging complex $[Rh_2((CNCH_2)_2CH_2)_4]$ [717375-02-5]. Carbene complexes are also known, eg, $[RhCl(P(C_6H_5)_3)_2(C(NC_2H_5CH_2)_2)]$ [54686-50-9].

Rhodium forms σ-bonded alkyl, *trans*-$[RhI(CNCH_3)_4CH_3]$ [45151-89-1] and $[RhI_2(P(C_6H_5)_3)_2CH_3]$ [47829-28-7]; aryl, $[Rh(P(CH_3)_3)_3C_6H_5]$ [71110-93-5]; and acyl, $[RhI(P(C_6H_5)_3)(COCH_3)C_5H_5]$ [34676-55-6], complexes, as well as alkenyl and alkynyl compounds. Alkynes readily undergo oxidative cyclodimerization in the presence of $[RhCl(P(C_6H_5)_3)_2]$ to form metallocyclopentadienyl complexes such as [36463-91-9], shown below.



Reaction with additional alkyne releases an organic anthraquinone (128). Numerous π-complexes are known. Examples include complexes of alkenes, $[Rh_2Cl(CH_2CH_2)_4]$ [12081-16-2]; dienes, $[Rh(cod)_2]^+$ [35338-22-8]; alkynes, $RhCl(P(C_6H_5)_3)_2(C_6H_5CCC_6H_5)]$ [12124-06-0]; allyls, $[Rh(C_3H_5)_3]$ [12082-48-3]; conjugated dienes, $[Rh(P(C_6H_5)_3)_2(1,4\text{-cyclohexadiene})]^+$ [32799-73-8]; cyclobutadienes, $[Rh_2Cl_2((C_6H_5C)_4)_2]$ [50477-60-6]; and many others. Many η^5-cyclopentadiene and η^6-arene complexes such as $[(Rh_3(CO)_3(C_5H_5)_3)H]^+$ [76082-92-3] and $[Rh(nbd)(C_6H_6)]^+$ [36683-23-2] are known. Although rhodacene is unstable at room temperature (129), rhodacenium hexafluorophosphate [37205-11-1], $[Rh(C_5H_5)_2]PF_6$, is a colorless crystalline solid.

6.4. Synthesis

The most important starting material for rhodium compounds is rhodium(III) chloride hydrate [20765-98-4], $RhCl_3nH_2O$. Other commercially available starting materials useful for laboratory-scale synthesis include $[Rh_2(OOCCH_3)_4]$ [5503-41-3], $[Rh(NH_3)_5Cl]Cl_2$ [13820-95-6], $[Rh_2Cl_2(CO)_4]$ [32408-34-7], and $[Rh_2Cl_2(cod)_2]$ [12092-47-6].

6.5. Uses

6.5.1. Catalysis

The readily accessible +1 and +3 oxidation states of rhodium make it a useful catalyst. There are several reviews of the catalytic properties of rhodium available (130–132). Rhodium-catalyzed methanol carbonylation (Monsanto process) accounted for 81% of worldwide acetic acid by 1988 (133). The Monsanto acetic acid process is carried out at 175°C and 1.5 MPa (200 psi). Rhodium is introduced as $RhCl_3$ but is likely reduced in a water

gas shift reaction (134) to the active catalytic species $[RhI_2(CO)_2]^-$ [38255-39-9]. The basic steps of the reaction (eqs. 1–6) are reaction of methanol (qv) and HI to form methyl iodide, oxidative addition of methyl iodide, migratory insertion of the methyl to the carbonyl, coordination of CO, reductive elimination of acetyl iodide, and hydrolysis of acetyl iodide to acetic acid. The iodide promoter is important for the success of the reaction because iodide is a good leaving group, a good nucleophile, and a good ligand for rhodium.

$$CH_3OH + HI \longrightarrow CH_3I + H_2O \qquad (1)$$

$$\left[RhI_2(CO)_2\right]^- + CH_3I \longrightarrow \left[RhI_3(CO)_2CH_3\right]^- \qquad (2)$$

$$\left[RhI_3(CO)_2CH_3\right]^- \longrightarrow \left[RhI_3(COCH_3)(CO)\right]^- \qquad (3)$$

$$\left[RhI_3(COCH_3)(CO)\right]^- + CO \longrightarrow \left[RhI_3(COCH_3)(CO)_2\right]^- \qquad (4)$$

$$\left[RhI_3(COCH_3)(CO)_2\right]^- \longrightarrow \left[RhI_2(CO)_2\right]^- + CH_3COI \qquad (5)$$

$$H_2O + CH_3COI \longrightarrow CH_3COOH + HI \qquad (6)$$

A related but distinct rhodium-catalyzed methyl acetate carbonylation to acetic anhydride (134) was commercialized by Eastman in 1983. Anhydrous conditions necessary to the Eastman acetic anhydride process require important modifications (24) to the process, including introduction of hydrogen to maintain the active $[RhI_2(CO)_2]^-$ catalyst and addition of lithium cation to activate the alkyl methyl group of methyl acetate toward nucleophilic attack by iodide.

Homogeneous rhodium-catalyzed hydroformylation (135, 136) of propene to *n*-butyraldehyde(qv) was commercialized in 1976. *n*-Butyraldehyde is a key intermediate in the synthesis of 2-ethylhexanol, an important plasticizer alcohol. Hydroformylation is carried out at <2 MPa (<290 psi) at 100°C. A large excess of triphenyl phosphine contributes to catalyst life and high selectivity for *n*-butyraldehyde ($>10:1$) yielding few side products (137). Normally, product separation from the catalyst $[Rh(P(C_6H_5)_3)_3(CO)H]$ [17185-29-4] is achieved by distillation.

In 1984 Rührchemie introduced a water-soluble catalyst, $[Rh(P(3\text{-}(NaO_3S)C_6H_4)_3)(CO)H]$ [103823-25-2], in a process producing 100,000 t/yr of *n*-butyraldehyde (138). Use of the water-soluble rhodium catalyst simplifies catalyst recovery and results in negligible rhodium losses, because the catalyst is not soluble in the organic product phase. Although a definitive mechanism has not been established, a plausible course based on model studies (139) includes dissociative loss of a ligand from the catalyst, coordination of propene, insertion into the metal hydride to form a rhodium propyl species, coordination of CO, migration of the propyl into the carbonyl, oxidative addition of H_2, and reductive elimination, forming *n*-butyraldehyde and a coordinatively unsaturated catalyst species.

Efficient enantioselective asymmetric hydrogenation of prochiral ketones and olefins has been accomplished under mild reaction conditions at low (0.01– 0.001 mol %) catalyst concentrations using rhodium catalysts containing chiral ligands (140, 141). Practical synthesis of several optically active natural products and medicines such as L-DOPA, (−)-deoxypodohyllotoxin, (+)-collinusin, (*R*)-rhenyephrine hydrochloride, and (*S*)-levamisole have been reported (141). The observed enantioselectivity is highly substrate- and catalyst-dependent. Much work has been devoted to developing improved chiral auxiliaries (142). The principal product enantiomer observed in the chiral bisphosphine-rhodium asymmetric hydrogenation of dehydroamino acids has been demonstrated to arise from the less stable catalyst–substrate intermediate (143).

Rhodium(II) acetate catalyzes C–H insertion, olefin addition, heteroatom-H insertion, and ylide formation of α-diazocarbonyls via a rhodium carbenoid species (144–147). Intramolecular cyclopentane formation via C–H insertion occurs with retention of stereochemistry (143). Chiral rhodium(II) carboxamides catalyze enantioselective cyclopropanation and intramolecular C–N insertions of α-diazoketones (148). Other reactions catalyzed by rhodium complexes include double-bond migration (140), hydrogenation of aromatic aldehydes and ketones to hydrocarbons (150), homologation of esters (151), carbonylation of formaldehyde (152) and amines (140), reductive carbonylation of dimethyl ether or methyl acetate to 1,1-diacetoxy ethane (153), decarbonylation of aldehydes (140), water gas shift reaction (69, 154), C–C skeletal rearrangements (132, 140), oxidation of olefins to ketones (155) and aldehydes (156), and oxidation of substituted anthracenes to anthraquinones (157). Rhodium-catalyzed hydrosilation of olefins, alkynes, carbonyls, alcohols, and imines is facile and may also be accomplished enantioselectively (140). Rhodium complexes are moderately active alkene and alkyne polymerization catalysts (140). In some cases polymer-supported versions of homogeneous rhodium catalysts have improved activity, compared to their homogenous counterparts. This is the case for the conversion of alkenes directly to alcohols under oxo conditions by rhodium–amine polymer catalysts (158).

6.5.2. Miscellaneous

Dimeric rhodium isocyanide complexes have been suggested for use to convert water to hydrogen and oxygen (159, 160). Photochemical activation of some rhodium complexes leads to intermolecular oxidative addition of aliphatic and aromatic C–H bonds under ambient conditions (161, 162). Rhodium complexes have been investigated for antibacterial and antitumor properties (163). However, none has been used in human clincial trials. Rhodium complexes have been used for site-specific DNA recognition and photoactivated strand scission (164). Rhodium plating has been used to deposit thin, brilliant white, tarnish-resistant, wear-resistant coatings for jewelry (165). Engineering applications utilize rhodium's good sliding contact characteristics or high stable reflectivity (165). Rhodium electroplating baths are proprietary, but are based on sulfate or phosphate salts (165).

7. Iridium Compounds

The most common oxidation states, corresponding electronic configurations, and coordination geometries of iridium are +1 (d^8) usually square plane although some five-coordinate complexes are known, and +3 (d^6) and +4 (d^5), both octahedral. Compounds in every oxidation state between −1 (d^{10}) and +6 (d^3) are known. Iridium compounds are used primarily to model more active rhodium catalysts.

7.1. Binary Compounds

The fluorides of iridium are IrF_3 [23370-59-4], IrF_4 [37501-24-9], the tetrameric pentafluoride $(IrF_5)_4$ [14568-19-5], and]IrF_6 [7789-75-7]. Chlorides of iridium include $IrCl_3$, which exists in anhydrous [10025-83-9] α- and β-forms, and as a soluble hydrate [14996-61-3], and $IrCl_4$ [10025-97-5]. Other halides include $IrBr_3$ [10049-24-8], which is insoluble, and the soluble tetrahydrate $IrBr_3{\cdot}4H_2O$; $IrBr_4$ [7789-64-2]; and IrI_3 [7790-41-2].

Iridium forms iridium dioxide [12030-49-8], IrO_2; a poorly characterized sesquioxide, Ir_2O_3 [1312-46-5]; and the hydroxides, $Ir(OH)_3$ [54968-01-3] and $Ir(OH)_4$ [25141-14-4]. Other binary iridium compounds include the sulfides, IrS [12136-40-2], Ir_2S_3 [12136-42-4], IrS_2 [12030-51-2], and IrS_3 [12030-52-3], as well as various selenides and tellurides.

7.2. Coordination Compounds

A large number of iridium complexes with nitrogen ligands have been isolated, particularly where Ir is in the +3 oxidation state. Examples of ammine complexes include $[Ir(NH_3)_6]^{3+}$ [24669-15-6], $[IrCl(NH_3)]^{2+}$ [29589-09-1], and *trans*-$[Ir(O_3SCF_3)_2(en)_2]^+$ [90065-94-4]. Compounds of *N*-heterocyclic ligands include *trans*-$[IrCl_4(py)_2]^-$ [24952-67-8], $[Ir(bipy)_3]^{3+}$ [16788-86-6], and an unusual C-metalated bipyridine complex, $[Ir(bipy)_2(C^3,N\text{-}bipy)]^{2+}$ [87137-18-6]. Isolation of this latter complex produced some confusion regarding the chemical and physical properties of $[Ir(bipy)_3]^{3+}$ (167).

Complexes of d^6 Ir(III) are kinetically inert and undergo octahedral substitution reactions slowly. The rate constant for aquation of $[IrBr(NH_3)_5]^{2+}$ [35884-02-7] at 298 K has been measured at $\sim 2 \times 10^{-10}$ s^{-1} (168). In many cases, addition of a catalytic reducing agent such as hypophosphorous acid greatly accelerates the rate of substitution via a transient, labile Ir(II) species (169). Optical isomers can frequently be resolved, as is the case of *cis*-$[IrCl_2(en)_2]^+$ [15444-47-0] (170). Ir(III) amine complexes are photoactive and undergo rapid photosubstitution reactions (171). Other iridium complexes containing nitrogen ligands include complexes of nitriles, $[Ir(P(C_6H_5)_3)_2(NCCH_3)CO]^+$ [51540-63-7]; nitrosyl, $[IrCl_2(P(C_6H_5)_3)_2(NO)]^+$ [27411-12-7]; dinitrogen, $[IrCl(P(C_6H_5)_3)_2N_2]$ [15695-36-0]; azide, *trans*-$[Ir(N_3)_2(en)_2]^+$ [26104-26-7]; and pyrazylborate, $[Ir_2Cl_4(HB(3,5\text{-}(CH_3)_2C_3N_2H_3)_3)_2]$ [73117-58-5]. A large number of phosphine complexes of iridium have been prepared. Examples are $[Ir(P(C_6H_5)_3)(CO)_3]^-$ [52352-68-8], $[IrCl(P(C_6H_5)_3)_2(CO)]$ [15842-08-7], and $[Ir(P(C_6H_5)_3)_3(CO)H]$ [17250-25-8], $[Ir(PC_6H_5)_3H_3]$ [16924-01-9]. Fewer arsine complexes such as $[Ir(As(C_6H_5)_3)Cl(CO)_2]$ [59809-93-7] and $[IrCl_2(As(C_6H_5)_3)_2(CO)]$ [15682-62-9] are known.

Iridium complexes having oxygen ligands are not nearly as extensive as those having nitrogen. Examples include acetylacetonates $[Ir(P(C_6H_5)_3)_2\ (acac)H_2]$ [64625-61-2], aqua complexes $[Ir(OH_2)_6]^{3+}$ [61003-29-0], nitrato complexes $[Ir(ONO_2)(NH_3)_5]^{2+}$ [42482-42-8], and peroxides $IrCl(P(C_6H_5)_3)_2(O_2\text{-}t\text{-}C_4H_9)_2(CO)]$ [81624-11-5]. Unlike rhodium, very few Ir(II) carboxylate-bridged dimers have been claimed and $[Ir_2(OOCCH_3)_4]$ has not been reported. Some Ir(I) complexes exhibit reversible oxidative addition of O_2 to form Ir(III) complexes. That chemistry has been reviewed (172). The most well-known and studied is Vaska's complex [14871-41-1], *trans*-$[IrCl(P(C_6H_5)_3)_2CO]$, which reversibly forms $[IrCl(P(C_6H_5)_3)(\eta^2\text{-}O_2)CO]$ [29933-65-1] in the presence of oxygen. Complexes containing sulfur ligands include dithiocarbamates $[Ir\{S_2CN(CH_2)_4\}_3]$ [39958-06-0]; thioethers, *mer*-$[IrCl_3(S(C_2H_5)_2)_3]$ [34177-65-6]; and carbon disulfide complexes, $[IrCl(P(C_6H_5)_2CH_3)(CS_2)(CO)]$ [81178-13-4].

Halide ligands are found in homoleptic complexes as well as in mixed ligands systems. Halide complexes of Ir(IV) such as $[IrCl_6]^{2-}$ [16918-91-5] are readily reduced to Ir(III) species, eg $[IrCl_6]^{2-}$ [14648-50-1], in neutral or basic solution, or in the presence of reducing agents such as KI, oxalate, or photochemical activation (173).

7.3. Organometallic Compounds

The predominant oxidation states of iridium in organometallics are +1 and +3. Iridium forms mononuclear and polynuclear carbonyl complexes including $[IrCl(P(C_6H_5)_3)_2(CO)_2]$ [14871-41-1], $[Ir_2Cl_4(CO)_2]^-$ [12703-90-1], $[Ir_4(CO)_{12}]$ [18827-81-1], and the conducting, polymeric $[IrCl(CO)_3]_n$ [32594-40-4]. Isonitrile and carbene complexes are also known.

Iridium forms σ-bonded alkyl, *fac*-$[Ir(P(CH_3)_2C_6H_5)_3(CH_3)_3]$ [15927-48-7]; aryl, $[IrI(Cp)(C_6H_5)(CO)]$ [64867-79-4]; acyl, $[IrCl_2(P(C_6H_5)_3)_2OOCCH_3]$ [36447-22-0]; carboxylato, $[IrI_2(bipy)(CO_2OCH_3)(CO)]$

[23733-10-0]; alkenyl; and alkynyl complexes. Many orthometallated complexes are known, such as $[IrHCl(P(C_6H_5)_2(C_6H_4))(P(C_6H_5)_3)_2]$ [24846-80-8]. In some cases orthometallation is reversible and gives rise to H–D exchange on the aromatic ring (172). Numerous π-complexes are known; examples include alkenes, $[Ir_2Cl_2(C_2H_4)_4]$ [39722-81-1]; dienes, $[Ir(cod)_2]^+$ [35138-23-9]; alkynes; allyls, $[Ir(\eta^3\text{-}C_3H_5)_3]$ [12108-64-4]; and conjugated dienes, $[IrCl(\eta^4\text{-1,3-butadiene})_2]$ [39732-20-2]. Complexes of η^5-cyclopentadiene (Cp) and η^6-arene such as $[Ir(P(C_6H_5)_3)(CO)Cp]$ [32612-68-3], $[IrBr_2(CO)Cp]$ [64867-78-3], and $[Ir(C_6H_6)((CH_3)_5C_5)]^{2+}$ [12715-71-8], are also known.

7.4. Synthesis

The principal starting material for synthesis of iridium compounds is iridium trichloride hydrate [14996-61-3], $IrCl_3 \cdot xH_2O$. Another useful material for laboratory-scale reactions is $[Ir_2Cl_2(cod)_2]$ [12112-67-3].

7.5. Uses

7.5.1. Catalysis

Iridium compounds do not have industrial applications as catalysts. However, these compounds have been studied to model fundamental catalytic steps (174), such as substrate binding of unsaturated molecules and dioxygen; oxidative addition of hydrogen, alkyl halides, and the carbon–hydrogen bond; reductive elimination; and important metal-centered transformations such as carbonylation, β-elimination, CO reduction, and oligomerization reactions. One of the most widely studied systems is the class of Vaska's compounds typified by *trans*-$[IrCl(P(C_6H_5)_3)(CO)]$ which reversibly adds O_2 yielding $[IrCl(P(C_6H_5)_3)_2(O_2)CO]$ [27628-97-3]. Oxygen complexes of this sort can catalytically oxidize olefins (175), ketones (176), NO (177), CO (178), and SO_2 (179). Another much-studied reaction is carbon–hydrogen bond activation (180). Complexes such as $[Ir(Cp(CH_3)_5)L]$, where $L = P(CH_3)_3$ or CO, oxidatively add arene and alkane carbon–hydrogen bonds (181, 182). Catalytic dehydrogenation of alkanes (183) and carbonylation of benzene (184) has also been observed. Iridium compounds have also been shown to catalyze hydrogenation (185) and isomerization of unsaturated alkanes (186), hydrogen-transfer reactions, and enantioselective hydrogenation of ketones (187) and imines (188).

7.5.2. Miscellaneous

Iridium dioxide, like RuO_2, is useful as an electrode material for dimensionally stable anodes (DSA) (189). Solid-state pH sensors employing IrO_2 electrode material are considered promising for measuring pH of geochemical fluids in nuclear waste repository sites (190). Thin films (qv) of IrO_2 are stable electrochromic materials (191).

8. Palladium Compounds

The most common oxidation state of palladium is +2 which corresponds to a d^8 electronic configuration. Compounds have square planar geometry. Other important oxidation states and electronic configurations include 0 (d^{10}), which can have coordination numbers ranging from two to four and is important in catalytic chemistry; and +4 (d^6), which is octahedral and much more strongly oxidizing than platinum (IV). The chemistry of palladium is similar to that of platinum, but palladium is between 10^3 to 5×10^5 more labile (192). A primary industrial application is palladium-catalyzed oxidation of ethylene (see Olefin polymers) to acetaldehyde (qv). Palladium-catalyzed carbon–carbon bond formation is an important organic reaction.

8.1. Binary Compounds

The fluorides of palladium are PdF_2 [13444-96-7], PdF_3 [12021-58-8], and PdF_4 [13709-55-2]. The difluoride and tetrafluoride are unusual. The former is paramagnetic and octahedral; the latter is eight-coordinate. The trifluoride contains both Pd(II) and Pd(IV). The only chloride is palladium dichloride [7647-10-1], $PdCl_2$, which occurs in a hydrated form, and two anhydrous forms, an α-form having a polymeric chain structure, and a β-form that consists of a Pd_6 core with edge-bridging chlorides. Solutions of the hydrate are readily reduced to metal by hydrogen and many organic compounds. Other halides include palladium dibromide [13444-94-5] and diiodide [7790-38-7]. Palladium monoxide [1314-08-5], PdO, is the only stable oxide of palladium. It is easily reduced to metal and used as a hydrogenation catalyst. Palladium also forms a dihydroxide, $Pd(OH)_2$ [12135-22-7]. Palladium forms sulfides, selenides, and tellurides. The best-characterized for these are PdS [12125-22-3], PdS_2 [12137-75-6], PdSe[12137-76-7], $PdSe_2$ [60672-19-7], PdTe [12037-94-4], and $PdTe_2$ [12037-95-5]. Borides, silicides, phosphides, and arsenides are also known (23, 24).

8.2. Coordination Compounds

Palladium forms numerous complexes with ammonia and with simple amines. Examples are $[Pd(NH_3)_4]^{2+}$ [15974-14-8], $[PdCl(dien)]^+$ [17549-31-4], *cis*-$[PdCl_2(NH_3)_2]$ [15684-18-1], and *trans*-$[PdCl_2(NH_3)_2]$ [13782-33-7]. Monoammine complexes such as $[PdCl_3(NH_3)]^-$ [15691-32-4] are stable but less common. Examples of aromatic amine complexes include *trans*-$[PdCl_2(pyr)_2]$ [14052-12-1], $[PdCl_2(bipy)]$ [14871-92-2], and nucleosides such as $[PdCl(dien)(guanosine)]^+$ [73601-42-0] (193). Complexes of Pd(IV) such as $[PdCl_2(NH_3)_4]^{2+}$ [70491-81-5] and $[PdCl_4(bipy)]$ [57209-01-5] may be prepared by chlorine oxidation of the corresponding $Pd(2+)$. The aromatic amine Pd(IV) complexes are more stable than ammine and aliphatic amine species, which are reduced to Pd(II) in water or thermally (194).

The Pd(II) compound chloro(tris[2-(dimethylamino)ethyl]amine)palladium(II) [66632-97-1] is a rare example of a Pd(II) compound having a coordination number greater than four (194, 195). Palladium forms complexes with nitriles, $[PdCl_2(NCC_6H_5)_2]$ [14220-64-5]; imines, *cis*-$[PdCl_2(t\text{-}C_4H_9N{=}CHCH{=}NC_4H_9\text{-}t)]$ [72905-45-4]; oximes, $[Pd(DMG)_2]$ [14740-97-7]; Schiff bases, [Pd(N-*n*-butylsalicylaldiminato)$_2$] [14363-25-8]; azides, $[Pd(N_3)_4]^{2-}$ [16843-41-7]; semicarbazones; hydrazones; and triazenes (194, 196). Numerous phosphine complexes have been isolated, including $[Pd_2Cl_4(P(C_2H_5)_3)_2]$ [15684-59-0], $[PdCl_2(P(CH_3)_3)_2]$ [25892-38-0], *trans*-$[PdCl_2(P(C_6H_5)_2CH_3)_2]$ [26973-01-3], $[Pd(PC_2H_5)_3H]^+$ [51404-97-8], and *trans*-$[PdCl(P(C_6H_5)_3)H]$ [16841-99-9]. In solution, *cis*- and *trans*-$[PdCl_2P_2]$ complexes, where $P = \text{phosphine}$, interconvert rapidly (197). Oxidation of Pd(II) phosphine and arsine complexes yields Pd(IV) complexes similar to those obtained with amines (198). Low valent Pd(0) complexes, $[Pd(P(C_6H_5)_3)_4]$ [14221-01-3], and binuclear Pd(I) complexes, $[Pd_2Cl_2(\text{bis(dimethylphosphino)methane})_2]$ [89178-59-6], containing bridging phosphine ligands and a metal–metal bond have been prepared. A variety of small molecules, including CO, CNR, SO_2, and CS_2, insert into the Pd–Pd bond (199) of this last species. Arsine and stibine complexes are similar to the phosphines.

Palladium coordinates oxygen ligands weakly. The aqua complexes are generally formed as intermediates in substitution reactions in water. The tetraaqua ion $[Pd(OH_2)_4]^{2+}$ [22573-07-5] is prepared by treating $[PdCl_4]^{2-}$ [14349-67-8] with $AgClO_4$ in water. Isolatable complexes containing oxygen ligands include $[Pd(DMSO\text{-}S)_2(DMSO\text{-}O)_2]$ [3079-58-4]; $[Pd_2(OH)_2(P(C_6H_5)_3)_4]$ [39151-60-5]; $[Pd_3(OOCCH_3)_6]$ [29950-51-4]; $[Pd(ox)_2]$- [15226-60-5]; $[Pd(acac)_2]$ [14024-61-4]; and $[Pd(P(C_6H_5)_3)_2(cat)]$ [64608-33-9]. Palladium binds to sulfur and selenium more strongly than to oxygen. Some representative complexes include the thiolates, $[Pd_6(S\text{-}n\text{-}C_3H_7)_{12}]$ [35359-97-8]; thioethers, $[Pd_2Br_4(S(CH_3)_2)_2]$ [21315-76-4]; thiocyanates $[Pd(SCN)_4]^{2-}$ [16057-01-5]; thioureas $[Pd(SC(NH_2)_2)_4]^{2+}$ [42941-76-4]; sulfoxides; sulfites, $[Pd(SO_3)_4]^{6-}$ [65466-59-3]; dithiocarbamates, $[Pd(S_2CN(C_2H_5)_2)_2]$ [15170-78-2]; dithiophosphinates, $[Pd(S_2P(C_2H_5)_2)_2]$ [89621-75-0]; and dithiolenes, $[Pd(S_2C_2(CN)_2)_2]^{2-}$ [19555-33-0]. Numerous other complexes with sulfur and selenium ligands are known (197).

Palladium forms halide complexes such as $[PdCl_4]^{2-}$ [14349-67-8] and $[PdCl_6]^{2-}$ [17141-41-2], and bridging complexes, $[Pd_2Br_6]^{2-}$ [33887-55-7]. Halide complexes can aquate in water. Hexachloropalladate salts release Cl_2 when heated as solids or in solution (200).

8.3. Organometallic Compounds

Mononuclear carbon monoxide complexes of palladium are relatively uncommon because of palladium's high lability, tendency to be reduced, and competing migratory insertion reactions in the presence of a Pd–C bond (201). A variety of multinuclear compounds are known (202), including $[Pd_2Cl_4(CO)_2]$ [75991-68-3], $[Pd_3(P(C_6H_5)_3)_3(CO)_3]$ [36642-60-1], and $[Pd_7(P(CH_3)_3)_7(\mu_3\text{-}CO)_3(\mu_2\text{-}CO)_4]$ [83632-51-3]. Isonitriles and carbenes are better σ-donors, and many compounds are known (203) such as $[PdI_2(CN\text{-}t\text{-}C_4H_9)_2]$ [24917-36-0], $[Pd_2(CNCH_3)_6]^{2+}$ [56116-47-3], $[Pd_2Cl_2(CN\text{-}t\text{-}C_4H_9)_4]$ [34742-93-3], $[Pd(CN\text{-}t\text{-}C_4H_9)_2]$ [24859-25-4], and $[Pd(C(NHCH_3)_2)_4]^{2+}$ [45256-27-7].

Palladium forms σ-bonded alkyl, $[Pd(C_2H_5)_2(bipy)]$ [102150-17-4], $[PdI\ (CH_3)_3(bipy)]$ [110182-93-9]; aryl, $[Pd_2Cl_2(2\text{-}(2\text{-pyridinyl})phenyl\text{-}C,N)_2]$ [2083286-4]; vinyl, $[PdCl(P(C_6H_5)_3)_2(CH{=}CCl_2)]$ [31871-49-5], acyl, $[PdCl(P(C_6H_5)_3)_2\ (COC_6H_5)]$ [50417-59-9]; and iminoacyl, $[PdI(P(C_4H_9)_3)_2(C(CH_3)NCC_6H_{11})_2]$ [42582-35-4], complexes. Palladium alkyls and aryls can be prepared by transmetallation of Pd(II) complexes using Grignard reagants, organolithium, or other organometallic species (see Grignard reactions); by oxidative addition by organic halides to a Pd(0) complex; by nucleophilic attack on coordinated olefins; and by orthometallation. Palladium alkyls and aryls tend to be very reactive, a property which has been used to advantage in organic synthesis. When the alkyl is contained in a chelate ring it is more stable. Some Pd(IV) alkyls have been prepared. Palladium acyl and iminoacyl are most often prepared by migratory insertion of an alkyl into a palladium carbonyl or isonitrile.

Palladium forms π-complexes of olefins, $[Pd_2Cl_4(CH_2{=}CHC_6H_5)_2]$ [12257-72-6]; dienes, $[PdCl_2(1,5\text{-}cod)_2]^{2+}$ [59687-80-8] and $[Pd_2(dba)_3]$ [51364-51-3]; acetylenes, $[Pd(P(C_6H_5)_3)_2((CCOOCH_3)_2)]$ [15629-88-6]; allyls, $[Pd(P(C_6H_5)_3)_2(C_3H_5)]^+$ [38497-96-0]; and cyclopentadienes $[Pd(CH_3Cp)(C_3H_5)]$ [92719-24-9]. Olefin complexes are generally very reactive and susceptible to nucleophilic attack. Diene complexes are somewhat more stable. The π-allyl ligand, the most common organometallic ligand for palladium, can be formed by deprotonation of a coordinated olefin that contains a β-hydrogen, nucleophilic attack on coordinated 1,3-dienes, hydropalladation of a diene by a palladium hydride, reaction of an alkyl halide or alcohol with a palladium salt in a protic solvent, oxidative addition of allyl halides with Pd(0) complexes, or transmetallation using an allyl Grignard. Palladacene is unknown but the Cp ligand is found in a variety of palladium complexes.

8.4. Synthesis

The most common starting materials for palladium complexes are $PdCl_2$ [7647-10-1] and $[PdCl_4]^{2-}$ [14349-67-8]. Commercially available materials useful for laboratory-scale synthesis include $[Pd_3(OOCCH_3)_6]$ [3375-31-3], $[PdCl_2(NCC_6H_5)]$ [14220-64-5], $[Pd(acac)_2]$ [14024-61-4], $[PdCl_2(cod)]$ [12107-56-1], and $[Pd(P(C_6H_5)_3)_4]$ [14221-01-3].

8.5. Uses

8.5.1. Catalysis

The most important industrial use of a palladium catalyst is the Wacker process. The overall reaction, shown in equations 7–9, involves oxidation of ethylene to acetaldehyde by Pd(II) followed by Cu(II)-catalyzed reoxidation of the Pd(0) by oxygen (204). Regeneration of the catalyst can be carried out *in situ* or in a separate reactor

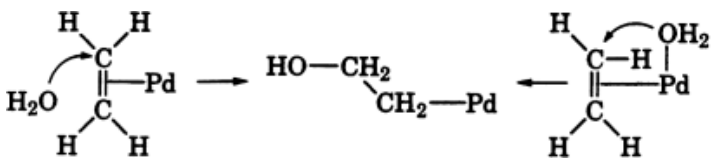
after removing acetaldehyde. The acetaldehyde must be distilled to remove chlorinated by-products.

$$C_2H_4 + PdCl_4^{2-} + H_2O \longrightarrow CH_3CHO + Pd^0 + 2\ HCl + 2\ Cl^- \qquad (7)$$

$$Pd^0 + 2\ CuCl_2 + 2\ Cl^- \longrightarrow PdCl_4^{2-} + 2\ CuCl \qquad (8)$$

$$2\ CuCl + 1/2\ O_2 + 2\ HCl \longrightarrow 2\ CuCl_2 + H_2O \qquad (9)$$

The acetaldehyde-forming step (eq. 7) involves nucleophilic attack by hydroxide or water on a coordinated Pd olefin complex followed by β-hydride elimination.



(10)

T[[dotb]he nature of the initial attack by the water (eq. **10**) is a matter of some controversy (205, 206). Stereochemical and kinetic studies of model systems have been reported that support trans addition of external water (207, 208) or internal addition of cis-coordinated water (209), depending on the particular model system under study. Other palladium-catalyzed oxidations of olefins in various oxygen donor solvents produce a variety of products including aldehydes (qv), ketones (qv), vinyl acetate, acetals, and vinyl ethers (204). However the product mixtures are complex and very sensitive to conditions.

Palladium-catalyzed coupling reactions have important synthetic applications (210–212). The prototypical reaction is the Heck reaction (213) whereby an organoPd(II) undergoes coupling with an olefin (eq. 11).

$$C_6H_5{-}Pd{-}X + CH_2{=}CH_2 \longrightarrow C_6H_5CH{=}CH_2 + HX + Pd^0 \qquad (11)$$

The utility of palladium-coupling reactions arises from the fact that several mild, stereospecific methodologies compatible with a variety of functional groups have been developed for coupling organopalladium complexes and electrophiles other than olefins (214–217). The reactive organopalladium complex is usually prepared *in situ* by transmetallation of a main group organometallic, eg, an organozinc, organotin, or organomercurial, using a Pd(II) salt, or by oxidative addition of Pd(0) into an R–X bond, where X is a leaving group, often halide or triflate. Hence palladium-catalyzed cross-coupling of organotin reagents using acid chlorides, benzyl halides, allyl halides, and vinyl halides, aryl halides, and aryl triflates occurs under mild conditions in high yields (215, 216). In the presence of CO, migratory insertion in the palladium alkyl intermediate leads to ketone formation (215) or ester formation (218, 219). Palladium-catalyzed arylation of enol ethers (217) and cross-coupling of organic halides with organoborates (220) and organosilanes (214) are other examples of palladium-catalyzed bond formation.

Other reactions (204) catalyzed by palladium include oxidative coupling of aromatic compounds to biphenyls; aromatic acetoxylation; oxidative carbonylation of olefins, aromatics, and alcohols; air oxidation of alcohols to acetals and aldehydes; allylation of active methylene groups (221); cycloaddition reactions (222); hydrostannylation (223); copolymerization of CO and olefins (224); and reductive carbonylation of methyl acetate to 1,1-diacetoxy ethane (153). Finally, ibuprofen [51146-56-6], 4-$(CH_3CH_2CH_2)C_6H_4CH(COOH)CH_3$, is

prepared commercially by Boots Hoechst Celanese using a palladium-catalyzed carbonylation. The carbonylation of 4-$(CH_3CH_2CH_2)C_6H_4CH(OH)CH_3$ is carried out in the presence of HCl and phosphoric acid at 125°C under 5.5 MPa (800 psi) of CO in the presence of catalytic $PdCl_2(P(C_6H_5)_3)_2$ [4056-88-3] (225, 226).

8.5.2. Miscellaneous

Reduction of a palladium salt by CO is the basis of a visual test for ambient carbon monoxide (227). Palladium compounds are used as photographic sensitizers (228). The low dimensional mixed valence compound $Cs_{0.83}[Pd(S_2C_2(CN)_2)]\cdot 0.5H_2O$ behaves as a semimetal at room temperature (229). Palladium compounds isostructural with potent platinum antitumor compounds have poor antitumor activity (230).

8.5.3. Plating and Coatings

Palladium films are used as electrical contacts and connectors and in circuit board fabrication (see Electrical connectors). Palladium, palladium–silver, and palladium–nickel alloys are used as less expensive substitutes for gold in some applications (231). Thin films also have applications as gas sensors (94). Typical electrolytes for plating baths include salts of $[Pd(NH_3)_4]^{2+}$, or $[Pd(NH_3)_2(NO_2)_2]$, called Pd–P–Salt in an ammoniacal medium. Alternatively, the Pd amine salt is prepared directly from $PdCl_2$. Palladium–silver baths can be prepared from $[Pd(NH_3)_2(NO_3)_2]$ and $AgNO_3$ in aqueous ammonia (232). Electroless plating (qv) baths contain a reducing agent such as hydrazine or hypophospite (233). Deposition of a thin, tarnish-resistant coating can be accomplished by immersion plating, using $H_2[Pd(NO_2)_2SO_4]$, known as DNS palladium solution (234). Volatile palladium compounds are used in chemical vapor deposition processes to deposit thin films of metallic palladium (94). Liquid palladium solutions employ discrete compounds such as $PdCl_2(S(n\text{-}C_4H_9)_2)_2$ [32335-75-4] or poorly defined sulforesinates.

9. Platinum Compounds

The most common oxidation states and corresponding electronic configurations of platinum are +2 (d^8), which is square planar, and +4 (d^6), which is octahedral. Compounds in oxidation states between 0 (d^{10}) and +6 (d^4) exist. Platinum hydrosilation catalysts are used in the manufacture of silicone polymers. Several platinum coordination compounds are important chemotherapeutic agents used for the treatment of cancer.

9.1. Binary Compounds

Three fluorides, PtF_4 [13455-15-7], PtF_5 [37782-184-8], and platinum hexafluoride [13693-05-5], PtF_6, are well documented. The last is a powerful oxidizing agent and can oxidize dioxygen and xenon (235). Two chlorides exist, platinum dichloride [10025-65-7], $PtCl_2$, and platinum tetrachloride [37773-49-2]. Platinum dichloride exists in an α- and β-form, the latter containing a Pt_6 core and edge-bridging chlorides. Platinum trichloride [25909-39-1], $PtCl_3$, contains Pt(II) and Pt(IV) centers. Other halides include two bromides, $PtBr_2$ [13455-12-4] and $PtBr_4$ [13455-11-3], and two iodides, PtI_2 [7790-39-8] and PtI_4 [7790-46-7]. The most common oxide is platinum dioxide [1314-15-4] (Adams catalyst), PtO_2. Three less well-defined oxides are PtO [12035-82-4], Pt_2O_3 [12725-92-7], and PtO_3 [77883-44-4]. Platinum also forms $Pt(OH)_2$ [12135-23-8]. Sulfides of platinum include PtS [12038-20-9] and PtS_2 [12038-21-0] (24, 25, 236, 237). Borides, silicides, phosphides, selenides, and tellurides have been prepared (23, 24).

9.2. Coordination Compounds

Platinum forms numerous stable ammine complexes, the most important of which is the antitumor agent cisplatin, *cis*-dichlorodiammineplatinum(II) [26035-31-4], *cis*-$[PtCl_2(NH_3)_2]$. Other examples of

complexes containing ammonia or aliphatic or aromatic amines include *trans*-$PtCl_2(NH_3)_2$ [14913-33-8], Magnus's green salt [13820-46-7], $[PtCl_4][Pt(NH_3)_4]$, $[PtCl(dien)]^+$ [17549-31-4], $[Pt(NH_3)_6]^{4+}$ [18536-12-4], $[PtCl_2(bipy)]$ [13965-31-6], and oligonucleotide complexes such as that with deoxyguanidyl guanosine monophosphate d(GpG) [99802-17-2], *cis*$-Pt(NH_3)_2(d(GpG))^+$. The pK_a of ammines coordinated to Pt(IV) is reduced sufficiently to permit acetylacetone to react with $[Pt(NH_3)_6]^+$ in the presence of base, forming $[Pt(NH_3)_4((HNCCH_3)_2CH))]^{4+}$ [56370-84-4] (238). Mixed valence complexes such as Wolfram's red salt [60428-75-3], $[(Pt(II(NH_2C_2H_5)_4)(Pt(IV)Cl_2(NH_2C_2H_5)_4)]^{4+}$, and platinum blues [71611-15-9], $[Pt_4(NH_3)_8(\alpha-\text{pyridone})_4]^{5+}$, are well known. The former consists of linear stacks of alternating platinum(II) and platinum(IV) centers bridged by chloride; the latter contains four platinum centers having an average oxidation state of 2.5 (239). Platinum forms complexes with many other nitrogen donor ligands such as nitriles, *cis*-$[PtCl_2(NCC_6H_5)_2]$ [15617-19-3]; nitrite, $[Pt(NO_2)_4]^{2-}$ [22289-82-3]; azides, $[Pt(N_3)_4]^2$ [45074-06-4]; imines; oximes, $[Pt(DMG)_2]$ [17632-92-7]; and imidates, *trans*-$[PtCl_2((E)\text{-}HNCCH_3(OCH_3))_2]$ [15022-74-9]. Phosphorus ligands are able to stabilize oxidation states of platinum between 0 and +4, although the higher oxidation states are less common. Zero-valent complexes having coordination numbers ranging from two to four depending on the steric demands of the ligand are known. Examples include $[Pt(P(t\text{-}C_4H_9)_3)_2]$ [60648-70-6], $[Pt(P(C_6H_5)_3)_3]$ [13517-35-6], and $[Pt(P(C_6H_5)_2CH_3)_4]$ [27121-53-5]. Other phosphine and phosphite complexes are $[PtCl_2(P(C_6H_5)_3)_2]$ [10199-34-5], $[Pt_2(P_2O_5H_2)_4Cl_2]^{4-}$ [98303-98-1], $[PtCl_4(P(C_6H_5)_3)_2]$ [78309-42-9], and A-frame complexes such as $[Pt_2Cl_2(dppm)_2]$ [61250-65-5], and $[Pt_2Cl_2(dppm)_2(\mu^2\text{-}CO)]$ [68851-47-8]. Arsine and stibine complexes are also known.

Oxygen ligands are relatively labile. Nonetheless, many stable complexes exist. Aqua complexes are frequently prepared as reactive intermediates for ligand substitution reactions but are generally not isolated. Hydroxide forms stable bridging complexes such as $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$ [62048-57-1], as well as some terminal complexes such as *c,t,c*-$[PtCl_2(OH)_2(NH_2\text{-}i\text{-}C_3H_7]$ [62928-11-4] and hexahydroxyplatinic acid [52438-26-3], $H_2Pt(OH)_6$. Other oxygen ligands that form platinum complexes include oxygen, $[Pt(P(C_6H_5)_3)_2O_2]$ [15614-67-2]; carboxylate, $[Pt(CBDCA)(NH_3)_2]$ [41575-94-4] and $[Pt_4(OOCCH_3)_8]$ [67286-38-8]; β-diketonate, $[Pt(O,O'\text{-}acac)_2]$ [15170-57-5]; catecholato, $[Pt(P(C_6H_5)_3)_2(cat)]$ [64608-33-9]; and nitrato, *cis*-$[Pt(NO_3)_2(NH_3)_2]$ [14286-03-4]. Sulfur ligands bind strongly to platinum and frequently form bridging complexes. Examples of compounds include thiocyantes, $[Pt(SCN)_4]^{2-}$ [3866899-4]; thioethers, *cis*-$[PtCl_2(S(CH_3)_2)_2$ [17836-09-8] and $[Pt_2Br_4(\mu\text{-}S(C_2H_5)_2)_2]$ [20004-38-0]; sulfoxides, $[PtCl_3(DMSO)]$ [31203-96-0]; dithiocarbamates, $[Pt(S_2CN(C_2H_5)_2)_2]$ [15730-38-8]; and 1,2-dithiolenes, $[Pt(S_2C_2(CN)_2)_2)]^{2-}$ [62906-12-1]. Sulfur ligands exhibit a strong trans effect that labilizes the trans ligands toward substitution. This feature forms the basis of the Kurnakov test (240) to distinguish cis and trans isomers of $[PtCl_2(NH_3)_2]$. After substitution of the chloride by thiourea, the ammines of the cis isomer are labilized and displaced by additional thiourea, yielding $[Pt\{SC(NH_2)_2\}_4]^{2+}$ [48069-54-1], whereas the trans isomer yields *trans*-$[Pt\{SC(NH_2)_2\}_2(NH_3)_2]^{2+}$ [56959-55-8].

Many mixed ligand complexes contain halide ligands. Some examples of homoleptic complexes are $[PtCl_4]^{2-}$ [13965-91-8], $[Pt_2Br_6]^{2-}$ [31826-84-3], and $H_2[PtCl_6]$ [16941-12-1]. Platinum forms stable hydride complexes such as $[PtH_2(P(C_2H_5)_3)_2]$ [62945-61-3], and the A-frame complex $[Pt_2(dppm)_2H_2(\mu\text{-}H)]^+$ [86392-85-0] containing both terminal and bridging hydride. Complexes of silicon and tin such as $[PtH(SiCH_3(C_6H_5)_2)(P(C_6H_5)_3)_2]$ [40869-78-1], *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ [44967-93-3], and the unusual five-coordinate, $[Pt(SnCl_3)_5]^{3-}$ [40770-13-6], are also known and are significant to catalytic chemistry.

9.2.1. Organometallic Compounds

Organometallic complexes of platinum are usually more stable than palladium complexes. Carbon monoxide complexes of platinum are formed more readily than with palladium. Mononuclear and polynuclear complexes in oxidation states 0 to +2 exist such as $[Pt(P(C_6H_5)_3)_3CO]$ [15376-99-5], $[Pt(P(C_6H_5)_3)_2(CO)_2]$ [15377-00-1], $[Pt_3(P(C_6H_5)_3)_4(CO)_3]$ [16222-02-9], $[Pt_{19}(CO)_{22}]^{4-}$ [71966-26-2], $[Pt_2Cl_4(CO)_2]$ [25478-60-8], and *trans*-$[PtCl(P(C_2H_5)_3)_2(CO)]^+$ [20683-71-0]. A few in the +4 oxidation state are known, eg, $[PtBr_3(CO)H_2]^-$.

Isonitrile complexes such as $[Pt_3(CN\text{-}t\text{-}C_4H_9)_6]$ [55664-26-1], $[PtBr(CN\text{-}t\text{-}C_4H_9)_3]^+$ [38317-64-5]; and carbene complexes such as $[PtCl_2(P(C_2H_5)_3)(C(OC_2H_5)(NHC_6H_5)_2)]$ [25530-58-9] are also readily prepared. Platinum forms σ-bonded alkyl, *trans*-$[PtCl(P(C_6H_5)(CH_3)_2)_2C_2H_5]$ [38832-88-1]; cycloalkyl, $[PtCl_2(CH_2)_3(py)_2]$ [12085-95-9]; aryl, *cis*-$[PtBr(P(C_6H_5)_3)_2C_6H_5]$ [57694-39-0] and $[PtI(C_6H_5)_2(CH_3)(bipy)]$ [58411-19-1], as well as alkenyl, alkynyl, and acyl complexes.

The olefin complexes of platinum are generally quite stable and have been extensively studied. Typically, compounds are prepared by ligand displacement from a Pt(0) or Pt(II) species, but a variety of methods have been developed (241). Examples of complexes include $[Pt(dba)_3]$ [11072-92-7], $[PtCl_3(CH_2CH_2)]^-$ [12275-00-2] (Zeisses salt), and $[PtCl_2(COD)]$ [12080-32-9]. Many olefin complexes yield stable nucleophilic addition products with oxygen and nitrogen nucleophiles in a step analogous to the first step of the catalytic Wacker process catalyzed by palladium. Platinum also forms η^2-complexes with dienes, allenes, acetylenes, carbonyls, and thiocarbonyls. Allyl complexes such as $[Pt(C_3H_4)_2]$ [12240-88-9] and $[Pt(P(C_6H_5)_3)_2(C_3H_4)]^+$ [12246-65-0] may be prepared by oxidative addition of allylic halides in the presence of a reducing agent, transmetallation, deprotonation of a coordinate olefin containing a β-hydrogen, or insertion of a Pt hydride into an allene or diene. Complexes of η^4-cyclobutadiene $[Pt(SnCl_3)_2(\eta^4\text{-}C_4(CH_3)_4)]$ and η^5-cyclopentadiene $[Pt(Cp)(CH_3)]$ [1271-07-4] are also known.

9.3. Synthesis

The most important starting materials for platinum compounds are potassium tetrachloroplatinate(II) [100025-98-6], $K_2[PtCl_4]$, and $H_2[PtCl_6]$ [16941-12-1]. Other useful starting materials are $PtCl_2(CCN_6H_5)_2$ [15617-19-3], $[PtCl_2(cod)]$ [12080-32-9], and $[PtCl_2(P(C_6H_5)_3)_2]$ [10199034-5].

9.4. Uses

9.4.1. Chemotherapy

Two platinum compounds, cisplatin, *cis*-$[PtCl_2(NH_3)]$, and carboplatin, $[Pt(CBDCA)(NH_3)_2]$, are approved for use in humans. Both compounds are particularly effective in the treatment of testicular tumors where disease-free status is achieved in more than 90% of patients having minimal-to-moderate disease at the start of treatment (242). Platinum compounds are also used in the treatment of ovarian, head and neck, prostate, bladder, lung, and cervical tumors (243). These compounds have been used as single-agent treatments, but are frequently employed in combination with other chemotherapeutics (see Chemotherapeutics, anticancer). The principal dose-limiting side-effects of cisplatin, introduced in 1972, are kidney toxicity, nausea and vomiting, myleosuppression, and in 20% of patients, hearing loss (244). Carboplatin was introduced in 1981 as an analogue to cisplatin. Carboplatin has good antitumor activity and significantly reduced kidney toxicity and reduced nausea and vomiting associated with it (245). Numerous other analogues of Pt(II) and Pt(IV), active in animal models having cisplatin-resistant tumors, have been prepared. Some are in human trials (246, 247). Development of an orally active platinum antitumor agent such as *c,t,c*-$[PtCl_2(OOCCH_3)_2(NH_2\text{-}c\text{-hexyl})(NH_3)]$ [129580-63-8] which as of this writing (ca 1995) is in clinical trials (247, 248), is also of interest. The biochemical origins of antitumor activity and resistance have been reviewed (244, 249). Platinum chemotherapeutics is an active area of research.

9.4.2. Catalysis

Platinum-catalyzed hydrosilation is used for cross-linking silicone polymers and for the preparation of functionally substituted silane monomers (250). The most widely used catalyst is chloroplatinic acid (Spier's catalyst), H_2PtCl_6. Other compounds that catalyze the reaction include Pt(II) and Pt(0) complexes such as $PtCl_2(cod)$ and $Pt(CH_2CHC_6H_5)_3$, and a catalyst which contains predominately η-vinyl Pt(0) species, prepared from $HPtCl_6$ and 1,3-divinyltetramethyldisiloxane (251). The mechanism of the reaction is not well understood. Whereas

the observation of asymmetric hydrosilation of 1-methylstyrene by a Pt(II) complex in the presence of a chiral phosphine suggests a homogenous pathway (252), other evidence suggests that in many systems, colloidal platinum, produced during an induction period, may be the active catalyst (253). Platinum halides in the presence of tin(II) chloride catalyze the hydrogenation, isomerization, and hydroformylation of alkenes in solution (254) and in melts (255, 256). The water gas shift reaction is catalyzed by $[Pt(P(i\text{-}C_3H_7))_3]$ [60648-72-8] (257). Other compounds such as PtO_2 (Adam's catalyst) are reduced by hydrogen to a metallic heterogeneous hydrogenation catalyst.

9.4.3. Plating and Coatings

Thin surface coatings of platinum and platinum alloys are used as decorative finishes and in critical applications where it is necessary to provide finishes resistant to corrosion or high temperature, eg, coatings on jet-engine turbine components (258). Compounds used in the electrodeposition of platinum are based on Pt(II) and Pt(IV) and include $H_2[PtCl_6]$ and its salts, eg, Pt–P–Salt, $[Pt(NH_3)_2(NO_2)_2]$; $H_2[Pt(SO_4)(NO_2)_2]$; Pt–Q–Salt, $[Pt(NH_3)_2(HPO_4)]$; and $[Pt(OH)_6]^{2-}$ (259, 260). Chloride-based baths have been superseded by P-Salt-based baths, which are more stable and relatively easily prepared. Q-Salt baths offer even greater stability and produce hard, bright films of low porosity. Plating under alkaline conditions employs salts of $[Pt(OH_6)]^{2-}$. These baths are easily regenerated but have low stability. Platinum films have uses in the electronics industry for circuit repair, mask repair, platinum silicide production, and interconnection fabrication (94). Vapor deposition of volatile platinum compounds such as $[Pt(hfacac)_2]$ and $[Pt(CO)_2Cl_2]$ is used to deposit thin films of metallic platinum on surfaces. Concentrated organic solutions of poorly defined platinum complexes of alkyl mercaptides or sulforesinates are used to coat ceramics and glass.

9.4.4. Miscellaneous

Chloroplatinic acid is used in the production of automobile catalysts. Platino-type prints based on reduction of Pt(II) to Pt(0) by a photosensitive reducing agent such as iron(III) oxalate are used in art photography (261, 262). Infrared imaging devices based on a platinum silicide detector have been developed (263).

10. Health and Safety

Compounds of most PGMs are only slightly to moderately toxic by oral ingestion (264), LD_{50} (rat): $RhCl_3$, 1300 mg/kg; $Na_2[IrCl_6]$, 500 mg/kg; $Na_2[PdCl_4]$, 500 mg/kg; *cis*-$[PtCl_2(NH_3)_2]$, 20 mg/kg; $Na_2[PtCl_6]$, 25 mg/kg; $RuCl_3$, 210 mg/kg (guinea pig). The most serious acute hazard arises from exposure to volatile RuO_4 (bp 40°C) and OsO_4 (bp 131°C), which deposit black RuO_2 or OsO_2 upon contact with tissue. These substances are especially hazardous to the eyes and respiratory system (265–267). Other volatile Os compounds, eg, OsF_6 (bp 45.9°C) and $OsCl_4$ (bp 130°C), pose a similar hazard (268). Finely divided osmium metal can react in air to form OsO_4. The acceptable 8-h exposure for OsO_4 is 2 $\mu g/m^3$(269).

Work using PGM compounds should be carried out in a properly functioning hood. Special care should be taken to avoid inhalation or contact of fumes with the eyes. Exposure to some anionic salts of platinum, eg, $[PtX_6]^{2-}$ and $[PtX_4]^{2-}$ where X = Cl, Br, or I, can lead to serious allergic reaction and sensitization (allergenicity Cl > Br > I) (270). Symptoms include rhinitis, conjuctivitus, asthma, urticara, and contact dermatitis. The allergic reaction may be immediate or may be delayed overnight. Whereas the allergic reaction can be life-threatening, there is no evidence of long-term effects if a sensitized individual is removed from exposure to platinum salts. Appropriate protective clothing should be worn and precautions should be taken to avoid inhalation or contact with the skin when working with these compounds. Compounds such as *cis*-$[PtCl_2(NH_3)_2]$, $[Pt(NH_3)_4]Cl_2$, and $K_2[Pt(NO_2)_4]$ are not allergenic (271). The threshold exposure limit of soluble platinum salts is 0.002 mg/m^3 on the basis of Pt (270). Platinum antitumor compounds are toxic. There have been no reports

of adverse toxic effects of platinum compounds owing to environmental exposure arising from the use of automobile catalysts (270).

10.1. Nomenclature

Abbreviation	Compound
acac	2,4-pentanedionato(1−)
(−)binap	(*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bipy	2,6-bipyridine
cat	catecholato(2−)
CBDCA	cyclobutane-1,1-dicarboxylate(2−)
cod	1,5-cyclooctadiene
cyclam	1,4,8,11-tetrazacyclotetradecane
dach	1,2-diaminocyclohexane
dba	1,5-diphenyl-1,4-pentadiene-2-one
diars	bis[diphenylarsine]ethane
dien	*N*-(2-aminoethyl)-1,2-ethanediamine
diim	ethanediimine
diphos	bis[diphenylphosphine]ethane
DMG	dimethyl glyoximato(1−)
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	methylenebis[diphenylphosphine]
EDTA	ethylenediaminetetraacetic acid anion(4−)
en	ethylenediamine
hfacac	1,1,1,5,5,5-hexafluoroacetyl acetonate(1−)
im	imidazolate(1−)
mhp	6-methyl-2-pyridonate(1−)
nbd	norbornadiene
OEP	2,3,7,8,12,13,17,18-octaethyl porphine(2−)
ox	oxalate(2−)
Pc	phthalocyanine(2−)
pop	$[P_2O_5H_2]^{2-}$
pyz	1,4-pyrazine
py	pyridine
terpy	2,2′:6′2″-terpyridine
sacsac	2,4-pentanedithionato(1−)
salen	1,2-ethylenebis(salicylideneiminato)(2−)
14-tms	1,4,8,11-tetramethyl-1,4,8,11-tetrazacyclotetradecane
TPP	*meso*-tetraphenylporphine(2−)

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