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Platinum Group Metals in Catalysis: Fabrication of Catalysts and Catalyst Precursors

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Abstract:

This short review article presents an overview of the preparation of platinum group metal complexes that are utilized as catalysts or catalyst precursors. The organization of this article begins with a description of the sources of the platinum group metals, goes through their basic refining and separation methodologies, and then into each individual metal's elaboration into value-added coordination and organometallic complexes that have demonstrated applications in homogeneous catalysis. The objective of this article is to explain how these catalysts are synthesized and the wide variety of organic transformations that are catalyzed by platinum group metal complexes. One conclusion that can be drawn from the article is that the further elaboration of the complexity of platinum group metal catalysts goes hand-in-hand with the selectivity of the particular organic transformation being catalyzed.

Introduction

Platinum group metals consist of the late second- and third-row transition series elements—ruthenium, osmium, rhodium, iridium, palladium, and platinum. Man's first knowledge of these elements dates back to ancient Egypt where archeologists had discovered a platinum band among silver hieroglyphic characters inlaid in a small box that dates back to ~720 B.C.[1] Platinum group metals were first deliberately mined in the 18th century in colonial South America and in the early 19th century in Russia. Platinum group metals and their salts have been used as catalysts for nearly 200 years. From as early as the 19th century, elemental platinum has been used as a catalyst in industrial processes such as the oxidation of ethanol to acetic acid or acetaldehyde, the oxidation of sulfur dioxide to sulfuric acid (the contact process), and catalytic combustion. The rationale behind the utilization of platinum group metals and their complexes as catalysts is their ability to catalyze reactions under milder conditions with higher selectivity as compared to other metals, their high stability in various oxidation states, functional-group tolerance, and their highly understood synthetic chemistry.

Platinum group metal complexes are capable of catalyzing a large variety of reactions including hydrogenations, hydrosilylations, oxidations, dehydrogenations, hydrogenolysis, carbon−carbon and carbon-heteroatom coupling, carbonylations, and hydroxylations.[2] Not only are these complexes utilized in the manufacture of bulk chemicals such as acetic acid (carbonylation) and *n*-butanal (hydroformylation), but they are also increasingly utilized in the fabrication of fine chemicals (the topic of this special feature section). Catalysis in and of itself plays an enormous role in our economy in terms of manufacturing and in environmental controls. The industrial use of catalysis in the United States generates a revenue that rivals the gross national product of an industrialized nation the size of Canada or Switzerland.[3] The science of homogeneous catalysis has made some dramatic breakthroughs in the past 20 years, especially in the areas of asymmetric catalysis, oxidation catalysis, carbonylation reactions, and olefin metathesis reactions. These areas all involve the utilization of platinum group metal complexes as catalysts or as catalyst precursors.

The purpose of this article is to provide a short and concise review covering the general fabrication of platinum group metals and their complexes with an emphasis on those complexes that are utilized as catalysts or catalyst precursors. The sources of these metals and their fabrication into higher-value-added products will be briefly described in this article.

Platinum Group Metal Sources

The aggregate supply of platinum group metals for 2001 was calculated to be a little over 450 metric tons.[4] The sources of the platinum group metals along with their amounts (in kg) are illustrated in Table 1.

From Table 1, the most significant source of platinum group metals is South Africa followed by Russia and then North America (primarily Canada). South Africa is the primary source of all the platinum group metals except for palladium, and that country is nearly the exclusive source for osmium, iridium, and ruthenium.

These metals are found in two different forms: as ore found along the chromite vein in pyroxene deposits in South Africa's Bushveld complex or as anode slimes derived as a byproduct of nickel refining.[5] The primary uses for the platinum group metals are in the automotive industry for

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(1) *Precious Metals Science and Technology*; Benner, L. S., Suzuki, T., Meguro, K., Tanaka, S., Eds.; IPMI Press: Allentown, PA, 1991; p 8.

(2) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd Ed.; Wiley: New York, 1992. (b) *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000. (c) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH Verlag: Weinheim, 2002.

(3) Godwin, H. A.; Hoffman, B.; Bowman-James, K. *The Frontiers of Inorganic Chemistry 2002*; Workshop sponsored by the National Science Foundation, Copper Mountain, CO, September 9−10, 2001; National Science Foundation: Washington, DC, 2002.

(4) *Platinum 2002*; Johnson Matthey Press: London, 2002.

(5) Hunt, L. B.; Lever, F. M. *Platinum Met. Rev.* **1969**, *13*, 126.

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Table 1. **Platinum group metal supply in 2001 tabulated by region of origin and amount (in kg)**

	South Africa	Russia	North America
Pt	127,520	46,660	3,760
Pd	62,520	135,000	26,440
Rh	14,060	3,900	720
Ir	2,670	−	−
Ru	10,860	−	−
Os	600	−	−

Table 2. **Platinum group metal demand (in 2001) by application (in kg)**

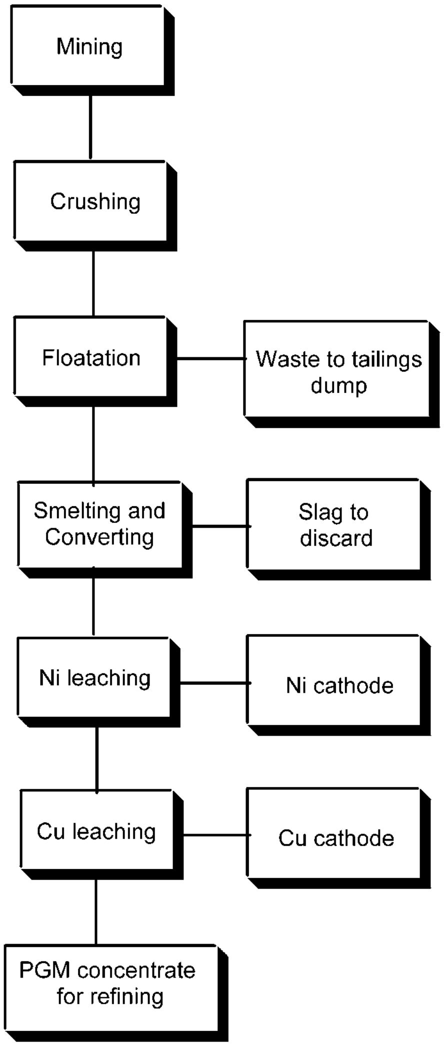
	automotive	jewelry /investment	chemical	electronics	glass	dental
Pt	78,380	80,890	12,910	11,970	8,860	−
Pd	158,940	9,490	7,310	21,770	−	20,840
Rh	17,600	−	1,370	190	1,210	−
Ir	280	−	870	1,520	−	−
Ru	−	−	4,760	4,170	−	−
Os	−	−	230	270	−	−

catalytic converters, in the electronics industry, in the glass industry for molds, in the chemical industry, for jewelry, and as investment instruments. A breakdown of the usage of platinum group metals by application is illustrated in Table 2.[4]

Platinum Group Metal Refining

As described earlier, platinum group metals are mined either on their own (which is only done in South Africa) or as a byproduct of nickel mining. The refining process that is described here will discuss the general process as performed in South Africa.[6] The crude ore is removed from the platinum-bearing iron-chromite reef layers within the basic pyroxene deposit of the Bushveld igneous rock complex along with small amounts of base metal sulfides. The platinum group metal content of the ore is typically 4−6 g/metric ton. Of this content, ∼50−60% is platinum, 20−25% is palladium, and the balance is composed of the other platinum group metals. The refining method used to separate the platinum group metal concentrate from the base metals and other rock is illustrated as a block diagram in Scheme 1.

Scheme 1. **Block diagram portraying the process of extracting the platinum group metal concentrate from the mined ore**



From here, the platinum group metal concentrate is separated into the individual components by a variety of different methods. The one that is illustrated in Scheme 2 is a solvent extraction procedure as reported by Cleare and Charlesworth.[7]

The platinum group metal concentrate is dissolved in hydrochloric acid under an atmosphere of chlorine. The suspension is then filtered to remove silver chloride, which is then further processed to produce silver metal. The filtrate is then extracted with methyl isobutyl ketone to selectively extract gold along with other base metal impurities that are removed by washing the organic layer with dilute hydrochloric acid solution. The gold is then reductively precipitated by a suspension of iron powder. To refine palladium from the platinum group metal concentrate, the concentrate is extracted with β-hydroxyoxime, and the organic layer is washed with dilute hydrochloric acid solution to remove the base metals. The organic layer is then extracted with concentrated hydrochloric acid solution to remove the palladium, and the palladium is precipitated with ammonia to generate the ammonium hexachloropalladate salt. This salt is then reduced with hydrogen to produce palladium metal. The platinum group metal concentrate solution is then neutralized with hydroxide solution, and ruthenium and osmium are distilled from the concentrate into a hydrochloric acid solution. This solution is then fractionally distilled to separate ruthenium from osmium. To separate platinum from the concentrate, the concentrate is sparged with sulfur dioxide to reduce the dissolved iridium(IV) to iridium(III). Then, platinum is extracted from the concentrate with trioctylamine. The organic layer is then extracted with concentrated hydrochloric acid solution to remove the platinum, and then

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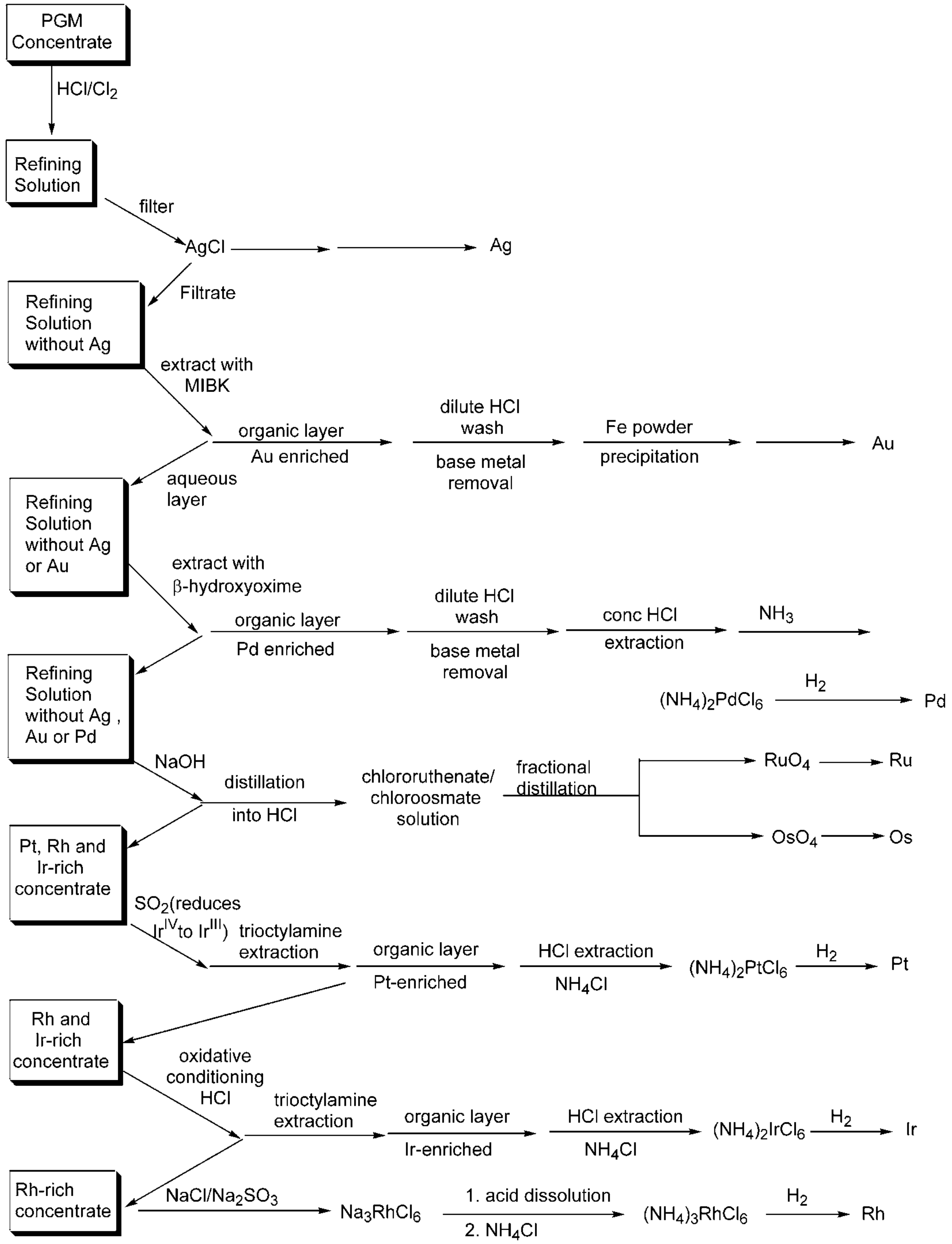
(6) Palmer, R. Western Platinum Mines, Ltd., personal communication.

(7) (a) Cleare, M. J.; Charlesworth, P.; Bryson, D. J. *J. Chem. Technol. Biotechnol.* **1979**, *29*, 210. (b) Charlesworth, P. *Platinum Met. Rev.* **1981**, *25*, 106. (c) *Precious Metals Science and Technology*; Benner, L. S., Suzuki, T., Meguro, K., Tanaka, S., Eds.; IPMI Press: Allentown, PA, 1991; p 383.

Scheme 2. **Refinement scheme for the chemical separation of the platinum group metals**

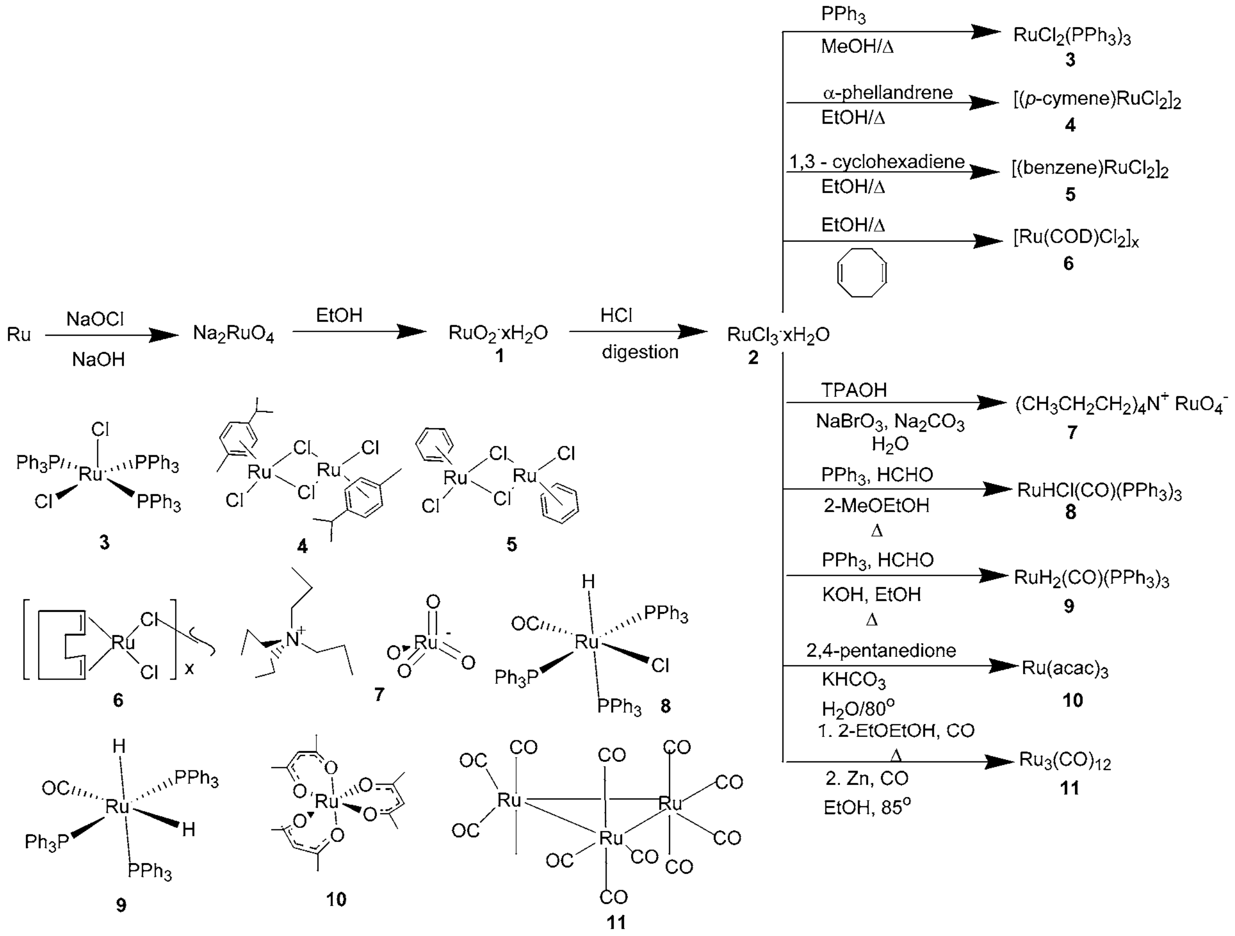


the platinum is precipitated with ammonium chloride to produce ammonium hexachloroplatinate, which is burned to generate platinum metal. To extract the iridium from the concentrate, the concentrate solution is oxidatively conditioned with hydrochloric acid to oxidize iridium to the +4 oxidation state. Then, iridium is selectively extracted with trioctylamine and then re-extracted with dilute hydrochloric acid to bring the iridium back into the aqueous phase as a chloro-complex. The iridium is then precipitated with ammonium chloride to generate ammonium hexachloroiridate and then reduced under hydrogen to generate iridium metal. Rhodium is then precipitated by a mixture of sodium chloride and sodium sulfite solution and filtered. The wet cake is dissolved in hydrochloric acid, and rhodium is precipitated by the addition of ammonium chloride to precipitate the ammonium hexachlororhodate salt. This salt is then reduced under hydrogen to generate rhodium metal. Typically the final purification steps in this process for each of the metals will be repeated one or two more times to attain the purity required for further value-added chemical products.

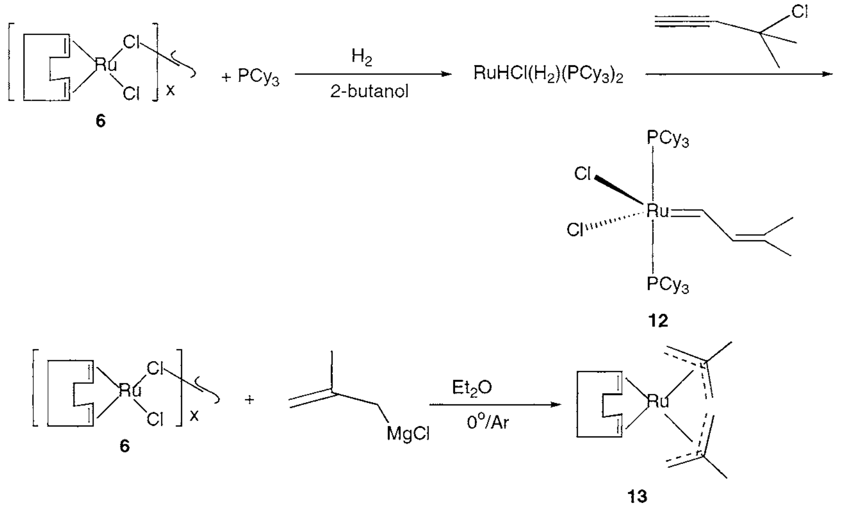
Platinum Group Metals: Introduction to Chemical Products

The platinum group metals are generally received via a commercial contract from a mining interest as electronic grade materials. For platinum and palladium, this is generally

Scheme 3. **Fabrication of ruthenium chemical products that have applications in catalysis**



Scheme 4. **Synthesis of further higher-value-added ruthenium products that are utilized in catalysis**



>99.95% purity while for rhodium, ruthenium, and iridium this is >99.9%, and for osmium, > 99.5%. From here, the chemical conversion of the metals all the way to high-value-added catalysts will be represented pictorially and explained on a metal-by-metal basis.

Ruthenium. Ruthenium complexes have been utilized as hydrogenation and olefin metathesis catalysts in many different applications. These types of catalytic applications and several others are elaborated on, along with the preparation of these catalysts in Schemes 3 and 4.

Ruthenium is dissolved by the reaction of the metal powder with chlorine in the presence of sodium hydroxide (to prevent volatilization of the ruthenium as ruthenium tetroxide) to generate sodium ruthenate solution which is then treated with a mild reducing agent to precipitate the binary ruthenium(IV) oxide as a hydrate ($RuO_2{\cdot}xH_2O$), **1**.[8] Ruthenium(IV) oxide hydrate, **1**, is utilized as a general starting point for all value-added ruthenium chemical products, is

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(8) Griffith, W. P. *The Chemistry Of The Rarer Platinum Metals*; Interscience: London, 1967; p 4.

available commercially, and is used as an oxidation catalyst in the presence of a powerful oxidant such as sodium periodate.[9,10] Ruthenium(IV) oxide hydrate is digested in warm concentrated hydrochloric acid solution and reduced in volume to form the hydrated ruthenium chloride ($RuCl_3 \cdot xH_2O$), **2**, salt as a brown/black hygroscopic crystalline solid. This product is generally an ill-defined mixture of oxochloro and hydroxychloro complexes in the III and IV oxidation states. Ruthenium(III) chloride hydrate, **2**, is used in a variety of different manners for catalysis. As a solution in butanol, it is utilized in metathesis polymerization of norbornene to form Norsorex, an elastomer that is produced by ElfAtochem in France at the rate of 5000 tons/annum.[11] **2** is also utilized in alkyne functionalization (e.g. the formation of vinyl carbamates with secondary amines, acetylene, and carbon dioxide),[12] oxidation catalysis in the presence of NMO,[13] and in olefin cleavage to form diacids. Ruthenium(III) chloride hydrate **2** is used as a starting reagent for a large number of ruthenium complexes utilized in catalysis. Dichlorotris(triphenylphosphine)ruthenium(II), **3**, is formed by the reaction of **2** with an excess of PPh_3 in refluxing MeOH.[14] **3**, is isolated as a red/black solid in nearly quantitative yield and adopts an unusual distorted octahedral geometry in which the vacant site is occupied by an agostic hydrogen of one of the phenyl groups of one of the PPh_3 ligands.[15]**3** is used as a catalyst for the oxidation of alcohols to aldehydes and ketones,[16] the reduction of diallyl α-oxalyl carboxylates with formic acid to form α-hydroxycarboxylic acids in high yield[17] and as an isomerization catalyst. Dichlorotris(triphenylphosphine)ruthenium(II) **3** is also utilized as a starting material for the formation of ruthenium complexes with chiral ligands and also for the formation of ruthenium carbene complexes for olefin metathesis. Dichloro(*p*-cymene)ruthenium(II) dimer, **4**, and Dichloro(benzene)ruthenium(II) dimer, **5**, are formed by the dehydrogenative coordination of the appropriate cyclohexadiene with **2** in refluxing EtOH.[18,19] These complexes are isolated as red to red/brown crystalline solids in high yield. These complexes are utilized in the hydrogenation of ketones and in transfer hydrogenations. In the presence of chiral ligands (e.g., BINAP), these complexes can perform these transformations in high enantiomeric excess.[20] Dichloro(*p*-cymene)ruthenium(II) dimer, **4**, is perhaps considered to be more advantageous than **5** due to the lower cost of α-phellandrene (a natural product derived from eucalyptus leaves) compared to 1,3-cyclohexadiene and to the greater solubility of **4** in organic solvents. Dichloro(1,5-cyclooctadiene)ruthenium(II) oligomer **6** is prepared by the reaction of 1,5-cyclooctadiene with **2** in refluxing EtOH.[21] The product is isolated as a brown insoluble polymer in nearly quantitative yield. As with **3**, **4**, and **5**, this complex is used as a catalyst precursor in the fabrication of ruthenium−BINAP complexes[22] and in the preparation of olefin metathesis catalysts.

Tetrapropylammonium perruthenate, **7**, is prepared by the reaction of **2** with an excess of $NaBrO_3$ and Na_2CO_3 in H_2O with the addition of the large cation to precipitate out the desired product.[23] Tetrapropylammonium perruthenate, **7**, is utilized as a mild catalytic oxidant for the conversion of alcohols to aldehydes and ketones.[24] Hydridochlorocarbonyltris(triphenylphosphine)ruthenium(II), **8**, is synthesized by the reaction of **2** with excess PPh_3 in the presence of formaldehyde in refluxing 2-methoxyethanol.[25] **8** has catalytic applications in the metathetical ring closure of silacycles[26] and the silylative coupling of vinyl alkyl ethers with vinyl silanes.[27] Dihydridocarbonyltris(triphenylphosphine)ruthenium(II), **9**, is prepared in much the same manner as **8** except that the reaction is performed in the presence of base (KOH) in refluxing EtOH.[25] Dihydridocarbonyltris(triphenylphosphine)ruthenium(II), **9,** has a potentially exciting application in the coupling of olefins to aromatic ketones via C−H activation.[28] Tris(2,4-pentanedionato)ruthenium(III) is synthesized by the reaction of **2** with excess 2,4-pentanedione in hot H_2O buffered with $KHCO_3$.[29] While **10** has seen application in the electronics and materials fields as a chemical vapor deposition agent, it has demonstrated catalytic utility in terpene rearrangements[30] and in the hydrogenation of esters to alcohols.[31] The reaction to form dodecacarbonyltriruthenium(0), **11**, can be achieved at ambient pressure in the presence of alcohols and zinc powder at elevated temperatures under a CO atmosphere.[32] Dodecacarbonyltriruthenium(0), **11**, is utilized as a carbonylation catalyst[33] and to acylate aromatic heterocycles via C−H activation in the presence of CO and olefins to form pyridyl ketones regiospecifically at the ortho position.[34]

Bis(tricyclohexylphosphine)-3-methyl-2-butenylideneruthenium(IV) dichloride, **12**, is an example of the family of ruthenium carbene complexes that are utilized in olefin

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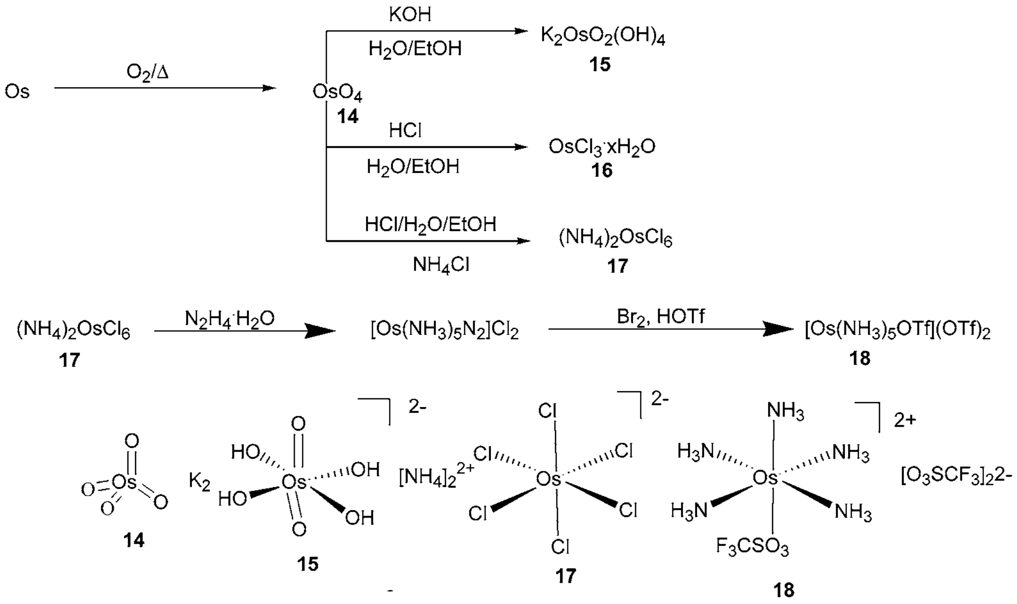
(9) Singh, A. K.; Varma, R. S. *Tetrahedron Lett.* **1992**, *33*, 2307.
(10) Hartmann, B.; Deprés, J. P.; Greene, A. E.; Friere de Lima, M. E. *Tetrahedron Lett.* **1993**, *34*, 1487.
(11) Marbach, A.; Hupp, R. *Rubber World* **1989**, (June), 30.
(12) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 314.
(13) Sharpless, K. B.; Akashi, K.; Oshima, K. *Tetrahedron Lett.* **1976**, 2503.
(14) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.
(15) La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778.
(16) Wang, G. Z.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun.* **1992**, 337.
(17) Shimizu, I.; Tekawa, M.; Maruyama, Y.; Yamamoto, A. *Chem. Lett.* **1992**, 1365.
(18) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
(19) Scaccianoce, L.; Braga, D.; Calhorda, M. J.; Grepioni, F.; Johnson, B. F. G. *Organometallics* **2000**, *19*, 790.
(20) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hari, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064.
(21) Bennett, M. A.; Wilkinson, G. *Chem. Ind.* (London) **1959**, 1516.
(22) Noyori, R.; Ohta, M.; Hisao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117.
(23) Bailey, A. J.; Griffith, W. P.; Mostafa, S. I.; Sherwood, P. A. *Inorg. Chem.* **1993**, *32*, 268.
(24) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.
(25) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. *Inorg. Synth.* **1974**, *15*, 48.
(26) Mise, T.; Takaguchi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 699.
(27) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677.
(28) Murai, S.; Kakiuchi, F.; Sekine; S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* (London) **1993**, *366*, 529.
(29) Figgis, B. N. *J. Chem. Soc (A)* **1966**, 432.
(30) Garcia-Granados, A.; Martinez, A.; Onorato, M. E. *J. Org. Chem.* **1987**, *52*, 606.
(31) Teunissen, H. T.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1367.
(32) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47.
(33) Byerley, J. J.; Rempel, G. L.; Takebe, N.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1482.
(34) Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. S. *J. Am. Chem. Soc.* **1992**, *114*, 5888.

Scheme 5. **Synthesis of osmium complexes that act as catalysts.**



metathesis. In this procedure, **6** is reacted with PCy_3 under a hydrogen atmosphere to generate the intermediate η^2-H_2 complex which is further reacted with a propargyl chloride to generate **12**.[35] The ruthenium carbene family of olefin metathesis catalysts have been named “Grubbs Catalysts” after their discoverer, R. H. Grubbs. These complexes have demonstrated wide usage in organic and polymer synthesis in that they are easier to handle than previous molybdenum and tungsten complexes, have significant functional group tolerance, and are able to catalyze all types of olefin metatheses (i.e., ring-closing metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, etc.)[36,37] Another example of the utilization of **6** as a catalyst precursor comes from the group of Genêt who prepared bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II), **13**, by the reaction of **6** with the Grignard reagent at 0° with concomitant extraction to isolate **13** as a light tan thermally sensitive solid.[38] **13** has been utilized as a pre-catalyst when in the presence of a chiral ligand, catalyzes enantioselective hydrogenation and has been utilized by PPG-Sipsy in the synthesis of candoxatril, a cardiovascular drug developed by Pfizer in the mid-1990s.[39,40]

Osmium. The utilization of osmium complexes in catalysis is dominated by the dihydroxylation transformation. The development of this process, especially with its enantioselective variant, was part of the focus of the 2001 Nobel Prize being awarded to K. Barry Sharpless. The synthesis of osmium complexes that behave as catalysts is shown in Scheme 5.

Osmium metal is reacted in a tube furnace at elevated temperatures in the presence of oxygen to generate osmium tetroxide, **14**, which is condensed and collected in a suitable receiving flask.[41] **14** is used as a starting material to synthesize potassium osmate, **15**, and osmium(III) chloride hydrate, **16**. **15** is synthesized from the reaction of **14** with KOH in aqueous EtOH and is isolated as a violet crystalline solid.[42] **16** is synthesized by the reaction of **14** with hydrochloric acid in aqueous EtOH to form chloroosmic acid (H_2OsCl_6). This red/yellow solution is reduced in volume to generate **16**, which much like **3**, is a mixture of oxochloro and chlorohydroxo complexes in various (III/IV) oxidation states. These osmium complexes are utilized as dihydroxylation and aminohydroxylation catalysts and in the presence of chiral ligands (e.g., cinchona alkaloids) as asymmetric catalysts.[2c,43] The asymmetric dihydroxylation process can be carried out on a commercial scale by Rhodia-Chirex (>10-kg scale) upon request.[44] Ammonium hexachloroosmate, **17**, is prepared by the dissolution of **14** in much the same way as **16** is prepared but the chloroosmate salt is precipitated from solution by the addition of NH_4Cl. **17** is reacted with hydrazine hydrate to form the pentaammine osmium dinitrogen complex, and this is reacted with molecular bromine in neat triflic acid to form triflatopentaammineosmium(III) triflate, **18**, in high yield.[45] **18** is also utilized in organic synthesis to promote dipolar cycloadditions with pyrroles.[46]

Rhodium. One of the first metals to be used in homogeneous catalysis was rhodium. Several important processes have been developed, including the Monsanto acetic acid

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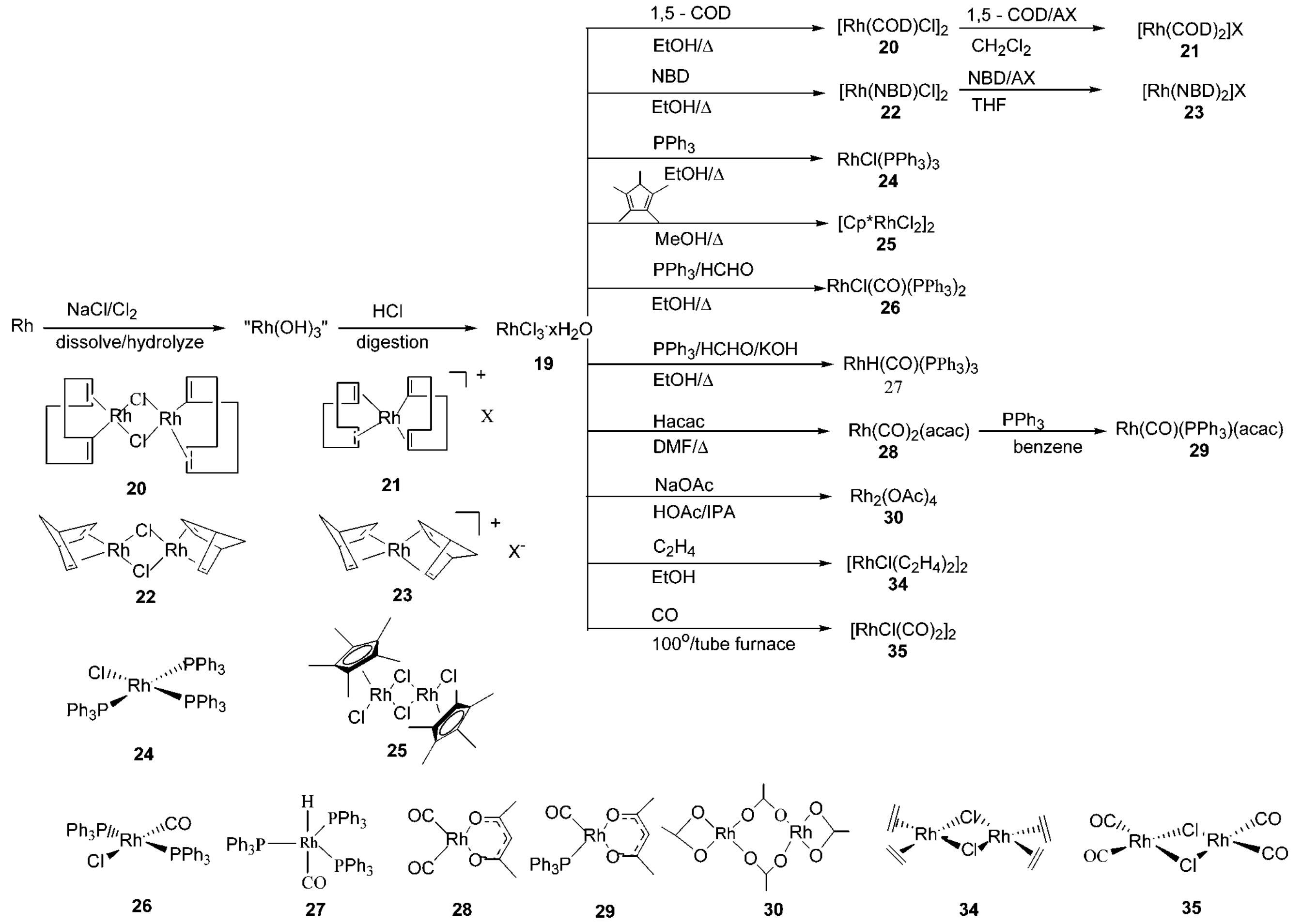
(35) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.
(36) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012.
(37) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413.
(38) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño De Andrade, M. C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 665.
(39) Builliard, M.; Laboue, B.; Lastennet, J.; Roussiasse, S. *Org. Process. Res. Dev.* **2001**, *5*, 438.
(40) Danilewicz, J. C.; Williams, M. T. Eur. Pat. 342850 A1, 1989; *Chem. Abstr.* **1990**, *112*, 197688.
(41) Griffith, W. P. *Platinum Met. Rev.* **1974**, *18*, 94.
(42) Ruff, O.; Bornemann, F. *Z. Anorg. Chem.* **1910**, *65*, 434.
(43) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.
(44) See information contained at http://www.chirex.com.
(45) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 29.
(46) Gonzalez, J.; Koontz, J. I.; Hodges, L. M.; Nilsson, K. R.; Neely, L. K.; Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405.

Scheme 6. **Fabrication of rhodium chemical products that have applications as catalysts**



process,[2a,c] the Union Carbide hydroformylation process,[2a,c] and homogeneous hydrogenation with Wilkinson's catalyst.[47] All the reactions discussed in this section are portrayed and the products shown in Schemes 6 and 7.

Rhodium metal is dissolved by roasting an intimate mixture of rhodium metal and sodium chloride under a chlorine atmosphere, dissolving the fusion cake, and then treating the solution with base to generate an ill-defined rhodium hydroxide species. This gelatinous solid is digested with concentrated hydrochloric acid solution and evaporated to a red crystalline hydrated rhodium(III) chloride hydrate salt $RhCl_3{\cdot}xH_2O$, **19**.[48] This salt, like the osmium and ruthenium analogues, is a mixture of oxochloro and chlorohydroxo complexes in multiple (III/IV) oxidation states. **19** is utilized as a catalyst precursor in such transformations as the hydrosilylation of ketones and the carbonylation and isomerization of olefins.[2] Most all of the rhodium-based catalysts/catalyst precursors are synthesized from **19**. Chloro(1,5-cyclooctadiene)rhodium(I) dimer, **20** is produced by the reaction of 1,5-cyclooctadiene with **19** in refluxing EtOH and is isolated as an orange crystalline solid via filtration in high yield.[49] The addition of excess 1,5-cyclooctadiene to a solution of **20** in dichloromethane followed by the addition of the appropriate counterion ($X = BF_4$, PF_6, OTf) as either a silver salt or an ammonium salt provides the bis(1,5-cyclooctadiene)rhodium(I) cation, **21**. The byproduct is then filtered off, and the product is recovered as a deep red crystalline solid in high yield.[50] The chloro(norbornadiene)rhodium(I) dimer, **22**, is synthesized in the much the same way as **20** except for the obvious substitution of bicyclo[2.2.1]hepta-2,5-diene for 1,5-cyclooctadiene.[51] The analogous cationic salt is fabricated in an analogous fashion to **21** in THF via the method of Schrock and Osborn.[52] The applications of these four complexes are wide-ranging. They have been utilized as catalyst precursors for the enantioselective hydrogenation of olefins (e.g., *l*-menthol), the hydrosilylation of ketones and in transfer hydrogenation and decarbonylation.[2] The bis(1,5-cyclooctadiene)rhodium(I) salt, **21**, has been utilized as a catalyst precursor for enantioselective isomerization (H migration) of allylamines to enamines[53] and as a hydroboration catalyst to produce secondary alcohols from olefins.[54]

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(47) Osborn, J. A.; Jardine, F. H.; Young, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* **1966**, 1711.

(48) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, pp 1587−1588.

(49) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(50) Schenck, T. G.; Downes, J. M.; Milne, C. R. C.; MacKenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.

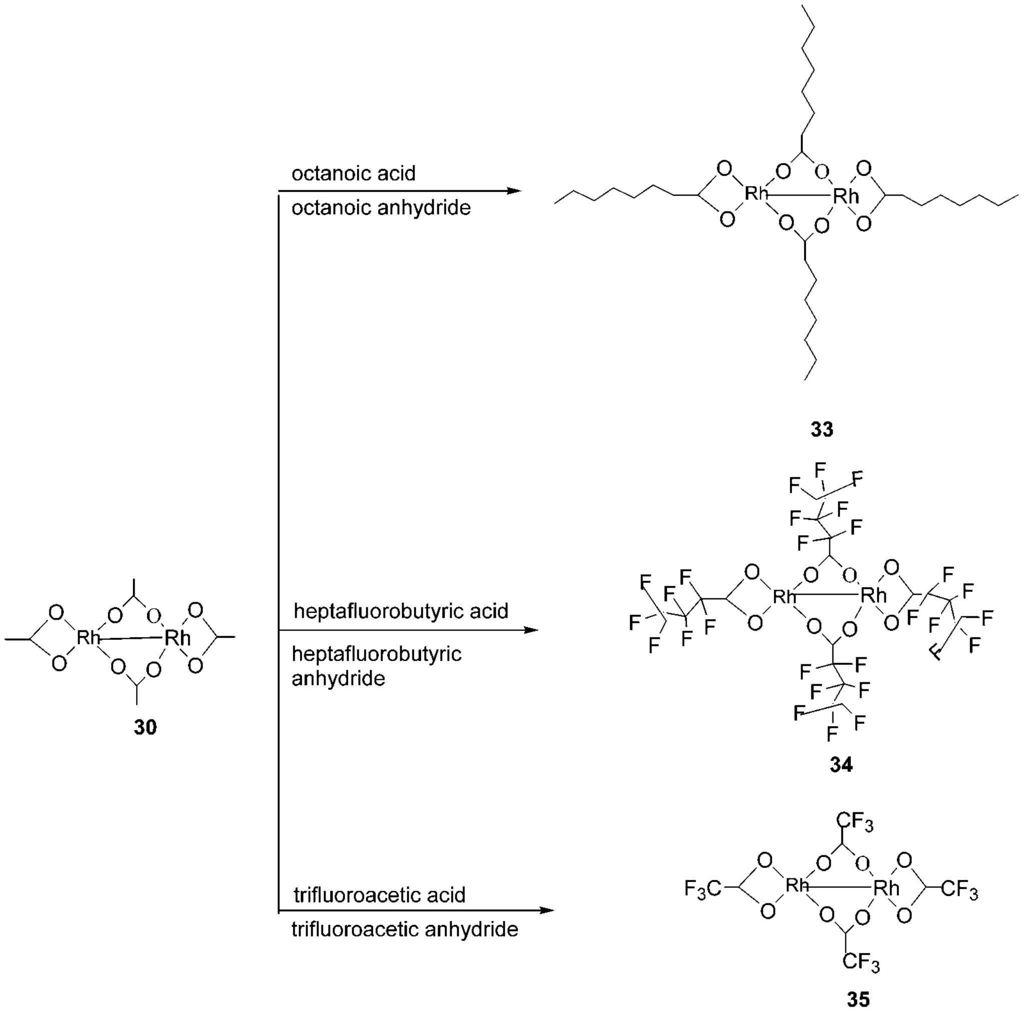
(51) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.

(52) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(53) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.

(54) . Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178.

Scheme 7. **Synthesis of various rhodium(II) carboxylates utilized in catalysis**



The synthesis of Wilkinson's catalyst **24** is performed by the reaction of **19** with excess PPh_3 in refluxing EtOH. The product is isolated as a burgundy-red crystalline solid in nearly quantitative yield.[55] This catalyst is important from a historical perspective in that it represents the first homogeneous hydrogenation catalyst that has been studied in detail concerning its mechanism of hydrogenation and its subsequent kinetics.[56] Wilkinson's catalyst has been utilized in many different catalytic applications, for example hydrogenations at ambient temperatures and pressures of unhindered olefins in a stereospecifically cis manner in the presence of other functional groups,[57] isomerizations,[58] decarbonylations in the presence of diphenyl phosphorazidate (to decarbonylate the catalytically inactive chlorocarbonylbis(triphenylphosphine)rhodium(I), **26**, that is formed in the reaction),[59] and hydrosilylations.[60]

The preparation of dichloro(pentamethylcyclopentadienyl)-rhodium(III) dimer, **25**, is achieved by the reaction of pentamethylcyclopentadiene with **19** in refluxing MeOH. The product is isolated as a red crystalline solid in high yield.[61] Dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer, **25**, has demonstrated application as a catalyst in hydrogenations and transfer hydrogenations. Chlorocarbonylbis(triphenylphosphine)rhodium(I), **26**, has been prepared by the reaction of **19** with excess PPh_3 in the presence of formaldehyde and is isolated as a bright-yellow solid in high yield.[62] **26** has found application as a carbonylation catalyst.[63] The preparation of hydridocarbonyltris(triphenylphosphine)-rhodium(I) is achieved by the reaction of **19** with excess PPh_3 in EtOH with formaldehyde and base (KOH). It is isolated as a bright golden/yellow solid in high yield.[64] This complex has found widespread use industrially as a hydroformylation catalyst (Union Carbide's LPO process) in the production of *n*-butanal, which is an intermediate utilized in the detergent and plastics (PVC) industries.[2] 2,4-Pentanedionatodicarbonylrhodium(I), **28**, is prepared by the reaction of **19** with 2,4-pentanedione in refluxing DMF

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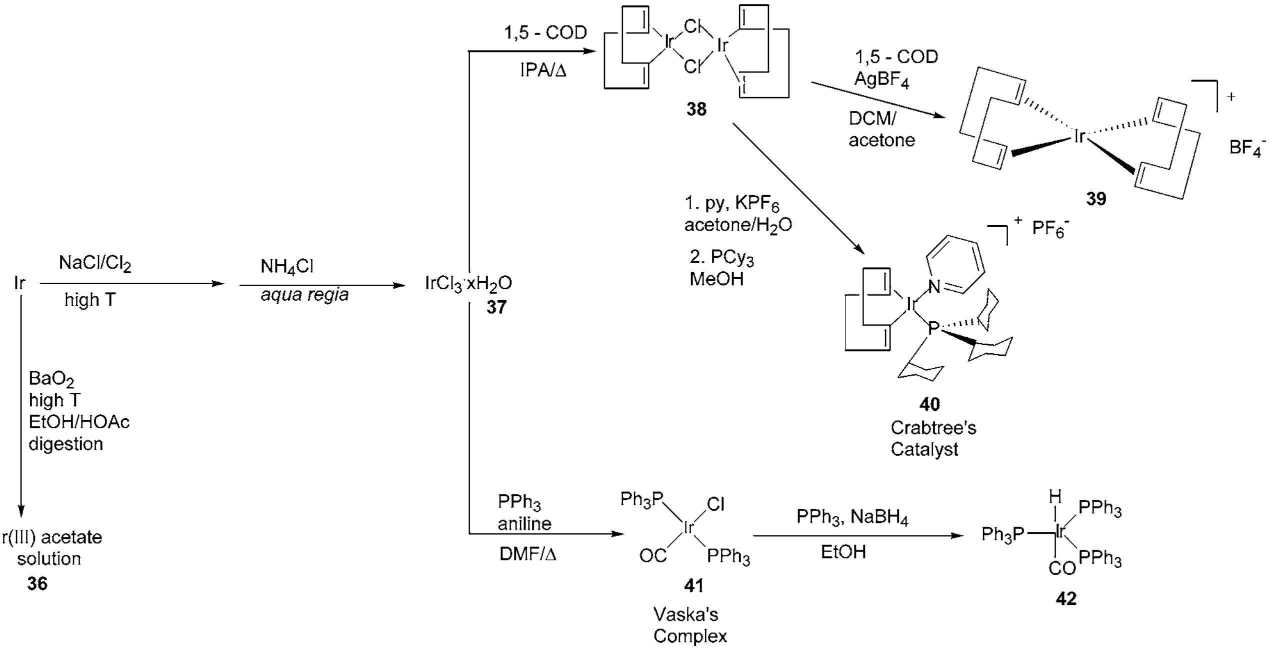
(55) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77.
(56) Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 3240.
(57) Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63.
(58) Grigg, R.; Mitchell, T. R. B.; Sutthivaivakit, S.; Tongpenyai, N. *J. Chem. Soc., Chem. Commun.* **1981**, 611.
(59) O'Connor, J. M.; Ma, J. *J. Org. Chem.* **1992**, *57*, 5075.
(60) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 2, p 1479.
(61) Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Chem. Soc. (A)* **1969**, 1299.
(62) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 79.
(63) (a) Kelkar, A. A.; Chaudhari, R. V. *J. Catal.* **1995**, *157*, 334. (b) Mulla, S. A. R.; Rode, C. V.; Kelkar, A. A.; Gupta, S. P. *J. Mol. Catal. A: Chem.* **1997**, *122*, 103.
(64) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. (D)* **1972**, 843.

Scheme 8. Synthesis of iridium complexes that display catalytic activity



(which is a CO source upon decomposition). It is isolated as a brilliant red/green dichroic solid in moderate yield.[65] **28** has been utilized as a precatalyst in the presence of a chiral ligand (e.g., BINAPHOS) to catalyze asymmetric hydroformylation in which the branched isomer is preferred.[66] **28** can be further elaborated to 2,4-pentanedionatocarbonyltriphenylphosphinerhodium(I), **29**, by the reaction of PPh_3 in benzene, which upon work up yields the product as a yellow crystalline solid.[67] **29** has seen applications as a hydroformylation catalyst which is known as ROPAC.

An unusual complex that has been utilized as a catalyst is the rhodium(II) acetate dimer **30**. This complex is prepared by the reaction of **19** with sodium acetate in hot (~ 1:1) acetic acid/2-propanol.[68] The product is isolated after workup as an emerald-green crystalline solid. This complex is utilized in metal carbene transformations such as cyclopropanations.[69] Chlorobis(ethylene)rhodium(I) dimer **31** is prepared by the reaction of ethylene with **19** in EtOH and is isolated as a dark red crystalline solid.[70] Chlorobis(ethylene)rhodium(I) dimer, **31**, has found applications as a hydroamination catalyst.[71] Chlorodicarbonylrhodium(I) dimer, **32**, is prepared by the solid-state reaction of CO with **19** at 100° in a tube furnace.[72] **32** has been utilized as a catalyst in [6 + 2] and [2 + 5] cycloadditions.[73]

Rhodium(II) carboxylates can be tuned to modify both solubility and reactivity. Rhodium(II) octanoate dimer, **33**, is prepared by ligand substitution of the acetate ligands on **30** for octanoate ligands by reaction in neat refluxing octanoic acid in the presence of octanoic anhydride (Scheme 7).[74] **33** has been utilized as a catalyst as a soluble alternative to **30**.[75] The fluoro-substituted carboxylate complexes, rhodium(II) heptafluorobutryate dimer, **34**, and rhodium(II) trifluoroacetate dimer, **35**, are utilized as cyclopropanation catalysts by rendering the rhodium center to be more electrophilic, therefore being more reactive but less selective.[74] One point of interest with these complexes is that **34** and **35** have measurable association constants with olefins, while **30** and **33** do not. These complexes are prepared in an analogous fashion as **33** as displayed in Scheme 7.[76,77]

Iridium. The major utilization of iridium and its complexes in catalysis is in the Cativa process[78] developed by BP and as a catalyst for enantioselective imine hydrogenation in the synthesis of (*S*)-metolachlor. The Cativa process utilizes an iridium(III) acetate solution as a carbonylation catalyst for the production of acetic acid. The complexes described in this section, and their general synthetic routes are portrayed in Scheme 8.

Iridium metal is converted to higher-value complexes by two different pathways. In the first method it is sintered with barium peroxide at high temperature and then digested with EtOH/acetic acid to render a green iridium(III) acetate solution **36**.[79] This solution is utilized by BP as the carbonylation catalyst in the Cativa process for methanol carbonylation in the manufacture of acetic acid. This process

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(65) Varshavskii, Y. S.; Cherkasova, T. G. *Russ. J. Inorg. Chem.* **1967**, *12*, 899.

(66) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033.

(67) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156.

(68) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(69) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385.

(70) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

(71) Steinborn, D.; Taube, R. *Z. Chem.* **1986**, *26*, 349.

(72) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(73) *Advances In Cycloadditions*; Harmata, M., Ed.; Jai Press: Greenwich, CT, 1999; Vol. 5, p 1.

(74) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K.-L. *J. Am. Chem. Soc.* **1990**, *112*, 1906.

(75) Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 453.

(76) Doyle, M. P.; Shankline, M. S. *Organometallics* **1994**, *13*, 1081.

(77) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19.

(78) Watson, D. J. In *Precious Metal Catalysis Seminar*; Durney, M. T., Shiflett, W. K., Tamblyn, W. H., Eds.; IPMI Press: Allentown, PA, 1997; p 83.

(79) Ezerskaya, N. A.; Kiseleva, I. N.; Simaneva, S. A.; Belyaev, A. N.; Bashmakov, V. I.; Troshina, O. N.; Belyaeva, V. K.; Morov, I. N.; Danilova, F. I.; Munina, V. N. *Russ. J. Inorg. Chem.* **1992**, *37*, 915.

has advantages over the older Monsanto rhodium technology in that it provides high carbonylation rates at low water concentrations with high catalyst stability (the catalyst is less prone to precipitation), it has fewer by-products, and the CO efficiency is improved.[80] In the second method, higher-value iridium complexes are produced by carrying out a series of transformations. A fusion of an intimate mixture of iridium metal and sodium chloride is done under a chlorine atmosphere at high temperature. This fusion cake is worked up by dissolution of the cake in water, and the precipitation of the iridium salt, by the addition of ammonium chloride to precipitate ammonium hexachloroiridate. This salt is then treated with aqua regia to generate chloroiridic acid solution.[81] This solution is reduced in volume to generate iridium(III) chloride hydrate, **37**, as a green/black hygroscopic solid. This complex, like ruthenium(III) chloride hydrate, **2**, osmium(III) chloride hydrate, **16**, and rhodium(III) chloride hydrate, **19**, is a mixture of oxochloro and chlorohydroxy complexes in various oxidation states. From this salt, two basic pathways are followed to the catalyst precursors **38**–**42**. In the first pathway, **38** is synthesized by the reaction of **37** with 1,5-cyclooctadiene in refluxing 2-propanol. This product is isolated as a red crystalline solid in high yield.[82] This complex is utilized as a catalyst precursor in enantioselective hydrogenation of imines, an example of this is performed by Novartis for the manufacture of (*S*)-metolachlor, which is the active agent in DUAL herbicide. This herbicide is manufactured on a scale of >10,000 tons/year.[83] Bis(1,5-cyclooctadiene)iridium(I) tetrafluoroborate **39** is synthesized from **38** in a procedure analogous to that for the synthesis of the rhodium analogue **21** from **20**.[50] This product, much like **21**, is utilized as a catalyst precursor when combined, for example, with a chiral ligand in the performance of enantioselective hydrogenations. Another product that can be fabricated from **38** is Crabtree's catalyst, **40**. This product is synthesized by the reaction of **38** with pyridine and KPF_6 in 1:1 acetone/water at ambient temperature. The intermediate from this reaction is isolated and then redissolved in MeOH and treated with PCy_3. Upon addition of PCy_3, a brilliant orange solid precipitates, and this product is isolated by filtration.[84] Crabtree's catalyst **40** is a very active hydrogenation catalyst that is even active for the hydrogenation of sterically hindered olefins.[85]

The second pathway involves the reaction of **37** with PPh_3 in the presence of aniline in refluxing DMF. The product Vaska's complex (chlorocarbonylbis(triphenylphosphine)iridium(I)), **41**, is isolated as a yellow crystalline solid in high yield.[86] This complex is catalytically active in the decarbonylation of formate esters to form alcohols and CO.[87] The iridium analogue **42** to the oxo catalyst **27** is prepared by the reaction of **41** with PPh_3 and sodium borohydride, providing hydridocarbonyltris(triphenylphosphine)iridium(I), **42**, as a light yellow solid in high yield. This complex has not displayed any activity as a hydroformylation catalyst but has been utilized as a hydrogenation catalyst.[88]

Palladium. As a theme, palladium complexes have been utilized as catalysts in a variety of situations that involve carbon–carbon bond-forming reactions, including carbonylations, carbon–carbon and carbon–heteroatom reactions, and allylic alkylations. The general fabrication of some of the more popular catalysts are shown in Scheme 9.

Palladium metal is dissolved in concentrated hydrochloric acid solution under an atmosphere of chlorine to generate chloropalladic acid solution **43** as a red/brown solution[89] which is evaporated to form palladium(II) chloride, **44**, a red/brown polymeric solid. **44** is utilized as a catalyst in bulk chemical production as a carbonylation catalyst (Wacker–Hoechst process) for the conversion of ethylene to acetaldehyde and the production of acetone from propene,[90] but it is also utilized in fine chemical manufacture in the carbonylation of complex molecules and the generation of glycol derivatives.[91] **44** is also the starting point for the synthesis of many other value-added catalysts. In warm MeCN, the $PdCl_2(MeCN)_2$, **45**, adduct is generated as an orange/yellow solid in nearly quantitative yield.[91] This complex is utilized as a catalyst in various cross-coupling reactions (Heck, Negishi, Grignard) and as a hydrocarboxylation catalyst. Dichlorobis(acetonitrile)palladium(II), **45**, is also utilized as a catalyst precursor in the synthesis of dichloro(bis(diphenylphosphino)ferrocene)palladium(II) dichloromethane adduct, **46**. **46** is synthesized by the reaction of **45** with the bis(diphenylphosphino)ferrocene ligand in an appropriate solvent.[92] **46** has found applications as a catalyst in Grignard coupling reactions,[93] Buchwald/Hartwig[94,95] and Stille coupling[96] reactions. It is also utilized in carbonylative coupling reactions.[97] As an alternative to **45**, dichlorobis(benzonitrile)palladium(II), **47**, can be generated by the reaction of **44** as an adduct with benzonitrile.[98] **47** is utilized as a soluble alternative to **44** and as a catalyst precursor. The reaction of **44** with PPh_3 in EtOH at 60° generates dichlorobis(triphenylphosphine)palladium(II), **48**, as a light yellow crystalline powder in nearly quantitative yield.[99] **48** is utilized as a catalyst in Sonogashira coupling of terminal alkynes

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(80) (a) Howard, M. J.; Jones, M. D.; Roberts, M. S.; Taylor, S. A. *Catal. Today* **1993**, *18*, 325. (b) Sunley, G. J.; Watson, D. J. *Catal. Today* **2000**, *58*, 293. (c) Jones, J. H. *Platinum Met. Rev.* **2000**, *44*, 94.

(81) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, pp 1593–1594.

(82) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

(83) Spindler, F.; Blaser, H.-U. *Enantiomer* **1999**, *4*, 557.

(84) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395.

(85) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

(86) Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 92.

(87) Zahalka, H. A.; Alper, H.; Sasson, Y. *Organometallics* **1986**, *5*, 2497.

(88) Li, R. X.; Li, X. J.; Wong, N. B.; Tin, K. C.; Zhou, Z. X.; Mak, T. C. W. *J. Mol. Catal. A: Chem.* **2002**, *178*, 181.

(89) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, p 1582.

(90) Jira, R. Acetaldehyde. In *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Wiley: New York, 1985; Vol. A1, p 31.

(91) *Synthesis of Organometallic Compounds. A Practical Guide*; Komiya, S. Ed.; Wiley: New York, 1998; p 285.

(92) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(93) Miller, J. A. *Tetrahedron Lett.* **2002**, *43*, 7111.

(94) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.

(95) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

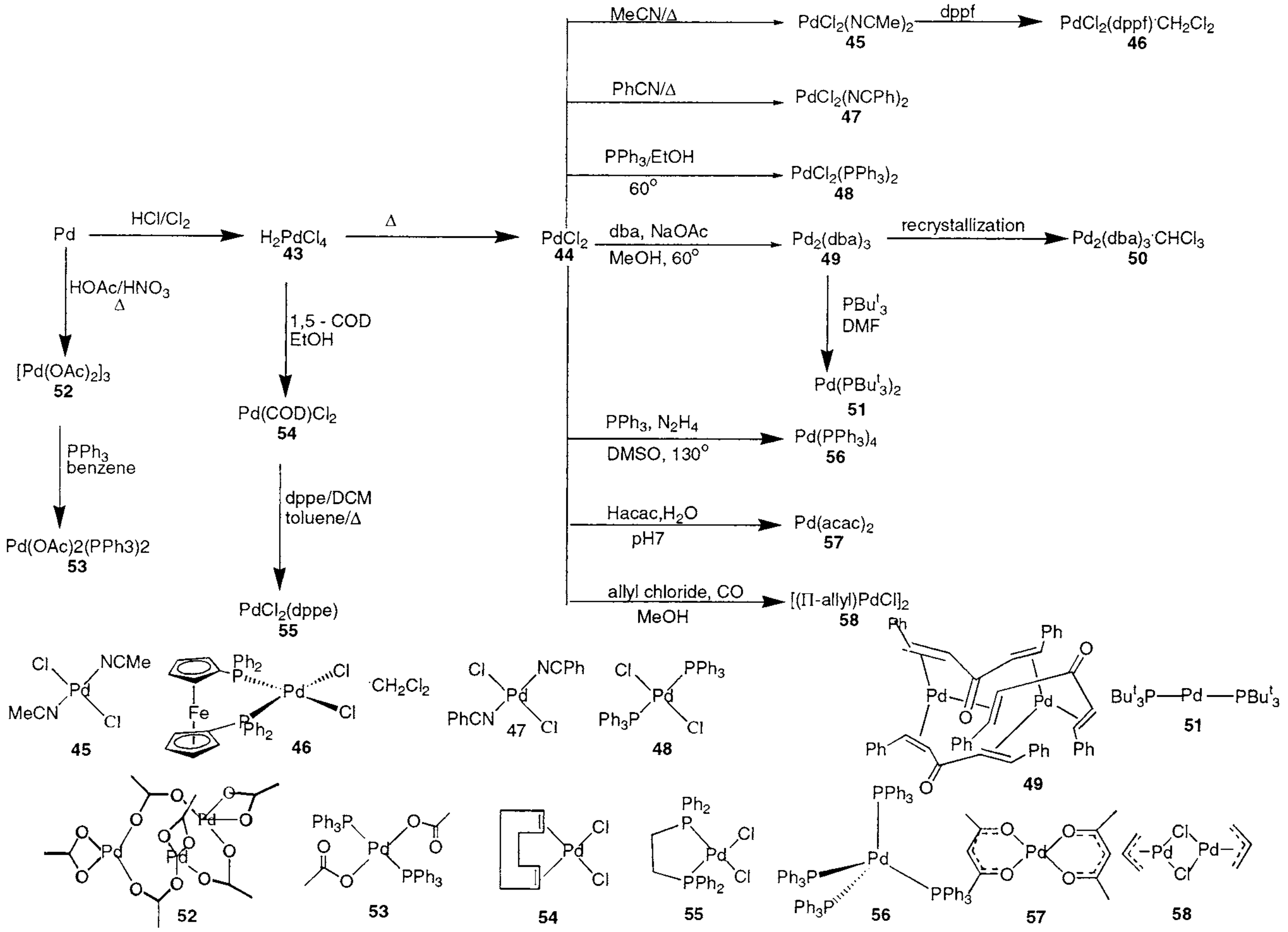
(96) Ito, Y.; Inouye, M.; Murakami, M. *Tetrahedron Lett.* **1988**, *29*, 5379.

(97) Ciatti, P. G.; Morera, E.; Ortar, G.; Rossi, S. S. *Tetrahedron* **1991**, *47*, 6449.

(98) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.

(99) Itatani, H.; Bailar, J. C., Jr. *J. Am. Oil Chem. Soc.* **1967**, *44*, 147.

Scheme 9. **General fabrication route to various palladium complexes that are utilized as catalysts**



with aryl halides[100] and as a carbonylation catalyst in the synthesis of certain lactones.[101] The reaction of **44** with dibenzylideneacetone and sodium acetate in MeOH at 60° generates tris(dibenzylideneacetone)dipalladium(0), **49**, in quantitative yield.[102] **49** ($Pd_2(dba)_3$) is a stable Pd(0) complex with easily dissociable ligands that has seen widespread use as a catalyst in all manners of carbon−carbon and carbon−heteroatom coupling reactions. **49** is quite an unusual complex in that it is a dimeric complex where both palladium metal centers are bonded to three C=C bonds of each dibenzylideneacetone ligand in a trigonal planar array so that each dibenzylideneacetone ligand is coordinated in a μ^2-η^2,η^2 fashion. The related complex, "$Pd(dba)_2$" has been proven by X-ray crystallography to be simply a mixture of **49** and $Pd(dba)_3$.[103] A specific catalytic utilization of particular importance is the reported Suzuki coupling of aryl chlorides in the presence of an Arduengo imidazolium salt to generate biphenyls,[104] an important fine chemical building block. In an area outside of coupling reactions, **49** has found applications as a catalyst for allylation reactions.[105] By recrystallization of tris(dibenzylideneacetone)dipalladium(0) from chloroform/diethyl ether, tris(dibenzylideneacetone)dipalladium(0) chloroform adduct, **50,** can be obtained as a purple crystalline solid.[102] The applications of **50** in catalysis are the same as those of **49**, but one unique utilization is in an asymmetric allylic alkylation process, where in the presence of a chiral ligand, the *allo* and *talo* isomers of the nucleoside skeleton of the polyoxin−nikkomycin complexes can be synthesized.[106] Another high-value complex bis(tri-*tert*-butylphophine)palladium(0) is a zerovalent palladium complex that contains two sterically hindered phosphines (PBu^t_3) coordinated to a palladium metal center in a linear fashion.[107] This catalyst has been utilized in the Negishi cross coupling of aryl and vinyl chlorides.[107]

A quite common Pd catalyst is the palladium(II) acetate salt **52**, which is synthesized by the reaction of palladium powder in refluxing acetic acid in the presence of nitric acid. The product is isolated as a tan crystalline solid after the cessation of brown (NO_x) fumes from the reaction mixture.[68] Palladium(II) acetate **52** has been demonstrated to possess a trimeric structure both by osmometry and by X-ray crystallography.[108] Palladium(II) acetate **52** is utilized as a catalyst

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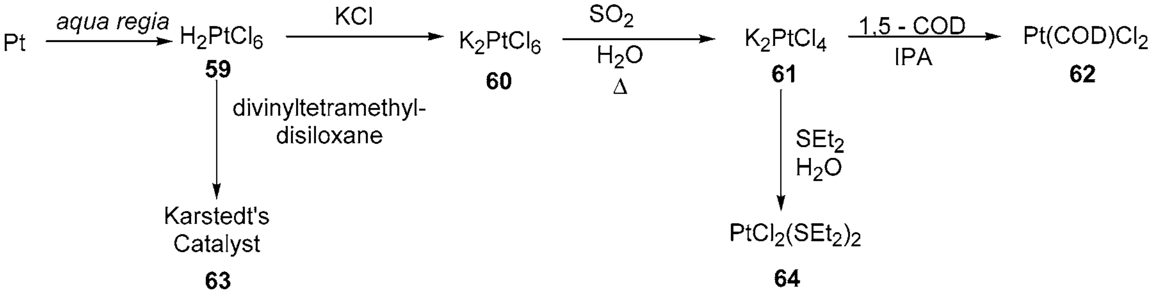
(100) Sonogashira, K. Sonogashira Coupling. In *Metal Catalyzed Cross Couplings*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1997; Chapter 5, p 203.
(101) Cowell, A.; Stille, J. K.; *J. Am. Chem. Soc.* **1980**, *102*, 4193.
(102) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(103) (a) Mazza, M. C.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2955. (b) Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891.
(104) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804.
(105) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523.
(106) Trost, B. M.; Shi, Z. *J. Am. Chem. Soc.* **1996**, *118*, 3037.
(107) Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719.

Scheme 10. **Synthesis of platinum complexes that demonstrate catalytic activity**



or in the presence of particular ligands or additives as a catalyst precursor in a wide variety of different transformations. One of the more interesting applications is as a catalyst for the telomerization of butadiene to form substituted 1,6- and 1,7-dienes.[109] By the addition of PPh_3 to **52** in benzene, the yellow complex diacetatobis(triphenylphosphine)palladium(II), **53**, is formed. **53** is utilized as a typical palladium catalyst but demonstrates an interesting application in a cyclization reaction to form either 1,3- or 1,4-dienes.[110] Another palladium catalyst of note is dichloro(1,5-cyclooctadiene)palladium(II), **54**, which is synthesized by the reaction of **43** with 1,5-COD in absolute EtOH.[111] **54** is utilized as a catalyst to protect hydroxyl groups.[112] **54** is also utilized to fabricate dichlorobis(diphenylphosphino)ethane-palladium(II), **55**, which is isolated as an off-white solid in high yield.[113] **55** has found application in a variety of organometallic (Grignard, Negishi, Stille) coupling reactions.[114,115]

From **44**, in the presence of excess PPh_3 and hydrazine in hot (130°) DMSO, tetrakis(triphenylphosphine)palladium(0), **56**, a yellow solid that exhibits thermal and air sensitivity, is isolated in high yield.[116] In many ways, the utilization of **49** has superseded **56** in applications in catalysis. However, **56** is utilized in catalysis for coupling reactions and especially the Sonogashira reaction and has an interesting application in catalyzing [3,3] sigmatropic rearrangements.[117] Bis(2,4-pentanedionato)palladium(II), **57**, is fabricated by the reaction of **44** with 2,4-pentanedione while carefully adjusting the base concentration.[118] Amongst various applications, one interesting use is in the cyclopropanation of α-diazo-β-ketoesters.[119] Another important catalyst is π-allylpalladium(II) chloride dimer, **58**, a yellow crystalline solid that is fabricated by the reaction of **44** with allyl chloride in MeOH in the presence of CO.[120] Amongst its many uses in catalysis, one application of note is in asymmetric alkylation,where the construction of a quaternary center by alkylation of an azlactone led to a new strategy that is used in the synthesis of a class of antifungal agents known as sphingosines.[121]

Platinum. In contrast to its second row congener, palladium, platinum has not seen a great amount of utilization in homogeneous catalysis. By far the greatest application is hydrosilylation in the production of silicone polymers and other related structures. An intriguing area that is experiencing greater attention is in the functionalization of alkanes via C−H activation (Shilov activation) to form, at least initially, methanol from methane.[122] Scheme 10 illustrates the synthetic pathway to the platinum complexes that demonstrate catalytic activity.

Platinum metal is dissolved in aqua regia to generate, after destruction of the nitrates, chloroplatinic acid solution. This yellow/orange solution can be crystallized by flash-cooling in liquid N_2 to yield chloroplatinic acid, **59**, as a yellow/orange hydrated crystalline solid.[123] This complex can be reacted with potassium chloride in water to yield potassium hexachloroplatinate, **60**, as a yellow crystalline powder in quantitative yield.[124] This intermediate is then reacted with sulfur dioxide in hot water to generate the platinum(II) salt potassium tetrachloroplatinate, **61**.[125] **61** is the platinum salt that was originally used by Shilov's group in their ground-breaking work on C−H activation of alkanes.[126] This salt is utilized as a starting material to synthesize dichloro(1,5-cyclooctadiene)platinum(II), **62**, by the addition of 1,5-COD to **61** in 2-propanol,[127] and dichlorobis(diethyl sulfide)-platinum(II) is synthesized by the addition of Et_2S to an aqueous solution of **61**. **62** is isolated as a colorless crystalline solid, while **64** is isolated as a yellow crystalline powder. Both **62** and **64** are utilized as hydrosilylation catalysts for the manufacture of silicone polymers. Karstedt's catalyst **63** is generated by the addition of divinyltetramethyldisiloxane in an inert solvent to **59** to generate the catalyst solution.[128]

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(108) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun*. **1970**, 658.
(109) Takaghashi, T.; Minami, I.; Tsuji, J. *Tetrahedron Lett.* **1981**, *22*, 2651.
(110) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781.
(111) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346.
(112) Ohshima, M.; Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1984**, 1535.
(113) Broadwood-Strong, G. T. L.; Chaloner, P. A.; Hitchcock, P. B. *Polyhedron* **1993**, *12*, 721.
(114) Kuribayashi, T.; Gohya, S.; Mizuno, Y.; Satoh, S. *J. Carbohydr. Chem.* **1999**, *18*, 393.
(115) Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1998**, 1863.
(116) Coulson, D. *Inorg. Synth.* **1972**, *13*, 121.
(117) Murahashi, S.; Makabe, Y.; Kunita, K. *J. Org. Chem.* **1988**, *53*, 4489.
(118) Okeya, S.; Ooi, K.; Matsumoto, K.; Nakamura, Y.; Kawagura, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085.
(119) Hoye, T. R.; Dinsmore, C. J.; Johnson, D. S.; Korkowski, P. F. *J. Org. Chem.* **1990**, *55*, 4518.
(120) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342.
(121) Trost, B. M.; Lee, C. B. *J. Am. Chem. Soc.* **1998**, *120*, 6818.
(122) Shilov, A. E.; Shulpin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Boston, 2000.
(123) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, p 1569.
(124) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, pp 1571.
(125) *Handbook Of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, p 1572.
(126) Shilov, A. E. *Activation and Functionalization of Saturated Hydrocarbons*; Riedel Press: Dordrecht, 1984.
(127) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.
(128) Karstedt, B. D. DE Patent 2,307,085, 1973; *Chem. Abstr.* **1973**, *80*, 16134j.

This catalytic method is utilized in the cross-linking reaction to generate cross-linked silicones that are utilized in such applications as automotive gaskets, pressure-sensitive adhesives, and many others.[129]

Summary

In conclusion, a brief outline of how platinum group metals are extracted out of the Earth, separated from the base metals, and refined and how they are separated from each other has been presented. Furthermore, the fabrication into high-value complexes that are used in homogeneous catalysis has been described. All catalysts described above are available in commercial quantities. The utilization of homogeneous catalysts in organic processes has been increasing over the last several years for various environmental and energy-efficiency-related reasons. Some of these include (1) by the simple concept of what a catalyst is, the kinetic barrier of a reaction profile will be lowered by use of homogeneous catalysis, and (2) on an industrial scale, the energy burden of that reaction will be lowered, and henceforth, energy is saved. A catalyzed process will generally undergo a reaction in a more selective manner than an uncatalyzed process and will therefore minimize product separation from undesired by-products and thus minimize waste. Moreover, traditional organic processes that have been developed in the past tended to use stoichiometric amounts of a reactant that could generate (especially in a large process) a large amount of a waste by-product. Along these lines, the concept of atom economy has come to the forefront over the past decade where reaction designs that utilize all the atoms in the reagents without any waste has been touted.[130] Homogeneous catalysis has been a major player in the practical development of this concept. In terms of active pharmaceutical ingredients, there has been regulatory pressure to synthesize these ingredients in an enantiopure form. Traditionally, one may synthesize a racemic mixture of the product and perform a resolution, thereby wasting 50% of the product but with advances in asymmetric synthesis and asymmetric catalysis, this waste-producing step may be avoided.

Homogeneous catalysis is a field that is constantly coming up with new advances. Among these advances are those in phase-transfer methodologies. These include the modification of ligands so that the catalysts are water-soluble and the utilization of nontraditional solvent technologies such as supercritical fluids and ionic liquids. All of these methodologies represent advances in product separation from the catalyst and perhaps also advances in selectivity and reactivity. Another new advancement has to do with combinatorial methods for high throughput screening (HTS). This methodology can look at a large-parameter space in a research program to look for, as an example, an enantioselective hydrogenation that may perform the best under the particular circumstances dictated by the reaction being catalyzed. These advances and others will certainly make the field of homogeneous catalysis and the subsequent fabrication of the identified catalysts a growing and exciting field for many years to come.

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(129) Lewis, L. N. In *Precious Metal Catalysis Seminar*; Durney, M. T., Shiflett, W. K., Tamblyn, W. H., Eds.; IPMI Press: Allentown, PA, 1997; p 7.

(130) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.