

Part I. Synthesis, Characterization, and Reactivity of Low Valent Organotitanium Complexes

Part II. Chemical Vapor Deposition of Rhodium Metal Thin Films

Yujian You

Final Seminar

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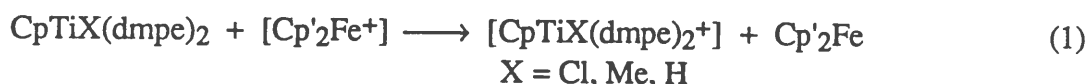
Part I

Heterogeneous Ziegler-Natta catalysts are used on a large scale industrially to manufacture polyolefins such as polyethylene and polypropylene [1, 2]. One of the first catalyst systems studied was prepared by treatment of TiCl_3 with triethylaluminum; variations of this procedure still form the basis of many of the catalysts used today. Many aspects of the chemical nature of these heterogeneous catalysts remain obscure: for example, even such a fundamental parameter as the oxidation state of the catalytically active titanium centers is not known with certainty, although most studies suggest that the +3 oxidation state is most active. Well-defined homogeneous alkene polymerization catalysts based on group 4 metallocene complexes in the +4 oxidation state are well-known, but there is not a single example of a well-defined group 4 complex in the +3 oxidation state that is active for the polymerization of alkenes. We have prepared the first cationic alkyltitanium(III) complexes and have explored their chemical properties.

Treatment of $[\text{CpTiCl}_2]_x$ with *n*-butyllithium in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) yields the new titanium(II) complex $\text{CpTiCl}(\text{dmpe})_2$. Subsequent treatment of this species with methyl lithium or *n*-butyllithium affords the alkyl and hydride analogues $\text{CpTiMe}(\text{dmpe})_2$ and $\text{CpTiH}(\text{dmpe})_2$, respectively. The X-ray crystal structures of $\text{CpTiX}(\text{dmpe})_2$ ($\text{X} = \text{Cl, Me, H}$) have been determined, and all possess unusually long metal-ligand distances; evidently all of these complexes are severely crowded. Analogous treatment of $[\text{Cp}^*\text{Ti}(\text{BH}_4)\text{Cl}]_2$ with *n*-butyllithium in the presence of a chelating phosphine affords the pentamethylcyclopentadienyl complexes, $\text{Cp}^*\text{Ti}(\text{BH}_4)(\text{PP})$, where PP is dmpe or (*t*-butyl)tris(dimethylphosphinomethyl)silane (trimpsil). In this case, the large size of the Cp^* ring prevents coordination of two equivalents of phosphine; in addition, the potentially tridentate trimpsil ligand is actually bidentate owing presumably to steric effects.

All of these titanium(II) complexes are catalysts for the oligomerization of alkenes. For example, ethylene is dimerized to 1-butene; subsequent coupling reactions of 1-butene with ethylene give the ethylene trimers 2-ethyl-1-butene and 3-methyl-1-pentene. The evidence most strongly supports a mechanism whereby these coupling reactions proceed via a metallacyclopentane intermediates. The oligomerization of alkenes (as opposed to the polymerization of alkenes) is a characteristic feature of the titanium(II) oxidation state.

Oxidation of the neutral titanium(II) complexes with dimethylferrocenium salts affords the first example of a cationic alkyltitanium(III) complex (Equation 1):



Salts of these cations with the fluorinated tetraphenylborate anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (FPB), are much more soluble in organic solvents than those of tetraphenylborate itself. Two other examples of cationic titanium(III) complexes $[\text{TiMe}_2(\text{dmpe})_2]\text{FPB}$ and $[\text{Cp}^*\text{Ti}(\text{BH}_4)(\text{dmpe})]\text{FPB}$ have been prepared by oxidation of the corresponding titanium(II) species. X-ray crystallographic studies of $[\text{CpTiH}(\text{dmpe})_2]\text{FPB}$, $[\text{TiMe}_2(\text{dmpe})_2]\text{FPB}$, and $[\text{Cp}^*\text{Ti}(\text{BH}_4)(\text{dmpe})]\text{FPB}$ (Figure 1) reveal that the titanium(III)

cations have structures similar to their neutral titanium(II) analogues except that the Ti-P bond distances are longer owing to a decrease in the extent of metal-ligand π -back-bonding.

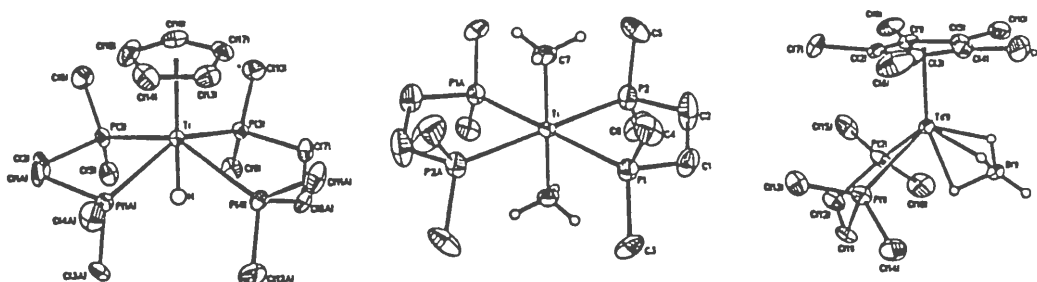


Figure 1. Structures of $[\text{CpTiH}(\text{dmpe})_2]\text{FPB}$, $[\text{TiMe}_2(\text{dmpe})_2]\text{FPB}$, and $[\text{Cp}^*\text{Ti}(\text{BH}_4)(\text{dmpe})]\text{FPB}$.

The reactions of the new cationic titanium(III) complexes with ethylene have been studied, but surprisingly no oligomerization or polymerization activity was observed. Several possible explanations of this behavior have been advanced.

Part II

The chemical vapor deposition (CVD) of thin films is a widely used process in the microelectronics industry [3]. Few detailed analyses of the chemical reactions responsible for film growth have been carried out, particularly for precursors that result in the deposition of transition metals and their binary and higher phases. A detailed understanding of these surface reactions can also assist in the design of improved precursors and in the control of film quality. Rhodium metalized surfaces have potential applications in the fields of microelectronics, optics, wear protection, and catalysis. We have studied the chemistry of rhodium(I) β -diketonate complexes as precursors for the deposition of rhodium thin films.

Several new rhodium(I) β -diketonate complexes have been prepared by displacing the ethylene ligands in $\text{Rh}(\text{hfac})(\text{CH}_2\text{CH}_2)_2$ (hfac = hexafluoroacetylacetonate) with vinyltrimethylsilane (VTMS), 1,2-bis(trimethylsilyl)acetylene (BTMSA), $\text{Cu}(\text{hfac})(\text{COT})$, and PMe_3 . In addition, $\text{Rh}(\text{hfac})(\text{CH}_2\text{CH}_2)_2$ reacts with excess PMe_3 and H_2 gas to afford the rhodium(III) hydride complex $[\text{cis-Rh}(\text{H})_2(\text{PMe}_3)_4]\text{hfac}$. These complexes have been examined as CVD precursors.

High purity rhodium films have been deposited on copper, aluminum, and silicon surfaces at 200 - 300 °C using $\text{Rh}(\text{hfac})(\text{CH}_2\text{CH}_2)_2$ and $\text{Rh}(\text{hfac})(\text{VTMS})_2$ as CVD precursors. Mass spectroscopic studies of the reaction byproducts show that the deposition occurs by a disproportionation reaction (Equation 2):



Mechanistic studies of $\text{Rh}(\text{hfac})(\text{CH}_2\text{CH}_2)_2$ on copper surfaces under ultra high vacuum (UHV) conditions have been carried out using X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) techniques. The studies show that the molecules remain intact on the surface at temperatures up to 130 K. The hfac groups are oriented perpendicular to the surface at 220 K. Reduction of rhodium(I) centers occurs at approximately 300 K. Subsequent decomposition of surface-bound hfac groups at higher temperatures generates CF_3 groups on the surface which desorb at 600 K. At 800 K, only a layer of amorphous carbon

Synthesis and Properties of Mononuclear and Polynuclear Indenyl Iridium Complexes

Matthew C. Comstock

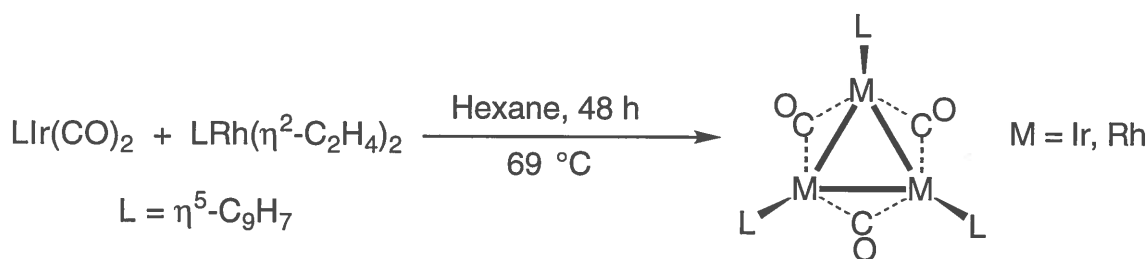
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Transition metal indenyl complexes generally show enhanced reactivity in associative substitution reactions compared to their cyclopentadienyl analogs, and this phenomenon has been termed the 'indenyl ligand effect.'¹

Interestingly, although the indenyl ligand effect has been vigorously researched in a multitude of mononuclear systems, related studies of polynuclear systems that incorporate indenyl metal fragments have not been reported. Therefore, we were interested in the synthesis and properties of metal cluster compounds that contain indenyl iridium fragments in order to investigate the possibility of enhancing cluster reactivity.

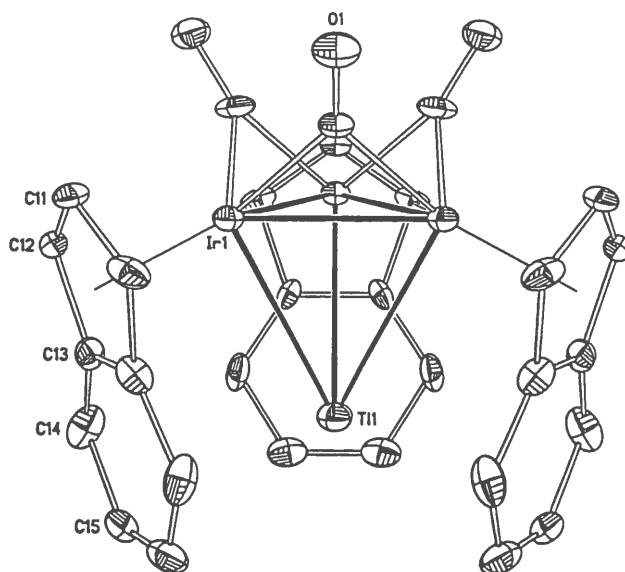
The reaction of $\text{Ir}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2(\eta^5\text{-C}_9\text{H}_7)$ provided $\text{Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$, and the reaction of $\text{Ir}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2(\eta^5\text{-C}_9\text{H}_7)$ provided the trinuclear clusters $\text{Ir}_{3-x}\text{Rh}_x(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ ($x = 0 - 2$) in good yields,² as well as $\text{Rh}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ which had been studied previously.³



These compounds react readily with carbon monoxide to form mononuclear products, whereas the corresponding cyclopentadienyl compounds are much less reactive.⁴ Thus, indenyl ligand substitution does enhance the reactivity of these clusters.

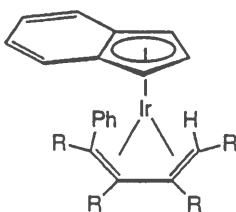
A fascinating diversity of structures has been observed for trinuclear compounds of the cobalt triad with the general formula $\text{M}_3(\text{CO})_3(\eta^5\text{-L})_3$, where L refers to $\eta^5\text{-C}_5\text{H}_5$ and related ligands.^{2, 5-7} The reaction of the triiridium cluster $\text{Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gave $[\text{Ir}_3(\mu\text{-H})(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3][\text{BF}_4]$. Subsequent deprotonation led to generation of $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$, which rapidly reverted to an equilibrium mixture of major isomer $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ and minor isomer $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. The solution dynamics and interconversion of both isomers were explored. Variable temperature ^1H and ^{13}C NMR experiments indicated that $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ undergoes a dynamic process that involves the intermediacy of a third isomer of $\text{Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. This study provides a unique set of relative energies in solution for three of the four observed forms for a $\text{M}_3(\text{CO})_3(\eta^5\text{-L})_3$ system.

The reactions of $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ with metal fragment electrophiles containing Cu, Ag, Au, and Hg provided cationic tetranuclear clusters, which show a rearrangement of the $\text{Ir}_3(\eta^5\text{-C}_9\text{H}_7)_3$ moiety to a C_s geometry. The reaction with TlPF_6 gave $[\text{Ir}_3\text{Tl}(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3][\text{PF}_6]$, which maintains the C_{3v} geometry of $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ and has the thallium ion encapsulated by the six-membered rings of the indenyl ligands (see below).



The search for other routes toward clusters containing indenyl ligands prompted the synthesis of $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ from the reaction of $\text{Ir}(\text{CO})(\eta^2\text{-C}_8\text{H}_{14})(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$. Deprotonation of $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ with KOH/EtOH and addition of $[\text{PPN}][\text{Cl}]$ provided $[\text{PPN}][\text{IrRe}_2(\mu\text{-H})(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)]$. Addition of PPh_3 to $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ led to the carbonyl substitution product $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)(\eta^5\text{-C}_9\text{H}_7)$, which contains the phosphine ligand on a rhenium atom, as well as to cluster fragmentation.

The reactions of $\text{Ir}(\text{CO})(\eta^2\text{-C}_8\text{H}_{14})(\eta^5\text{-C}_9\text{H}_7)$ with C_2R_2 were explored as an indirect method toward alkyne complexes of $\text{Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. The mononuclear and dinuclear compounds, $\text{Ir}(\text{CO})(\eta^2\text{-C}_2\text{R}_2)(\eta^5\text{-C}_9\text{H}_7)$ and $\text{Ir}_2(\text{CO})_2(\mu\text{-C}_2\text{R}_2)(\eta^5\text{-C}_9\text{H}_7)_2$ were obtained. Also, alkyne coupling and activation of a C-H bond in the arene solvent formed a novel mononuclear compound containing a substituted butadiene ligand (see below).



References

1. (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208.
- (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.
- (c) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198-200*, 219.
- (d) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

2. Comstock, M. C.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 3805.
3. (a) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648; *Angew. Chem.* **1977**, *89*, 671.
(b) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.
4. Shapley, J. R.; Adair, P. C.; Lawson, R. J.; Pierpont, C. G. *Inorg. Chem.* **1982**, *21*, 1701.
5. Wadepohl, H.; Gebert, S. *Coord. Chem. Rev.* **1995**, *143*, 535.
6. Braga, D.; Grepioni, F.; Wadepohl, H.; Gebert, S.; Calhorda, M. J.; Veiros, L. F. *Organometallics* **1995**, *14*, 5350.
7. Robben, M. P.; Geiger, W. E.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 5615.