

Late Transition Metal Complexes as Precursors to Metallic Thin Films and as Promoters of Carbon-Silicon and Carbon-Phosphorus Bond Activation Processes

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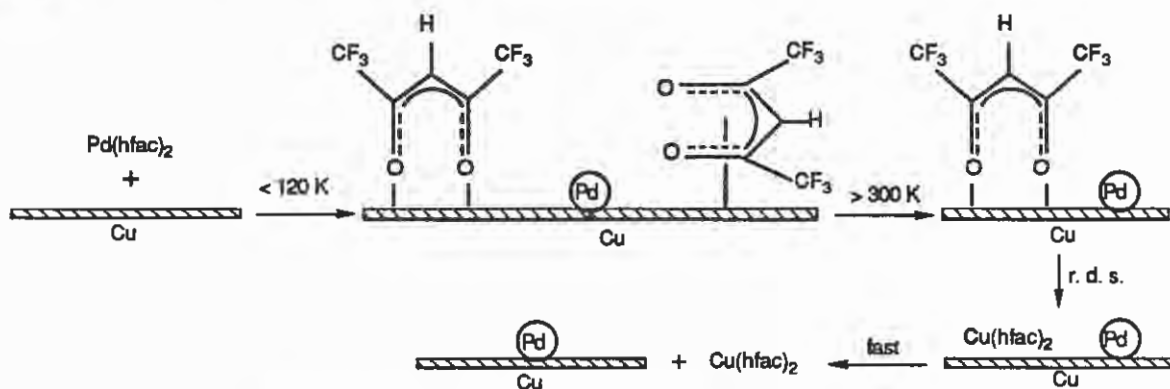
There is great current interest in the fabrication of metal and ceramic thin films via metal-organic chemical vapor deposition (MOCVD) because MOCVD methods offer several advantages such as low deposition temperatures, fast growth rates, and the ability to effect the coverage of irregular surfaces conformally and, in some cases, selectively [1-5]. The films of platinum group metals are of particular interest owing to their potential uses as interconnects in microelectronic devices [6-8].

Bis(hexafluoroacetylacetonato)palladium(II), Pd(hfac)₂, selectively deposits palladium on copper (and iron) substrates at 10⁻⁴ torr and 200 °C to 425 °C via the redox transmetalation reaction [9]:



The volatile silver(I) complexes Ag(hfac)(PMe₃) and Ag(hfac)(PMe₃)₂ yield silver deposits on copper and iron substrates by similar redox transmetalation reactions. In contrast, passage of platinum(II) hexafluoroacetylacetonate, Pt(hfac)₂, over copper under similar conditions does not result in the deposition of platinum metal.

Mechanistic studies reveal that Pd(hfac)₂ is reduced by the copper surface to generate palladium atoms and surface-bound hfac groups below 120 K; the hfac groups then abstract a surface copper atom to form the Cu(hfac)₂ product. On a polycrystalline Cu surface, the rate limiting step for the transmetalation reaction is the formation of Cu(hfac)₂ molecules from the surface copper atoms and surface-bound hfac groups. On a Cu(111) single crystal surface, however, the diffusion of Pd atoms into the bulk is rate determining below 600 K. The reactions of Pd(hfac)₂ with copper surfaces are also very sensitive to the surface coverage of hfac groups: low surface hfac coverages (< 0.1%) favor the thermolytic decomposition of surface bound hfac groups, while higher hfac coverages promote the higher-order transmetalation reaction. The primary driving force for the transmetalation reaction is a favorable redox potential [10,11].



Scheme I. Mechanism for the transmetalation of Pd(hfac)₂ on Cu surfaces

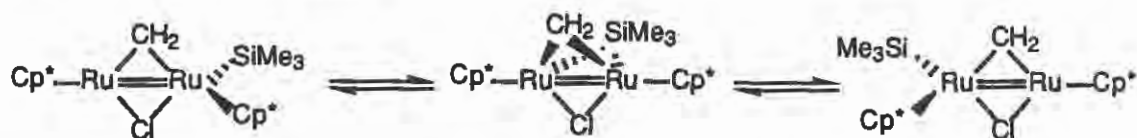
Comproportionation of M(PMe₃)₄ and [M'(hfac)(PMe₃)₂][hfac] yields the novel dinuclear complexes [MM'(PMe₃)₆][hfac]₂ (where M, M' = Pd or Pt). These dinuclear complexes

adopt structures in which the two metal centers are connected by a metal-metal bond and the six terminal PMe_3 ligands complete two mutually perpendicular square-planar coordination environments. Reaction of $\text{Pt}(\text{PMe}_3)_4$ and $\text{Pt}(\text{hfac})_2$ affords the novel diplatinum complex $[\text{Pt}_2(\mu\text{-hfac})(\text{PMe}_3)_4][\text{hfac}]$ which is actually a mixed valence complex: the bridging hfac group binds to the Pt^{II} center via the two oxygens and to the Pt^0 center as an alkene via its methine and one of the carbonyl carbons. Sublimation of these complexes at 10^{-3} Torr and $100 - 150^\circ\text{C}$ results in cleavage of P-C bonds of the PMe_3 ligands and formation of $[\text{MMe}(\text{PMe}_3)_3][\text{hfac}]$ ($\text{M} = \text{Pd}$ or Pt):

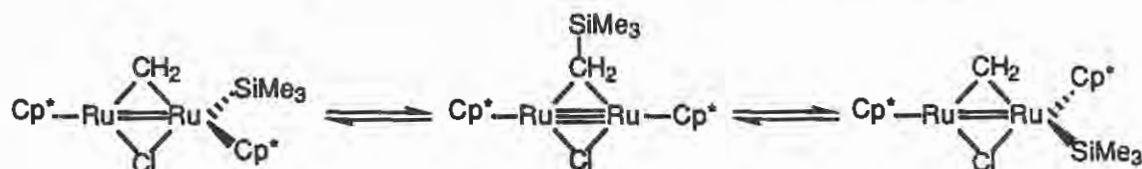


These thermolysis results imply that some metal-organic precursors that contain trialkylphosphine groups could give films that are contaminated by carbon and phosphorus [12].

Reaction of $[\text{Cp}^*\text{RuCl}]_4$ with $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ gives the methylene/silyl complex $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\text{SiMe}_3)(\mu\text{-Cl})$ via the unusual cleavage of the $\alpha\text{-C-Si}$ bond of the CH_2SiMe_3 group [13,14]. The variable-temperature ^1H and ^{13}C NMR spectroscopy shows that this molecule undergoes two dynamic processes. The lower temperature process ($\Delta H^\ddagger = 9.0 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 0.5 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1}$) involves hopping of the silyl ligand between the two ruthenium centers:



The higher temperature process ($\Delta H^\ddagger = 12.0 \pm 0.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -7 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$) involves the reversible reformation of the C-Si bond between the silyl and methylene ligands:



Treatment of $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\text{SiMe}_3)(\mu\text{-Cl})$ with PMe_3 , CO , and HO_2CCF_3 gives products in which the C-Si bond has reformed: the Lewis bases give the mononuclear Ru^{II} products $\text{Cp}^*\text{Ru}(\text{CH}_2\text{SiMe}_3)\text{L}_2$ and $\text{Cp}^*\text{RuClL}_2$, while HO_2CCF_3 gives the alkylidene complex $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CHSiMe}_3)(\mu\text{-O}_2\text{CCF}_3)(\mu\text{-Cl})$. The most convincing evidence for the reversible silyl group migration in $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\text{SiMe}_3)(\mu\text{-Cl})$ is that $[\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\text{PMe}_3)(\mu\text{-Cl})][\text{O}_2\text{CCF}_3]$ is non-fluxional despite being isoelectronic and isosteric with the methylene/silyl complex. Treatment of $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\text{SiMe}_3)(\mu\text{-Cl})$ with acetylene yields the first unsubstituted metallabenzene complex $\text{Cp}^*_2\text{Ru}_2(\eta^2, \eta^5\text{-C}_5\text{H}_5)(\text{SiMe}_3)$. The ^1H and ^{13}C NMR spectra and X-ray crystal structure clearly indicate that the ruthenabenzene ring is delocalized and aromatic [15].

Protonation of $\text{Cp}^*\text{Ru}(\text{L}_2)\text{Me}$ [where L_2 is bis(dimethylphosphino)methane (dmpm) or bis(diphenylphosphino)methane (dppm)] with HO_2CCF_3 readily results in reductive elimination of methane; no ruthenium(IV) hydridomethyl intermediates can be detected. The dinuclear aluminohydride complex $\text{Cp}^*_2\text{Ru}_2(\mu\text{-dppm})(\mu\text{-AlH}_5)$ has also been prepared and characterized by X-ray crystallography. Treatment of this aluminohydride complex with methanol affords the ruthenium polyhydride complex $\text{Cp}^*_2\text{Ru}_2(\mu\text{-dppm})\text{H}_6$.

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