

CHAPTER 5

Organometallic Pd^{III} Complexes in C–C and C–Heteroatom Bond Formation Reactions

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5.1 Introduction

Palladium complexes are extensively employed as efficient catalysts for a wide range of synthetically useful organic transformations such as C–H functionalization, C–C coupling, and hydrocarbon oxidation reactions.^{1–3} Whereas catalytic processes involving Pd complexes in oxidation states +2 and 0 have been recognized and studied for several decades,^{2,4–7} more recent studies have shown that high-valent Pd species can also act as catalytically active intermediates in various organic transformations.^{8–13} For example, the reactivity of isolated organometallic Pd^{IV} complexes has been studied for the past two decades,^{14–23} and Pd^{IV} intermediates have been shown to be involved in a variety of functional group-directed C–H functionalization reactions (see Chapter 4 of this book).^{8–13} By contrast, much less is known about the organometallic chemistry of Pd^{III} complexes and only a limited number of isolated mononuclear and dinuclear organometallic Pd^{III} complexes have been reported to date.^{24,25} Moreover, dinuclear Pd^{III} complexes have been recently proposed as reactive intermediates in oxidative C–H functionalization reactions,^{24,26–29}

RSC Catalysis Series No. 11

C–H and C–X Bond Functionalization: Transition Metal Mediation

Edited by Xavi Ribas

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Published by the Royal Society of Chemistry, www.rsc.org

while mononuclear Pd^{III} intermediates have been proposed in oxidatively induced C–C bond formation, O₂ activation or insertion, radical Kumada coupling and other reactions.^{24,25}

Herein, we overview the synthesis and reactivity of isolated mononuclear and dinuclear Pd^{III} complexes and describe the various C–C and C–heteroatom bond formation reactions in which the intermediacy of Pd^{III} species has been demonstrated or invoked.

5.2 Mononuclear Pd^{III} Complexes

5.2.1 Electronic and Structural Properties of Pd^{III} Coordination Complexes

The electronic configuration of Pd in oxidation states +2, +3, and +4 is d⁸, d⁷, and d⁶, respectively (Figure 5.1). Pd^{II} complexes are typically square planar, while the paramagnetic Pd^{III} d⁷ centers prefer a Jahn–Teller distorted octahedral geometry and the diamagnetic Pd^{IV} d⁶ centers exhibit an octahedral geometry.

While the first confirmed Pd^{III} species was the ionic compound NaPdF₄ obtained in 1982 in the solid state,³⁰ the first structurally characterized molecular Pd^{III} coordination compounds were the mononuclear homoleptic complexes of type [L₂Pd^{III}]³⁺ supported by the tridentate macrocyclic ligands 1,4,7-trithiacyclononane and 1,4,7-triazacyclononane (Scheme 5.1).^{31,32} These complexes were obtained by electrochemical or chemical oxidation with HClO₄ and their reactivity in one-electron redox processes was investigated.^{31–33} EPR characterization suggests that the unpaired electron resides predominantly at the metal center,^{32,33} although it was shown recently that the sulfur atoms of the macrocyclic ligands may contribute significantly to the singly occupied molecular orbital of the Pd^{III} complex.³⁴ In addition, the X-ray structures reveal a tetragonally distorted octahedral geometry, consistent with a Jahn–Teller distorted Pd^{III} d⁷ center.^{31,32}

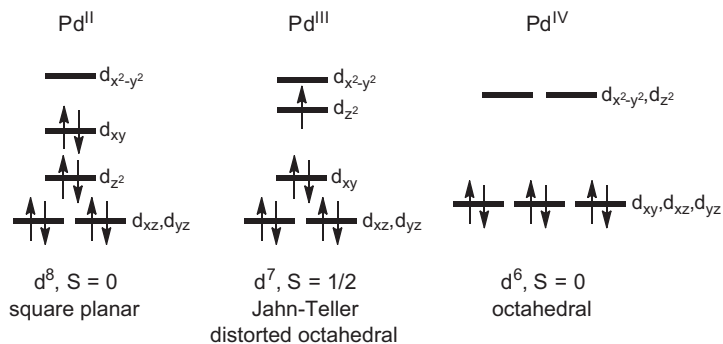
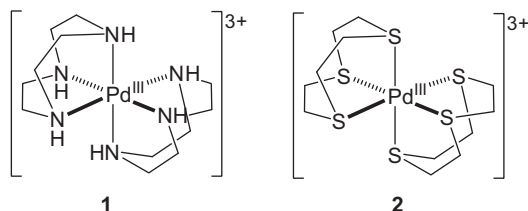
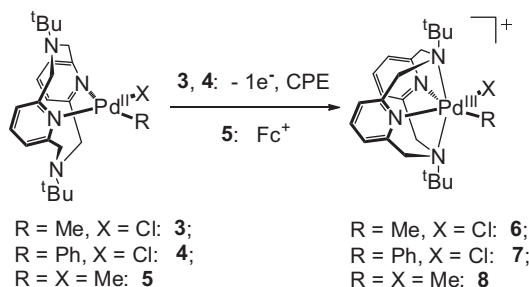


Figure 5.1 Representative d electron configuration of Pd^{II}, Pd^{III}, and Pd^{IV} oxidation states.



Scheme 5.1 Pd^{III} coordination compounds supported by N- or S-donor tridentate macrocyclic ligands.



Scheme 5.2 Synthesis of organometallic (^tBu₄N)Pd^{III} complexes (CPE – controlled potential electrolysis; Fc⁺-ferrocenium).

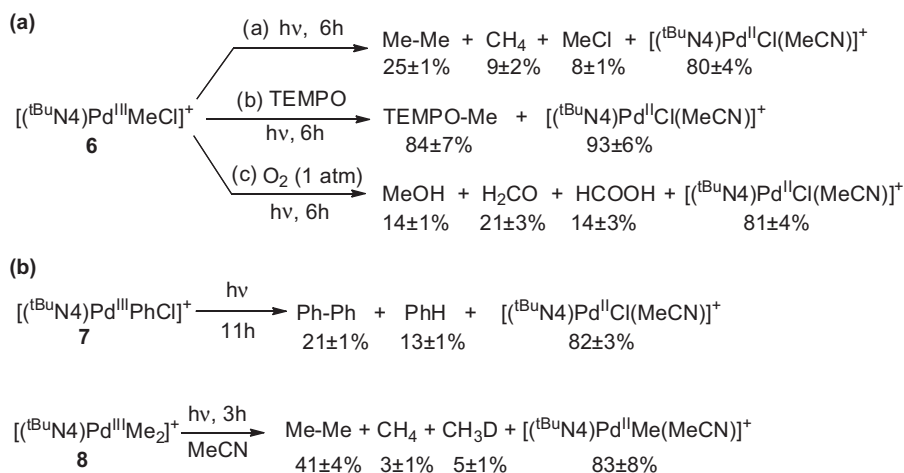
5.2.2 Reactivity of Isolated Organometallic Pd^{III} Complexes

Although the intermediacy of mononuclear Pd^{III} organometallic species was proposed in a number of C–C and C–heteroatom bond formation reactions, the first isolated mononuclear organometallic Pd^{III} complexes were reported by Mirica *et al.* in 2010.³⁵ The tetradentate macrocyclic ligand *N,N'*-di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane (^tBu₄N4) was employed in order to stabilize the distorted octahedral geometry of a Pd^{III} d⁷ center. The complexes [(^tBu₄N4)Pd^{III}RX]⁺ (**6**: R = Me, X = Cl; **7**: R = Ph, X = Cl; **8**: R = X = Me) were obtained by controlled potential electrolysis (CPE) or chemical oxidation with ferrocenium (Fc⁺) of the corresponding Pd^{II} precursors (^tBu₄N4)Pd^{II}RX (**3**: R = Me, X = Cl; **4**: R = Ph, X = Cl; **5**: R = X = Me) (Scheme 5.2). The resulting Pd^{III} complexes were stable in the absence of light in the solid state and in solution for several weeks. The structures of these Pd^{III} complexes reveal a distorted octahedral geometry with elongated Pd–N_{axial} distances, as expected for a d⁷ Pd^{III} center. In addition, the EPR spectra of the [(^tBu₄N4)Pd^{III}RX]⁺ species exhibit anisotropic signals with $g_{\text{ave}} = 2.12\text{--}2.13$, confirming a Pd^{III} center with a d₂₂ ground state.

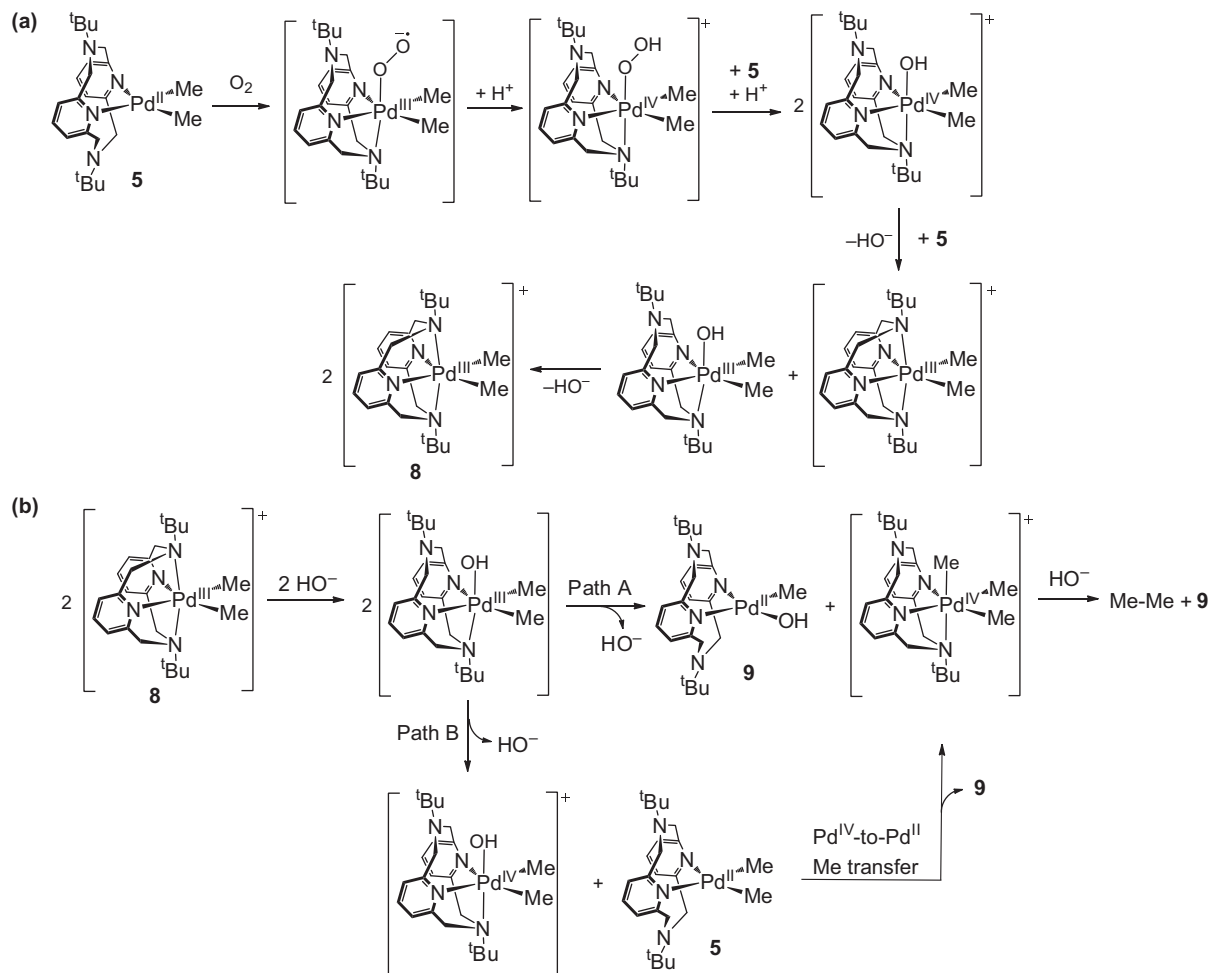
The isolated Pd^{III} complexes are stable in the dark, however they exhibit C–C (and C–Cl) bond formation reactivity in the presence of visible light.³⁵ For example, when a solution of [(^tBu₄N4)Pd^{III}MeCl]BF₄ in MeCN is exposed to

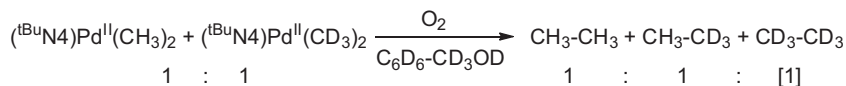
visible light, formation of ethane (25% yield), MeCl (8%), and methane (9%) occurs, along with the Pd^{II} product $[(^t\text{BuN}4)\text{Pd}^{\text{II}}\text{Cl}(\text{MeCN})]^+$ (80%, Scheme 5.3a). Reactivity studies suggest a radical mechanism for the observed light-induced reactions. For example, the formation of ethane from $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{MeCl}]\text{BF}_4$ is completely suppressed in the presence of the radical trap TEMPO (TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl), and the TEMPO–Me adduct forms as the major product (Scheme 5.3a). Notably, O₂ was also reported to act as an efficient Me radical trap and irradiation of $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{MeCl}]\text{BF}_4$ in the presence of O₂ generates a number of oxygenated products such as methanol, formaldehyde, and formic acid (Scheme 5.3a). Similar C–C bond formation photoreactivity was observed for $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{PhCl}]^+$ to generate biphenyl in 21% yield along with benzene (13%) and $[(^t\text{BuN}4)\text{Pd}^{\text{II}}\text{Cl}(\text{MeCN})]^+$ (82%) (Scheme 5.3b). Interestingly, while biaryl elimination from monoaryl Pd complexes is known (*vide infra*), the elimination of ethane from a monomethyl Pd complex has not been reported previously and is currently of great interest due to its relevance to catalytic methane oligomerization.³⁶

In addition, irradiation of a solution of $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{Me}_2]^+$ generated ethane and the monomethyl complex $[(^t\text{BuN}4)\text{Pd}^{\text{II}}\text{Me}(\text{MeCN})]^+$ in 41% and 83% yield, respectively (Scheme 5.3b). Such a reactivity resembles the Me group transfer and ethane elimination reactions induced by chemical oxidation of PdMe₂ complexes in which Pd^{III} intermediates were proposed but not detected (*vide infra*),^{37,38} thus confirming that Pd^{III} complexes are viable intermediates in such processes. Interestingly, the Pd^{II} dimethyl complex $(^t\text{BuN}4)\text{Pd}^{\text{II}}\text{Me}_2$ (**5**) also exhibits a non-radical ethane elimination induced by oxidation with O₂ or peroxides through the intermediate formation of a $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{Me}_2]^+$ complex **8**.³⁹ The oxidation of $(^t\text{BuN}4)\text{PdMe}_2$ with O₂ in C₆H₆–MeOH leads

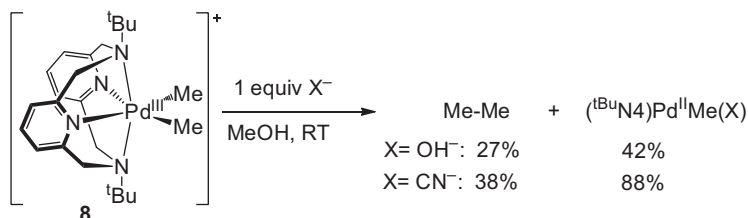


Scheme 5.3 Photoreactivity of $[(^t\text{BuN}4)\text{Pd}^{\text{III}}\text{MeRX}]^+$ complexes.

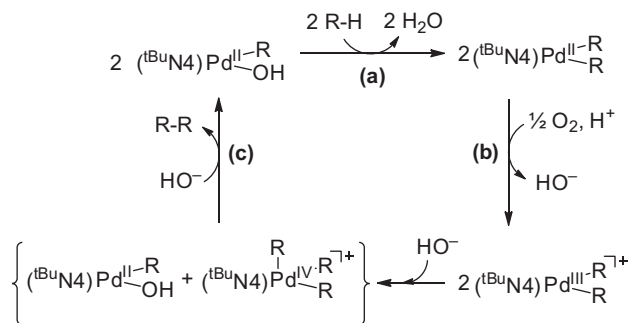




Scheme 5.6 Crossover reactivity of $(^t\text{Bu}_4\text{N})\text{Pd}^{\text{II}}\text{Me}_2$ and $[(^t\text{Bu}_4\text{N})\text{Pd}^{\text{III}}\text{Me}_2]^+$.



Scheme 5.7 Anion-induced C–C bond formation from $[(^t\text{Bu}_4\text{N})\text{Pd}^{\text{III}}\text{Me}_2]^+$.



Scheme 5.8 Proposed catalytic cycle for the aerobic oxidative coupling of C–H bonds that involves (a) C–H bond activation, (b) aerobic Pd^{II} oxidation, and (c) C–C bond formation.

bonds of acetone and terminal alkynes leading to the formation of a new $\text{Pd}^{\text{II}}\text{-C}$ bond. Based on this observed reactivity, a catalytic cycle for the aerobic oxidative coupling of C–H bonds that involves both Pd^{III} and Pd^{IV} intermediates can be envisioned (Scheme 5.8). In this proposed catalytic process, the formation of transient Pd^{III} species is expected to promote aerobic oxidation, while Pd^{IV} intermediates are necessary for efficient C–C bond formation.³⁹

Overall, these results show that isolated Pd^{III} methyl and phenyl complexes exhibit C–C bond formation reactivity, and the mechanisms of these transformations may involve either radical or non-radical pathways for the C–C bond elimination step. While the radical pathway for the C–C bond formation proceeds through an initial photoinduced $\text{Pd}^{\text{III}}\text{-C}$ bond homolysis, the

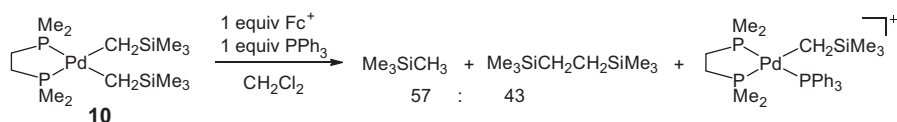
non-radical C–C elimination most likely involves the formation of Pd^{IV} intermediates.

5.2.3 Proposed Pd^{III} Intermediates in C–C Bond Formation Reactions

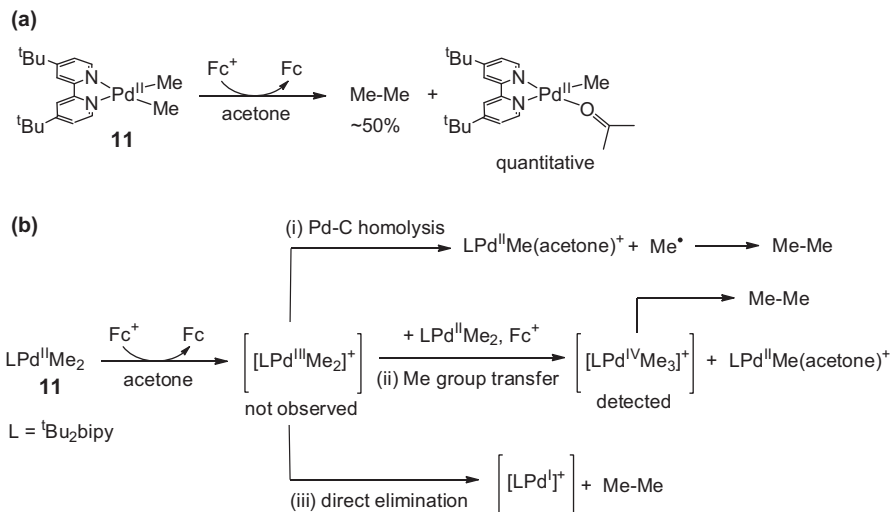
5.2.3.1 Proposed Pd^{III} Intermediates in C_{sp³}–C_{sp³} Coupling

The oxidatively induced C–C bond formation from dialkyl Pd^{II} complexes with phosphine ligands has been studied by Trogler and Seligson.³⁷ Oxidation of (dmpe)Pd(CH₂SiMe₃)₂ (dmpe = 1,2-bis(dimethylphosphino)ethane) complex **10** with Fc⁺ in the presence of 1 equiv. PPh₃ gave a mixture of Si(CH₃)₄, Me₃SiCH₂CH₂SiMe₃, and the Pd^{II} monoalkyl product [(dmpe)Pd^{II}(CH₂SiMe₃)(PPh₃)]⁺ (Scheme 5.9). A mechanism involving a Me₃SiCH₂ radical was proposed, as the oxidation of MgCH₂SiMe₃ with Fc⁺ produced Si(CH₃)₄ and Me₃SiCH₂CH₂SiMe₃ in a ~1:1 ratio. Interestingly, a more selective C–C bond formation was observed in the absence of PPh₃, to give Me₃SiCH₂CH₂SiMe₃ as the major product accompanied by complete decomposition of a metal complex. The oxidation of the analogous dimethyl complex (dmpe)PdMe₂ was reported to produce ethane.³⁷

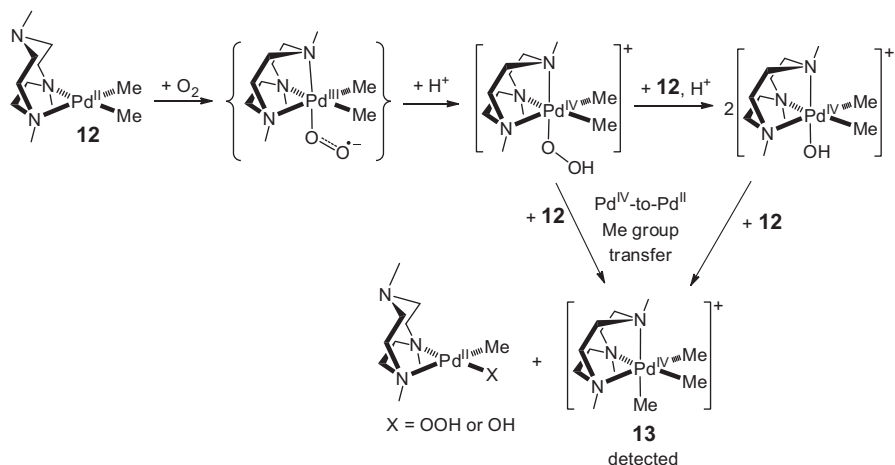
The selective ethane formation from the (^tBu₂bipy)Pd^{II}Me₂ complex **11** induced by one-electron oxidation has been recently reported by Sanford, Mayer, *et al.*³⁸ Oxidation of (^tBu₂bipy)Pd^{II}Me₂ with one-electron oxidants such as Fc⁺, the thianthrenyl radical cation, or Ag⁺ was shown to produce ethane in ~50% yield and the monomethyl product [(^tBu₂bipy)Pd^{II}Me(acetone)]⁺ quantitatively (Scheme 5.10a). Several mechanisms were considered for the C–C bond formation (Scheme 5.10b), all involving the initial one-electron oxidation of a Pd^{II}Me₂ complex to form an undetected Pd^{III}Me₂ intermediate. In path (i), subsequent Pd–Me bond homolysis generates a Me radical and ethane is produced by combination of two Me radicals. In path (ii), a Me group transfer occurs upon reaction of the Pd^{III}Me₂ species with **11** and 1 equiv. of Fc⁺ to generate [(^tBu₂bipy)Pd^{IV}Me₃]⁺ and [(^tBu₂bipy)Pd^{II}Me(solvent)]⁺, followed by reductive elimination from the former species. Path (iii) involves direct C–C reductive elimination from a Pd^{III} center to afford ethane and a Pd^I product. Path (i) was ruled out since the yield of ethane remains almost unchanged in the presence of Me radical traps 1,4-cyclohexadiene or styrene. Moreover, low temperature NMR studies and crossover experiments suggest that path (ii) is operative. Oxidation of (^tBu₂bipy)Pd^{II}Me₂ with Fc⁺ at –80 °C generates a new species assigned as the [(^tBu₂bipy)Pd^{IV}Me₃(solvent)]⁺ species along



Scheme 5.9 Oxidatively induced C–C bond formation from (dmpe)Pd^{II}(CH₂SiMe₃)₂.



Scheme 5.10 (a) Oxidatively induced ethane elimination from $(t\text{Bu}_2\text{bipy})\text{PdMe}_2$ and (b) mechanisms considered for ethane formation.



Scheme 5.11 Proposed mechanism for oxidation of $(\text{Me}_3\text{tacn})\text{PdMe}_2$ (**12**) with O_2 to generate **13**.

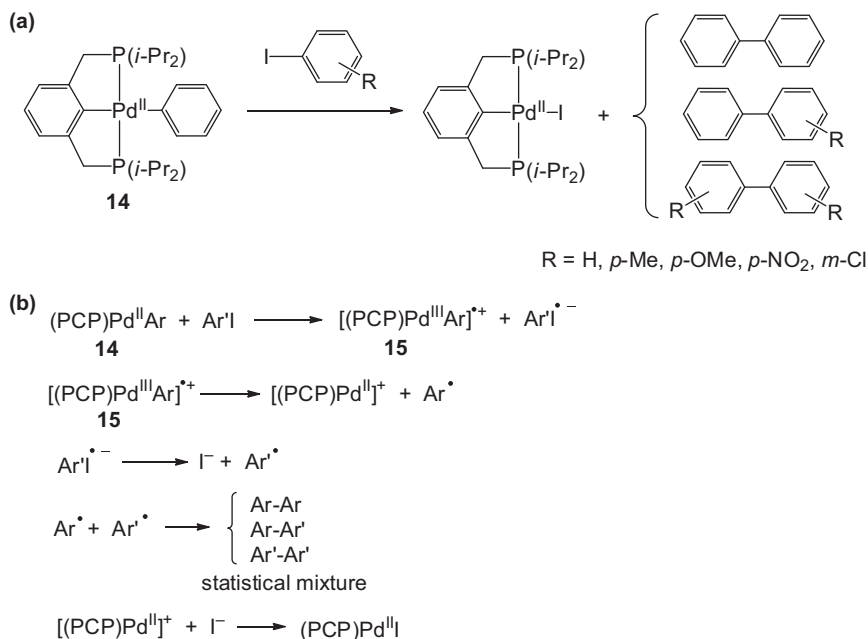
with $[(t\text{Bu}_2\text{bipy})\text{Pd}^{\text{II}}\text{Me}(\text{soln})]^+$. While $[(t\text{Bu}_2\text{bipy})\text{Pd}^{\text{IV}}\text{Me}_3(\text{soln})]^+$ is stable at -80°C , it eliminates ethane and $[(t\text{Bu}_2\text{bipy})\text{Pd}^{\text{II}}\text{Me}(\text{soln})]^+$ upon warming up to -30°C . In addition, oxidation of a 1 : 1 mixture of $(t\text{Bu}_2\text{bipy})\text{Pd}^{\text{II}}(\text{CH}_3)_2$ and $(t\text{Bu}_2\text{bipy})\text{Pd}^{\text{II}}(\text{CD}_3)_2$ with Fc^+ generates a 1 : 2 mixture of CH_3CH_3 and CH_3CD_3 , indicative of a Me group transfer consistent with path (ii).

The transient formation of a Pd^{III} intermediate was also recently proposed by Mirica *et al.* during the aerobic oxidation of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$, **12** ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane, Scheme 5.11).⁴⁴ The

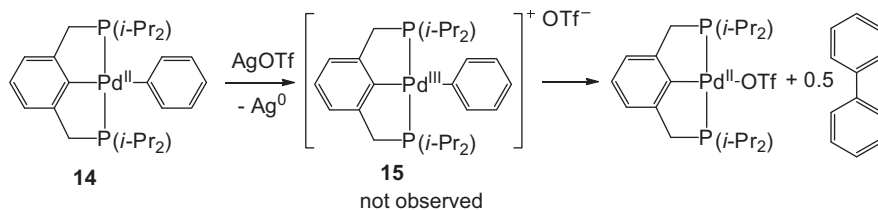
inner-sphere oxidation of the Pd^{II} center by O₂ is proposed to form a Pd^{III}-O₂^{•-} species – as suggested by detection of an EPR-active radical adduct trapped by DMPO, followed by further oxidation of the metal center to form detected Pd^{IV}-OOH and Pd^{IV}-OH intermediates and ultimately the [(Me₃tacn)Pd^{IV}Me₃]⁺ species **13**, which eliminates ethane at elevated temperatures.⁴⁴

5.2.3.2 Pd^{III} Intermediates in Oxidative Transformations of Pd^{II} Aryl Complexes

The mechanism of aryl–aryl coupling of Pd aryl complexes in presence of aryl iodides or one-electron oxidants has been studied by Milstein *et al.*⁴⁵ The reaction of (PCP)Pd^{II}(Ph) (PCP = 2,6-(*i*-Pr₂PCH₂)₂C₆H₃) (**14**) with aryl iodides results in the formation of (PCP)Pd^{II}(I) and a biaryl product. The use of substituted aryl iodides results in the formation of a mixed biaryl and homo-coupled products in a nearly statistical ratio (Scheme 5.12a), suggesting a radical mechanism involving an initial one-electron transfer from the electron-rich Pd phenyl complex **14** to the aryl iodide to form [(PCP)PdPh]^{•+} (**15**), which undergoes Pd–C bond homolysis to generate Ph radicals (Scheme 5.12b). Fragmentation of aryl iodide radical anion produces aryl radical and iodide,



Scheme 5.12 (a) Biaryl formation upon reaction of (PCP)PdPh with aryl iodides and (b) proposed radical mechanism.



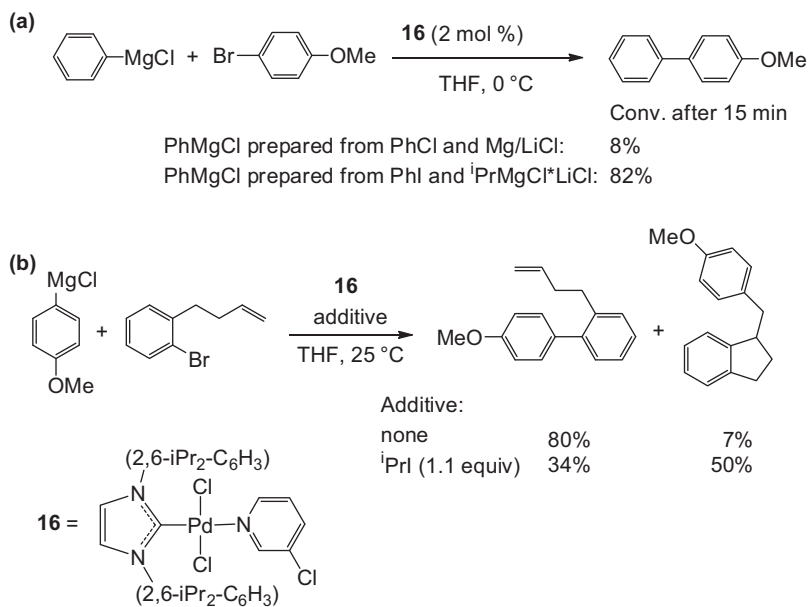
Scheme 5.13 One-electron oxidation of (PCP)PdPh with Ag^+ and Ph–Ph bond formation.

and the combination of Ph and aryl radicals then furnishes a statistical mixture of biaryls. A similar mechanism has been proposed for Ni-catalyzed aryl halide coupling.^{46,47}

Complex **14** also reacts with one-electron oxidants such as galvinoxyl and AgOTf, and formation of a transient Pd^{III} species $[(\text{PCP})\text{Pd}^{\text{III}}\text{Ph}]^+$ was proposed (Scheme 5.13).⁴⁵ As no products resulting from the reaction of a phenyl radical with the deuterated solvent was observed, the authors suggested the formation of aryl-bridged intermediates prior to C–C bond formation. The possibility of such bridged intermediates was also considered for the reactions involving aryl iodide as an oxidant (*vide supra*).

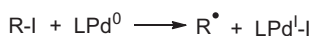
5.2.3.3 Pd^{III} Intermediates in Kumada Coupling

A recent report by Knochel *et al.* indicated that Kumada coupling catalyzed by Pd compounds such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene(3-chloropyridyl)palladium(II) dichloride (**16**) shows a dramatic rate acceleration in the presence of ^1PrI .⁴⁸ While a slow reaction between *p*-bromoanisole and phenylmagnesium chloride that was prepared from PhCl and Mg/LiCl was observed, significantly faster reactions were obtained with PhMgCl prepared by I/Mg exchange from PhI and $^1\text{PrMgCl}\cdot\text{LiCl}$, which generates ^1PrI as a stoichiometric byproduct (Scheme 5.14a). The same effect was observed in the presence of other alkyl iodides such as methyl iodide, neopentyl iodide, 1-iodoadamantane, or cyclohexyl iodide, and a radical mechanism was proposed. Indeed, use of a radical clock reaction test produced a mixture of the coupled and the cyclized product, the latter likely resulting from the ring closure between the aryl radical and an olefin (Scheme 5.14b). The proposed mechanism involves an initiation reaction between a Pd(0) complex and ^1PrI to form a Pd^{I} intermediate that reacts with aryl bromide to generate a Pd^{II} species and an aryl radical, which can be trapped by the Pd^{II} species to produce a Pd^{III} monoaryl complex (Scheme 5.15). The subsequent transmetalation with Ar_2MgBr produces a Pd^{III} biaryl intermediate that reductively eliminates the coupling product and regenerates the Pd^{I} species. However, it remains to be seen whether Pd^{III} species can undergo direct

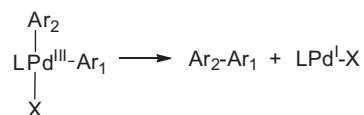
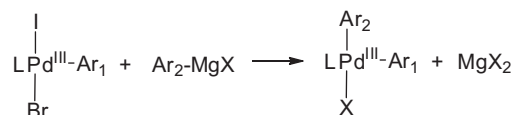
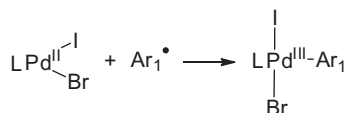


Scheme 5.14 (a) Effect of ⁱPrI on Pd-catalyzed Kumada coupling and (b) radical clock test for the presence of aryl radicals.

Initiation



Propagation



Scheme 5.15 Proposed mechanism for the Pd-catalyzed radical Kumada coupling.

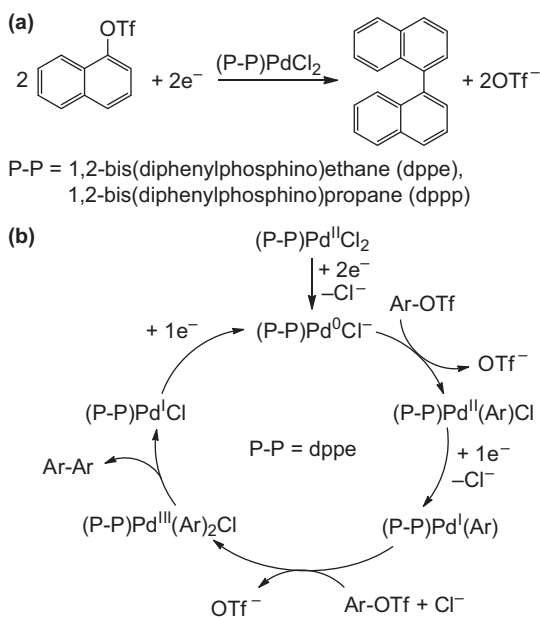
reductive elimination to form C–C or C–heteroatom bond, as to date no isolated mononuclear Pd^{III} species were shown to exhibit such reactivity.

5.2.3.4 Pd^{III} Intermediates in Homocoupling of Aryl Triflates

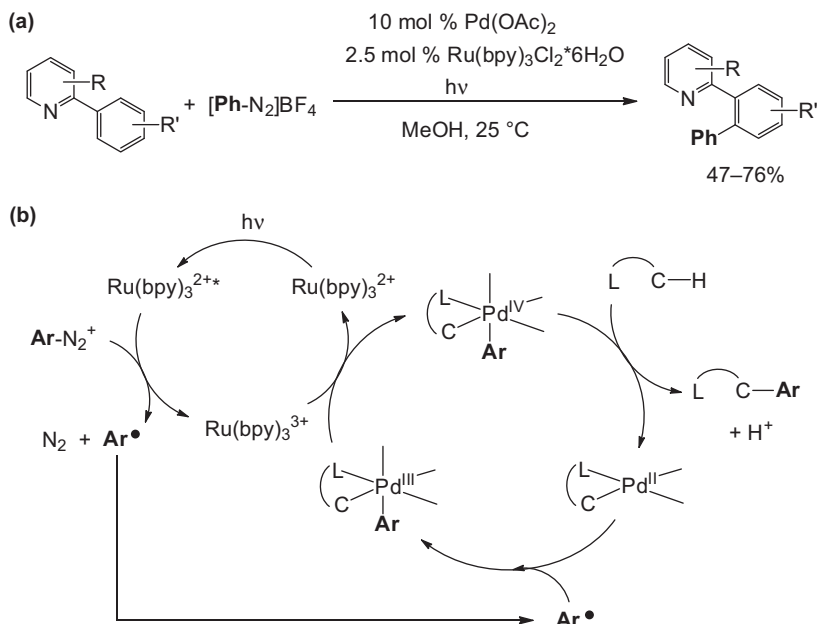
The Pd^{III} intermediates were proposed in the electrosynthesis of binaphthyls by reductive coupling of naphthyl triflates catalyzed by Pd complexes with bidentate phosphine ligands (P-P)PdCl₂ (P-P = dppe, dppp; Scheme 5.16a).⁴⁹ Electrochemical studies suggest a mechanism that involves an initial activation of the catalyst by two-electron reduction to form a Pd(0) species, which reacts with aryl triflate to generate a Pd^{II} monoaryl complex (Scheme 5.16b). CV studies indicate that the reduction of the (dppe)Pd^{II} monoaryl complex is a one-electron process,⁵⁰ and a mechanism similar to the (dppe)NiCl₂-catalyzed aryl halide coupling was proposed⁵¹ that involves the formation of Pd^I and Pd^{III} species, followed by the C–C reductive elimination of biaryl from a Pd^{III}Ar₂ intermediate (Scheme 5.16b).⁴⁹

5.2.3.5 Pd^{III} Intermediates in Other Arylation Reactions

Pd^{III} intermediates were proposed by Sanford *et al.* in a photocatalyzed C–H arylation reaction using diazonium salts in the presence of Pd(OAc)₂ and a Ru(bpy)₃Cl₂ photocatalyst (Scheme 5.17a).⁵² The proposed mechanism



Scheme 5.16 (a) Pd-catalyzed reductive coupling of naphthyl triflates and (b) proposed mechanism.



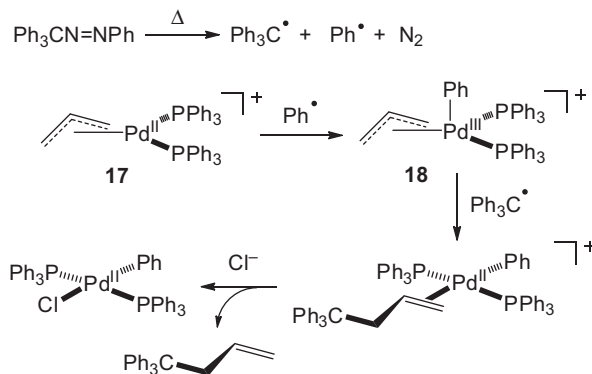
Scheme 5.17 (a) Pd/Ru-catalyzed C-H arylation with aryldiazonium salts and (b) proposed mechanism.

involves the reduction of diazonium salt with the photoexcited Ru(bpy)₃^{2+*} species to generate an aryl radical, which reacts with the palladacycle to produce a Pd^{III} intermediate (Scheme 5.17b). A subsequent one-electron oxidation of the Pd^{III} species is proposed to form a Pd^{IV} intermediate that is responsible for the C–C bond reductive elimination.⁵²

Yu *et al.* reported Pd-catalyzed C–H bond arylation and ethoxy-carbonylation reactions that are proposed to involve the generation of aryl or ethoxyacyl radicals and formation of high-valent Pd intermediates, although it remains unclear whether Pd^{III} or Pd^{IV} species form under these conditions.^{53,54}

Interestingly, formation of a Pd^{III} intermediate by reaction of a Pd^{II} precursor with a phenyl radical source, phenylazotriphenylmethane (PAT), was also proposed by Baird *et al.*⁵⁵ Thermal decomposition of PAT forms both Ph and trityl radicals that react with the Pd^{II}-allyl complex **17** to give a Pd^{II}Ph species and 4,4,4-triphenyl-1-butene (Scheme 5.18). The proposed mechanism involves an initial attack of the Ph radical at the Pd^{II} center to generate a Pd^{III}Ph(allyl) species **18**, which reacts with the trityl radical to give the observed products (Scheme 5.18).

Overall, the formation of Pd^{III} intermediates was proposed in a number of C_{sp3}–C_{sp3} and C_{sp2}–C_{sp2} coupling reactions and such intermediates can be formed by either oxidation of Pd^{II} precursors with one-electron oxidants, oxidative addition of ArX (X = halide or triflate) to Pd^I species, or reaction of



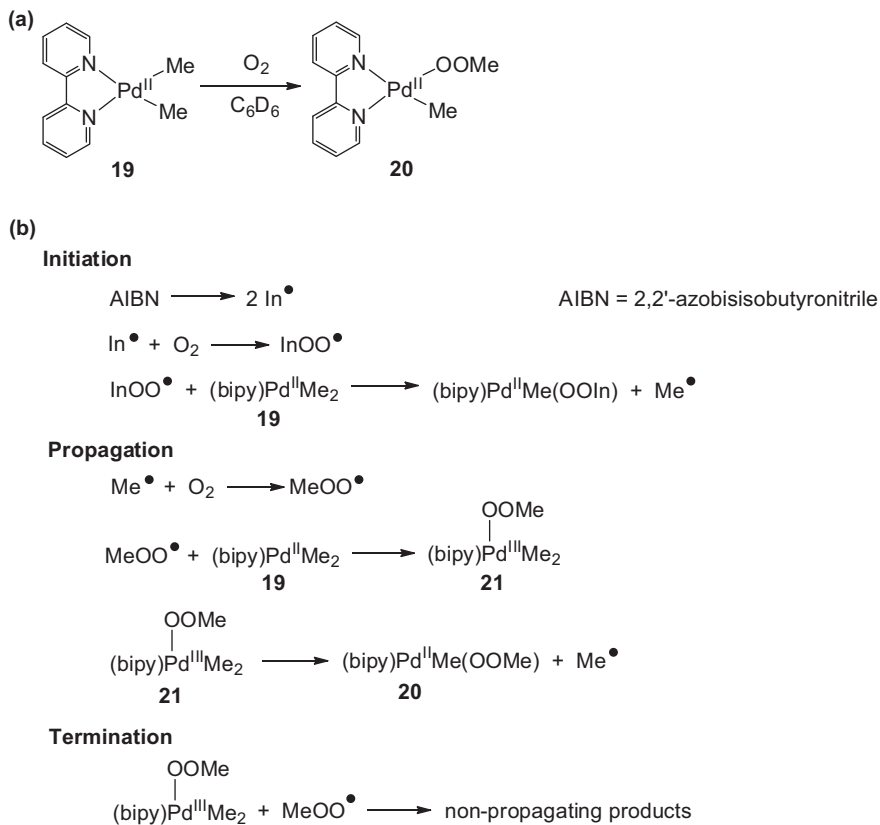
Scheme 5.18 Proposed formation of a Pd^{III} intermediate in presence of phenyl radical.

Pd^{II} complexes with carbon-centered radicals. The formation of the Pd^{III} intermediates in a number of C–C coupling reactions can thus be considered as a viable alternative to the commonly accepted Pd⁰/Pd^{II} mechanisms.⁵⁶ It is important to note that the Ag⁺ salt additives that are commonly employed in Pd-catalyzed C–H functionalization reactions can also act as one-electron oxidants and promote formation of Pd^{III} species.

5.2.4 Proposed Pd^{III} Intermediates in C–Heteroatom Bond Formation Reactions

5.2.4.1 Pd^{III} Intermediates in the Radical O₂ Insertion into a Pd–Me Bond

The radical insertion of dioxygen into the Pd–C bond of a dimethyl Pd^{II} complex was reported by Goldberg *et al.*⁵⁷ When a solution of (bipy)Pd^{II}Me₂ (**19**) in benzene was exposed to O₂ (1–10 atm) at RT, formation of the Pd^{II} methylperoxo complex (bipy)Pd^{II}Me(OOMe) (**20**) was observed in up to ~70% yield (Scheme 5.19a). The reaction was accelerated in the presence of light or radical initiator additives, and reproducible reaction rates were obtained in the presence of excess AIBN radical initiator. Detailed kinetic studies suggest a radical chain mechanism in which a chain propagation step involves a stepwise associative homolytic substitution at the Pd center (Scheme 5.19b). Addition of the MeOO radical to a square planar Pd^{II} center generates a five-coordinate Pd^{III} intermediate **21**, which then extrudes a Me radical with concomitant formation of (bipy)Pd^{II}Me(OOMe) (**20**). Analogous reactions of alkylperoxo radicals with first row transition complexes leading to a one-electron oxidation of a metal center have been reported previously,^{58–60} and also proposed in the radical-chain aerobic oxidation of a Pt^{II} complex in the presence of ⁱPrI.⁶¹



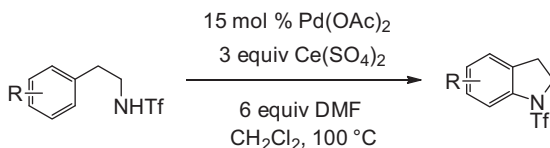
Scheme 5.19 (a) Reaction of (bipy)PdMe₂ (**19**) with O₂ and (b) proposed mechanism for the insertion of O₂ into the Pd–Me bond.

5.2.4.2 Pd^{III} Intermediates in Catalytic C–H Functionalization Reactions

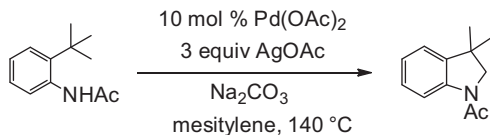
Yu *et al.* reported intramolecular C–H amination reactions catalyzed by Pd(OAc)₂ in the presence of the one-electron oxidant Ce(SO₄)₂ (Scheme 5.20).⁶² The formation of a Pd^{III} intermediate was proposed, although it remains unclear whether its further oxidation to Pd^{IV} occurs before the C–N reductive elimination step.⁶²

The involvement of high-valent Pd intermediates as an alternative to the more common Pd⁰/Pd^{II} catalytic cycles was also discussed by Glorius in the C–H amination in the presence of AgOAc, which can act as a one-electron oxidant (Scheme 5.21).⁶³

In general, the oxidation of Pd^{II} complexes with one-electron oxidants may yield either Pd^{III} or Pd^{IV} species, depending on the relative stability of the two oxidation states and the ligand environment. For example, stable Pd^{IV}



Scheme 5.20 Pd-catalyzed intramolecular C–H amination in presence of $\text{Ce(SO}_4)_2$.



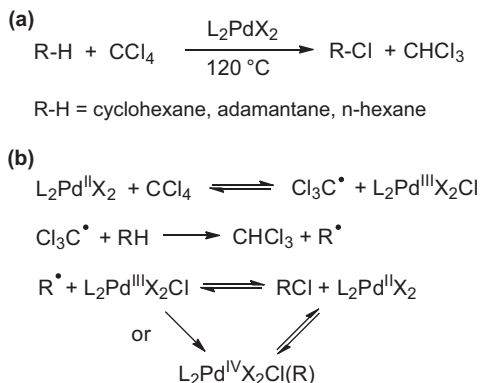
Scheme 5.21 Pd-catalyzed intramolecular C–H amination in presence of AgOAc .

complexes were obtained by oxidation with Fc^+ of palladacycles $\text{LPd}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{C}_6\text{H}_4)$ ($\text{L} = \text{hydrotris(pyrazolyl)borate anion, Tp}^-$), since the Tp^- ligand is known to stabilize Pd^{IV} complexes.⁶⁴ In addition, examples of disproportionation of Pd^{III} to Pd^{IV} and Pd^{II} species,^{65–67} as well as the comproportionation of Pd^{IV} and Pd^{II} to form Pd^{III} species are known.³³ Therefore, it may not be possible to unambiguously assign the oxidation state of high-valent Pd intermediates, and both Pd^{III} and Pd^{IV} species may be involved in oxidatively-induced C–C or C–heteroatom bond formation reactions.

5.2.4.3 Pd^{III} Intermediates in C–Cl Bond Formation Reactions

The transient formation of a Pd^{III} intermediate was proposed in a number of reactions involving CCl_4 or CCl_3Br as the oxidant, such as the C–H chlorination of saturated hydrocarbons with CCl_4 catalyzed by $(\text{L})_2\text{PdX}_2$ ($\text{L} = \text{PPh}_3$, $p\text{-Tol}_3\text{P}$, MeCN ; $\text{X} = \text{Cl, Br, I}$; Scheme 5.22a).^{68,69} Based on the reaction selectivity, a mechanism was proposed in which the Pd^{II} complex reacts with CCl_4 to produce a transient $\text{Pd}^{\text{III}}\text{Cl}$ species and a CCl_3 radical, which reacts with the C–H bond of an alkane to generate chloroform and an alkyl radical that then reacts with the $\text{Pd}^{\text{III}}\text{Cl}$ species to give alkyl chloride and regenerate the Pd^{II} complex (Scheme 5.22b).

A similar mechanism was proposed for the Kharasch addition of CCl_3Br to alkenes catalyzed by Pd^{II} complexes.^{70,71} For example, the Pd^{II} complexes $(\text{Me}_3\text{tacn})\text{PdCl}_2$ and $(\text{Me}_3\text{tacn})\text{PdBr}_2$ ($\text{Me}_3\text{tacn} = N,N',N'$ -trimethyl-1,4,7-triazacyclononane) were shown to be good catalysts for the radical addition of CCl_3Br to alkenes, most likely due to their low $\text{Pd}^{\text{II/III}}$ oxidation potentials.⁷¹ While the proposed catalytic mechanism involves a mononuclear trihalide Pd^{III} intermediate that was not detected, a dinuclear Pd^{III} species was observed in the reaction mixture (*vide infra*).



Scheme 5.22 (a) Pd-catalyzed C–Cl bond formation and (b) proposed mechanism.

5.3 Dinuclear Pd^{III} Complexes

5.3.1 Electronic Properties of Dinuclear Pd^{III} Complexes

The interaction of two square planar Pd^{II} d⁸ centers along the *z*-axis leads to mixing of the d orbitals and a molecular orbital diagram in which both the bonding and antibonding molecular orbitals are filled (Figure 5.2), and thus no metal–metal bonding interaction is expected for such complexes. However, due to symmetry-allowed mixing of Pd 5p_{*z*} and 5s orbitals into the 4d_{*z*²} orbital, weak metal–metal bonding interactions may be present in such complexes.⁷² One-electron or two-electron oxidation of Pd^{II} dinuclear species removes electrons from antibonding orbitals and generates mixed-valent Pd^{II}–Pd^{III} or Pd^{III}–Pd^{III} complexes with Pd–Pd bond orders of 0.5 or 1, respectively.^{24,25}

5.3.2 Dinuclear Pd^{II} Complexes

Cyclometalated Pd^{II} complexes are common precursors in Pd-mediated oxidative C–H bond functionalization reactions. In this context, the geometry of bridged dinuclear Pd complexes depends on the nature of the bridging ligands and directly affects their redox reactivity. For example, while the dichloro-bridged palladacycle **22** is essentially planar and exhibits no metal–metal interactions, the acetato- (**23**) or trifluoroacetate-bridged complexes adopt an open “clamshell” geometry with two Pd centers in close proximity (2.862 Å Pd⋯Pd distance for complex **23**) and exhibit weak attractive d⁸–d⁸ interactions between two Pd centers and π-stacking interactions between two phenylpyridine ligands (Scheme 5.23).⁷²

Interestingly, weak d⁸–d⁸ interactions between two cationic Pd^{II} centers were also observed for Pd^{II} complexes supported with the macrocyclic tetradentate ligand 2,11-dithia[3.3](2,6)pyridinophane (N2S2), **24** and **25** (Scheme 5.24).⁷³

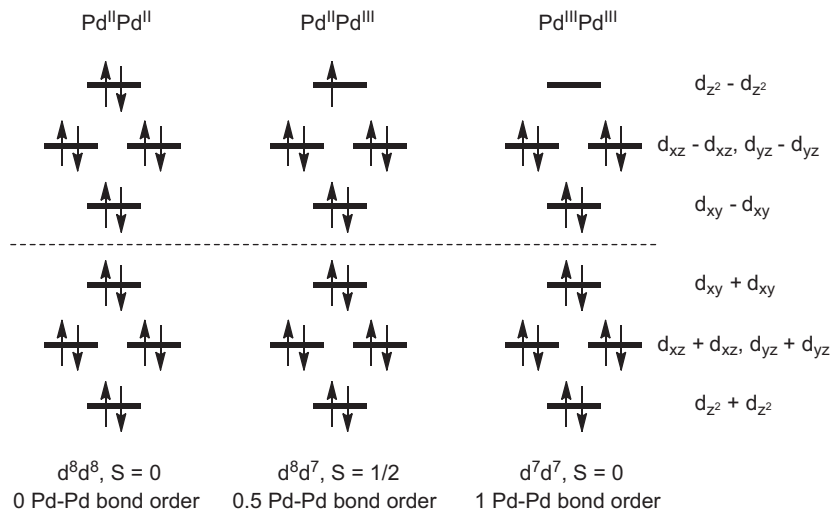
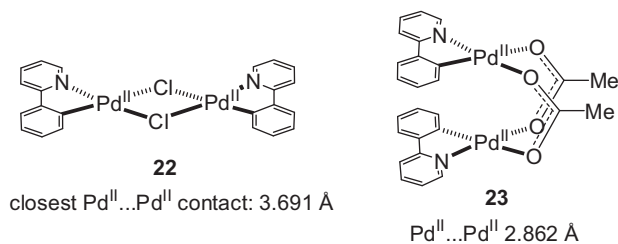
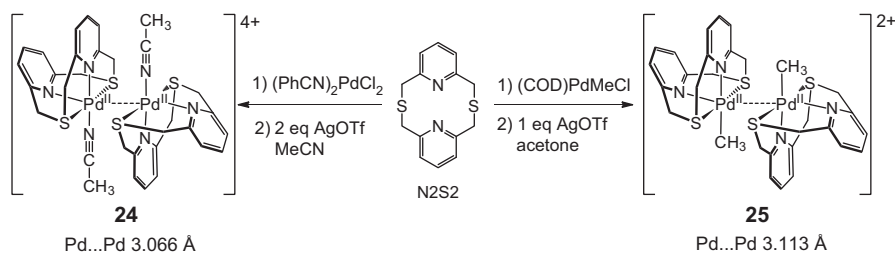


Figure 5.2 Molecular orbital diagram for $\text{Pd}^{\text{II}}\text{Pd}^{\text{II}}$, $\text{Pd}^{\text{II}}\text{Pd}^{\text{III}}$, and $\text{Pd}^{\text{III}}\text{Pd}^{\text{III}}$ dinuclear complexes with interacting metal centers. The z axis is along the Pd-Pd vector and the dashed line represents the separation between bonding and antibonding molecular orbitals.



Scheme 5.23 Examples of dinuclear bridged Pd^{II} complexes with planar (**22**) or “clamshell” (**23**) geometry.



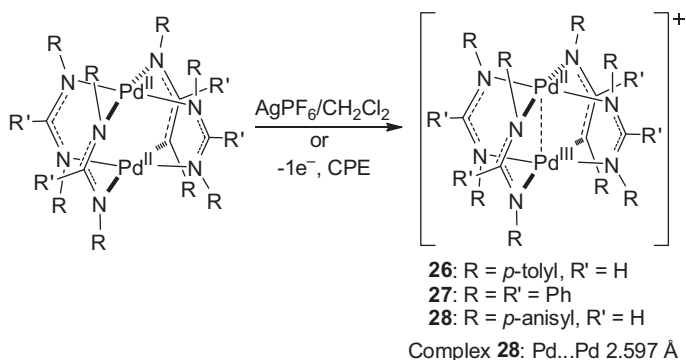
Scheme 5.24 Dinuclear (N2S2) Pd^{II} complexes with weak d^8-d^8 interactions.

These interactions are not supported by any bridging ligands and were proposed to play a role in the observed oxidatively-induced Me group transfer reactivity leading to the Pd^{IV} species [(N2S2)Pd^{IV}Me₂]²⁺.⁷³

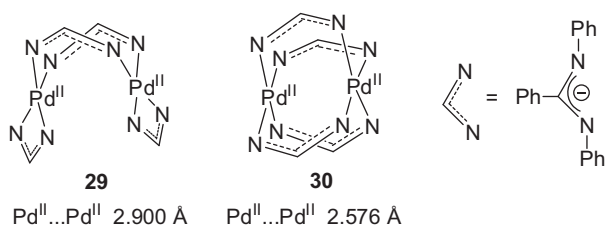
5.3.3 Mixed-Valent Pd^{II}–Pd^{III} Complexes

The first isolated mixed-valent Pd^{II}–Pd^{III} complexes were the amidinate-bridged dinuclear complexes **26–28** obtained by chemical or electrochemical oxidation of the corresponding tetrabridged Pd^{II} precursors (Scheme 5.25).^{74–77} These paramagnetic complexes were characterized by X-ray crystallography and high-field EPR spectroscopy that confirmed a metal-centered oxidation,^{74–77} while DFT calculations suggest a Pd–Pd bond order of 0.5 for such complexes.⁷⁷

Detailed electrochemical studies suggest that the number of ligands bridging the two Pd centers has a pronounced effect on the redox properties of these complexes. Thus, the oxidation of the dibridged complex **29** was shown to be a two-electron process that corresponds to the oxidation of the two non-interacting Pd centers (Scheme 5.26), in line with the long Pd...Pd distance of



Scheme 5.25 Synthesis of mixed-valent Pd^{II}–Pd^{III} complexes.



Scheme 5.26 Dinuclear Pd^{II} complexes with bridging *N,N'*-diphenylbenzamidinate ligands.

2.900 Å. By contrast, the tetrabridged complex **30** undergoes a reversible one-electron oxidation corresponding to a Pd^{II}–Pd^{II}/Pd^{II}–Pd^{III} oxidation at a potential that is 0.37 V less positive compared to **29**, and supported by the shorter Pd...Pd distance of 2.576 Å enforced by the four bridging ligands.⁷⁶

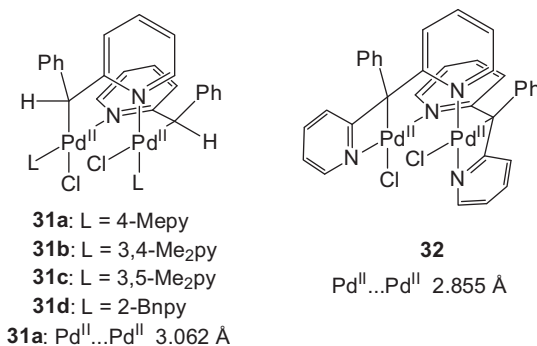
5.3.4 Dinuclear Pd^{III}–Pd^{III} Complexes with a Pd^{III}–Pd^{III} Bond

In 1996, Bond, Canty *et al.* reported electrochemical studies of the dinuclear palladacyclic complexes **31** and **32** (Scheme 5.27).⁷⁸ These studies suggest a stepwise oxidation to Pd^{II}–Pd^{III} and Pd^{III}–Pd^{III} dinuclear species, respectively, although both oxidation products were unstable and could not be isolated. The CV of complex **32** revealed that the first one-electron oxidation was chemically reversible, indicative of a limited stability of the mixed-valent Pd^{II}–Pd^{III} product, however, electrolysis of this complex results in an overall two-electron oxidation, presumably due to the disproportionation of the mixed-valent intermediate to Pd^{II}–Pd^{II} and Pd^{III}–Pd^{III} species.⁷⁸

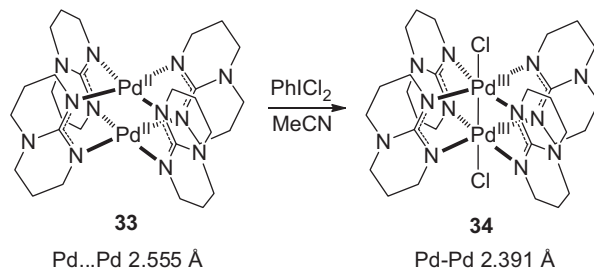
Similarly, the CV study of the diacetato-bridged 2-phenylpyridyl complex **23** and its 2-tolylpyridyl analog revealed two one-electron oxidation steps corresponding to sequential formation of Pd^{II}–Pd^{III} and Pd^{III}–Pd^{III} species. The mixed-valent species was proposed to undergo disproportionation to Pd^{III}–Pd^{III} and Pd^{II}–Pd^{II} resulting in a decreased intensity for the second oxidation wave.⁷²

In 1998, Cotton reported the first isolated Pd^{III}–Pd^{III} complex **34**, which was obtained by chemical oxidation of the dinuclear Pd^{II}–Pd^{II} precursor **33** with PhICl₂ (Scheme 5.28).⁷⁹ Complex **34** exhibits a Pd–Pd single bond that is supported by four bridging 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidinate ligands.

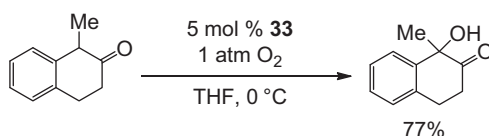
In 2011, Ritter *et al.* found that complex **33** catalyzes the aerobic hydroxylation of the α-carbonyl tertiary C–H bonds (Scheme 5.29).⁸⁰ Moreover, UV-vis studies suggest formation of a transient Pd^{III}–Pd^{III} intermediate, and



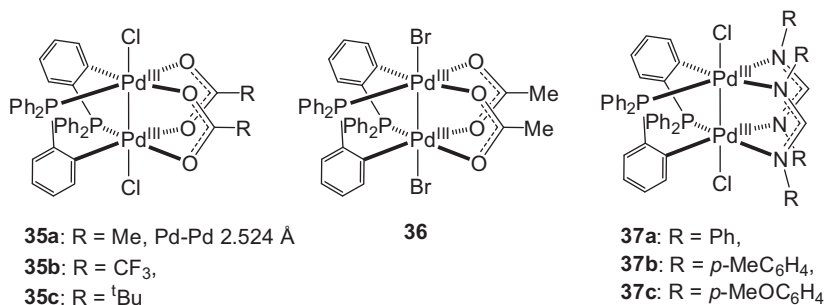
Scheme 5.27 Dinuclear Pd^{II} complexes with bridging pyridine-2-yl(phenyl)methyl-*C,N* and bis(pyridine-2-yl)phenylmethyl-*C,N,N'* ligands.



Scheme 5.28 Synthesis of the first isolated dinuclear Pd^{III}-Pd^{III} complex by Cotton *et al.*



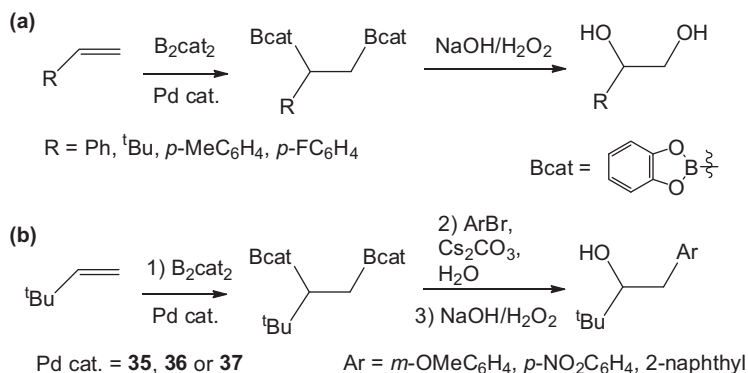
Scheme 5.29 Alpha-hydroxylation of carbonyl compounds catalyzed by **33**.



Scheme 5.30 Dinuclear Pd^{III} complexes with bridging orthometalated triphenylphosphine ligands.

O₂ uptake and ¹⁸O₂ labeling experiments imply that both oxygens from O₂ are incorporated into the product. Although the mechanism of this transformation remains to be elucidated, the absence of peroxide or hydroperoxide products and a lack of reactivity for Ph₃CH suggest that a radical metal-mediated autooxidation mechanism is unlikely.

In 2006, Cotton, Lahuerta, Ubeda *et al.* reported the first organometallic Pd^{III}-Pd^{III} complexes **35a-c**, with the Pd^{III} centers being supported by two bridging orthometalated triphenylphosphine ligands and two carboxylate groups (Scheme 5.30).⁸¹ The observed short Pd-Pd distances of 2.524–2.543 Å imply a single bond between the two Pd centers that is supported by DFT calculations. In addition, several analogs (**36–37**) were synthesized using acetate



Scheme 5.31 (a) Diboration/oxidation and (b) tandem diboration/arylation/oxidation catalyzed by dinuclear Pd^{III} complexes.

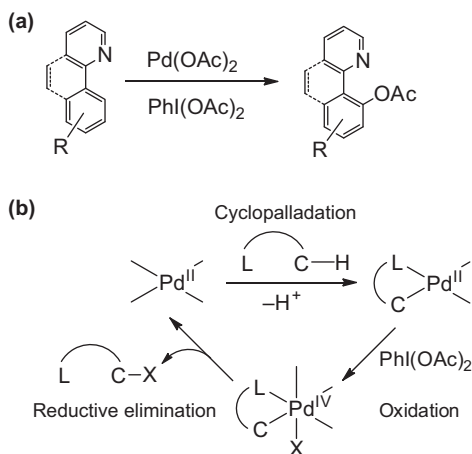
or formamidinate bridging ligands (Scheme 5.30).^{82,83} Complexes **35–37** were employed as pre-catalysts for the diborylation and tandem borylation/arylation of alkenes (Scheme 5.31).^{82,83} The Pd^{III} complexes were shown to be reduced to Pd^{II} by the diboron reagents under the catalytic reaction conditions and thus most likely serve as precursors for the active catalyst.

5.3.5 Dinuclear Pd^{III} Complexes in Catalytic C–H Functionalization Reactions

5.3.5.1 Pd^{III} Intermediates in C–H Acetoxylation

Palladium complexes have been known to catalyze aromatic C–H bond functionalization in the presence of strong oxidants since the 1960s and the involvement of Pd^{IV} intermediates has been proposed.^{84–90} General methods for the regioselective ligand-directed functionalization of C_{sp²}–H and C_{sp³}–H bonds to esters, ethers, halides, and amines in the presence of oxidants such as PhI(OAc)₂, *N*-chlorosuccinimide (NCS), or *N*-bromosuccinimide (NBS) was reported initially by Sanford *et al.*,^{8,11,91} and then by Yu *et al.*,^{92,93} Gaunt *et al.*,⁹⁴ and others.^{10–13,95} For example, the regioselective acetoxylation of 2-phenylpyridine and benzo[h]quinoline was accomplished using Pd(OAc)₂ as the catalyst and PhI(OAc)₂ as the oxidant (Scheme 5.32a).⁸ As no product was formed in the presence of benzoquinone or Cu(OAc)₂ – typical oxidants used in Pd^{II}/Pd⁰-mediated reactions – and no reaction occurred in the absence of the oxidant, a Pd^{II}/Pd^{IV} catalytic cycle was proposed that involves C–H activation and formation of a palladacycle, which is oxidized by PhI(OAc)₂ to form a Pd^{IV} species followed by reductive C–O elimination (Scheme 5.32b).

In 2009, Ritter *et al.* demonstrated that the two-electron oxidation of the dinuclear palladacycle **23** with PhI(OAc)₂ at low temperature yields a structurally characterized dinuclear Pd^{III}–Pd^{III} product **39** that was stable



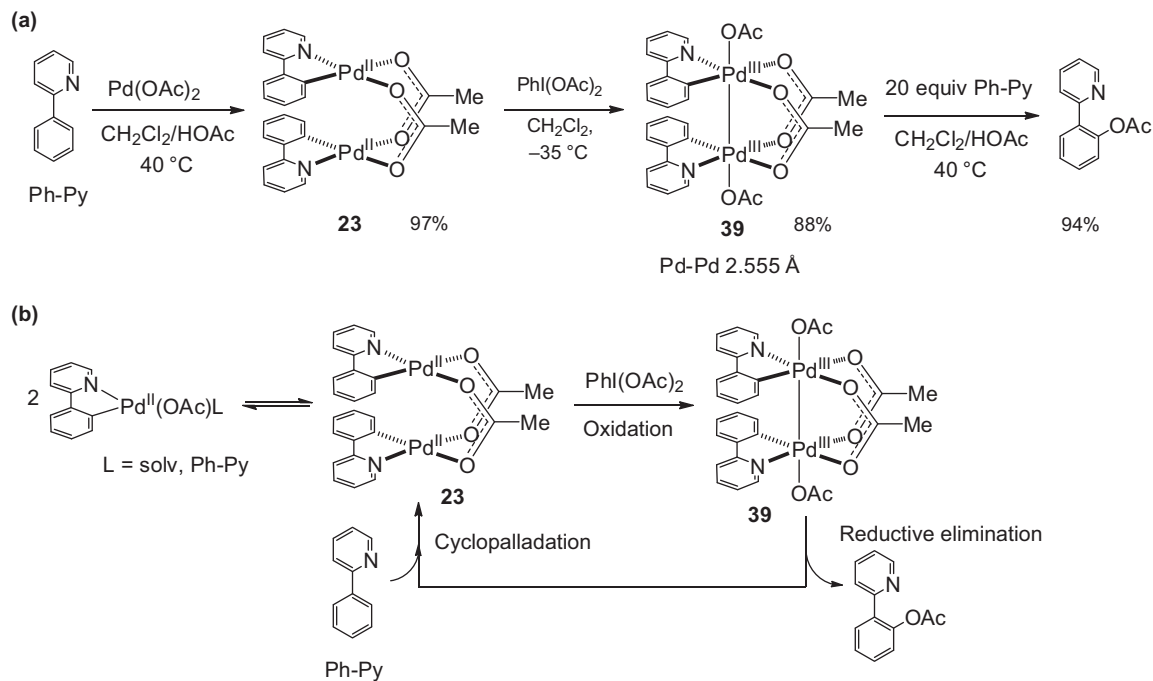
Scheme 5.32 (a) Pd-catalyzed C–H bond acetoxylation and (b) Pd^{II}/Pd^{IV} catalytic cycle proposed by Sanford *et al.*

below $-10\text{ }^{\circ}\text{C}$ (Scheme 5.33a).²⁷ The Pd–Pd distance in **39** is 2.555 \AA , 0.307 \AA shorter *vs.* the Pd^{II}–Pd^{II} precursor **23**. The complex **39** is diamagnetic, consistent with the presence of a Pd^{III}–Pd^{III} single bond. Warming up the solution of **39** to $40\text{ }^{\circ}\text{C}$ leads to C–O reductive elimination and yields the acetoxyated product (Scheme 5.33a). Based on these results, a catalytic cycle was proposed involving (i) cyclopalladation to give **23**, (ii) bimetallic oxidation of **23** with PhI(OAc)₂ to generate **39**, and (iii) bimetallic C–O reductive elimination (Scheme 5.33b). The complex **39** was shown to be a kinetically competent catalytic intermediate, although a potential involvement of a transient Pd^{IV} species could not be excluded.

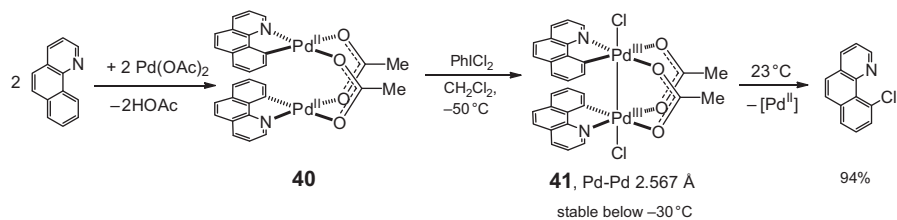
5.3.5.2 Pd^{III} Intermediates in C–H Halogenation

The oxidation of the palladacycle **40** with PhICl₂, leading to formation of the structurally characterized diamagnetic Pd^{III}–Pd^{III} complex **41**, was also reported (Scheme 5.34).²⁶ Complex **41** is stable at low temperature, yet it reductively eliminates 10-chlorobenzo[h]quinoline at $23\text{ }^{\circ}\text{C}$ in high yield (Scheme 5.34), and the authors proposed a direct C–Cl reductive elimination without prior dissociation to mononuclear Pd^{III} species or disproportionation to Pd^{IV} and Pd^{II} complexes.²⁶ Detailed experimental and computational studies suggest a synergistic effect of the bimetallic core in both oxidation and C–Cl reductive elimination that lowers the overall energy barrier of these transformations.²⁹ The complex **41** could also be formed under catalytic conditions, in the presence of excess benzo[h]quinoline.²⁶

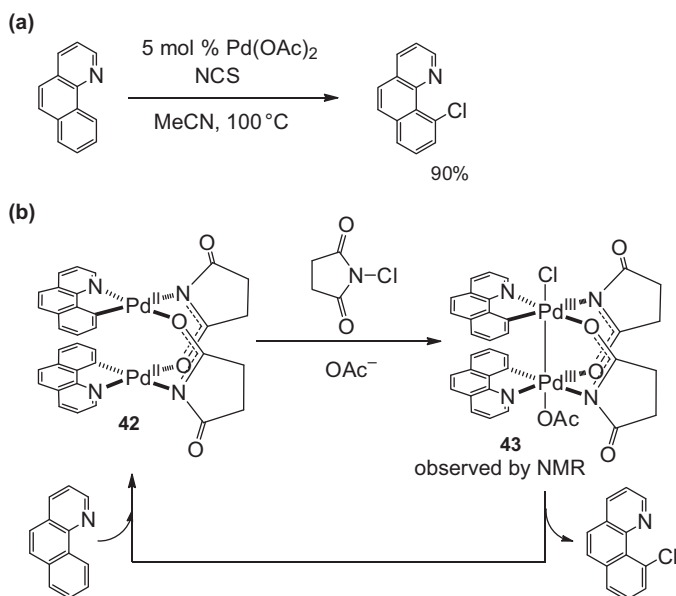
The mechanism of C–H bond chlorination with *N*-chlorosuccinimide (NCS) as an oxidant was also investigated, and formation of the Pd^{III}–Pd^{III} dinuclear



Scheme 5.33 (a) Dinuclear Pd^{II} and Pd^{III} intermediates in C–H bond acetoxylation and (b) bimetallic Pd^{II}/Pd^{III} catalytic cycle proposed by Ritter *et al.*



Scheme 5.34 Dinuclear Pd^{II} and Pd^{III} intermediates in C–H bond chlorination.



Scheme 5.35 (a) Pd-catalyzed C–H bond chlorination with NCS and (b) proposed bimetallic Pd^{II}/Pd^{III} catalytic cycle.

intermediate **43** was detected by NMR (Scheme 5.35).⁹⁶ The resting state of the catalyst is a dinuclear succinimide anion-bridged complex **42**. Mechanistic studies of the catalytic chlorination reveal a turnover-limiting oxidation of **42** by NCS, while the first order of the reaction rate in **42** implies this dinuclear complex is directly involved in an acetate-assisted bimetallic oxidation by NCS (Scheme 5.35b).

Formation of dinuclear and/or mononuclear Pd^{III} intermediates can also be considered in a number of other cases in which Pd^{IV} intermediates were proposed initially, for example, in catalytic chlorination of C–H bonds of arylpyridines or acetanilides with NCS^{8,97–99} or CuCl₂¹⁰⁰ as an oxidant.

5.3.5.3 Pd^{III} Intermediates in C–H Arylation and Trifluoromethylation

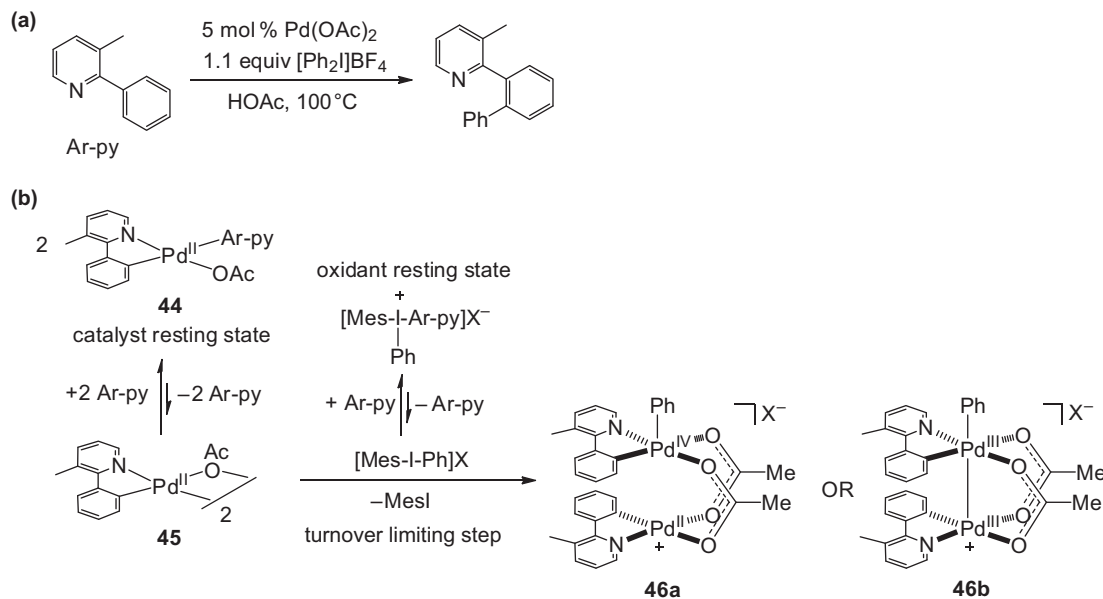
Ortho-phenylation of C–H bonds with diaryliodonium salts catalyzed by $Pd(OAc)_2$ was demonstrated for a number of substrates such as arylpyridines (Scheme 5.36a), quinolines, pyrrolidinones, oxazolidinones, and benzodiazepines.^{28,101–103} Mechanistic studies of the ortho-phenylation of 3-methyl-2-phenylpyridine reveal that the mononuclear complex **44** is the catalyst resting state (Scheme 5.36b).²⁸ The catalytic reaction rate shows a second order dependence on **44**, and the turnover limiting step was proposed to be the oxidation of the dinuclear Pd^{II} species **45** to give the dinuclear Pd^{IV} – Pd^{II} complex **46a**, which can alternatively be formulated as the isoelectronic Pd^{III} – Pd^{III} species **46b**. Subsequent reductive C–C elimination from **46** affords the arylated product and regenerates the Pd^{II} catalyst.

Computational studies were employed to elucidate the electronic structure and reactivity of dinuclear complexes of type **A** and **B** (Scheme 5.37) as a function of ligand environment, as these species are proposed in various Pd -catalyzed C–H functionalization reactions.^{104,105} The Pd^{IV} – Pd^{II} bonding character in complex of type **A** was found to be favored when X is a strong σ -donor, while the Pd^{III} – Pd^{III} bonding character was found to be predominant when X is a weak σ -donor ligand.¹⁰⁵

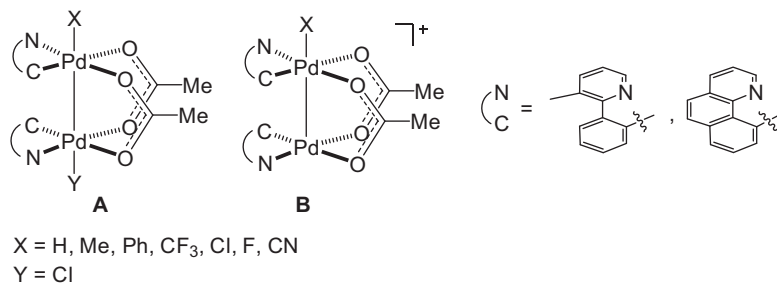
The arylation of C_{sp^2} –H and C_{sp^3} –H bonds using aryl iodides in the presence of a stoichiometric amount of Ag salts was also developed (Scheme 5.38).^{101,106–109} These reactions were proposed to involve oxidative addition of the aryl iodide to Pd^{II} to give a $Pd^{IV}(Ar)(I)$ product, however, one-electron oxidation to form Pd^{III} intermediates cannot be ruled out.^{101,106–109}

Interestingly, the formation of the mononuclear Pd^{IV} complex **47** by treatment of the dinuclear Pd^{II} precursor **40** with 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (Togni reagent)¹¹⁰ was proposed to involve the transient formation of a Pd^{III} – Pd^{III} species **48** followed by Pd^{III} – Pd^{III} bond heterolysis, as suggested by a recent combined experimental and computational study (Scheme 5.39).¹¹¹ Thus, such dinuclear Pd^{III} complexes may play a role as intermediates in Pd -catalyzed C–H bond trifluoromethylation reactions using electrophilic trifluoromethylating reagents.^{111–113}

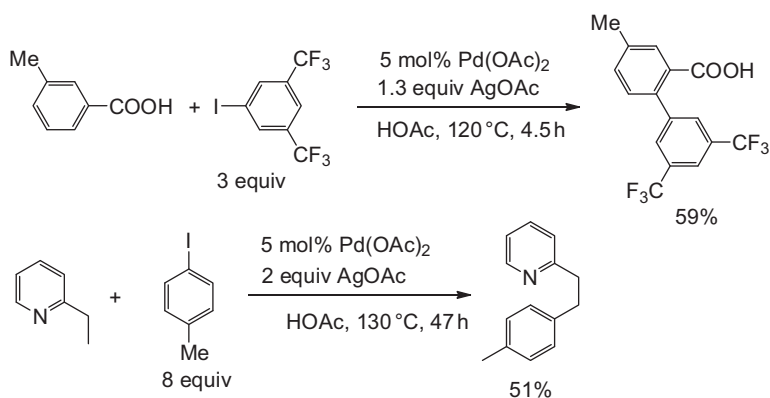
Overall, the generation of dinuclear Pd^{III} – Pd^{III} intermediates by two-electron oxidation of palladacycle Pd^{II} precursors and their facile C–O, C–Cl, and C–Br elimination reactivity suggests that Pd^{III} – Pd^{III} species may be involved in a range of Pd -catalyzed C–H oxidative functionalization reactions and should be considered as a viable alternative to Pd^{II}/Pd^{IV} catalytic cycles. The formation of dinuclear Pd^{III} – Pd^{III} species is generally dictated by the ligand environment and the presence of bridging ligands that bring together the two Pd centers. By contrast, the formation of mononuclear Pd^{IV} complexes by two-electron oxidation of the mononuclear Pd^{II} precursors was also observed in many cases.⁹ Thus, it can be difficult to assign the observed reactivity to either dinuclear Pd^{III} or mononuclear Pd^{IV} species, as both oxidation states can be generated by an overall two-electron oxidation of two or one mononuclear Pd^{II} precursors, respectively.^{9,10,12,104,105,114}



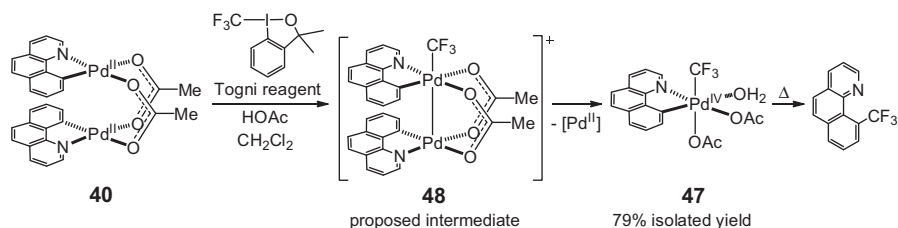
Scheme 5.36 (a) Pd-catalyzed C–H arylation with diaryliodonium salts and (b) proposed mechanism for C–H arylation of 3-methyl-2-phenylpyridine.



Scheme 5.37 Proposed geometries for dinuclear Pd^{III} diacetato-bridged complexes.



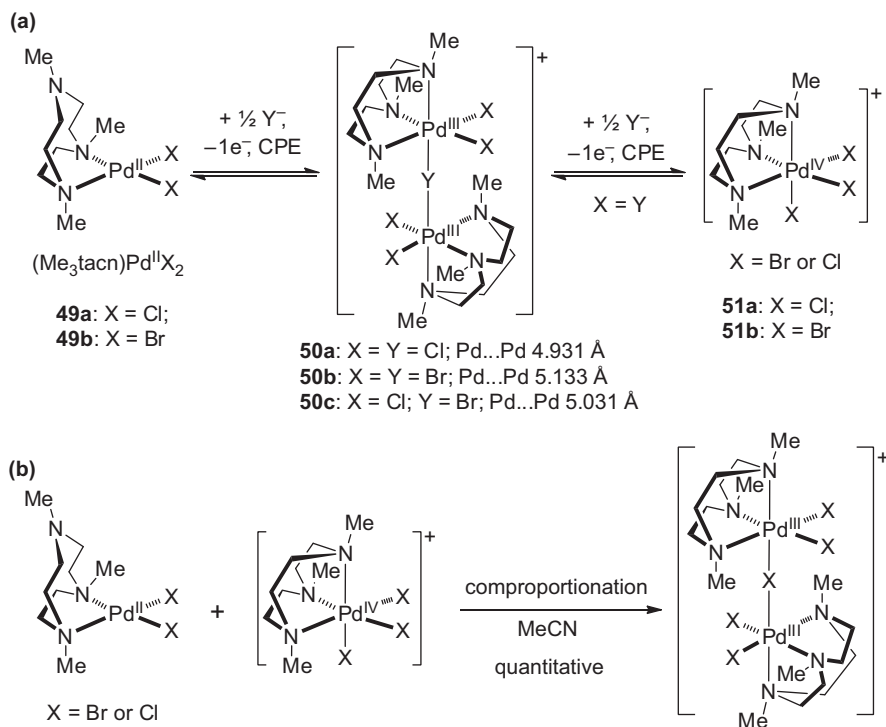
Scheme 5.38 Pd-catalyzed arylation of C–H bonds in presence of Ag⁺ salts.



Scheme 5.39 Proposed formation of a dinuclear high-valent Pd intermediate during the oxidation of a Pd^{II} precursor to a mononuclear Pd^{IV} species.

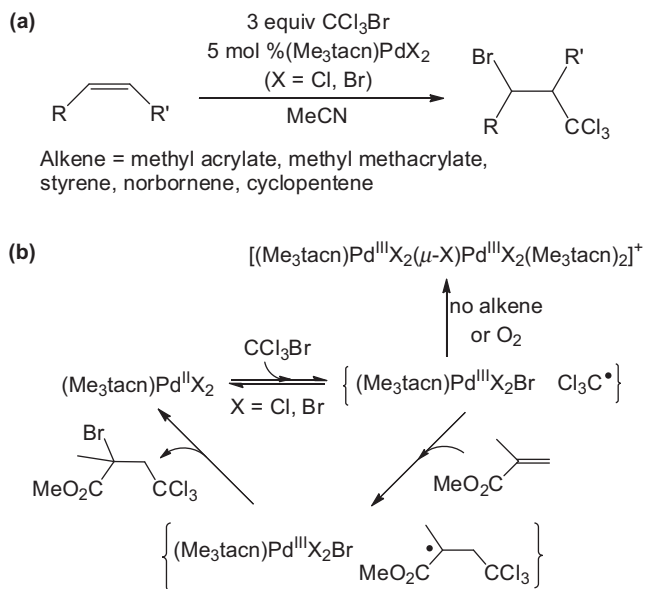
5.3.6 Dinuclear Pd^{III} Complexes Without a Pd–Pd Bond

In 2011, Mirica *et al.* reported a series of dinuclear Pd^{III} complexes **50a–c** that were synthesized by electrochemical oxidation of mononuclear Pd^{II} precursors (Scheme 5.40).⁷¹ These complexes employ the tridentate macrocyclic ligand *N,N',N'*-trimethyl-1,4,7-triazacyclononane, Me₃tacn, and the two Pd^{III} centers



Scheme 5.40 (a) Reversible synthesis of [(Me₃tacn)₂Pd^{III}₂X₄(μ-Y)]⁺ and [(Me₃tacn)Pd^{IV}X₃]⁺ complexes (X, Y = Cl, Br) and (b) comproportionation reactivity.

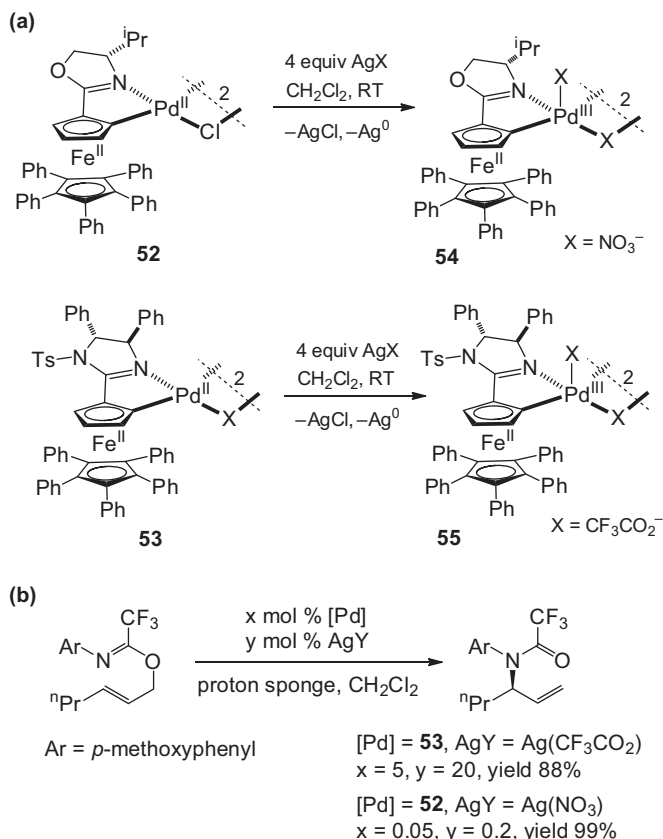
are bridged by a single halide ligand, representing the first examples of dinuclear Pd^{III} species that are not stabilized by a Pd–Pd bond. The two Pd^{III} centers exhibit a distorted octahedral geometry and are strongly antiferromagnetically coupled through the bridging halide ligand. Further electrochemical oxidation of these complexes in the presence of external halide affords the mononuclear Pd^{IV} complexes **51a–b**, which were structurally characterized (Scheme 5.40a). Interestingly, the interconversion between these Pd^{II}/Pd^{III}/Pd^{IV} species is reversible: reduction of the mononuclear Pd^{IV} complex generates a dinuclear Pd^{III} species and eventually the mononuclear Pd^{II} species. Moreover, the Pd^{IV} complexes react rapidly with 1 equiv. of Pd^{II} complex to quantitatively generate the dinuclear Pd^{III} complex (Scheme 5.40b), suggesting that the latter species is more stable than the corresponding mononuclear Pd^{IV} and Pd^{II} complexes under an analogous ligand environment. The facile interconversion of dinuclear Pd^{III} and mononuclear Pd^{IV} species suggests that for a given ligand environment both types of intermediates can be present, with direct implications into the proposed involvement of analogous intermediates in Pd-catalyzed C–H oxidative functionalization reactions (*vide supra*).¹¹¹



Scheme 5.41 (a) Pd-catalyzed Kharasch radical addition of CCl_3Br to alkenes and (b) proposed mechanism.

Interestingly, the Pd^{II} complexes **49a–b** catalyze the Kharasch radical addition of CCl_3Br to alkenes (Scheme 5.41a).⁷¹ The proposed catalytic cycle involves an electron transfer/halogen transfer from CCl_3Br to Pd^{II} to generate a Pd^{III} species and a CCl_3 radical (Scheme 5.41b). Although no mononuclear Pd^{III} species were detected under catalytic conditions, the formation of dinuclear Pd^{III} species was detected by UV-vis at RT in the absence of the alkene substrate. Moreover, a higher yield of the dinuclear Pd^{III} species was obtained in the presence of O_2 , which can act as a radical trap for the CCl_3 radical. As the kinetic analysis revealed a first order dependence of the reaction rate on Pd^{II} , formation of the dinuclear Pd^{III} species could be a means of stabilizing the mononuclear Pd^{III} intermediates involved in the catalytic cycle (Scheme 5.41b).

A recent report showed that the paramagnetic dinuclear Pd^{III} complexes **54** and **55** are active catalysts for asymmetric aza-Claisen rearrangement (Scheme 5.42).¹¹⁵ When the chloride-bridged pentaphenylferrocene oxazoline (**52**) and imidazoline (**53**) palladacycle precursors were treated with 4 equiv. Ag^+ , formation of the dinuclear paramagnetic complexes **54** and **55** was observed (Scheme 5.42a). Characterization of these complexes by XAS, EPR, and Mössbauer spectroscopy suggests that the ligand ferrocene unit remains intact upon oxidation, while two Pd^{II} centers are oxidized to Pd^{III} . The oxidized complexes show an enhanced catalytic activity compared to the Pd^{II} species, presumably¹⁰⁵ due to their higher Lewis acidity.¹¹⁵



Scheme 5.42 (a) Synthesis of dinuclear paramagnetic Pd^{III} complexes and (b) Pd-catalyzed asymmetric aza-Claisen rearrangement.

5.4 Summary and Outlook

This chapter provides an overview of the organometallic chemistry of isolated Pd^{III} complexes and the proposed involvement of Pd^{III} intermediates in various organometallic transformations. The first mononuclear organometallic Pd^{III} complexes were isolated and characterized in 2010 and shown to exhibit C–C bond formation reactivity. Moreover, mononuclear Pd^{III} intermediates have been observed during the dioxygen-induced C–C bond elimination from Pd^{II} precursors. In addition, the involvement of mononuclear Pd^{III} intermediates has been proposed in a wide range of C–C and C–heteroatom bond formation reactions.

The first isolated dinuclear organometallic Pd^{III} complexes have been reported in 2006, and such dinuclear Pd^{III} species were shown to act as catalytically active intermediates in a range of C–H functionalization reactions, suggesting that Pd^{III} species may be more prevalent than previously

anticipated. In addition, dinuclear Pd^{III} complexes that are not stabilized by a Pd–Pd bond and their role in catalytic processes have also been reported. Importantly, the facile interconversion between Pd^{III} and Pd^{IV} complexes has been demonstrated, suggesting that the intermediacy of either Pd^{III} or Pd^{IV} species cannot always be unambiguously confirmed or ruled out. Finally, we envision that in the near future the chemistry of the less-common oxidation states of Pd, such as Pd^{III}, Pd^{III} will lead to novel organometallic reactions that employ odd-electron oxidation states and involve one-electron oxidation or reduction steps.

Acknowledgements

We thank the Department of Chemistry at Washington University, the American Chemical Society Petroleum Research Fund (49914-DNI3), and Department of Energy Catalysis Science Program (DE-FG02-11ER16254) for financial support. L.M.M. is a Sloan Fellow.

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