

Reactions of allylpalladium(II) complexes with free radicals

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Allylpalladium(II) compounds react readily in benzene with free phenyl and trityl radicals, generated from the thermal decomposition of phenylazotriphenylmethane, and with free cyclohexyl radicals, generated from the photolysis of (cyclohexyl)(pyridine)cobaloxime; the reactions appear to involve initial attack of the radicals at palladium, followed by secondary processes which convert the coordinated allyl ligands preferentially to terminal rather than internal alkenes.

Free radicals have been invoked as reactive intermediates in a wide variety of reactions involving organotransition metal compounds, e.g. oxidative addition reactions,^{1a} $S_{\text{M}}2$ induced coupling of organic halides with carbonyl compounds,^{1b} reduction of organic halides by complexes of chromium(II),^{1c} and hydrogenation and hydrometallation of aromatic alkenes^{1d} and conjugated dienes.^{1e} Recent years have also seen increasing interest in free radicals as *reactants* with unsaturated organic ligands, e.g. with coordinated aromatic,^{2a} allylic,^{2b} carbenoid^{2c} and alkyne^{2d} ligands although there is as yet no general understanding of the reactions of free radicals with coordinated ligands. We have therefore undertaken an investigation of reactions of a variety of free radicals with allylic palladium(II) compounds of the types $[(\eta^3\text{-allyl})\text{PdCl}]_2$, $(\eta^3\text{-allyl})\text{PdCl}(\text{PPh}_3)$ and $[(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$, the latter being of interest because the enhanced susceptibility of the allyl groups in these types of compounds to nucleophilic attack has proven very useful in synthetic organic methodology.³

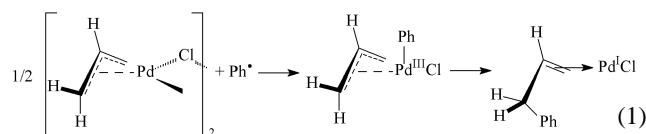
Our initial studies have utilized triphenylmethyl (trityl) and phenyl radicals, derived *via* the thermal decomposition of phenylazotriphenylmethane ($\text{PhN}=\text{NCPH}_3$, PAT),⁴ and cyclohexyl radicals, generated from visible light photolysis of (cyclohexyl)(pyridine)cobaloxime [$c\text{-C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$].⁵ Both procedures generate free radicals in good yields and under relatively mild conditions, and molar ratios of radical source to palladium of 2–3:1 ensured that reactions of the palladium substrates proceeded to completion.

Reaction of $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ with PAT in benzene or benzene- d_6 at 60 °C resulted in the formation of palladium metal, 3-phenylprop-1-ene, 1-phenylprop-1-ene, chlorotriphenylmethane (in high yield by GC) and a small amount of 4,4,4-triphenylbut-1-ene but no chlorobenzene. By monitoring the reaction products as a function of time, it was found that 3-phenylprop-1-ene was formed initially in *ca.* 90% yield (NMR) and that 1-phenylprop-1-ene was formed by subsequent isomerization of the kinetic product. Control experiments showed that this isomerization reaction is catalyzed by palladium metal, and thus the primary reaction involves the formation of 3-phenylprop-1-ene, $\text{PhCH}_2\text{CH}=\text{CH}_2$.

In contrast, the analogous reactions of $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ in the presence of either 1 or 2 equivalents of PPh_3 per palladium were found to produce 4,4,4-triphenylbut-1-ene (>90% yield by NMR) and $[\text{PdPh}(\mu\text{-Cl})(\text{PPh}_3)_2]$ ^{6a} or *trans*- $\text{PdPhCl}(\text{PPh}_3)_2$,^{6b,c} respectively. In addition, the reaction of $[(\eta^3\text{-2-methylallyl})\text{PdCl}]_2$ with PAT in the presence of PPh_3 produced *trans*-2-methyl-4,4,4-triphenylbut-1-ene and $\text{PdPhCl}(\text{PPh}_3)_2$, while the reaction of $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]^+\text{Cl}^-$ produced 4,4,4-triphenylbut-1-ene and *trans*- $\text{PtPhCl}(\text{PPh}_3)_2$.^{6d}

Assuming a similar first step in all of these reactions, the results may be rationalized on the basis of initial attack of

phenyl radical on palladium. In the absence of triphenylphosphine, it seems likely that initial phenyl radical coupling with the palladium to form a palladium(III) intermediate is followed by reductive coupling of the phenyl group with a terminal carbon atom of the allyl ligand to give an intermediate chloropalladium(I) complex [eqn. (1)]. In possibly a concerted



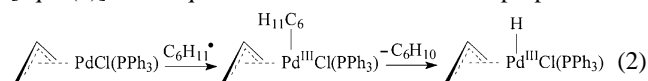
process, the chlorine atom is abstracted from the intermediate by free trityl radical to form chlorotriphenylmethane, palladium metal and free 3-phenylbut-1-ene.

Initial abstraction of a chlorine atom from $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ by trityl radical can presumably be ruled out since no chlorobenzene was formed. Although one might anticipate that the initially formed trityl radical could react with $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ before significant amounts of the intrinsically more reactive phenyl radical are formed, in fact the relative rates of formation of the two radicals are very similar^{4d} and pre-empting of any reactive site by the trityl radical seems unlikely. On the other hand, with analogous triphenylphosphine-containing phenylpalladium(III) intermediates such as $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}^{\text{III}}(\text{Ph})\text{Cl}(\text{PPh}_3)]$ or $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}^{\text{III}}(\text{Ph})(\text{PPh}_3)_2]^+$, steric hindrance by the bulky phosphine ligands may prevent attack on the coordinated chlorine atoms by the bulky trityl radical. Instead, the latter apparently couples in these cases with the sterically less congested allyl ligand to form 4,4,4-triphenylbut-1-ene, again possibly *via* a concerted process but not, presumably, *via* initial trityl radical attack as there is no obvious reason why at least *some* phenyl radical involvement to give 3-phenylprop-1-ene would not occur. Interestingly, in a control experiment, it was found that trityl radical, added as the corresponding dimer with which it is in equilibrium,⁷ does react with $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ in the presence of PPh_3 , the trityl and allyl groups combining to form exclusively 4,4,4-triphenylbut-1-ene. On the other hand, the formation of 4,4,4-triphenylbut-1-ene apparently does not involve trityl coupling with free allyl radicals as no hexa-1,5-diene, the product of allyl free radical coupling,⁸ was formed.

In contrast to the above, photolysis of $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$ with visible light in the presence of $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ (PPh_3 :Pd ratios 1:1, 2:1) in benzene or benzene- d_6 at 25 °C did not give 3-cyclohexylprop-1-ene and/or cyclohexyl-palladium complexes, but rather propene, cyclohexene and palladium(0) species. Similar reactions of $[(\eta^3\text{-1-methylallyl})\text{PdCl}]_2$, $[(\eta^3\text{-2-methylallyl})\text{PdCl}]_2$ and $[(\eta^3\text{-2-phenylallyl})\text{PdCl}]_2$ (PPh_3 :Pd ratios 1:1) resulted in the exclusive formation of but-1-ene, isobutene and 2-phenylprop-1-ene respectively, while reaction of $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$ (PPh_3 :Pd ratio 1:1) resulted in the formation of a mixture of 3-phenylprop-1-ene and 1-phenylprop-1-ene at 25 °C but only 3-phenylprop-1-ene at 5 °C if the PPh_3 :Pd ratio were 2:1. The reaction of $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ with $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$ gave propene and palladium metal while reaction of $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$ gave 1-phenylprop-1-ene and palladium metal; as above, isomerization of a terminal alkene kinetic product to internal alkene may be catalyzed by palladium metal. Control

experiments showed that the allyl–palladium compounds are stable under the above conditions in the absence of $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$.

Assuming a mechanism analogous to the above and considering the nature of the products, these reactions probably involve initial attack of the cyclohexyl radical at the metal to form a cyclohexyl–Pd(III) species, followed by β -hydrogen elimination of cyclohexene to form a hydrido–allylpalladium(III) complex [eqn. (2)]. Subsequent reductive elimination of propene could



result in the palladium(I) species $\text{PdCl}(\text{PPh}_3)$, which could undergo a second attack by a cyclohexyl radical to form the palladium(II) cyclohexyl compound $\text{PdCl}(\text{C}_6\text{H}_{11})(\text{PPh}_3)$, which could also undergo β -hydrogen elimination of cyclohexene to give the hydride $\text{PdHCl}(\text{PPh}_3)$.

Although cyclohexene is anticipated as a byproduct in these reactions, it is expected to be formed in any case as a product of the photolysis of $c\text{-C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$ ⁵ and we therefore cannot take its formation as evidence for the postulated mechanism. While neither the putative hydride $\text{PdHCl}(\text{PPh}_3)$ nor its dimer appear to have been reported, the ¹H NMR spectrum of a reaction mixture in benzene-*d*₆ exhibited a resonance at δ –13, indicative of a palladium hydride. This *same* resonance is also observed in reactions involving $[(\eta^3\text{-1-methylallyl})\text{PdCl}]_2$, $[(\eta^3\text{-2-methylallyl})\text{PdCl}]_2$, $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$ and $[(\eta^3\text{-2-phenylallyl})\text{PdCl}]_2$, consistent with the general mechanism proposed. Also consistent is an observation that the reaction of $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$ with $\text{C}_6\text{H}_{11}\text{Co}(\text{DMG})_2(\text{py})$ gives comparable amounts of propene and *trans*- $\text{PtHCl}(\text{PPh}_3)_2$, identified by comparison of its hydride resonance (δ –15.2) with that of an authentic sample,⁹ in addition to cyclohexene.

Seemingly anomalous, however, is the exclusive formation of but-1-ene in the reaction of $[(\eta^3\text{-1-methylallyl})\text{PdCl}]_2$ and of 3-phenylprop-1-ene in the reaction of $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$. While these products are consistent with the reductive elimination step implied above, reductive elimination of alkenes from allylpalladium(II) hydrido complexes normally results in the formation of the thermodynamically preferred internal alkenes.^{3b} Thus the fact that the reactions discussed here give solely terminal alkenes is perhaps evidence that the reactions do indeed involve allylpalladium(III) hydrido species, although it is not readily obvious why formation of the terminal alkenes should become kinetically preferred. A better understanding of these processes must await further labelling and stereochemical studies which are underway.

Although the mechanisms are as yet uncertain, the reactions lead in all cases to preferential conversion of the allylic ligands to terminal alkenes. Since compounds of the type $[(\eta^3\text{-1-RC}_3\text{H}_4)\text{PdCl}]_2$ (R = alkyl, aryl) are readily prepared from,

e.g. alkenes $\text{RCH}=\text{CHCH}_3$ ^{3a} and allylic acetates $\text{RCH}=\text{CHCH}_2\text{OAc}$,^{3a} the chemistry involving hydrogen transfer from the cyclohexyl radical would seem in effect to provide a route for both the isomerization of the alkene or the hydrogenolysis of the allylic acetate, *via* η^3 -allylpalladium compounds, to terminal alkenes $\text{RCH}_2\text{CH}=\text{CH}_2$. Both types of reactions have potential utility, as we note that hydrogenolysis of allylpalladium complexes by hydride sources normally results in the formation of internal alkenes unless the source is formate ion.¹⁰

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