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Reactions of free radicals with η^3-allylpalladium(II) complexes: phenyl and trityl radicals

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The compounds (η^3-allyl)PdCl(PPh_3) and [(η^3-allyl)Pd(PPh_3)$_2$]Cl react with phenyl and trityl radicals generated from the thermal decomposition of phenylazotriphenylmethane (PhN=NCPh$_3$, PAT) in benzene at 60 °C. The products are the palladium phenyl compounds, [PdPhCl(PPh_3)]$_2$ and *trans*-PdPhCl(PPh_3)$_2$, respectively, and 4,4,4-triphenyl-1-butene, the latter being the result of coupling of the trityl radical with the allyl ligands. In contrast, [(η^3-allyl)PdCl]$_2$ reacts with phenyl and trityl radicals under the same conditions to form palladium metal, trityl chloride and 3-phenylpropene, which is subsequently catalytically isomerized to 1-phenylpropene. These disparate results are interpreted in all cases in terms of initial attack by phenyl radicals on the palladium(II) to give phenyl–palladium(III) intermediates, and it is the secondary reactions, influenced by the presence or absence of coordinated PPh_3 ligands, which provide variety in the products. The reaction of [(4-methoxy-1,3-η^3-cyclohexenyl)PdCl]$_2$ gives a mixture of *trans*-3-methoxy-6-phenylcyclohexene and *trans*-4-methoxy-3-phenylcyclohexene, consistent with initial formation of a phenyl–palladium(III) intermediate followed by phenyl migration to the η^3-cyclohexenyl ligand (reductive elimination).

Introduction

Free radical additions to carbon-carbon double and triple bonds provide a range of well developed and synthetically useful organic transformations, and the subject has been reviewed extensively.[1] Free radicals have also been invoked as reactive intermediates in a wide variety of reactions involving transition metal compounds, *e.g.* oxidative addition reactions,[2] SmI_2 induced coupling of organic halides with carbonyl compounds,[3] reduction of organic halides by complexes of chromium(II),[4] and hydrogenation and hydrometallation of aromatic alkenes[5] and conjugated dienes.[6] Complementing this activity, recent years have also seen increasing interest in addition reactions of free radicals on complexes of a variety of unsaturated, coordinated organic compounds such as arene,[7] allylic,[8] carbenoid[9] and alkenyne[10] ligands. Examples of such radical addition reactions are shown in Fig. 1, where other steps in what are all complex processes are omitted. The field of free radical additions to organometallic compounds has been reviewed,[11] and it is clear that there is as yet really no general knowledge or understanding of the reactions of free radicals with coordinated ligands.

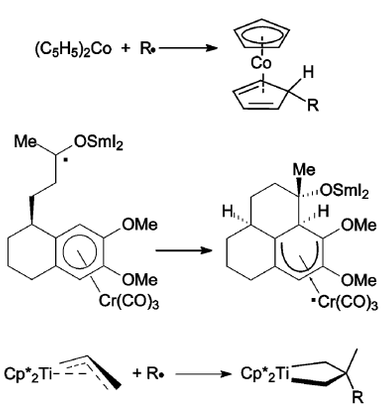

Fig. 1 Addition reactions of free radicals with coordinated unsaturated ligands.

η^3-Allyllic palladium(II) complexes have been employed extensively in synthetic organic chemistry. This is in large part because of their ability to participate in a variety of synthetically useful reactions,[12] and neutral compounds of the types [(η^3-allyl)PdCl]$_2$ (**A**) and (η^3-allyl)PdCl(PPh_3) (**B**) and cationic complexes of the type [(η^3-allyl)Pd(PPh_3)$_2$]$^+$ (**C**) (all shown in Fig. 2) have been studied intensively to date. While the two types of neutral compounds **A** and **B** exhibit limited activity towards nucleophiles, cationic complexes of type **C** react readily as in eqn. (1) (Nu^- = various C-, O- and N-based nucleophiles).

$$[(\eta^3\text{-allyl})Pd(PPh_3)_2]^+ + Nu^- \longrightarrow \text{allyl–Nu} + \text{“}Pd(PPh_3)_2\text{”} \quad (1)$$

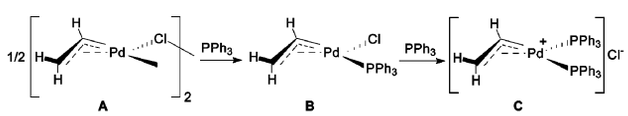

Fig. 2 Compounds present on the addition of triphenylphosphine to [(η^3-allyl)PdCl]$_2$ (**A**).

Nucleophilic attack on complexes of type **C** has been thoroughly investigated and results in a range of extremely useful in synthetic methodologies.[12] Although there is a plethora of nucleophiles that can be added to allyl–palladium complexes as in eqn. (1),[12] in fact all such reactions proceed *via* one of two mechanisms. Of relevance here, there are those which involve direct addition of the nucleophile to the η^3-allyl ligand (exo attack, Fig. 3(a)) and those which involve initial attack at the palladium followed by migration of the coordinated nucleophile to the η^3-allyl ligand (endo attack, Fig. 3(b)).[12]

In view of the wide range of chemistry exhibited in reactions of free radicals with unsaturated molecules, both free[1] and coordinated,[11] coupled with the above mentioned, intense interest in the synthetic utilization of allyl–palladium complexes, we have begun an investigation of reactions of organic free radicals with neutral and cationic allylic palladium compounds of types **A**, **B** and **C**. It was anticipated that interesting and useful coupling/addition reactions of free radicals with allylic ligands would be observed, and that products not available by conventional palladium–allyl chemistry might be formed.

We wished first to ascertain if free radicals would react at all with the unsaturated allylic ligands present in these compounds and, if so, what would be the products and the effects of the various ligand environments and the positive charge. We have begun our studies utilizing phenylazotriphenylmethane (PhN=

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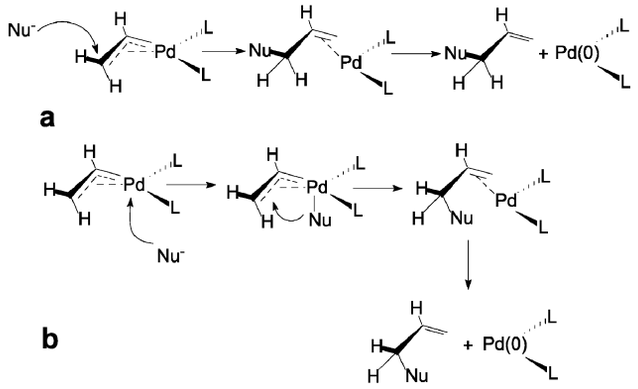


Fig. 3 (a) Exo nucleophilic attack on an allyl group; (b) endo nucleophilic attack on an allyl group (L = PPh_3).

$NCPh_3$: henceforth PAT) as a very convenient source of phenyl *and* triphenylmethyl (henceforth trityl) radicals.[13] PAT decomposes in inert solvents on heating by releasing phenyl and trityl radicals in addition to molecular nitrogen (eqn. (2)).[13]

$$PhN{=}NCPh_3 \longrightarrow Ph^{\bullet} + Ph_3C^{\bullet} + N_2 \qquad (2)$$

This reaction is known to be a two-step process which involves initial homolytic dissociation of the weaker N–CPh_3 bond to produce a trityl radical and a phenyldiazenyl radical, $PhN{=}N^{\bullet}$. The carbon–nitrogen bond of the latter then undergoes homolysis to result in a phenyl radical and molecular nitrogen. The phenyl radical is highly reactive but the trityl radical is persistent and remains in solution in equilibrium with its head-to-tail dimer, 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.[14] Therefore, while it may appear that any reactions involving PAT would involve predominantly the initially formed trityl radical, the fact that the latter exists in solution in equilibrium with its dimer means that radical reactions derived from PAT may involve reactions with either the phenyl or the trityl radical or both.

We now report in detail on the reactions of allylic palladium compounds of types **A**, **B** and **C** with phenyl and trityl radicals. We have earlier communicated some of our initial finding on this and related chemistry;[15] a subsequent paper will discuss reactions of these same types of allyl–palladium compounds with the cyclohexyl radical.

Experimental

Experiments were conducted under an inert atmosphere of oxygen-free N_2 or Ar, further purified by passing through a column of BASF catalyst heated to 140 °C and a column of 5A molecular sieves. Manipulations of air-sensitive materials employed standard Schlenk-line techniques, a Vacuum Atmosphere glovebox and an Mbraun Labmaster glovebox. Solvents were dried and distilled over sodium metal except dichloromethane, which was dried over calcium hydride, and methanol, which was dried over magnesium methoxide; all were thoroughly deoxygenated prior to use by freeze–thaw–pump cycles or by saturation with N_2 or Ar.

NMR spectra were acquired on Bruker ACF 200, Avance 300, AM 400 or Avance 500 NMR spectrometers. The residual proton and the carbon resonances of deuterated solvents served as internal references for ^1H and ^{13}C resonances, respectively, while ^{31}P resonances were referenced externally to 85% H_3PO_4. Mass spectra were obtained on a Quatro Fisons Pro Quadropole mass spectrometer in EI^+ mode. GC-MS experiments were carried out on a Fisons GC 8000 coupled to a Fisons MD 800 spectrometer operating in EI^+ mode or a Varian GC-MS (CP-3800 GC and Saturn 2000 MS).

Except as noted below, all chemicals were purchased from Aldrich and were used without further purification. Deuterated solvents were purchased from MSD isotopes and Cambridge Isotopes Limited, while $PdCl_2$ was obtained on loan from Johnsonn Mathey. The following complexes were synthesized *via* standard literature preparations: $Pd(PPh_3)_4$,[16] $[PdPh(PPh_3)(\mu\text{-}OAc)]_2$,[17] $[(\eta^3\text{-allyl})PdCl]_2$,[18] [(4-methoxy-1,3-$\eta^3$-cyclohexenyl)$PdCl]_2$,[19] $(\eta^3\text{-allyl})PdCl(PPh_3)$,[18d] $[(\eta^3\text{-allyl})Pt(PPh_3)_2]Cl$,[20] phenylazotriphenylmethane (PAT)[13] and 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (trityl dimer).[14] PPh_3 was recrystallized from methanol.

Reactions of $(\eta^3\text{-allyl})PdCl(PPh_3)$ and $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ with PAT

In a typical procedure, a solution of 0.200 g $[(\eta^3\text{-allyl})PdCl]_2$ (5.50×10^{-4} mol), 0.575 g PPh_3 (2.2×10^{-3} mol), and 0.770 g PAT (2.2×10^{-3} mol) (ratio Pd : PPh_3 : PAT = 1 : 2 : 2) in 50 mL benzene was stirred at 60 °C for 1.5 h, during which time the solution changed from yellow to orange and a small amount of a black solid formed. The solvent was removed under reduced pressure to leave a gummy orange residue which was extracted with pentane until the extracts were colourless (5 × 10 mL). There resulted a pale yellow solution and a yellow–white residue. The solid material was collected and recrystallized from dichloromethane–pentane to give 0.261 g *trans*-$PdPhCl(PPh_3)_2$ (32% yield). ^1H NMR ($CDCl_3$): δ 6.23 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *m*-H of Pd–Ph), 6.36 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-H of Pd–Ph), 6.62 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *o*-H of Pd–Ph), 7.2–7.6 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 121.7 (s), 127.6 (s), 127.84 (vt), 129.7(s), 131.2 (t), 134.6 (vt), 136.4 (t), 154.0 (t). ^{31}P NMR ($CDCl_3$): δ 24.2 (s). The ^1H NMR data are identical to those of a sample of the compound synthesized as in the literature.[21]

The solvent was removed from the pentane extract to give a yellow, oily residue. From this 0.10 g 4,4,4-triphenyl-1-butene (65% yield) was separated from byproducts arising from the decomposition of PAT by chromatography on an alumina column using a 2 : 1 pentane–benzene solution as eluent. ^1H NMR (C_6D_6): δ 5.72 (ddt, $-CH_2CH{=}CH_2$, $^3J_{H-H}$ = 6.4, 19.6, 8.8 Hz), 5.04 (dq, $-CH_2CH{=}CH(anti)$, $^3J_{H-H}$ = 19.6, 1.4, 1.4 Hz), 4.97(dq, $-CH_2CH{=}CH(syn)$, $^3J_{H-H}$ = 8.8, 1.4, 1.4 Hz), 3.32 (dt, CH_2 $^3J_{H-H}$ = 6.4, 1.4 Hz), 7.0–7.4 (m, 30H, Ph). The ^1H NMR data are identical to those of a sample of the compound synthesized as in the literature.[22]

In a complementary experiment, an NMR-scale reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with two equivalents each of PAT and PPh_3 per palladium was run in C_6D_6 at 60 °C. Monitoring by ^1H and ^{31}P NMR spectroscopy showed that *trans*-$PdPhCl(PPh_3)_2$ and 4,4,4-triphenyl-1-butene were formed essentially quantitatively and that the reaction was complete within 1.5 h.

In a reaction in which $[(\eta^3\text{-allyl})PdCl]_2$ was treated with two equivalents of PAT and *one* equivalent of PPh_3 per Pd, 4,4,4-triphenyl-1-butene and $[PdPh(PPh_3)(\mu\text{-}Cl)]_2$ (53% yield) were obtained. The latter is a white compound which was identified by preparing it as in the literature[23] as well as by conversion to *trans*-$PdPhCl(PPh_3)_2$ by reaction with PPh_3 in benzene. ^1H NMR of $[PdPh(PPh_3)(\mu\text{-}Cl)]_2$ ($CDCl_3$): δ 7.51–7.17 (m, 15H, H (Ph)), 6.9 (br s, 2H), 6.6 (br s, 3H). ^{31}P NMR ($CDCl_3$): δ 31.9 (br s).[23]

Complementing this, a solution of 0.15 g $(\eta^3\text{-allyl})PdCl(PPh_3)$ (3.37×10^{-4} mol) and 0.236 g PAT (6.78×10^{-4} mol) in 0.75 mL benzene was heated at 60 °C for 1.5 h, and the solvent was removed *in vacuo* to give an orange residue. The residue was extracted with pentanes, giving an orange solution and leaving a pale yellow solid. The solvent was removed from the extract and the ^1H NMR spectrum showed the only allyl product was 4,4,4-triphenyl-1-butene. The pale yellow solid left after the extraction was collected and washed thoroughly with benzene. It was identified as $[PdPh(PPh_3)(\mu\text{-}Cl)]_2$ (40% yield) by comparison to an authentic sample and by conversion to *trans*-$PdPhCl(PPh_3)_2$.

Reactions of $[(\eta^3\text{-allyl})PdCl]_2$ with PAT

In an NMR-scale reaction, $[(\eta^3\text{-allyl})PdCl]_2$ was treated at 60 °C in C_6D_6 in an NMR tube with one equivalent of PAT in the absence of PPh_3. A small amount of a black precipitate appeared within 5 min and a metallic mirror had formed on the side of the NMR tube within 2 h. The ^{1}H NMR spectrum of the reaction mixture was broad as a result, and the sample was filtered to give a clear, orange solution. The ^{1}H NMR spectrum of the solution exhibited the resonances of 1-phenylpropene (~80% of the total allyl products), 3-phenylpropene (~10% of the total allyl products), and 4,4,4-triphenyl-1-butene (~10% of the total allyl products), all identified by comparisons with ^{1}H NMR spectra of authentic samples. The relative proportions of these products were confirmed by GC-MS, which also demonstrated the presence of trityl chloride as a major product. The NMR reaction was repeated, and in this case 3-phenylpropene was added after the reaction was complete. After further heating at 60 °C for 2 h, a ^{1}H NMR spectrum showed that the 3-phenylpropene had been converted to 1-phenylpropene.

In a complementary experiment, a solution of 0.01 g $[(\eta^3\text{-allyl})PdCl]_2$ (2.7×10^{-5} mol), 0.053 g PAT (1.5×10^{-4} mol) and 22.5 μL 3-chloropropene (2.75×10^{-4} mol) in 0.75 mL C_6D_6 was heated at 60 °C for 2 h, by which time no metallic palladium had formed but the solution had turned orange and an orange product had begun to precipitate. The sample was filtered and a ^{1}H NMR spectrum was found to exhibit the resonances of 1-phenylpropene (~10% of allyl products), 3-phenylpropene (~80% of allyl products) and 4,4,4-triphenyl-1-butene (~10% of allyl products) as the major allyl products. The sample was analyzed using GC-MS, which showed that 3-phenylpropene and trityl chloride were the major products. The orange product was identified as $[(\eta^3\text{-trityl})PdCl]_2$ *via* conversion to the known $(\eta^3\text{-trityl})Pd(acac)$.[24] A repeat of the reaction in the presence of a 25 : 1 molar excess of 3-chloropropene resulted in the formation predominantly 3-phenylpropene in addition to $[(\eta^3\text{-trityl})PdCl]_2$.[24]

Reactions of [(4-methoxy-1,3-η^3-cyclohexenyl)$PdCl_2$] with PAT

A yellow solution of 0.02 g [(4-methoxy-1,3-η^3-cyclohexenyl)-$PdCl]_2$[19] (4.01×10^{-5} mol) and 0.03 g PAT (8.62×10^{-5} mol) in 0.75 mL C_6D_6 was heated at 60 °C for 10 min, forming a black/green slurry. The slurry was filtered through alumina and the filtrate was shown by ^{1}H NMR spectroscopy to contain *trans*-3-methoxy-6-phenylcyclohexene[25a] and *trans*-4-methoxy-3-phenylcyclohexene[25a] in a ratio of ~5 : 1. ^{1}H NMR of *trans*-3-methoxy-6-phenylcyclohexene ($CDCl_3$): δ 7.2–7.8 (m, 5H, H (Ph)), 5.8–5.95 (m, 2H, CH), 3.91 (br m, 1H, C*H*–OMe), 3.43 (m, 1H, C*H*–Ph), 3.41 (s, 3H, OCH_3), 2.10 (m, 2H, CH_2), 1.6 (m, 2H, CH_2). ^{1}H NMR of *trans*-4-methoxy-3-phenylcyclohexene ($CDCl_3$): δ 7.2–7.8 (m, 5H, H (Ph)), 5.90–5.55 (m, 2H, CH), 3.43 (m, 1H, C*H*–Ph), 3.35 (br m, 1H, C*H*–OMe), 3.28 (s, 3H, OCH_3), 1.9 (m, 4H, CH_2).

These compounds were identified by comparison to a literature reference[25a] and by their synthesis *via* the reaction of a solution of 0.065 g [(4-methoxy-1,3-η^3-cyclohexenyl)$PdCl]_2$ (1.30×10^{-4} mol) and 0.108 g PPh_3 (4.12×10^{-4} mol) in 2.5 mL THF at 0 °C with 0.15 mL of 3 M PhMgBr in ether (4.5×10^{-4} mol). The resulting greenish slurry was stirred for 30 min at 0 °C and then filtered to give a yellow solution. The solvent was removed and the resulting yellow powder was shown by ^{1}H NMR spectroscopy to contain the above-mentioned *trans*-3-methoxy-6-phenylcyclohexene and *trans*-4-methoxy-3-phenylcyclohexene.

Reaction of $[(\eta^3\text{-allyl})Pt(PPh_3)_2]Cl$ with PAT

A mixture of 0.152 g $[(\eta^3\text{-allyl})Pt(PPh_3)_2]Cl$ (1.88×10^{-4} mol) and 0.135 g PAT (3.76×10^{-4} mol) in 50 mL benzene was heated at 60 °C for 2 h to give an orange–green solution. The solvent was removed *in vacuo* and the resulting whitish yellow residue was extracted with pentane to give 4,4,4-triphenyl-1-butene, identified by ^{1}H NMR spectroscopy. The less soluble product was shown by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy ($CDCl_3$) to be the known compound *trans*-$PtPhCl(PPh_3)_2$ (0.15 g, 94% yield).[26] A complementary NMR-scale reaction in C_6D_6 at 60 °C showed that *trans*-$PtPhCl(PPh_3)_2$ and 4,4,4-triphenyl-1-butene were formed quantitatively.

Reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with trityl dimer

A solution of 0.106 g $[(\eta^3\text{-allyl})PdCl]_2$ (2.90×10^{-4} mol), 0.289 g PPh_3 (1.10×10^{-3} mol) and 1.40 g trityl dimer (2.90×10^{-3} mol) in 50 mL C_6H_6 was refluxed for 1.5 h. The solvent was removed and a ^{1}H NMR spectrum showed that 4,4,4-triphenyl-1-butene had formed. Some unreacted $(\eta^3\text{-allyl})Pd(PPh_3)_2Cl$ was also present, but no other palladium-containing product could be identified.

Results and discussion

While nucleophilic addition reactions to allyl–palladium complexes of types **A**, **B** and **C** have been thoroughly investigated,[12] addition of organic radicals to these complexes has not been explored previously. In this study, we have therefore investigated the reactions of these same types of allyl–palladium complexes **A**, **B** and **C** with phenyl and trityl radicals, formed *via* the thermal decomposition of PAT. This was done with two major objectives in mind, to gain an understanding of the nature of radical interactions with allyl–palladium species, and, if possible, to develop synthetically useful organic reactions. The reactions studied here were carried out by reacting allylic compounds of type **A** with phenyl and trityl radicals in the presence of zero, one and two molar equivalents of PPh_3 per palladium, *i.e.* with compounds of types **A**, **B** and **C**, respectively, since we find that PPh_3 coordination occurs much more rapidly than does PAT decomposition. As we shall show below, the nature of the products varies as the PPh_3 : palladium ratio changes, demonstrating that different palladium substrates are involved. Furthermore, coupling of the allylic fragments with the radicals is shown to involve endo attack in one case, at least.

Reactions in the presence of one and two equivalents of PPh_3 per palladium

We shall address reactions of $(\eta^3\text{-allyl})PdCl(PPh_3)$ (**B**) and $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ (**C**) first, thus making possible a comparison with addition reactions of nucleophiles. The reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with a two-fold excess of PAT in the presence of two equivalents of PPh_3 per palladium in C_6H_6 at 60 °C resulted in the formation of the known compound *trans*-$PdPhCl(PPh_3)_2$.[21] Examination of the organic products by ^{1}H NMR spectroscopy suggested the presence of a single major allyl containing product in addition to several byproducts resulting from decomposition of PAT. The thermal decomposition of PAT in benzene has been shown to produce biphenyl, triphenylmethane and 1-phenyl-4-triphenylmethyl-2–5-cylcohexadiene.[13] The allylic product was separated from these and identified by ^{1}H NMR spectroscopy as 4,4,4-triphenyl-1-butene.[22]

The same reaction was also carried out on an NMR-scale and monitored by ^{1}H NMR spectroscopy. The first ^{1}H NMR spectrum, run within 5 min of mixing of reagents, showed the complete formation of $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$,[18] and thus phosphine coordination occurs much more rapidly than does the decomposition of PAT. The resonances of *trans*-$PdPhCl(PPh_3)_2$ and $CH_2{=}CHCH_2CPh_3$ were evident within 30 min and these compounds had formed essentially quantitatively within 1.5 h. Thus the overall the reaction is represented by eqn. (3).

$$[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl + PAT \longrightarrow \textit{trans}\text{-}PdClPh(PPh_3)_2 + CH_2{=}CHCH_2CPh_3 + N_2 \quad (3)$$

There are two reasonable mechanistic routes to the observed products. These involve either initial addition of the trityl radical to the allyl group to directly form 4,4,4-triphenyl-1-butene (Fig. 4(a)), or initial attack of the phenyl radical on the palladium (Fig. 4(b)). The initial intermediate in Fig. 4(a) is a palladium(I) alkene complex, from which the π bonded ligand would presumably dissociate to give the free 4,4,4-triphenyl-1-butene which is observed. The resulting palladium(I) species $[Pd^{I}(PPh_3)_2]^+$ would then couple with a phenyl radical to form the coordinatively unsaturated $[Pd^{II}(PPh_3)_2Ph]^+$, which would readily coordinate the chloride ion to form the observed product, *trans*-$PdPhCl(PPh_3)_2$.

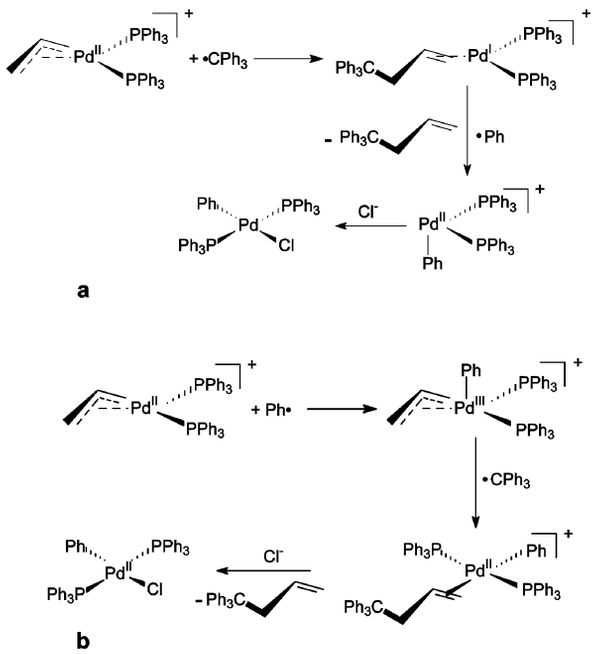


Fig. 4 Possible mechanism for the reaction of $[(\eta^3\text{-allyl})Pd(PPh_3)_2]^+Cl^-$ with trityl and phenyl radicals (a) assuming initial reaction of the trityl radical (exo), (b) assuming initial reaction of the phenyl radical (endo).

The alternative mechanism, shown in Fig. 4(b), involves initial reaction of the phenyl radical with the palladium. This seems more plausible since, if the initial reaction does indeed involve direct addition of the trityl radical to the allyl group, then one would also expect at least some attack of phenyl radical to give 3-phenylpropene, which is not observed. Reaction of the phenyl radical with the palladium centre would result in the formation of an allylpalladium(III) intermediate which apparently couples with trityl radical to form 4,4,4-triphenyl-1-butene. Following dissociation of the latter, the palladium product would be the same intermediate $[Pd^{II}(PPh_3)_2Ph]^+$ proposed in Fig. 4(a). Again coordination of chloride ion would lead to the formation of the observed palladium product.

To complement this study, preformed $[(\eta^3\text{-allyl})Pt(PPh_3)_2]Cl$[20] was also reacted with trityl and phenyl radicals *via* the decomposition of PAT. This reaction was expected to proceed similarly to the reaction of the analogous palladium complex, and indeed it did although $[(\eta^3\text{-allyl})Pt(PPh_3)_2]Cl$ is only minimally soluble in benzene and the reaction began as a slurry. The solution resulting at the end of the reaction was worked up similarly to the analogous palladium reaction, and the products were found to be 4,4,4-triphenyl-1-butene and *trans*-$PtPhCl(PPh_3)_2$.[26] Thus the palladium and platinum allyl complexes behave similarly.

In order to compare the reactions of compounds of types **B** and **C** of Fig. 2, we also carried out a series of experiments in which $[(\eta^3\text{-allyl})PdCl]_2$ was reacted with PAT as above but in the presence of only one molar equivalent of PPh_3 per palladium. In these cases, the only allyl product was 4,4,4-triphenyl-1-butene while the palladium product was $[PdPh(PPh_3)(\mu\text{-}Cl)]_2$, identified spectroscopically, by its synthesis *via* a known route,[23] and by its reaction with PPh_3 to give *trans*-$PdPhCl(PPh_3)_2$. The same products were also obtained using preformed $(\eta^3\text{-allyl})PdCl(PPh_3)$, and thus the overall reaction is represented by eqn. (4).

$$(\eta^3\text{-allyl})PdCl(PPh_3) + PAT \longrightarrow \tfrac{1}{2}[PdPh(PPh_3)(\mu\text{-}Cl)]_2 + CH_2{=}CHCH_2CPh_3 + N_2 \quad (4)$$

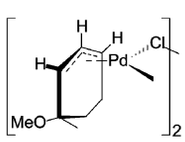
These reactions proceed as readily as do the reactions in the presence of two equivalents of PPh_3 per palladium, demonstrating that the cationic bisphosphine complex is not required and thus that the radical addition/coupling processes are not subject to the same controls as are nucleophilic addition reactions. In fact the great similarity in the allyl-radical coupling products from the radical reactions with $(\eta^3\text{-allyl})PdCl(PPh_3)$ and $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ suggests essentially identical mechanisms for the two types of allylic compounds.

Reactions in the absence of PPh_3

Quite different results were obtained, however, when $[(\eta^3\text{-allyl})PdCl]_2$ was reacted with phenyl and trityl radicals *in the absence* of PPh_3. The most immediately apparent difference was the rapid appearance of palladium metal although, after two hours, GC-MS and ^1H NMR monitoring in C_6D_6 showed that 1-phenylpropene was the major allylic product (~80%), in addition to 3-phenylpropene (~10%) and 4,4,4-triphenyl-1-butene (~10%). GC-MS also showed that trityl chloride was also formed as a major product during the reactions. The reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with PAT may broadly be represented by eqn. (5).

$$[(\eta^3\text{-allyl})PdCl]_2 + PAT \longrightarrow PhCH{=}CHCH_3 + PhCH_2CH{=}CH_2 + 4,4,4\text{-triphenyl-1-butene} + N_2 + Pd(0) + Ph_3CCl \quad (5)$$

It seemed possible in this case that direct attack by the highly reactive phenyl radical was occurring on the allyl ligand. Therefore, in order to ascertain whether the coupling between the phenyl radical and the allyl ligand proceeds *via* net exo or endo attack, as defined in Fig. 3, we utilized $[(4\text{-methoxy-}1,3\text{-}\eta^3\text{-cyclohexenyl})PdCl]_2$ (**D**).[19] Attack on the allylic ligand of this compound by a phenyl radical, either directly (exo) or indirectly *via* an initially formed phenyl-palladium intermediate (endo), is expected to occur at C-1 and C-3 and to give 3-methoxy-6-phenylcyclohexene and 4-methoxy-3-phenylcyclohexene.



D

These two possibilities are illustrated in Figs. 5(a) and (b), where it is seen that endo attack would give the *trans* isomeric products while exo attack would give the *cis* isomers. The compounds *trans*-3-methoxy-6-phenylcyclohexene and *trans*-4-methoxy-3-phenylcyclohexene are known and their ^1H NMR spectra have been reported.[25a] They have been prepared *via* the reaction of compound **D**, activated with chelating, neutral diimine ligands,[25a] with a source of phenyl carbanion in a reaction known to give endo products *via* initial attack at the metal followed by carbanion migration to the allylic ligand.[25a] To obtain the two *trans* isomers for purposes of comparison, we therefore reacted $[(4\text{-methoxy-}1,3\text{-}\eta^3\text{-cyclohexenyl})Pd(PPh_3)_2]^+$ with phenylmagnesium bromide, obtaining products exhibiting ^1H NMR spectra consistent with literature data for the two *trans* isomers.

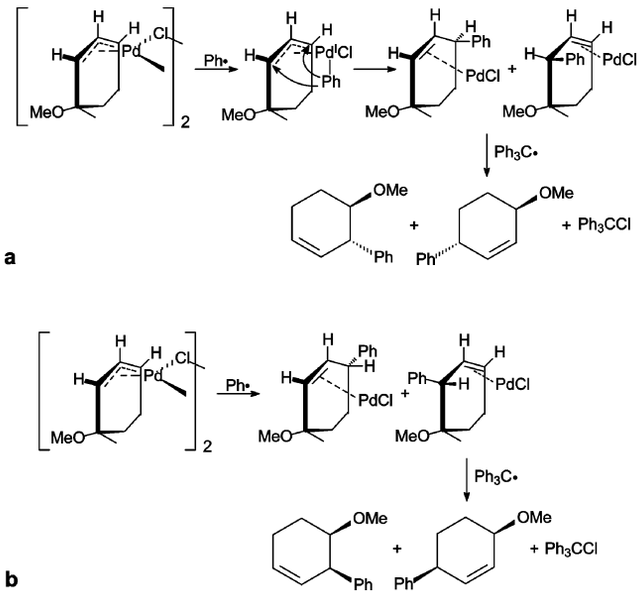


Fig. 5 Reaction of the phenyl radical with [(6-methoxy-1,3-η^3-cyclohexenyl)PdCl]$_2$ (a) *via* a mechanism involving initial attack at the palladium, (b) *via* a mechanism involving initial attack at the coordinated allyl group.

We then reacted **D** with PAT, much as above although over shorter time periods (10, 20 min) because **D** itself is somewhat thermally unstable under these conditions. We also wished to minimize possible palladium metal-catalyzed isomerization of the product (see below). The products of the two phenylation reactions of **D**, utilizing carbanionic and radical sources, were then compared (^{1}H NMR spectroscopy, GC-MS) and found to be identical, consistent with the formation of the *trans* endo products in both cases. Therefore, unless the corresponding *cis* isomers exhibit ^{1}H NMR spectra identical to those of the *trans* isomers, the reaction of (4-methoxy-1,3-η^3-cyclohexenyl)PdCl]$_2$ with PAT appears to proceed as illustrated in Fig. 5(a) rather than as in Fig. 5(b). While the alternative *cis* isomeric compounds have not been reported, isomeric pairs of several other disubstituted cyclohexenyl compounds are known and generally exhibit both different ^{1}H chemical shifts and different GC retention times.[19,25b,c] Thus the above conclusions are very reasonable.

It is probable that the analogous reaction of [(η^3-allyl)PdCl]$_2$ (eqn. (5)) also proceeds *via* initial attack at the palladium to form a phenylpalladium(III) intermediate, as with (η^3-allyl)-PdCl(PPh$_3$) and [(η^3-allyl)Pd(PPh$_3$)$_2$]Cl, rather than *via* direct addition of a phenyl radical to the coordinated allyl ligand. However, in contrast to the analogous reactions of the phosphine containing complexes, here the phenyl group subsequently couples with the allyl ligand to give 3-phenylpropene rather than remaining bonded to the palladium. The process by which 3-phenylpropene is formed presumably involves phenyl ligand migration to the allyl ligand in what is essentially a reductive elimination process. For trityl chloride formation to occur, the trityl radical must abstract the chlorine as the "PdCl" is formed. The phenyl–allyl coupling and the chlorine abstraction processes are probably concerted as a simple halogen abstraction reaction by the trityl radical from the metal would almost certainly be rather endothermic.[27]

There are probably several reasons for the quite different secondary processes observed in the presence and absence of PPh$_3$. Tertiary phosphines have long been known for their ability to stabilize alkyl– and aryl–metal compounds with respect to a variety of thermal decomposition processes,[28] and therefore, in a PPh$_3$-free compound, it seems reasonable that reductive elimination *via* initial phenyl migration is intrinsically more facile. Complementing this higher lability of the PPh$_3$-free system, it is likely that the planar trity radical cannot abstract the chlorine atom from the palladium when coordinated PPh$_3$ is present because of steric hindrance by the bulky PPh$_3$ ligands. Also, of course, in [(η^3-allyl)Pd(PPh$_3$)$_2$]Cl the chloride is not available for abstraction as it is probably ion paired to the complex cation, not covalently bonded to the palladium. In any case, phenyl radical migration from the palladium to the allyl group results in the formation of 3-phenylpropene as the kinetic product.

Catalytic isomerization of 3-phenylpropene

To assess the possibility that the major, thermodynamically more stable product 1-phenylpropene was formed by palladium metal catalyzed isomerization of the kinetic product, 3-phenylpropene, a reaction of [(η^3-allyl)PdCl]$_2$ with PAT was carried out for 2 h. At this point 1-phenylpropene was the major allyl product, and 3-phenylpropene was added and the mixture was heated for a further 2 h at 60 °C. A ^{1}H NMR spectrum then showed that all of the 3-phenylpropene had been converted to 1-phenylpropene. The mechanism probably involves an allylic intermediate as in Fig. 6.[29]

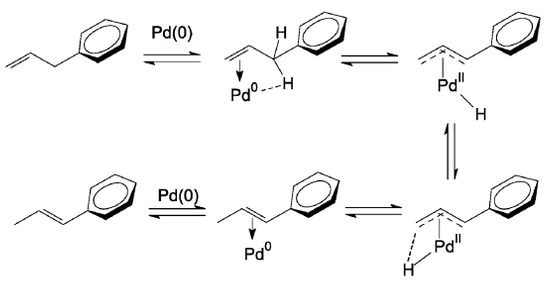


Fig. 6 Proposed mechanism for the catalytic isomerization of 3-phenylpropene to 1-phenylpropene.

It seemed unfortunate that the 3-phenylpropene, formed as the kinetic product of the reaction of [(η^3-allyl)PdCl]$_2$ with phenyl and trityl radicals, is isomerized catalytically by the palladium metal also formed, and we wondered if we might be able to intercept the palladium metal by carrying out the reaction in the presence of 3-chloropropene. It has long been known that allylic halides undergo oxidative addition reactions to Pd(PPh$_3$)$_4$ to give compounds of the type [(η^3-allyl)Pd(PPh$_3$)$_2$]Cl,[12] and we realized that if 3-chloropropene would react similarly with the palladium metal formed in eqn. (5), it would regenerate [(η^3-allyl)PdCl]$_2$. This would result in shutting down the isomerization of 3-phenylpropene by removing the palladium metal catalyst, and might possibly also result in the coupling reaction becoming catalytic in palladium.

We therefore carried out a reaction of [(η^3-allyl)PdCl]$_2$ with PAT (C_6D_6, 60 °C) in the presence of five equivalents of 3-chloropropene per palladium. In pleasant contrast to the analogous reaction carried out in the absence of 3-chloropropene, palladium metal did not precipitate but rather an orange solution and subsequently an orange precipitate were formed. ^{1}H NMR spectroscopy and GC-MS analyses again showed that 1-phenylpropene, 3-phenylpropene and 4,4,4-triphenyl-1-butene were formed, but in this case 3-phenylpropene was the *major* allyl product (~80% yield). A reaction with 25 equivalents of 3-chloropropene per palladium also resulted in 3-phenylpropene being formed exclusively, while a control experiment showed that PAT does not react directly with 3-chloropropene under these conditions.

The same reaction was then carried out in the presence of 50 equivalents of 3-chloropropene and 25 equivalents of PAT. The volatile products were collected by vacuum distillation and shown (GC-MS) to be exclusively 3-phenylpropene. Also obtained was an orange residue, the ^{1}H NMR spectrum of which exhibited only phenyl resonances. This product therefore

seemed likely to be $[(\eta^3\text{-trityl})PdCl]_2$, formed *via* oxidative addition of Ph_3Cl to palladium(0).[24] To characterize the compound, it was reacted with Tl(acac) to form the known $(\eta^3\text{-trityl})Pd(acac)$.[24] The ^1H NMR spectrum of the product from this reaction contained singlets from the acac group at δ 5.09, 1.76 and 1.84, consistent with the literature spectrum of $(\eta^3\text{-trityl})Pd(acac)$.

The results imply that a catalytic cycle is present, quite likely as shown in Fig. 7. On the basis of the GC-MS experiments, it appears as though approximately 15 turnovers in 1.5 h were achieved with a 50 : 1 ratio of 3-chloropropene to Pd.

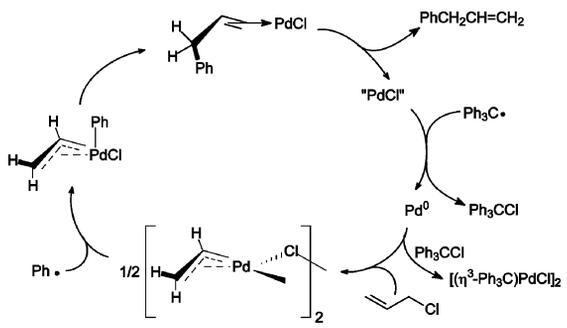


Fig. 7 Catalytic cycle of reaction of $[(\eta^3\text{-allyl})PdCl]_2$, PAT and 3-chloropropene, showing also the role of trityl chloride in subverting the catalysis.

The reaction of $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ with the trityl dimer

The reaction of $[(\eta^3\text{-allyl})PdCl]_2$ with trityl dimer in the presence of two equivalents of PPh_3 at 60 °C was carried out as a test of the ability of the trityl radical to react directly with a coordinated allyl group. Although the reaction was allowed to run for 1.5 h, much longer than is required for complete reactions of PAT, only a small amount of 4,4,4-triphenyl-1-butene was produced and a substantial amount of unreacted $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ was also isolated. All attempts to identify a palladium product from this reaction were unsuccessful.

While this result suggests that the trityl radical can react directly with the allyl group of $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$, it is clear that the reaction proceeds at a much lower rate than the reaction of $[(\eta^3\text{-allyl})Pd(PPh_3)_2]Cl$ with the combination of phenyl and trityl radicals derived from the thermal decomposition of PAT.

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