

# Reactions of free radicals with $\eta^3$ -allylpalladium(II) complexes: cyclohexyl radicals

Simon J. Reid, Michael C. Baird \*

Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

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## Abstract

Allyl palladium complexes of the types  $[(\eta^3\text{-allyl})\text{PdCl}]_2$ ,  $(\eta^3\text{-allyl})\text{PdCl}(\text{PPh}_3)$  and  $[(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$  (allyl =  $\text{C}_3\text{H}_5$ , 1-Me $\text{C}_3\text{H}_4$ , 2-Me $\text{C}_3\text{H}_4$ , 1-Ph $\text{C}_3\text{H}_4$ , 2-Ph $\text{C}_3\text{H}_4$ ) react with cyclohexyl radicals derived from the visible light photolysis of (c-hex)-Co(DMG) $_2$ (py). The reactions proceed via initial attack of the free radical at the metal center, followed by  $\beta$ -hydrogen elimination and subsequent reductive elimination of propene, 1-butene, isobutene, 3-phenylpropene and 2-phenylpropene, respectively. The 3-phenylpropene can be catalytically isomerized to the thermodynamically more stable 1-phenylpropene by either palladium metal or palladium(0) products, but the formation of 1-butene and 3-phenylpropene as primary products is unusual. A mechanism, differing in many ways from that proposed previously for analogous reactions of phenyl and trityl radicals, is proposed for the overall reaction and supported by use of the labeled cobaloxime, (2,2,6,6-D $_4$ -c-hex)Co(DMG) $_2$ (py).

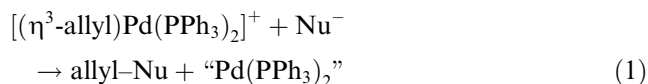
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## 1. Introduction

Free radicals have been invoked as reactive intermediates in a wide variety of reactions involving transition metal compounds, e.g., oxidative addition reactions [1], SmI $_2$  induced coupling of organic halides with carbonyl compounds [2], reduction of organic halides by complexes of chromium(II) [3], and hydrogenation and hydrometallation of aromatic alkenes [4] and conjugated dienes [5]. In addition, there has in recent years been increasing interest in addition reactions of free radicals on complexes of a variety of unsaturated, coordinated organic compounds such as arene [6], allylic [7], carbenoid [8] and alkenyne [9] ligands. The latter studies complement to a growing extent many better developed studies of free radical addition reactions to unsaturated carbon–carbon bonds, which provide a range of synthetically useful organic transformations [10].

In spite of this activity [11], there is as yet really no general knowledge or understanding of the reactions of free radicals with coordinated ligands and we recently began an investigation of reactions of free radicals with neutral and cationic  $\eta^3$ -allylic palladium compounds of types **A**, **B** and **C** (Fig. 1). Palladium compounds containing  $\eta^3$ -allylic ligands were chosen because of the susceptibility of such compounds to nucleophilic attack [12]. Indeed, cationic complexes of type **C** react readily as in Eq. 1 with a wide variety of C-, O- and N-based nucleophiles Nu $^-$  although the neutral compounds **A** and **B** exhibit relatively limited activities



Nucleophilic attack on complexes of type **C** has been thoroughly investigated and results in a range of extremely useful synthetic methodologies; as a result,  $\eta^3$ -allylic palladium(II) complexes of type **C** have been employed extensively in synthetic organic chemistry [12]. It was anticipated that equally interesting and useful coupling/addition reactions of free radicals with allylic ligands might be observed, and that products not

\*Corresponding author. Tel.: +1-613-533-2616; fax: +1-613-533-6669.

E-mail address: [bairdmc@chem.queensu.ca](mailto:bairdmc@chem.queensu.ca) (M.C. Baird).

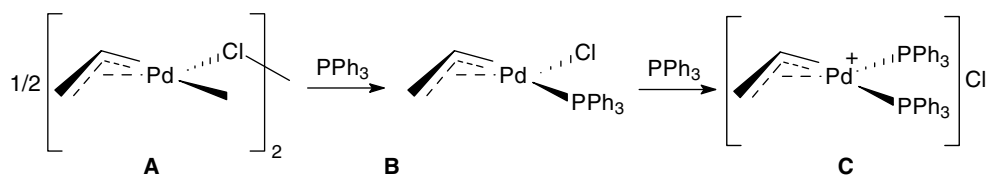
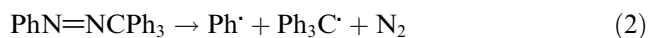


Fig. 1. Compounds present on the addition of triphenylphosphine to  $[(\eta^3\text{-allyl})\text{PdCl}]_2$  (A).

available by conventional palladium allyl chemistry might be formed since, e.g., base-sensitive functional groups should not be affected.

We began our studies utilizing phenylazotriphenylmethane,  $\text{PhN}=\text{NCPh}_3$  (PAT), as a source of phenyl and triphenylmethyl (trityl) radicals [13]. PAT decomposes in inert solvents on heating by releasing phenyl and trityl radicals in addition to molecular nitrogen (Eq. 2) [13]



We found [14] that compounds of the types  $(\eta^3\text{-allyl})\text{PdCl}(\text{PPh}_3)$  and  $[(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$  react readily with phenyl and trityl radicals in benzene at 60 °C, the products being the palladium phenyl compounds,  $[\text{PdPhCl}(\text{PPh}_3)]_2$  and *trans*- $\text{PdPhCl}(\text{PPh}_3)_2$ , respectively, and 4,4,4-triphenyl-1-butene. In contrast,  $[(\eta^3\text{-allyl})\text{PdCl}]_2$  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 were interpreted generally in terms of initial attack by phenyl radicals on the palladium(II) to give phenyl-palladium(III) intermediates followed by a variety of secondary reactions, depending on the degree of coordination of  $\text{PPh}_3$  ligands.

We have continued our studies by exploring the chemistry of the same types of allyl-palladium compounds **A**, **B** and **C**, with the cyclohexyl radical, chosen because of its greater nucleophilic character relative to the phenyl and trityl radicals [10]. As a source of cyclohexyl radicals, we have utilized the compound cyclohexylbis(dimethylglyoximate)(pyridine)cobalt(III),  $(c\text{-hexyl})\text{Co}(\text{DMG})_2(\text{py})$ , **D** of Fig. 2, a member of a

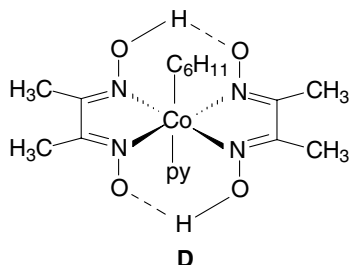
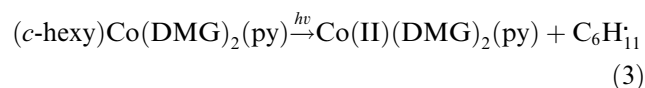


Fig. 2. Structure of  $(c\text{-hexyl})\text{Co}(\text{DMG})_2(\text{py})$ .

class of so-called alkylcobaloxime compounds  $\text{RCo}(\text{DMG})_2(\text{L})$  ( $\text{R} = \text{alkyl}$ ,  $\text{L} = \text{ligand}$ ) known to undergo cobalt-carbon bond homolysis on irradiation with visible light at ambient temperatures to give a carbon centred radical and the cobalt(II) compound  $\text{Co}(\text{DMG})_2(\text{L})$  (as in Eq. 3 for  $\text{R} = \text{cyclohexyl}$ ) [15]



We have earlier communicated some of our initial finding on this chemistry [16] and have reported in detail the chemistry of allyl-palladium compounds with phenyl and trityl radicals [14]. We now discuss an investigation of the analogous chemistry with cyclohexyl radicals, finding significant differences in reaction pathways.

## 2. Experimental

Experiments were conducted under an inert atmosphere of oxygen-free  $\text{N}_2$  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  $\text{N}_2$  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  $^1\text{H}$  and  $^{13}\text{C}$  resonances, respectively, while  $^{31}\text{P}$  resonances were referenced externally to 85%  $\text{H}_3\text{PO}_4$ .  $^2\text{H}$  NMR spectra were run in non-deuterated solvents with the naturally occurring abundance of deuterium in the solvent serving as the internal reference. Mass spectra were obtained on a Quatro Fisons Pro Quadrupole mass spectrometer in  $\text{EI}^+$  mode. GC-MS experiments were carried out on a Fisons GC 8000 coupled to a Fisons MD 800 spectrometer operating in  $\text{EI}^+$  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 as received. Deuterated solvents were purchased from MSD isotopes and Cambridge Isotopes Limited, while PdCl<sub>2</sub> was obtained on loan from Johnson Matthey. The following complexes were synthesized via standard literature preparations: [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> [17], (η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)Cl [17d], [(η<sup>3</sup>-allyl)Pt(PPh<sub>3</sub>)<sub>2</sub>]Cl [18], [(η<sup>3</sup>-1-methylallyl)PdCl]<sub>2</sub> [17a,19], [(η<sup>3</sup>-2-methylallyl)PdCl]<sub>2</sub> [17a,20], [(η<sup>3</sup>-1-phenylallyl)PdCl]<sub>2</sub> [17b,21], [(η<sup>3</sup>-2-phenylallyl)PdCl]<sub>2</sub> [22], *trans*-PtHCl(PPh<sub>3</sub>)<sub>2</sub> [23] and (c-hex)Co(DMG)<sub>2</sub>(py) (**D**) [15a]. <sup>1</sup>H NMR of **D** (CDCl<sub>3</sub>) δ 18.05 (s, 2H, OH), δ 8.50 (d, 2H, H-1, <sup>3</sup>J<sub>H1-H2</sub> = 4.0 Hz), δ 7.61 (t, 1H, H-3, <sup>3</sup>J<sub>H3-H2</sub> = 6.1 Hz), δ 7.20 (t, 2H, H2, <sup>3</sup>J<sub>H1-H2</sub> = 4.0 Hz, <sup>3</sup>J<sub>H3-H2</sub> = 6.1 Hz), δ 2.07 (s, 12H, H(Me)), δ 0.7–1.95 (m, 11H, C<sub>6</sub>H<sub>11</sub>). Literature [15a] <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.56 (d, 2H, *J* = 4 Hz), δ 7.66 (m, 1H), δ 7.26 (m, 1H), δ 2.14 (s, 12H), δ 0.7–2.0 (m, 11H).

(2,2,6,6-D<sub>4</sub>-c-hex)Co(DMG)<sub>2</sub>(py) was prepared in the same manner as for (c-hex)Co(DMG)<sub>2</sub>(py) except that 2,2,6,6-D<sub>4</sub>-cyclohexyl bromide was used in place of cyclohexyl iodide. 2,2,6,6-D<sub>4</sub>-cyclohexyl bromide was prepared via a literature preparation using the following general route [24]. 2,2,6,6-D<sub>4</sub>-cyclohexanone was first prepared via Na<sub>2</sub>CO<sub>3</sub> catalyzed hydrogen/deuterium exchange, at the 2,2,6 and 6 positions, of cyclohexanone in D<sub>2</sub>O. 2,2,6,6-D<sub>4</sub>-cyclohexanone was then reduced to 2,2,6,6-D<sub>4</sub>-cyclohexanol with NaBH<sub>4</sub> rather than LiAlH<sub>4</sub> which was used in the literature. 2,2,6,6-D<sub>4</sub>-cyclohexanol was finally converted to 2,2,6,6-D<sub>4</sub>-cyclohexyl bromide with PPh<sub>3</sub> and Br<sub>2</sub>. (2,2,6,6-D<sub>4</sub>-c-hex)Co(DMG)<sub>2</sub>(py) was then prepared using the standard literature procedure [15a]. Yield 1.05 g (36%) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 18.05 (s, 2H, OH), 8.49 (d, 2H, H-1, <sup>3</sup>J<sub>H1-H2</sub> = 4.0 Hz), 7.57 (t, 1H, H-3, <sup>3</sup>J<sub>H3-H2</sub> = 6.1 Hz), 7.19 (t, 2H, H-2, <sup>3</sup>J<sub>H1-H2</sub> = 4.0 Hz, <sup>3</sup>J<sub>H3-H2</sub> = 6.1 Hz), 2.06 (s, 12H, H(Me)), 0.7–1.95 (m, ≈ 9–10 H, C<sub>6</sub>H<sub>11</sub>). <sup>2</sup>H NMR (CDCl<sub>3</sub>) δ 1.85, 1.68, 1.47, 1.23, 0.82.

Photochemical experiments were carried out in Schlenk flasks and NMR tubes, maintained at 25 °C in a water bath and placed ~8 cm from a 300 W Sylvania light bulb. The whole apparatus was wrapped in aluminum foil to allow maximum illumination.

### 2.1. Reaction of (η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)Cl with cyclohexyl radicals

A solution of 0.151 g [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> (4.13 × 10<sup>-4</sup> mol), 0.261 g PPh<sub>3</sub> (8.24 × 10<sup>-4</sup> mol) and 0.450 g **D** (1.57 × 10<sup>-3</sup> mol) in 15 mL benzene was photolysed as above for 4 h, at which time the solvent was vacuum distilled from the reddish brown solution. A <sup>1</sup>H NMR spectrum of the residue exhibited resonances at δ 41.7, 27.0, 21.3; 15.9, -3.3, -13 and -23.9, in addition to many unassigned resonances, some quite broad, in the region δ

0–10. There were also several resonances in the <sup>31</sup>P NMR spectrum, indicating that more than one palladium compound had formed. GC-MS of the distillate showed that only very low amounts of 3-cyclohexylpropene and cyclohexenyl chloride were present. Similar results were obtained using preformed (η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)Cl.

In an NMR scale reaction, a solution of 0.010 g [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> (2.7 × 10<sup>-5</sup> mol), 0.014 g PPh<sub>3</sub> (5.33 × 10<sup>-5</sup> mol), and 0.030 g **D** (6.7 × 10<sup>-5</sup> mol) in 1 mL C<sub>6</sub>D<sub>6</sub> in an NMR tube was photolysed as above for 3 h. The solution turned from orange to deep red, but <sup>1</sup>H NMR monitoring revealed no resonances attributable to 3-cyclohexylpropene; as **D** disappeared, propene and cyclohexene were formed in yields up to 80% in some cases. The <sup>1</sup>H NMR spectrum was very similar to that described above.

In a complementary NMR experiment, a solution of 0.010 g [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> (2.7 × 10<sup>-5</sup> mol), 0.014 g PPh<sub>3</sub> (5.33 × 10<sup>-5</sup> mol), and 0.030 g **D** (6.7 × 10<sup>-5</sup> mol) in 1 mL C<sub>6</sub>D<sub>6</sub> in an NMR tube was photolysed as above for 3 h. At this point, 2 μL 3-chloropropene (2.5 × 10<sup>-5</sup> mol) were added to the mixture and the resonance of the starting material, (η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)Cl, immediately reappeared but no resonances of 3-chloropropene were evident. A further 2.5 h of photolysis resulted in the formation of more propene at the expense of the allyl starting material. This procedure was repeated, demonstrating that the reaction was catalytic in palladium to at least a limited extent.

### 2.2. Reaction of [(η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)<sub>2</sub>]Cl with cyclohexyl radicals

A solution of 0.050 g [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> (1.37 × 10<sup>-4</sup> mol), 0.155 g PPh<sub>3</sub> (5.91 × 10<sup>-4</sup> mol) and 0.145 g **D** (1.57 × 10<sup>-3</sup> mol) in 15 mL benzene was photolysed as above for 4 h. The reaction mixture was worked up as above, and the <sup>1</sup>H NMR spectrum of the resulting reddish brown residue differed somewhat from that of the residue resulting from the reaction of (η<sup>3</sup>-allyl)Pd(PPh<sub>3</sub>)Cl in that weak multiplets in the region δ 4.7–4.9 were present while the resonance at δ -13 was sometimes absent. An NMR reaction run as above in C<sub>6</sub>D<sub>6</sub> revealed also the formation of propene and cyclohexene in ~25% yield.

### 2.3. Reactions of [(η<sup>3</sup>-allyl)PdCl]<sub>2</sub> with cyclohexyl radicals

A reaction as above but with no PPh<sub>3</sub> added resulted in the formation of palladium metal, propene and cyclohexene. A similar reaction of [(η<sup>3</sup>-1-phenylallyl)PdCl]<sub>2</sub> also resulted in the formation of palladium metal in addition to 1-phenylpropene.

2.4. Reactions of  $(\eta^3\text{-1-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ ,  $(\eta^3\text{-2-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ ,  $(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ , and  $(\eta^3\text{-2-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  with cyclohexyl radicals

The procedure outlined above for an NMR scale reaction at 25 °C was followed in all cases. The reactions were generally somewhat slower, and in all cases  $^1\text{H}$  NMR spectroscopy showed that D disappeared while cyclohexene was formed. In the cases of the 1-methylallyl, 2-methylallyl and 2-phenylallyl compounds, 1-butene, isobutene and 2-phenylpropene, respectively, were obtained in high yields; all were identified by  $^1\text{H}$  NMR spectroscopy. In the case of the 1-phenylallyl compound, 1-phenylpropene and 3-phenylpropene were obtained in a  $\sim 1:1$  ratio. In all cases, the  $^1\text{H}$  NMR spectra also exhibited resonances at  $\delta$  41.7, 27.0, 21.3 15.9,  $-3.3$ ,  $-13$  and  $-23.9$ . In a reaction of  $(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  at 6 °C, a mixture of 3-phenylpropene and 1-phenylpropene were formed in a 3:1 ratio. In contrast, a similar reaction of  $[(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$  at 6 °C produced only 3-phenylpropene.

2.5. Reaction of  $[(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$  with deuterated cyclohexyl radicals derived from (2,2,6,6- $d_4$ -c-hex)Co(DMG) $_2$ (py)

This reaction was carried out as above at 6 °C. Again 3-phenylpropene was evident in the  $^1\text{H}$  NMR spectrum, while a  $^2\text{H}$  NMR spectrum exhibited a resonance of 3-phenylpropene at  $\delta$  3.14 and of cyclohexene at  $\delta$  5.68, 1.82 and 1.09 (Fig. 3). For purposes of comparison, a natural abundance  $^2\text{H}$  NMR spectrum of a solution of 3-phenylpropene in benzene was also run. A GC-MS was also run on the product of the above reaction, and

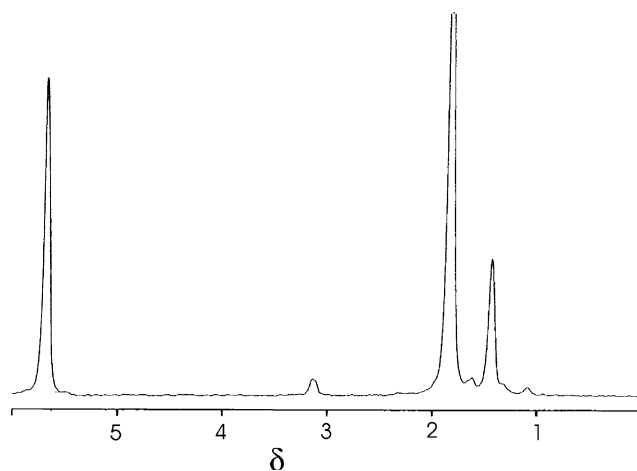


Fig. 3.  $^2\text{H}$  NMR spectrum showing the resonance at  $\delta$  3.14 of  $\text{CH}_2=\text{CH}-\text{CHD}-\text{Ph}$ , the product of the reaction of  $(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  with (2,2,6,6- $\text{D}_4$ -c-hex)Co(DMG) $_2$ (py).

showed there was a substantial percentage of the 3-phenylpropene with a mass increase of one, corresponding to mono-deuteration.

2.6. Reaction of  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$  with cyclohexyl radicals

An orange slurry of 0.211 g  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$  ( $2.66 \times 10^{-4}$  mol) and 0.232 g D ( $9.11 \times 10^{-4}$  mol) in 50 mL  $\text{C}_6\text{H}_6$  was irradiated as above for 4 h. The solvent was removed from the resulting reddish brown solution to give a brown residue, the  $^1\text{H}$  NMR spectrum of which exhibited inter alia resonances at  $\delta$  41.7, 27.0, 21.3 15.9,  $-3.3$ ,  $-23.9$  and  $-16.32$ . The latter was a 1:6:1 triplet ( $^1J_{\text{Pt-H}} = 1197$  Hz). The reaction was also carried out on an NMR scale in  $\text{C}_6\text{D}_6$ ; the observed products were propene, cyclohexene and  $\text{PtHCl}(\text{PPh}_3)_2$  in high yields, but no cyclohexane or bicyclohexyl.

### 3. Results and discussion

To extend our previous investigation of the reactions of palladium allyl complexes of the types A, B and C with phenyl and trityl radicals [14], we now report a study of the reactions of the same types of allyl palladium compounds with the cyclohexyl radical. Cobaloximes,  $\text{RCo}(\text{DMG})_2(\text{L})$ , generally have rather weak Co-C bonds which undergo homolytic cleavage on irradiation by visible light to form alkyl radicals  $\text{R}\cdot$  and the cobalt(II) compound  $\text{Co}(\text{DMG})_2(\text{L})$ . Thus cyclohexyl radicals are formed by visible light photolysis of the cobaloxime, D [15], and have been shown to exhibit chemical properties identical to those of cyclohexyl radicals generated from other methods of radical production [25].

In view of our earlier work in which it was found that attack by phenyl radicals on  $\eta^3$ -allyl palladium compounds generally occurred at the metal rather than at the allylic ligand [14], we anticipated that cyclohexyl radicals would also add preferentially at the metal. What was very unclear was what would happen next. It has been previously demonstrated that photolysis of compounds of the type  $[(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$  (allyl = propenyl, 1-methylpropenyl, 2-methylpropenyl, 1-phenylpropenyl, 2-phenylpropenyl) using a high-pressure Xe-Hg arc lamp results in the formation of the corresponding 1,5-hexadienes [26] via allyl radical intermediates. However, control experiments with the 300 W Sylvania bulb used in the present experiments show that the palladium allyl complexes used in this study are stable under the conditions employed here, involving visible light photolysis.

Earlier work has also shown that reactions of  $\eta^3$ -allylpalladium compounds of type A with  $\text{PPh}_3$  to form compounds of types B and C occur relatively rapidly

[14]. Thus many of the reactions carried out here involved mixtures of **A** and  $\text{PPh}_3$ , although in some cases preformed  $\text{PPh}_3$  complexes were used. As anticipated, similar results were found in both cases.

### 3.1. Reactions of $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ and $[(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$ with cyclohexyl radicals

The photolytic reactions of  $[(\eta^3\text{-allyl})\text{PdCl}]_2$  and  $(\text{c-hex})\text{Co}(\text{DMG})_2(\text{py})$ , in benzene and benzene- $d_6$  and in the presence of one equivalent of  $\text{PPh}_3$  per palladium, resulted in the formation of propene and cyclohexene in high yields but essentially no products of coupling of the cyclohexyl and allyl groups. The reaction of preformed  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  proceeded similarly, also resulting in the formation of propene and cyclohexene. In all cases, the reaction mixtures turned red during photolysis and eventually yielded reddish brown residues on removal of the solvent.

The  $^1\text{H}$  NMR spectra of the solid product mixtures were rather complex, and included resonances with unusual chemical shifts at  $\delta$  41.7, 27.0, 21.3, 15.9,  $-3.3$ ,  $-13$  and  $-23.9$ . The resonance at  $\delta$   $-13$  may alternatively be attributable to a palladium hydride (see below) [28], but most of these unusual resonances are reasonably assigned as contact shifted resonances [27] of one or more cobalt(II) byproducts. Unfortunately, there appear to be no NMR data such species in the literature, nor would EPR spectroscopy be of use [27]. However, the solutions are clearly paramagnetic, and while there were many resonances in the  $\delta$  0–10 part of the  $^1\text{H}$  NMR spectra, many were quite broad and none could be assigned. Furthermore, all attempts to isolate or identify any of products, i.e., by extraction, chromatography, or recrystallization, proved unsuccessful. Several resonances were also observed in the  $^{31}\text{P}$  NMR spectrum, consistent with a mixture of products being formed. Reactions carried out similarly but in the presence of two equivalents of  $\text{PPh}_3$  per palladium, i.e., involving  $[(\eta^3\text{-al-$

$\text{ly})\text{Pd}(\text{PPh}_3)_2]\text{Cl}$ , produced products exhibiting similarly complex, unassignable  $^1\text{H}$  NMR spectra.

A mechanism rationalizing the formation of propene and cyclohexene formation from reaction of  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  is shown in Fig. 4. Following our previous study [14], it is likely that the initial step involves reaction of the cyclohexyl radical directly with the palladium to form the palladium(III) intermediate  $(\eta^3\text{-allyl})\text{Pd}(\text{c-hex})\text{Cl}(\text{PPh}_3)$ . The latter would reasonably undergo  $\beta$ -hydrogen elimination to form cyclohexene and the palladium(III) hydride,  $(\eta^3\text{-allyl})\text{PdHCl}(\text{PPh}_3)$ , which could subsequently reductively eliminate propene to give  $\text{Pd}^{\text{I}}(\text{PPh}_3)\text{Cl}$  as shown. The latter species would then undergo further reactions as will be discussed below.

As an alternative process, one might anticipate that the palladium cyclohexyl intermediate,  $(\eta^3\text{-allyl})\text{Pd}(\text{III})(\text{c-hex})\text{Cl}(\text{PPh}_3)$  would undergo reductive elimination of the cyclohexyl and allyl groups to form 3-cyclohexylpropene. Although product mixtures were examined carefully for this product, it was not formed to a significant extent.

While  $\text{Pd}^{\text{I}}(\text{PPh}_3)\text{Cl}$  is proposed as a product in the mechanism outlined above, this compound was not detected and would be expected to react very rapidly, possibly with a second cyclohexyl radical to form  $\text{Pd}^{\text{II}}(\text{C}_6\text{H}_{11})(\text{PPh}_3)\text{Cl}$  as in Fig. 5. The latter might well undergo  $\beta$ -hydrogen elimination to form  $\text{Pd}^{\text{II}}\text{HCl}(\text{PPh}_3)$ , a species which could reductively eliminate HCl to give a palladium(0) product,  $\text{Pd}^0(\text{PPh}_3)$ .

In the reactions of **D** discussed above, cyclohexene is formed but not cyclohexane or bicyclohexyl. The latter compounds would also be formed if free cyclohexyl radicals achieved sufficient concentrations that bimolecular self reactions could occur; cyclohexane and cyclohexene would be formed via disproportionation while bicyclohexyl would be formed via combination reactions of cyclohexyl radicals [29]. The absence of cyclohexane and bicyclohexyl therefore provides evidence that

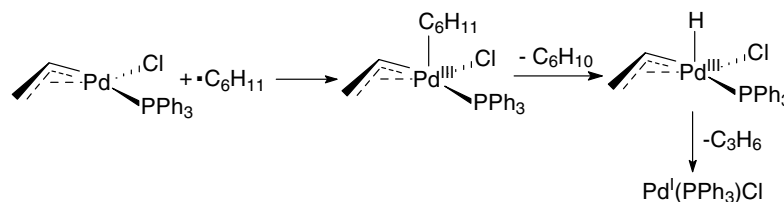


Fig. 4. Mechanism of the reaction of the cyclohexyl radical with  $(\eta^3\text{-allyl})\text{PdCl}(\text{PPh}_3)$ .

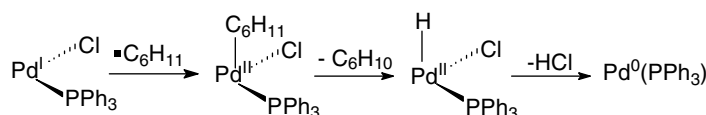


Fig. 5. Reaction of  $\text{Pd}(\text{PPh}_3)\text{Cl}$  with a second cyclohexyl radical.

cyclohexene is not formed via disproportionation, but rather via the mechanism proposed in Figs. 4 and 5 or via photochemical decomposition of **D**. Control experiments showed that photolysis of **D** in the absence of allyl palladium compounds did indeed result in the formation of some cyclohexene (but no cyclohexane or bicyclohexyl), results which have been reported previously [30].

### 3.2. Reaction of $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ with cyclohexyl radicals in the presence of 3-chloropropene

If a palladium(0) species such as “Pd<sup>0</sup>(PPh<sub>3</sub>)” is indeed formed during the reaction of  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  with cyclohexyl radicals derived from **D**, it should be possible to render the reaction catalytic by carrying it out in the presence of added 3-chloropropene which would oxidatively add to reform the starting  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ . To lend support to the hypothesis concerning the intermediacy of palladium(0) species, we therefore added 3-chloropropene to a reaction mixture in which essentially all of the  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  had reacted. The resonances of this compound reappeared as those of the 3-chloropropene disappeared, and further photolysis resulted in the formation of more propene. This process was repeated a second time, and thus the reaction can be rendered catalytic to at least a limited extent.

### 3.3. Reactions of $(\eta^3\text{-1-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ , $(\eta^3\text{-2-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ and $(\eta^3\text{-2-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ with cyclohexyl radicals

In the photolytic reaction of  $(\eta^3\text{-1-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  with **D**, a <sup>1</sup>H NMR spectrum of the reaction mixture showed that the  $(\eta^3\text{-1-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  disappeared while 1-butene and cyclohexene were formed. Similarly the reactions of  $(\eta^3\text{-2-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  and  $(\eta^3\text{-2-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  re-

sulted in the formation of isobutene and cyclohexene and 2-phenylpropene and cyclohexene, respectively. Thus these reactions appear to proceed via the same mechanism as does the reaction of  $(\eta^3\text{-allyl})\text{Pd}(\text{PPh}_3)\text{Cl}$ .

It is interesting and surprising that the reaction of  $(\eta^3\text{-1-methylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  resulted in the formation of 1-butene but not *cis*- or *trans*-2-butene. Similarly the reaction of  $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$  produced a mixture of 3-phenylpropene and *trans*-1-phenylpropene at 25 °C but predominantly the thermodynamically less stable isomer, 3-phenylpropene, at 6 °C. When the reaction was carried out with  $[(\eta^3\text{-allyl})\text{PdCl}]_2$ , only the thermodynamically more stable *trans*-1-phenylpropene was formed, in addition to palladium metal, and we suspected that 3-phenylpropene was the primary product formed from  $\beta$ -hydrogen elimination and that it was subsequently isomerized by Pd<sup>0</sup>(PPh<sub>3</sub>) or palladium metal to *trans*-1-phenylpropene. We find that the reaction of  $[(\eta^3\text{-allyl})\text{PdCl}]_2$  and (c-hex)Co(DMG)<sub>2</sub>(py), in the absence of PPh<sub>3</sub> resulted in formation of palladium metal, propene, and cyclohexene, and we have previously observed that 3-phenylpropene undergoes palladium metal-catalyzed isomerism to 1-phenylpropene, probably via an allylic intermediate [14].

It has been reported that  $(\eta^3\text{-allyl})\text{palladium(II)}$  hydride species normally undergo reductive elimination to form 2-alkenes rather than the thermodynamically less stable 1-alkene analogues [12c]. Thus the coordinated hydride migrates to the less hindered terminus of the  $\eta^3\text{-allylic}$  ligand, and the 2-alkene is obtained from the reductive elimination process. While it is not at all clear why the same regiochemistry is not observed here, the result does imply a mechanism other than reductive elimination from palladium(II) and may be taken tentatively as implicit evidence for an alternative mechanism, such as is shown in Fig. 4.

As a final test of the mechanism proposed above, the photolysis experiment of  $[(\eta^3\text{-1-phenylallyl})\text{PdCl}]_2$  was repeated using (2,2,6,6-D<sub>4</sub>-c-hex)Co(DMG)<sub>2</sub>(py). If re-

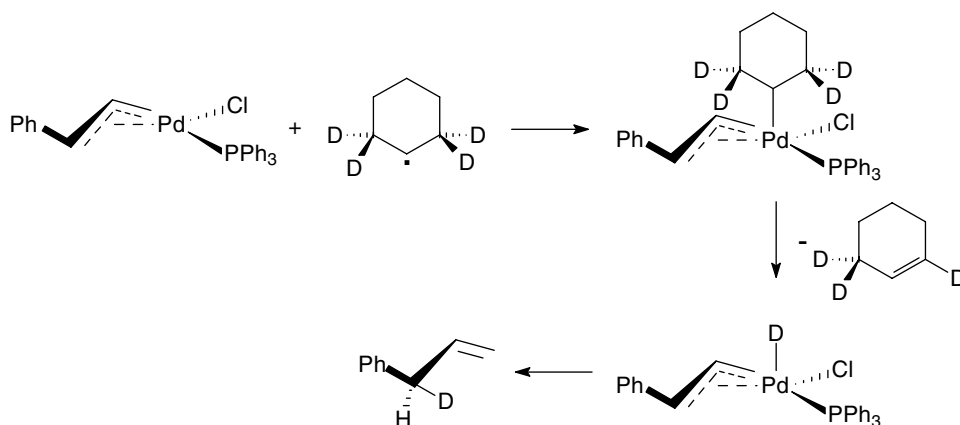


Fig. 6. Formation of CH<sub>2</sub>=CHCHDPh via the photolytic reaction of  $(\eta^3\text{-1-phenylallyl})\text{Pd}(\text{PPh}_3)\text{Cl}$  and (2,2,6,6-D<sub>4</sub>-c-hex)Co(DMG)<sub>2</sub>(py).

ductive elimination of propene follows  $\beta$ -elimination from a cyclohexyl-palladium intermediate as in Fig. 5, then placement of deuterium atoms on the C-2 atoms should result in the formation of 3-deutero-3-phenylpropene, as in Fig. 6.

The  $^2\text{H}$  NMR spectrum of the product mixture exhibited resonances at  $\delta$  5.8, 1.85 and 1.4, attributable to partially deuterated cyclohexene, and at  $\delta$  3.14, attributable to the deuterium on C-3 of  $\text{CH}_2=\text{CH}-\text{CHD}-\text{Ph}$  (Fig. 3). There were no vinylic resonances in the region  $\delta$  4.5–6.5, observed in a natural abundance  $^2\text{H}$  NMR spectrum of 3-phenylpropene. The formation specifically of  $\text{CH}_2=\text{CH}-\text{CHD}-\text{Ph}$  supports the mechanism proposed for this reaction as it is consistent with a  $\beta$ -deuterium elimination followed by reductive elimination (Fig. 6). The sample was also analyzed using GC-MS, and the mass spectrum obtained showed that 3-phenylpropene was formed predominantly with one hydrogen atom replaced by a deuterium atom.

#### 3.4. Reaction of $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$ with cyclohexyl radicals

We have pointed out above that a product resonance at  $\delta$  -13 provides tentative evidence for a hydrido-palladium species, although the resonance could not in fact be attributed specifically to a known compound. An analogous experiment was therefore carried out using  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$ , as the anticipated hydride in this case,  $\text{PtHCl}(\text{PPh}_3)_2$ , is a stable compound which would be isolable [23]. The reaction of  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$  with  $(\text{c-hex})\text{Co}(\text{DMG})_2(\text{py})$  was therefore carried out, the initially formed slurry forming a red solution. Evaporation of the solvent and analysis of the solid residue by  $^1\text{H}$  NMR spectroscopy showed that no allylic products were present, but the spectrum did exhibit a resonance in the hydride region ( $\delta$  -15), attributable to  $\text{PtHCl}(\text{PPh}_3)_2$  [23] although spin-spin coupling to the phosphorus nuclei was not observed. The subsequent addition of free  $\text{PPh}_3$  to a solution of  $\text{PtHCl}(\text{PPh}_3)_2$  prepared as in the literature [23] showed that spin-spin coupling phosphorus does indeed disappear under these conditions, presumably because of exchange between free and coordinated  $\text{PPh}_3$ . When the reaction of  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$  with  $(\text{c-hex})\text{Co}(\text{DMG})_2(\text{py})$  was performed on an NMR scale, propene and cyclohexene were formed in addition to  $\text{PtHCl}(\text{PPh}_3)_2$ . Thus the reaction of  $[(\eta^3\text{-allyl})\text{Pt}(\text{PPh}_3)_2]\text{Cl}$  with  $(\text{c-hex})\text{Co}(\text{DMG})_2(\text{py})$  appears to proceed via a mechanism similar to that of the palladium system.

#### 4. Conclusions

It has been shown that palladium allyl and platinum allyl complexes, containing zero, one or two coordinated

triphenylphosphine ligands, react with cyclohexyl radicals derived from  $(\text{c-hex})(\text{py})\text{Co}(\text{DMG})_2$ . These reactions proceed via initial attack of the radical at the metal center, followed by various secondary processes. The reactions of palladium and platinum allyl complexes with the cyclohexyl radical involve an initial attack of the radical with the palladium center, followed by  $\beta$ -hydrogen elimination and subsequent reductive elimination of  $\text{RCH}_2\text{CH}=\text{CH}_2$ . Since compounds of the type  $[(\eta^3\text{-RC}_3\text{H}_4)\text{PdCl}]_2$  ( $\text{R} = \text{alkyl, aryl}$ ) are readily prepared from, e.g., alkenes  $\text{RCH}=\text{CHCH}_3$  and allylic acetates  $\text{RCH}=\text{CHCH}_2\text{Oac}$ , the chemistry involving hydrogen transfer from the cyclohexyl radical would seem in effect to provide a route for both hydrogenolysis of alkenes or allylic acetate, via  $\eta^3$ -allylpalladium compounds, to terminal alkenes  $\text{RCH}_2\text{CH}=\text{CH}_2$ .

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