

Formation of $[(\eta^3\text{-CPh}_3)\text{PdCl}]_2$ via the Reaction of $\text{Pd}(\text{COD})\text{Cl}_2$ with the Trityl Radical

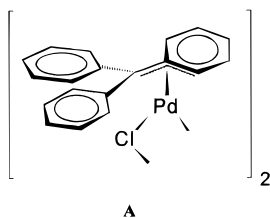
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Summary: The diene compound $\text{Pd}(\text{COD})\text{Cl}_2$ (COD = 1,5-cyclooctadiene) reacts with a benzene solution of the trityl radical $\cdot\text{CPh}_3$ to yield, surprisingly, trityl chloride and the η^3 -benzylic compound $[(\eta^3\text{-CPh}_3)\text{PdCl}]_2$, previously synthesized via a more conventional route.

Although addition reactions of alkyl radicals to electron-deficient olefins have found many useful synthetic applications in recent years,¹ there have been only sporadic reports of attempted radical reactions with coordinated aromatic,² allylic,^{2a,3} carbenoid,⁴ and alkenyne⁵ ligand systems. We have, therefore, recently begun an investigation of reactions of radicals with coordinated olefins, starting with an examination of the reactions of $\text{Pd}(\text{COD})\text{Cl}_2$ (COD = 1,5-cyclooctadiene).⁶ To our surprise, reaction of $\text{Pd}(\text{COD})\text{Cl}_2$ with the trityl radical, which exists in thermal equilibrium with its head-to-tail dimer,⁷ yielded not a product of *e.g.*, addition of trityl to the COD, but rather the known $[(\eta^3\text{-CPh}_3)\text{PdCl}]_2$ (**A**), containing an η^3 -benzylic linkage to the metal.⁸



Experimental Section

Experiments were conducted under an inert atmosphere of oxygen-free grade nitrogen, further purified through a heated BASF catalyst and molecular sieves. Manipulations of air-sensitive materials followed standard Schlenk line techniques and included the use of a Vacuum Atmosphere glovebox. The benzene solvent used was dried and distilled over sodium metal and was thoroughly deoxygenated prior to use by saturation with N_2 or repeated freeze–thaw cycles.

Infrared spectra were acquired on a Bruker IFS 25 FT-IR spectrometer and NMR spectra on Bruker ACF 200 (200.1

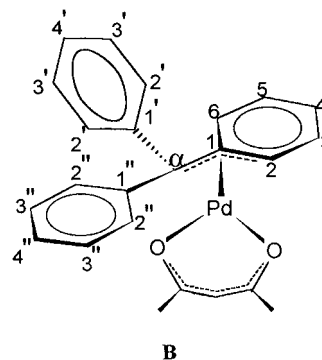
MHz, ^1H ; 50.3 MHz, $^{13}\text{C}\{^1\text{H}\}$) and AM 400 (400.1 MHz, ^1H ; 100.6 MHz, $^{13}\text{C}\{^1\text{H}\}$) FT-NMR spectrometers using CDCl_3 unless stated otherwise. The residual proton and the carbon resonances of deuterated solvents served as internal references for ^1H and ^{13}C resonances, respectively. GC-MS experiments were carried on a Fisons GC 8000 coupled to a Fisons MD800 spectrometer operating in the EI mode.

The compounds $\text{Pd}(\text{COD})\text{Cl}_2$,⁶ $[(\eta^3\text{-CPh}_3)\text{Pd}(\text{acac})]_2$,⁸ thallium acetylacetonate,⁹ and trityl dimer⁷ were prepared as described in the literature, the latter via the reduction of trityl chloride with zinc powder in benzene in the dark. In order to ensure that no trityl chloride remained, the reactions utilized a large excess of zinc and were stirred for 10–18 h.

Synthesis of $[(\eta^3\text{-CPh}_3)\text{PdCl}]_2$. A typical reaction involved refluxing a mixture of 0.21 g of $\text{Pd}(\text{COD})\text{Cl}_2$ (0.74 mmol) and 0.93 g of trityl dimer (1.91 mmol monomer equivalent) in 150 mL of benzene for 1.5 h. After the reaction mixture was refluxed, it was concentrated under reduced pressure to about 40 mL and cooled overnight in a refrigerator. The resulting orange-brown, crystalline product was collected by filtration, washed well with benzene, and dried (0.31 g, 42% yield).

Results and Discussion

In a refluxing benzene solution of the trityl radical, a slurry of the yellow, insoluble $\text{Pd}(\text{COD})\text{Cl}_2$ dissolved over 1.5 h, the solution turning orange. After concentration and cooling to about 280 K, an orange-brown, crystalline precipitate formed, the ^1H NMR spectrum of which exhibited only phenyl resonances (δ 7.1–7.45). Suspecting, therefore, that the material was the known $[(\eta^3\text{-CPh}_3)\text{PdCl}]_2$ (**A**),⁸ we also prepared this compound via the reaction of $\text{Pd}_2(\text{PhCH}=\text{CHCOCH}=\text{CHPh})_3$ with trityl chloride,^{8b} obtaining apparently the same poorly soluble product (NMR). Further proof of identity was sought and obtained by converting both materials to the more soluble and, hence, more readily characterized acetylacetonato derivative, $[(\eta^3\text{-CPh}_3)\text{Pd}(\text{acac})]$ (**B**).⁸



Synthesis of **B** from both batches of **A**, via metathetical displacement of chloride using thallium acetylac-

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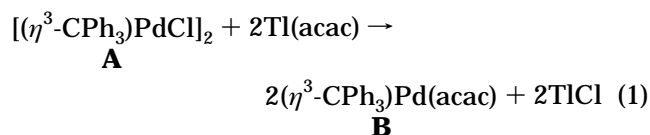
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Table 1. $^{13}\text{C}\{^1\text{H}\}$ NMR Data (δ)

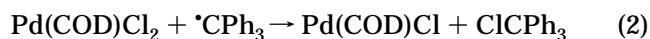
chemical shift	tentative assignt	lit. ^{12b}
28.3, 28.4	Me	28.3
73.4	C $_{\alpha}$	73.3
98.9	CH	98.8
102.1	C(2)	102.3
115.9	C(1)	116.0
126.7, 127.1, 127.2, 127.7, 127.8, 127.9, 128.1, 128.9	C(3',3''), C(2',2''), C(4,4',4''), C(6)	126.7, 127.9, 129.9
133.7	C(3,5)	133.7
142.9	C(1',1'')	143.1
187.0, 187.2	CO	187.1

etonate (Tl(acac)), proceeded as previously described (eq 1),⁸ giving two identical samples of orange-yellow crys-



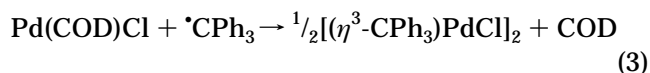
tals of **B** of the structure shown.^{8c} In addition to phenyl resonances (δ 7.1–7.6, 15H), the room temperature ^1H NMR spectra of both exhibited singlets at δ 5.09 (1H), 1.76 (3H), and 1.84 (3H) attributable to the acac ligand and comparing well with literature data.⁸ In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (-30°C) of the sample prepared via the Pd(COD)Cl₂/trityl route exhibited the resonances listed in Table 1. This compound is fluxional, rapid exchange of the metal between the pairs of edges of each of the three phenyl groups giving rise to the observation of averaged spectra at room temperature but of individual aryl carbon resonances at -30°C .⁸ As can be seen, the chemical shifts observed here generally agree well with the literature data, although we were also able to resolve extra phenyl resonances and to separate pairs of acac methyl and carbonyl carbon resonances; only singlet methyl and carbonyl resonances were reported previously.^{8b}

The palladium product **A** could form via chlorine abstraction by a trityl radical from Pd(COD)Cl₂ as in eq 2. GC-MS analyses of the supernatant from the



reaction showed the presence of trityl chloride, absent in control samples. Interestingly, in some reactions, palladium metal was also observed, suggesting the possible abstraction of both chlorine atoms.

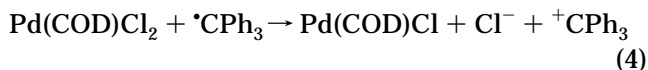
The initial chlorine abstraction reaction would then be followed by coupling of a second trityl radical with the resulting Pd(I) intermediate and subsequent rearrangement to the final η^3 -allylic structure (eq 3).



Compounds of palladium(I) are extremely rare,¹⁰ but an odd-electron species such as Pd(COD)Cl might couple with an organic radical as in eq 3.¹¹

There has, however, been ample demonstration that metal-centered radicals generally abstract halogen atoms from organic halides,¹¹ and at first sight, it seems perhaps unlikely that a trityl radical can abstract a chlorine atom from Pd(COD)Cl₂. However, the reaction may involve initial addition of the trityl radical to the metal atom of Pd(COD)Cl₂ to form a palladium(III) intermediate Pd(COD)(CPh₃)Cl₂, which could undergo chlorine abstraction by a second trityl radical in a concerted process involving η^1 to η^3 conversion of the coordinated trityl group.

Alternatively, the reaction could involve direct electron transfer from the trityl radical to palladium(II) (eq 4), followed by secondary processes involving the chem-



istry of eq 3 and combination of the resulting chloride anion and trityl carbenium ions. In either case, the type of chemistry reported here is to our knowledge without precedent.

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