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SHORT PAPER

Alkane activation by homogeneous palladium complexes

James K Beattie, Anthony F Masters and Meredith L Sparkes
Department of Inorganic Chemistry, University of Sydney, New South Wales 2006, Australia

The conversion of adamantane exclusively to 1-adamantyl trifluoroacetate in a refluxing trifluoroacetic acid solution of palladium acetate at 1 atm of air or nitrogen was confirmed. The conversion can be made quantitative. The 1-adamantyl trifluoroacetate was hydrolysed to yield 1-adamantanol in 90 % isolated yield. The adamantane functionalization is accompanied by concomitant formation of a palladium mirror.

Keywords: Alkane, activation, catalysis, adamantane, adamantanol, palladium acetate

INTRODUCTION

The metal-mediated activation of hydrocarbons is a subject of quite considerable contemporary interest.[1] The interest stems from the potential industrial utilization of methane and from efforts to understand the mode of action of the enzyme methane mono-oxygenase, which catalyses the oxidation of methane to methanol by dioxygen.[2,3] Recently, several catalytic systems, based on homogeneous transition-metal complexes, have been reported to activate methane and other alkanes under mild conditions.[4–12] The mechanisms of these reactions are generally only speculative; a variety of mechanisms appear to be possible,[1] including radical chemistry,[9,12,13] Fenton-type and related chemistry,[14–16] non-radical oxidative hydroxylation,[11,19] oxidative addition and electrophilic displacement.[4,5,20]

Recently, the non-catalytic conversion of alkanes to alcohols under mild conditions was reported. Specifically, Sen *et al.* reported the conversion of methane in 60 % yield to methyl trifluoroacetate by a solution of palladium(II) acetate $[Pd(O_2CCH_3)_2]$ in trifluoroacetic acid at 80 °C and 56–70 atm.[4,5] Hydrolysis of the methyl trifluoroacetate yielded methanol. These claims were later queried by Moiseev and co-workers,[6] who reported the catalytic oxidation of methane by cobalt(III) trifluoroacetate $[Co(O_2CCF_3)_3]$ in trifluoroacetic acid at 30 atm and 130 °C, and who attributed the palladium-mediated results of Sen *et al.* to reactions of 'unknown admixtures in the reagents'. Sen and co-workers have subsequently reiterated their earlier claims and demonstrated that $[Pd(O_2CCH_3)_2]$ in trifluoroacetic acid catalyses the oxidation of methane by peroxytrifluoroacetic acid (generated from hydrogen peroxide and trifluoroacetic acid anhydride) to methyl trifluoroacetate at 90 °C and 60 atm.[10] The palladium trifluoroacetate-mediated oxidative dehydrogenation of cyclohexane to benzene with concomitant reduction of the palladium(II) to palladium(0) in trifluoroacetic acid at 92 °C was reported by Shilov and co-workers[1,21] in 1974 (Eqn [1]):

$$3[Pd(O_2CCF_3)_2] + C_6H_{12} \rightarrow 3\,Pd(0) + C_6H_6 + 6\,CF_3CO_2H \qquad [1]$$

n-Hexane is also oxidized in this system.[1,21] A similar palladium acetate/trifluoroacetic acid-mediated reaction with cyclohexane as substrate is effectively suppressed by CO (at both 1 and 62 atm), yielding minor amounts of benzoic and cyclohexanecarboxylic acids.[22]

The $[Pd(O_2CCF_3)_2]/CF_3CO_2H$ system has also been shown to convert adamantane non-catalytically to its trifluoroacetate ester in 52 % yield.[4] The development of a catalytic reaction from this stoichiometric reaction is of interest. However, quantiative conversion of adamantane in the stoichiometric reaction is desirable to optimize the potential catalytic reaction.

We report here our results on the stoichiometric functionalization of adamantane mediated by palladium species, and offer some resolution of the conflicting disclosures discussed above.

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EXPERIMENTAL

Manipulations were carried out in air or, where noted, under an atmosphere of dry nitrogen using standard Schlenk techniques.[23] The solvents used were analytical grade, and were dried and distilled under nitrogen. Diethyl ether (Merck) was distilled from sodium benzophenone ketyl. Dichloromethane (Merck) was distilled from calcium hydride; pentane (Merk) and n-hexane (Ajax) were distilled from sodium.

Adamantane (Aldrich), palladium acetate (Aldrich) and 1-adamantanol (Merck) were used as received.

Palladium sponge was prepared from palladium (Johnson Matthey) by the method of Hosokawa *et al.*[24] Palladium acetate was also prepared from palladium sponge via the method of Stephenson *et al.*[25] A trifluoroacetic acid solution of 1-adamantanyl trifluoroacetate was prepared by refluxing 1-adamantanol (2.049 g, 13.5 mmol) in trifluoroacetic acid (*ca* 5 cm^3) for 1 h.

Adamantane (0.109 g, 0.8 mmol) and palladium acetate (0.18 g, 0.8 mmol, from either source) were heated at reflux in trifluoroacetic acid (*ca* 10 cm^3). The reaction was monitored by thin-layer chromatography until the adamantane was completely consumed (about 3 h, depending on the age of the palladium acetate). The solution was cooled, and water (10 cm^3) added to hydrolyse the 1-adamantyl trifluoroacetate. The solution was filtered, and the 1-adamantanol extracted into ether ($3 \times 50\ cm^3$). The combined ether extracts were washed with water, sodium carbonate (10 % aqueous solution), and saturated sodium chloride solution. The organic phase was dried over calcium chloride, and the ether removed on a rotary evaporator to give 1-adamantanol, which was characterized by ^1H NMR and gas chromatography by comparison with an authentic sample.

^1H NMR spectra were recorded at 200 MHz, using a Bruker AC200 spectrometer. Spectra were recorded at ambient temperature in deuterated chloroform with tetramethylsilane as an internal standard. FTIR spectra of samples suspended in potassium bromide discs were recorded using a Digilab FTS 20/80 spectrometer. Gas-chromatographic analyses were obtained using a Hewlett–Packard 5890A gas chromatograph equipped with an SGE 25 m QC2/BP1 0.2 mm capillary column, a flame ionization detector and a Hewlett–Packard 3393A reporter integrator. Products were identified by comparisons with the retention times of authentic samples.

RESULTS AND DISCUSSION

We have chosen adamantane as substrate in these investigations for experimental convenience, and as a useful probe of any potential regioselectivity of the oxidative functionalization process.[11] Thus, statistical reaction will result in a value of 3 for the ratio of products resulting from substitution at secondary carbons to those resulting from substitution at tertiary carbons (the C_2/C_3 ratio).

The reaction of adamantane (0.08 M) in a reluxing trifluoroacetic acid solution of $[Pd(O_2CCH_3)_2]$ (0.08 M), followed by hydrolysis, yielded exclusively 1-adamantanol as the only GC- and NMR-detectable product. The conversion of adamantane was close to 100 % within 3 h. The isolated yield of 1-adamantanol was 90 %. These results compare with the experiments reported by Sen *et al.*,[4] in which a 52 % conversion of adamantane (0.223 mmol), adamantane concentration approximately 0.06 M, palladium:adamantane molar ratio 1:1), also to the 1-substituted product, was achieved in 2 h. The high selectivity to 1-adamantanol contrasts with, for example, systems employing an iron catalyst, acetic acid, pyridine, zinc dust and oxygen, in which 1-adamantanol- (2 %), 2-adamantanol- (9 %), adamantanone- (17 %) and pyridine-coupled products (72 %) are obtained, or with *cis*-$[Ru(L)_2S_2/H_2O_2$, with which 1- and 2-adamantanol and adamantanone are produced.[9,19]

We have employed several separately prepared fresh samples of palladium acetate, as well as a commercial sample, and find the products to be essentially independent of the source of the palladium acetate. However, we have noted that the fresher the palladium acetate sample, the faster the consumption of adamantane, which is consistent with observations reported by Sen *et al.*[4] These workers emphasized that the freshness of the palladium acetate sample was '. . . particularly critical for methane oxidation . . .'. This point may offer some resolution of the conflict between the results of Sen *et al.* and those of Moiseev and co-workers.

The activation of adamantane occurs exclusively at the most reactive *tertiary* C–H bonds, to give 1-adamantanol trifluoroacetate and, subsequently, 1-adamantanol.

The palladium-mediated reaction of adamantane with the trifluoroacetate ion is accompanied by the deposition of a palladium mirror on the walls of the reaction vessel. (Eqn. [2]):

$$[Pd(O_2CCF_3)_2] + C_{10}H_{16} \rightarrow C_{10}H_{15}O_2CCF_3 + F_3CCO_2H + Pd(0) \qquad [2]$$

Given that the non-catalytic reaction is near-quantitative, it would be of interest to attempt the re-oxidation of the Pd(0), in whatever form it was produced, to make the reaction catalytic in palladium.

CONCLUSIONS

Near-quantitative conversions of adamantane to 1-adamantyl trifluoroacetate can be achieved in a refluxing solution of palladium acetate in trifluoroacetic acid. The 1-adamantane can be hydrolysed to 1-adamantanol, to give an overall stoichiometry (Eqn [3]) of:

$$C_{10}H_{16} + H_2O + [Pd(O_2CCF_3)_2] \rightarrow C_{10}H_{15}OH + 2\,CF_3CO_2H + Pd \qquad [3]$$

The reaction occurs exclusively at the *tertiary* C–H position of adamantane, and no other products were detected.

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