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Activation of unsaturated alkyl chlorides by photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals. Transient absorbance kinetics studies of the formation of η^3-allyl and "oxaallyl" palladium complexes

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Abstract

The reactions of photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals with the unsaturated alkyl chlorides, RCl = allyl chloride and chloroacetone, have been investigated by laser flash photolysis. Irradiation ($\lambda > 290$ nm) of acetonitrile solutions of $[Pd_2(CNMe)_6][PF_6]_2$ (**1**), in the presence of allyl chloride yields a mixture of the η^3-allyl complex $[Pd(C_3H_5)(CNMe)_2][PF_6]$ and $[PdCl(CNMe)_3][PF_6]$. In the presence of chloroacetone, Cl-atom abstraction by photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals yields the "oxaallyl" complex $[Pd(CH_2C(O)Me)(CNMe)_2][PF_6]$ and $[PdCl(CNMe)_3][PF_6]$. The disappearance of **1** in the presence of RCl occurs with a limiting quantum yield of 0.07 ± 0.01 ($R = C_3H_5$) and 0.05 ± 0.01 ($R = MeC(O)CH_2$) at 313 nm. The rate of disappearance of $[Pd(CNMe)_3]^{\cdot +}$, generated by laser flash photolysis (355 nm), depends on [RCl]. The reaction is first-order over the concentration range 0.062-1.23 *M* for allyl chloride and 0.63-1.89 *M* for chloroacetone. The rate constants for the bimolecular reactions with allyl chloride and chloroacetone are 500 and 200 M^{-1} s^{-1}, respectively. Mechanisms for the reactions of photogenerated $[Pd(CNMe)_3]^{\cdot +}$ with allyl chloride and chloroacetone are interpreted in terms of rate limiting Cl-atom abstraction to form $[PdCl(CNMe)_3][PF_6]$ followed by rapid combination of a second $[Pd(CNMe)_3]^{\cdot +}$ radical with the resulting allylic radical.

Introduction

The photochemistry of metal-metal bonds is an area of fundamental interest [1]. Over the past several years we have investigated the photochemistry associated with

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the Pd^I–Pd^I σ-bond of $[Pd_2(CNMe)_6][PF_6]_2$ (**1**) [2–4]. Excitation into the $\sigma \rightarrow \sigma^*$ electronic absorption band of **1** generates a pair of $[Pd(CNMe)_3]^{\cdot +}$ radicals (eq. 1).

$$[Pd_2(CNMe)_6]^{2+} \xrightarrow{h\nu} 2\,[Pd(CNMe)_3]^{\cdot +} \qquad (1)$$

Photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals have been demonstrated to undergo halogen atom (X = Cl, Br) transfer reactions (eq. 2) [2,3] and also participate in

$$[Pd(CNMe)_3]^{\cdot +} + CX_4 \longrightarrow [Pd(CNMe)_3X]^{+} + {}^{\cdot}CX_3 \qquad (2)$$

electron-transfer reactions, with "viologen" electron acceptors, A (eq. 3) [4].

$$[Pd(CNMe)_3]^{\cdot +} + A \xrightarrow{MeCN} [Pd(CNMe)_3(NCMe)]^{2+} + A^{\cdot -} \qquad (3)$$

An interesting question pertaining to the reactivity of photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals is whether their 15-valence electron configuration can be exploited in reactions with potential 3-electron donating ligands. We now describe our studies of the reactivity of photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals with potential 3-electron donor, allylic substrates. The photochemical syntheses of the allyl- and "oxaallyl"-palladium complexes $[Pd(C_3H_5)(CNMe)_2][PF_6]$ (**2**) and $[Pd(CH_2C(O)CH_3)(CNMe)_2][PF_6]$ (**3**) by reactions of photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals with allyl chloride and chloroacetone are described. The kinetics of these photochemical reactions have also been investigated by transient absorbance spectroscopy and are described.

Experimental

General procedures

Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR with a Model 3600 data station with 0.2 or 0.05 mm CaF_2 solution IR cells or KBr pellets. ^1H NMR and $^{13}C(^1H)$ NMR spectra were recorded at 200 and 50.3 MHz, respectively, on a Varian XL-200 spectrophotometer. Conductivity data were obtained on 10^{-3} *M* acetonitrile solutions of complex employing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. Elemental analyses were preformed by Dr. H.D. Lee of the Microanalytical Laboratory, Department of Chemistry, Purdue University.

Materials

Acetonitrile (Fischer Scientific) was distilled from CaH_2 prior to use. Tetrahydrofuran (Fischer Scientific) was distilled from sodium and benzophenone. Anhydrous diethyl ether (Mallinckrodt) was used as received. $[Pd_2(CNMe)_6][PF_6]_2$ (**1**) [5] and $[Pd(CNMe)_3Cl][PF_6]$ (**4**) [2] were prepared by the literature methods. Methyl isocyanide was prepared by the dehydration of *N*-methylformamide [6]. Allyl chloride (Aldrich) and chloroacetone (Eastman Organic Chemicals) were filtered through activated carbon prior to use. Tetraallyltin (Aldrich) was used as received.

Photolyses

Bulk photolysis and quantum yield samples were degassed by three freeze-pump-thaw cycles and placed under nitrogen. Manipulations of photolyzed samples were carried out using standard Schlenk and glovebox techniques under dry nitrogen. Lamps used for photolysis were an Oriel 6141 1000 W Hg(Xe) arc lamp fitted with an Oriel 7240 monochromator and, for bulk photolyses, an Ace/Hanovia 550 W medium-pressure Hg lamp fitted with pyrex and water filters. All photolyses were preformed at 10 °C. Quantum yields at 313 nm were determined using $Mn_2(CO)_{10}$ as an actinometer [2,7] and compared well with values obtained at 266 nm with a frequency quadrupuled Nd-YAG laser and Scientech 362 power energy meter.

Transient absorbance studies

The laser flash photolysis system employed in these studies is based on a Quanta Ray DCR-1 Nd-YAG pulsed laser (1064 nm, 7 ns pulse width) equipped with second, third, and fourth harmonic generating crystals. Laser energy is measured by a Scientech Model 362 power meter equipped with a pyroelectric probe. A 150W Xenon arc lamp (Photon Technologies) is used to measure transient absorbance in a geometry perpendicular to the laser beam. The Xenon arc output is passed through a water filter with pyrex windows to remove IR and < 290 nm radiation. A mechanical shutter (Vincent Associates, Model 225) limits irradiation of the sample by the Xe arc. A Jobin Yvon monochromator (200–800 nm) and a six dynode string, capacitively coupled RCA 1P28 photomultiplier tube complete the optical train. The signal from the photomultiplier anode is passed through a 15 kΩ terminator to the differential amplifier of a Tektronix 5000 series 2 MHz storage oscilloscope. A DC offset voltage from a battery and a variable resistor is applied to the $(-)$ input of the differential amplifier to null the large DC signal from the photomultiplier. Data are recorded with a Tektronix Model C-5 oscilloscope camera on Polaroid film.

Samples for laser flash photolysis were degassed by three freeze-pump-thaw cycles in evacuable cells and sealed under N_2. Samples were 1 m*M* in **1** and 0.12 m*M* to 1.89 *M* in saturated alkyl chloride. Data were analyzed in terms of a first-order rate law by least-squares fits of ln(absorbance) versus time. Data through the first two or more half-lives were employed. The k_{obs} values used in Fig. 2 (vide supra) are the mean of 3–5 experiments.

Preparation of $[Pd(C_3H_5)(CNMe)_2][PF_6]$ *(**2**)*

An acetonitrile solution (20 ml) of **1** (200 mg, 0.267 mmol) and allyl chloride (1.64 ml, 20 mmol) was photolyzed with broad band radiation. The photoreaction was monitored by FTIR, observing the disappearance of absorbance at 2237 cm^{-1} corresponding to ν(CN) for **1**. The photoreaction was essentially complete after 2–3 days. The reaction volatiles were removed via bulb-to-bulb distillation. The reaction residue was extracted with tetrahydrofuran and filtered. The filtrate was concentrated. Diethyl ether was then added to initiate precipitation and the solution was cooled to -10 °C to obtain 120 mg of a tan solid which was a (1/1) mixture of **2** and $[Pd(CNMe)_3Cl][PF_6]$ (**4**). The reaction volatiles were examined by ^1H NMR and showed only MeNC and allyl chloride in the acetonitrile solvent. No hexadienes were observed.

Complex **2** can also be synthesized by the reaction of **4** with tetraallyltin. Complex **4** (103 mg, 0.25 mmol) was slurried in 10 ml tetrahydrofuran. Tetraallyltin (17 μl, 0.07 mmol) was added via microliter syringe to the white slurry. The reaction was stirred for 1 h and the yellow solution was filtered. The filtrate was concentrated, diethyl ether was added via syringe and the solution was cooled to

$-20\,^\circ$C to obtain 78 mg (83% yield) of a yellow solid.

$[\mathrm{Pd(C_3H_5)(CNMe)_2}][\mathrm{PF_6}]$ (**2**). IR [THF]: ν(CN) 2244(br) $\mathrm{cm^{-1}}$; [KBr]: ν(CN) 2244(s) $\mathrm{cm^{-1}}$, ν(PF) 839(vs) $\mathrm{cm^{-1}}$. Λ_{1mM} [MeCN] 174 ohm $\mathrm{s^{-1}\,cm^2\,mol^{-1}}$. ^{1}H NMR ($\mathrm{CD_3CN}$, $-43\,^\circ$C): δ 5.60 (m, $^3J(\mathrm{H_cH_a})$ 14 Hz, $^3J(\mathrm{H_cH_s})$ 7 Hz, 1H, $\mathrm{H_c}$), 4.73 (br d, $^3J(\mathrm{H_cH_s})$ 7 Hz, 2H, $\mathrm{H_s}$), 3.48 (s, 6H, CN*Me*), 3.24 (br d, $^3J(\mathrm{H_cH_a})$ 14 Hz, 2H, $\mathrm{H_a}$); ($\mathrm{CD_3CN}$, $68\,^\circ$C): δ 5.63 (p, $^3J(\mathrm{H_cH_{a(s)}})$ 10 Hz, 1H, $\mathrm{H_c}$), 4.05 (very br,3.5H, $\mathrm{H_a + H_s}$), 3.51 (t, ^2J(HN) 2 Hz, 6.5H, CN*Me*); ($\mathrm{CD_2Cl_2}$): δ 5.55 (m, $^3J(\mathrm{H_cH_a})$ 13 Hz, $^3J(\mathrm{H_cH_s})$ 7 Hz, 1H, $\mathrm{H_c}$), 4.76 (d, $^3J(\mathrm{H_cH_s})$ 7 Hz, 2H, $\mathrm{H_s}$), 3.53 (~ t, ^2J(HN) 2 Hz, 6H, CN*Me*), 3.24 (d, $^3J(\mathrm{H_cH_a})$ 13 Hz, 2H, $\mathrm{H_a}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_3CN}$, $28\,^\circ$C): δ 123.7 (s, $\mathrm{HC(\mathit{C}H_2)_2}$], 70.6 (s, $\mathrm{H\mathit{C}(CH_2)_2}$), 30.4 (br, $\mathrm{CN\mathit{C}H_3}$), the isonitrile carbon, $\mathrm{\mathit{C}NCH_3}$, was not observed. Anal. Found: C, 22.37; H, 3.08; N, 7.00 $\mathrm{C_7H_{11}N_2PdF_6P}$ calcd.: C, 22.44; H, 2.97; N, 7.48%.

Preparation of $[\mathrm{Pd(CH_2C(O)CH_3)(CNMe)_2}][\mathrm{PF_6}]$ *(3)*

An acetonitrile solution (20 ml) of **1** (200 mg, 0.267 mmol) and chloroacetone (1.60 ml, 20 mmol) was photolyzed with broad band radiation. The reaction was monitored and worked up as described above to obtained 76 mg of an orange solid which was a (1/1) mixture of **3** and **4**. The reaction volatiles consisted of only MeNC and chloroacetone in acetonitrile solvent. No hexanediones were observed.

$[\mathrm{Pd(CH_2C(O)CH_3)(CNMe)_2}][\mathrm{PF_6}]$ (**3**): IR [THF]: ν(CN) 2258 $\mathrm{cm^{-1}}$; [KBr]: ν(CN) 2266(m) $\mathrm{cm^{-1}}$, ν(CO) 1575(w) $\mathrm{cm^{-1}}$, ν(PF) 840(vs) $\mathrm{cm^{-1}}$. ^{1}H NMR [$\mathrm{CD_3CN}$, $28\,^\circ$C]: δ 3.53 (t, ^2J(HN) 2 Hz, 6H, CN*Me*), 3.20 (d, ^2J(HH) 4 Hz, 1H, CH), 2.89 (d, ^2J(HH) 4 Hz, 1H, CH), 2.14 (s, 3H, $\mathrm{CH_3}$).

Results and discussion

Preparation and characterization of photoproducts

Broad band photolyses ($\lambda > 290$ nm) of acetonitrile solutions of **1** in the presence of 1 *M* allyl chloride give an intimate mixture of two palladium complexes. One complex is the known species $[\mathrm{Pd(CNMe)_3Cl}][\mathrm{PF_6}]$ (**4**), which was previously demonstrated to result from Cl-atom abstraction by photogenerated $[\mathrm{Pd(CNMe)_3}]^{\cdot+}$ radicals [2]. The second product is a new allylpalladium complex **2** (eq. 4). The identity of **2** is confirmed by its independent synthesis from **4** and tetraallyltin in 80% yield (eq. 5). All spectroscopic properties of photochemically and chemically prepared samples of **2** are identical. Purification of photochemically prepared samples of **2** however is complicated by the presence of **4**, which has similar solubility and chromatographic properties. The complete physical characterization of complex **2** was therefore conducted with synthetic samples, prepared by eq. 5.

$[\mathrm{Pd_2(CNMe)_6}]^{2+}$ + 

$\xrightarrow[-\mathrm{CNMe}]{h\nu}$

(**1**)

$$[\mathrm{Pd(C_3H_5)(CNMe)_2}]^+ + [\mathrm{Pd(CNMe)_3Cl}]^+ \qquad (4)$$

(**2**) (**4**)

$$[\mathrm{PdCl(CNMe)_3}]^+ + \tfrac{1}{4}\mathrm{Sn(C_3H_5)_4} \xrightarrow[-\mathrm{CNMe}]{}$$

(**4**)

$$[\mathrm{Pd(C_3H_5)(CNMe)_2}]^+ + \tfrac{1}{4}\mathrm{SnCl_4} \qquad (5)$$

(**2**)

The conductivity of **2** in acetonitrile is consistent with its formulation as a 1/1 electrolyte. The solid state FTIR spectrum of **2** shows a single isocyanide ν(CN) band at 2244 cm^{-1}. The ^1H NMR (CD_3CN) of **2** at 29° C shows a pentet at δ 5.61 (J(HH) 10 Hz) for the unique allylic proton and a very broad resonance ($>$ 1 ppm wide) centered at δ -4.05 for the *syn* and *anti* allylic (J(HN) 2 Hz). The spectroscopic data indicate that the allylpalladium complex **2** is fluxional in solution between the η^3- and η^1-allyl conformations.

The results of a variable temperature ^1H NMR study of **2** in acetonitrile-d_3 are presented in Fig. 1. Above 18° C, the *syn* and *anti* protons of the allyl group, H_s and H_a, exhibit a broad resonance centered at δ 4.05. Below 18° C, this resonance splits into two broad resonances of equal intensity (δ 4.73 for H_s and δ 3.24 for H_a). At lower temperatures (< -14° C) the H_s and H_a resonances each split into doublets due to coupling with the unique allylic proton H_c. The $\eta^3 \leftrightarrow \eta^1$ allyl exchange rate constant at 18° C (coalescence temperature) is calculated to be 660 s^{-1}, using the relationship $k_{ex} = [\pi(2)^{-1/2}]\Delta\nu$, where $\Delta\nu$ is the peak separation at -43° C. The free energy of coalescence $\Delta G_c^{\ddagger}$ at 18° C is thus calculated to be 13 kcal mol^{-1} on the basis of the relationship $\Delta G_c^{\ddagger} = 2.3\ R\ T_c\ [10.32 + \log(T_c/k_{ex})]$ [8]. The unique allylic proton, H_c, signal also shows a temperature dependence. At high temperatures $>$ 18° C, H_c exhibits a binomial pentet at δ 5.63. As the temperature is lowered this pentet broadens and becomes more complex due to unequal coupling with the *syn* and *anti* protons. The ^1H NMR spectrum at 68° C is intermediate

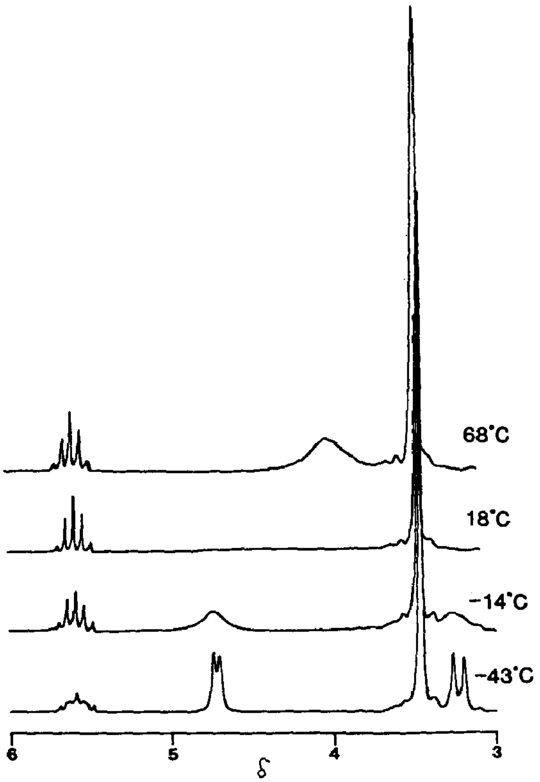
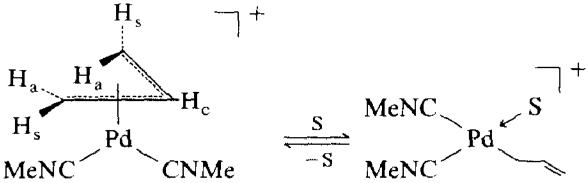


Fig. 1. Variable-temperature ^1H NMR spectra of **2** in acetonitrile-d_3.

between the low-temperature spectrum at −43° C and the expected, limiting AX_4 spectrum, characteristic of very rapid η^3- and η^1-allyl interconversion. Coordination of acetonitrile-d_3 solvent facilitates the $\eta^3 \leftrightarrow \eta^1$ allyl conversion, eq. 6. We note that in the relatively non-coordinating solvent CD_2Cl_2 the ^1H NMR spectrum of **2** at 25° C closely resembles the limiting −43° C acetonitrile-d_3 solution η^3-allyl spectrum.

A result of this study is that the 15 valence electron $[Pd(CNMe)_3]^{\cdot+}$ radical does not react with a 3 π-electron allyl radical to give an 18 e⁻ $[Pd(\eta^3\text{-}C_3H_5)(CNMe)_3]^+$ species, but gives instead a $[Pd(\eta^3\text{-}C_3H_5)(CNMe)_2]^+$ species alternating between 16 e⁻ η^3-allyl and solvated η^1-allyl conformations, eq. 6. This result is consistent which the general tendency of low valent palladium complexes to exist as 16e⁻ species.

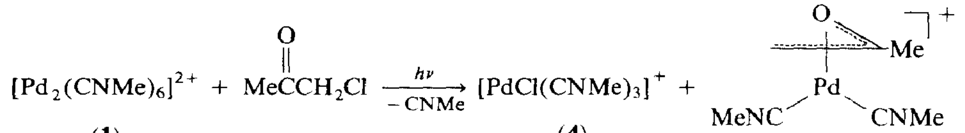


(2)

(S = NCMe)

(6)

Broad band photolyses of acetonitrile solutions of **1** in the presence of 1 *M* chloroacetone give a mixture of **4** and the acetone enolate, "oxaallyl", complex **3** (eq. 7).



(1)

(4)

(3)

(7)

The similar solubilities and chromatographic properties of **3** and **4** complicated the purification of **3**. Attempts to independently prepare **3** by reaction of **4** with $^-CH_2C(O)CH_3$ were also unsuccessful. For example, the reaction of **4** with $Li[CH_2C(O)CH_3]$ in tetrahydrofuran at −78° C yielded only the electron-transfer product **1**. Similarly, a mixture of **1** and an unidentified palladium complex was obtained from the reaction of **4** with $K[CH_2C(O)CH_3]$ in tetrahydrofuran at 25° C.

However, the identity of complex **3** can be established by IR and NMR spectroscopic data. The solid state IR spectrum shows an isocyanide ν(CN) band at 2266 cm^{-1}. The IR spectrum also reveals the acetone enolate ν(CO) band at 1575 cm^{-1}. The ^1H NMR (CD_3CN) of **3** as a 1/1 mixture with **4** at 29° C shows a singlet at δ 2.14 for the enolate methyl group. Also observed are two doublets (*J*(HH) 4 Hz) at δ 2.89 (1H) and δ 3.20 (1H) corresponding to inequivalent methylene protons. The methyl isocyanide signal is observed at δ 3.53 as a triplet (*J*(HN) 2 Hz). These spectroscopic data suggest that the acetone enolate moiety in **3** possesses an η^3-conformation similar to several previously reported "oxaallyl" complexes [9–11]. However, the observation of a single methyl isocyanide signal indicates that the η^3-"oxaallyl" is capable of rotating at 29° C.

The overall efficiencies of the photoactivations of allyl chloride and chloroacetone were determined in a quantum yield studies. The limiting quantum yield for the disappearance of 1 at 313 nm, Φ_d^{313}, in the presence of allyl chloride ($> 0.01\ M$) is 0.07 ± 0.01. The quantum yield, Φ_d^{313}, for the disappearance of 1 in the presence of chloroacetone is 0.05 ± 0.01.

Photochemical kinetics

Laser flash photolysis studies were undertaken to probe in detail the mechanism of the photoactivation of allyl chloride and chloroacetone by $[Pd(CNMe)_3]^{\cdot +}$ radicals. Laser excitation (355 nm) of an acetonitrile solution of 1 gives rise to a transient absorbance at 405 nm due to the formation of $[Pd(CNMe)_3]^{\cdot +}$ radicals [4]. The transient absorbance of $[Pd(CNMe)_3]^{\cdot +}$ decays according to second-order kinetics with a recombination rate constant $k_r = 1 \times 10^9\ M^{-1}\ s^{-1}$ [4]. The presence of allyl chloride or chloroacetone dramatically accelerates the rate of disappearance of $[Pd(CNMe)_3]^{\cdot +}$. The photochemical kinetics of 1 were examined over the allyl chloride concentration range, 0.12 mM to 1.23 M and the chloroacetone range 0.013–1.89 M. Plots of k_{obs}, the observed first-order decay rate constant, as a function of allyl chloride and chloroacetone concentration are presented in Fig. 2.

Our results suggest that photoactivation of allyl chloride and chloroacetone proceeds via initial Cl-atom abstraction. Flash photolysis of 1 produces $[Pd(CNMe)_3]^{\cdot +}$ radicals in the initial step (eq. 8). Our experimental evidence

$$[Pd_2(CNMe)_6]^{2+} \xrightarrow{h\nu} 2\,[Pd(CNMe)_3]^{\cdot +} \tag{8}$$

$$2\,[Pd(CNMe)_3]^{\cdot +} \xrightarrow{k_r} [Pd_2(CNMe)_6]^{2+} \tag{9}$$

$$[Pd(CNMe)_3]^{\cdot +} + RCl \xrightarrow{k_1} [Pd(CNMe)_3Cl]^{+} + R^{\cdot} \tag{10}$$

$$[Pd(CNMe)_3]^{\cdot +} + R^{\cdot} \xrightarrow{k_2} [Pd(CNMe)_3R]^{+} \tag{11}$$

$$[Pd(CNMe)_3R]^{+} \xrightarrow{k_3} [Pd(CNMe)_2R]^{+} + CNMe \tag{12}$$

$$2\,R^{\cdot} \xrightarrow{k_4} RR \tag{13}$$

($R^{\cdot}$= allyl or acetone enolate radical)

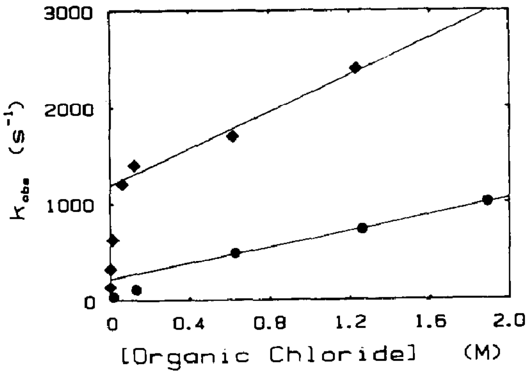


Fig. 2. Plots of k_{obs}, the pseudo-first-order rate constant for disappearance of Nd-YAG laser (355 nm) generated $[Pd(CNMe)_3]^{\cdot +}$ at 405 nm, versus $[C_3H_5Cl]$ (◆) and $[C_3H_5OCl]$ (●) in acetonitrile.

suggests that a photogenerated $[Pd(CNMe)_3]^{\cdot+}$ radical abstracts a chlorine atom from allyl chloride or chloroacetone, RCl, to produce one of the observed reaction products, the palladium(II) chloride complex **4** and an unsaturated alkyl radical (eq. 10). The allyl or acetone enolate radical, $R^{\cdot}$, then combines with the second $[Pd(CNMe)_3]^{2\cdot+}$ radical (eq. 11) at a rate which must be competitive with $[Pd(CNMe)_3]^{\cdot+}$ recombination (eq. 9) and alkyl radical dimerization (eq. 13), since no hexadienes or hexanediones from alkyl radical dimerization were detected in these experiments. The $[Pd(CNMe)_3R]^+$ species apparently loses CNMe to afford the observed allyl or "oxaallyl" complexes **2** or **3** (eq. 12).

A steady-state approximation for $[[Pd(CMe)_3]^{\cdot+}]$ in the chlorine atom abstraction mechanism outlined in eq. 8–13 leads to the rate expression in eq. 14, which

$$k_{obs} = 2k_r\left[[Pd(CNMe)_3]^{\cdot+}\right] + 2\ k_1[RCl] \tag{14}$$

predicts that k_{obs} will depend on both the $[Pd(CNMe)_3]^{\cdot+}$ and RCl concentrations. Therefore, k_{obs} will exhibit mixed first- and second-order kinetic behavior, especially at low [RCl]. However, at high [RCl] the contribution of $2k_r[[Pd(CNMe)_3]^{\cdot+}]$ to k_{obs} will become negligible and a simplified pseudo-first-order expression, eq. 15, becomes valid.

$$k_{obs} = 2\ k_1\ [RCl] \tag{15}$$

Eq. 14 and 15 are consistent with the data in Fig. 2. Note k_{obs} does not vary linearly at low allyl chloride or chloroacetone concentrations; however at high [RCl], k_{obs} does obey a linear relationship. The rate constant, k_{obs}, varies linearly with allyl chloride concentration over a range 0.062–1.23 M with a slope of 1000 M^{-1} s^{-1}. For chloroacetone, k_{obs} varies linearly over the concentration range 0.63–1.89 M with a slope of 400 M^{-1} s^{-1}. Thus, the bimolecular rate constants for the reactions of $[Pd(CNMe)_3]^{\cdot+}$ with allyl chloride and chloroacetone, k_1, are 500 and 200 M^{-1} s^{-1}, respectively.

The bimolecular rate constants exhibit an inverse relationship to the carbon–chlorine bond dissociation energies, D[C–Cl], of the α,β-unsaturated alkyl chlorides. For allyl chloride, D[C–Cl] is reported to be 60.4 kcal mol^{-1} [12] while D[C–Cl] for chloroacetone is estimated to be ~ 81 kcal mol^{-1} [16,17*]. These data suggest that carbon–chlorine bond strength and not organic radical stability is the determining factor in the rates of these photoactivation reactions [19]. This relationship between rate constant and D[C–Cl] is consistent with observations by Brown [21] and Ford [22]. The atom transfer (inner sphere electron transfer) rate constants for the $Mn(CO)_{5-n}L^{\cdot}_n$ and $(C_5H_5)W(CO)^{\cdot}_3$ radicals show a similar inverse relationship with the C–X bond dissociation energy for a series of organic halides. Also note, if outer sphere electron-transfer [13,14] played an important role in the photoactivation of α,β-unsaturated alkyl chlorides, then k_1(chloroacetone) > k_1(allyl chloride) would be expected, reflecting the increased driving force for the rate determining electron transfer, $E°$ $(MeC(O)CH_2Cl^{0/-})$ ~ -1.15 V, $E°$ $(C_3H_5Cl^{0/-})$ ~ -1.8 V, vs. SCE [15].

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* Reference number with asterisk indicates a note in the list of references.

Summary and conclusions

This study indicates that 15-valence electron $[Pd(CNMe)_3]^{\cdot +}$ radicals activate unsaturated alkyl chlorides by Cl-atom abstraction to generate the corresponding allylic radicals. Combination of the allylic radicals with a second $[Pd(CNMe)_3]^{\cdot +}$ radical affords allyl or η^3-oxaallyl species which lose one MeNC ligand to afford the more stable 16 electron species **2** and **3**. The kinetic studies are consistent with a rate determining chlorine atom abstraction and suggest that the carbon–chlorine bond dissociation energy is an important factor influencing rate constants. Although photogenerated $[Pd(CNMe)_3]^{\cdot +}$ radicals are also known to react by outer sphere electron transfer pathways [4], outer sphere electron transfer does not appear to play an important role in the activation of unsaturated alkyl chlorides.

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$$D[CH_3C(O)CH_2Cl] = \Delta H_f^\circ[CH_3C(O)CH_2^\cdot\ (g)] + \Delta H_f^\circ[Cl^\cdot\ (g)] - \Delta H_f^\circ[CH_3C(O)CH_2Cl\ (g)]$$

$\Delta H_f^\circ[CH_3C(O)CH_2^\cdot\ (g)] = -6.0$ kcal mol^{-1} [16], $\Delta H_f^\circ[Cl^\cdot\ (g)] = 28.9$ kcal mol^{-1} [19], and $\Delta H_f^\circ[CH_3C(O)CH_2Cl\ (g)]$ was estimated from group additivity properties as described by Benson [20] to be -58.1 kcal mol^{-1}; thus $D[CH_3C(O)CH_2Cl] \sim 81$ kcal mol^{-1}.

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