

Direct Observation of C–O Reductive Elimination from Pt(IV)

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Reductive elimination is a fundamental organometallic reaction and a critical product-release step in a number of industrially important catalytic processes.¹ In particular, reductive elimination reactions which form C–O bonds from Pt(IV) have been proposed as product-forming steps in the functionalization of alkanes by Pt(II) catalysts (Shilov's oxidations and the system recently reported by Catalytica).^{2–4} Only a limited number of examples of reductive eliminations which form carbon-heteroatom (C–O, C–N, C–S) bonds from model complexes are known. These reactions primarily occur at low valent d⁸ metal centers (Pd(II), Ni(II)) and involve aryl and acyl carbon groups.⁵ Examples of carbon-heteroatom reductive couplings which occur from high valent d⁶ metal centers such as Pd(IV),⁶ Pt(IV), Rh(III), or Ir(III),⁷ as well as those which involve alkyl carbon groups, are extremely rare.^{3,5c,8} This contribution reports the first direct observation and study of high yield alkyl C–O reductive elimination from a d⁶ octahedral Pt(IV) metal center.

The Pt(IV) complex, dppePtMe₃OAc (**1**), was prepared from dppePtMe₃I and AgOAc.⁹ Crystals of **1** suitable for an X-ray diffraction study were grown by evaporation from a toluene solution in air. The ORTEP view is included in the Supporting Information.^{10,11} A water molecule is shown to be hydrogen-bonded to the acetate moiety (O–O distance = 2.75 Å).

The thermolyses of anhydrous samples of **1** at 99 °C were studied in a variety of solvents (Table 1). In the relatively nonpolar solvents benzene-*d*₆ and THF-*d*₈, the primary products are those

(1) Parshall, G. W.; Iteel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley-Interscience: New York, 1992.

(2) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel: Dordrecht, The Netherlands, 1984.

(3) Mechanistic support has been presented for the product forming step in Shilov's oxidations being nucleophilic attack at a Pt(IV) carbon group by an external heteroatom species. This reaction which results in C–X bond formation and generation of a Pt(II) species is sometimes classified as a reductive elimination. Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75 and references therein.

(4) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560.

(5) See: (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046–2067 and references therein. (b) Widenhofer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504 and references therein. (c) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1998**, *120*, 7657 and references therein. (d) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

(6) (a) Canty, A. J.; Jin, H. *J. Organomet. Chem.* **1998**, *565*, 135. (b) Canty, A. J.; Jin, H.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1998**, *37*, 3975.

(7) (a) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (b) Thompson, J. S.; Randall, S. L.; Atwood, J. D. *Organometallics* **1991**, *10*, 3906.

(8) The microscopic reverse, oxidative addition of an alkyl C–O bond (RCO₂R') to form a d⁶ octahedral compound, has been reported. (a) Iteel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Khin-Than, A.; Colpitts, D.; Ferguson, G.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 1454.

(9) See supporting material for characterization of **1**, **5** and dppePtMe(O₂CCF₃) (**6**).

(10) 1·H₂O (C₃₁H₃₈O₃P₂Pt), MW = 715.64, colorless rhombohedron, triclinic, space group = *P*1, *a* = 10.043(2) Å, *b* = 12.581(3) Å, *c* = 13.538(3) Å, α = 66.15(2)°, β = 70.32(2)°, γ = 78.16(2)°, *V* = 1468.3(6) Å³, *Z* = 2, *R*₁ = 0.0369 [*I* > 4σ(*I*)], w*R*² = 0.1179, GOF (on *F*²) = 0.695.

(11) Selected bond lengths(Å): Pt–C (trans to OAc) 2.079(7); Pt–C (cis to OAc) 2.087(7), 2.092(7); Pt–O 2.162(5); O–C 1.272(9); C=O 1.228(9). Select angles(deg): P–Pt–P 83.62(6); Pt–C–O 125.1(4); O–C=O 124.8(7), O=C–C 119.1(7), O–C–C 116.1(7).

(12) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

resulting from C–O reductive elimination; methyl acetate and dppePtMe₂ (**2**) are formed in ≥88% yield. Competitive with this C–O bond forming process is a C–C reductive elimination yielding ethane and dppePtMe(OAc) (**3**).¹³ In the more polar solvents acetone-*d*₆ and nitrobenzene-*d*₅, the C–C reductive elimination dominates. Rates of reaction are also substantially faster in the more polar solvents.

Higher percentages of methyl acetate (94–98 vs 88–89%) were obtained when 2% cross-linked polyvinylpyridine (PVP), an acid scavenger, was added to the benzene-*d*₆ and THF-*d*₈ thermolysis experiments. This inhibition of ethane elimination by PVP suggested that the C–C reductive elimination pathway might be acid-catalyzed. Indeed, the addition of a small amount of HOTf (0.1 equiv, 3.4 mM) or the Lewis acid, AgOTf (0.1 equiv, 5.6 mM), caused a dramatic increase in the rate of C–C elimination. Under these conditions, exclusive ethane elimination proceeded at room temperature. In contrast, the addition of a small amount of acetic acid (0.1 equiv, 5.3 mM) caused a lesser enhancement of the initial C–C coupling rate but also increased the initial rate of C–O reductive elimination (*k*_{obs} = 2.7 × 10^{−5} s^{−1} at 99 °C vs 1.25 × 10^{−5} s^{−1} without added acid; C–O:C–C = 80:20). Subsequently, the acetic acid was consumed by reaction with the Pt(II) dimethyl product, **2** (to produce methane (s, δ 0.15) and **3**).¹⁴ The rate of reaction then slowed to a final rate (*k*_{obs} = 1.25 × 10^{−5} s^{−1}) identical to that without added acid and the C–C coupling dropped to 10%. Thus, the rate and product ratios observed in the thermolysis of **1** are very sensitive to the presence of Brønsted and Lewis acids.

Thermolysis of **1** in the more polar solvent acetone-*d*₆ produced primarily C–C reductive elimination (95–99%). Although these reactions consistently followed first-order kinetic behavior, a high variability in the rate constant was observed (at 99 °C, *k*_{obs} = 6.2–11 × 10^{−4} s^{−1}).¹⁵ We have not as yet identified the exact cause of this variability.^{16,17} However, when a constant acetate concentration was maintained by the addition of acetate ions ([N(*n*-Bu)₄]OAc, 0.38 or 0.60 M), a reproducible reaction rate was observed (*k*_{obs} = 4.0 (± 0.1) × 10^{−5} s^{−1}).^{18,19} Under these conditions, ethane production was completely inhibited and methyl acetate and **2** were formed in quantitative yield.

The reaction mechanism shown in Scheme 1 is consistent with all of our data. In agreement with substantial literature precedent, C–C reductive elimination from Pt(IV) proceeds via a five-coordinate intermediate.^{20,21} Dissociation of acetate from **1** is supported by the inhibition of ethane elimination in the presence of a high concentration of acetate ions and also by the dramatic solvent effect. The C–C coupling rate increases by over 3 orders of magnitude from benzene-*d*₆ to nitrobenzene-*d*₅ (Table 1).²² Finally, the accelerative effect of added acid on the C–C coupling reaction can be explained by Lewis acid coordination to the acetate group (similar to H₂O coordination in the crystal structure). This interaction should promote dissociation of the acetate, increasing *k*₁. When the counterion is OTf[−], *k*_{−1}[OAc] and *k*₂[OAc] decrease as the acetate ion is more strongly bound to the acid, further augmenting the C–C coupling rate.^{23a} However, when the counterion is OAc[−], the acetate dependent steps are not substantially inhibited (and may be accelerated) which explains the less dramatic increase in the C–C coupling rate with with HOAc vs HOTf and AgOTf.

(13) **3** and **4**-*h*₅: Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

(14) The reaction of **2** with HOAc has also been independently demonstrated.

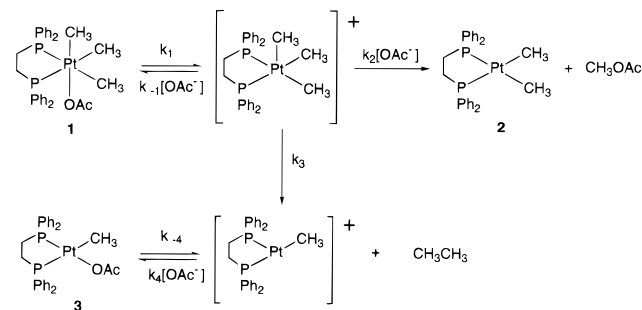
(15) A similar variation in rates was observed at 79 °C (*k*_{obs} = 3.4–19 × 10^{−5} s^{−1}).

(16) A side reaction between the primary Pt(II) product, dppePtMe(OAc) (**3**) and acetone-*d*₆ to form dppePtMe(CD₂COCD₃) (**4**)¹³ and DOAc further complicates the analysis. However, production of acetic acid during the reaction would be expected to cause a deviation from first-order behavior (see text) rather than simple variability between experiments.

Table 1. Thermolysis Rate Constants and Product Yields for **1** (99 °C)

solvent	polarity (A + B) ^a	k_{obs} (10^5 s^{-1})	% C–O	$k_{\text{C–O}}$ (10^5 s^{-1}) ^c	% C–C	$k_{\text{C–C}}$ (10^5 s^{-1}) ^c
C ₆ D ₆ ^b	0.73	1.25 ± 0.04	88–98	1.18 ± 0.05	2–12	0.07 ± 0.04
THF- <i>d</i> ₈ ^b	0.84	1.28 ± 0.03	88–96	1.16 ± 0.07	4–12	0.12 ± 0.06
acetone- <i>d</i> ₆	1.06	62–110	1–5	2–4	95–99	60–110
C ₆ D ₅ NO ₂	1.14	140 ± 10	<0.5	d	99.5+	140 ± 10

^a Relative polarity scale for protio solvents.¹² ^b Some reactions contained PVP (see text). ^c Reference 22. ^d Insufficient product was generated to accurately determine the rate constant.

Scheme 1

The mechanism for C–O reductive elimination suggested in Scheme 1 is analogous to that previously presented for C–I reductive elimination from the related compound, dppePtMe₃I.²⁰ As shown by the experiments with added [N(*n*-Bu)₄]OAc, the rate of methyl acetate production from **1** is independent of the acetate ion concentration. This is consistent with the path involving acetate dissociation detailed in Scheme 1.²³ While a pathway involving direct reductive elimination of methyl acetate from **1** should also be independent of acetate ion concentration, the acceleration of the C–O reductive elimination in the presence of HOAc argues against direct elimination. In contrast, acetic acid coordination to the acetate group of **1** should increase k_1 in Scheme 1 as described above, thereby increasing the overall C–O coupling rate.

To further consider the dissociation of the acetate group as an integral part of the C–O and C–C coupling reactions, the thermolysis of the trifluoroacetate analogue of **1**, dppePtMe₃(O₂CCF₃) (**5**)⁹ was studied in benzene-*d*₆ at 99 °C. Thermolysis of **5** in the presence of PVP proceeds much faster ($k_{\text{obs}} = 2.8 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$) than that of **1** and results in a much lower C–O coupling percentage of 49(±2)%. The rate of C–O coupling is approximately an order of magnitude faster, and the rate of C–C coupling is roughly 100 times that of the acetate analogue, **1**.²⁴ Thus, the greater lability of the trifluoroacetate group increases the rate of both eliminations. In contrast, studies of C–O and C–N reductive eliminations from Pd(II) in which coupling is proposed to occur without preliminary heteroatom dissociation report that the more electron-withdrawing heteroatom groups react more slowly than their more electron-donating analogues.^{5a,b}

The evidence presented strongly suggests preliminary acetate dissociation and the involvement of a common five-coordinate cationic intermediate in both C–C and C–O reductive elimination reactions from **1**. The coupling of an alkyl moiety with an acetate or trifluoroacetate fragment represents a promising product-release pathway in alkane functionalization involving high-valent late-metal complexes.²⁵ Methyl acetate and methyl trifluoroacetate are

both derivatives of methanol which may be protected from overoxidation similarly to the methyl bisulfate product in the Catalytica methane functionalization process.^{4,25} Investigations of these and other novel carbon-heteroatom couplings from octahedral d⁶ metal centers continue in our laboratories.

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Supporting Information Available: Spectroscopic data for compounds **1**, **5**, and **6** and crystal structure data for **1** (13 pages, print/PDF). See any current masthead page for ordering instructions and Web access information.

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(17) Possible sources of variability in k_{obs} (acetone-*d*₆): (a) Trace amounts of a Lewis acidic impurity could cause erratic kinetic behavior. (b) The acetone reactions may not be strictly first order. In contrast to thermolysis in less polar solvents, >95% of the reaction proceeds via a pathway that depends on the concentration of acetate anions.^{23a} This will be a function of the concentration of **1**, that of the major product, dppePtMe(OAc) (**3**) and of any acetic acid¹⁶ produced (Scheme 1).

(18) The disappearance of starting material was monitored by ¹H NMR for two half-lives, beyond which, the dynamic range of the NMR spectrometer hindered accurate data collection.

(19) During the course of the thermolysis reaction, conversion of [(*n*-Bu)₄N]OAc to (*n*-Bu)₃N and BuOAc occurs at a rate approximately an order of magnitude slower than the Pt(IV) reductive eliminations.

(20) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889 and references therein.

(21) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 4522 and references therein.

(22) $k_{\text{C–O}} = k_{\text{obs}}(\% \text{ C–O}/100)$ and $k_{\text{C–C}} = k_{\text{obs}}(\% \text{ C–C}/100)$ were calculated using the final product ratios as measured by integration of ¹H NMR signals for Pt(II)–Me groups and of methyl acetate against an internal standard. Product ratios estimated by ³¹P NMR through the majority of the reaction were consistent with the final ratios. However, spectra taken at very early reaction times indicated higher amounts of C–C coupling. The low signal-to-noise ratios at early reaction times makes quantitation difficult. A trace amount of acid consumed during the reaction could be responsible for a higher initial C–C coupling rate as could a variable acetate concentration (see ref 17).

(23) (a) See the Supporting Information for a derivation for the rate law corresponding to the mechanism in Scheme 1. (b) If $(k_{-1} + k_2)[\text{OAc}] \gg k_3$, then $k_{\text{C–O}} \approx k_1 k_2 / (k_{-1} + k_2)$.

(24) An even faster rate and higher C–C coupling percentage is observed for the triflate analogue. dppePtMe₃(OTf) is reported to react below room temperature in acetone-*d*₆ to yield exclusively ethane and dppePtMe(OTf).²¹

(25) This strategy of deactivating the products of alkane functionalization toward further oxidation via esterification as RO₂CCF₃ or ROSO₃H has been employed successfully in a number of systems. See references in recent review article: Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.