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Reductive Elimination and Dissociative *β*-Hydride Abstraction from Pt(IV) Hydroxide and Methoxide Complexes

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The platinum(IV) hydroxide and methoxide complexes *fac*-(dppbz)PtMe$_3$(OR) (dppbz = *o*-bis(diphenylphosphino)benzene; R = H (**1**), CH$_3$ (**2**)) have been prepared and characterized. Thermolysis of hydroxide **1** produces (dppbz)PtMe$_2$ (**3**) and methanol in a rare example of directly observed sp^3 carbon−oxygen reductive elimination from a metal center to form an alcohol. Competitive carbon−carbon reductive elimination to form (dppbz)PtMe(OH) (**5**) and ethane also occurs. In contrast, the major reaction observed upon thermolysis of the methoxide analog **2** is neither carbon−oxygen nor carbon−carbon reductive elimination. Instead, products expected from formal *β*-hydride elimination followed by carbon−hydrogen reductive elimination are detected. Mechanistic studies suggest the operation of an alternative mechanism to that most commonly accepted for this fundamental reaction; a dissociative *β*-hydride abstraction pathway is proposed.

Introduction

Reductive elimination and *β*-hydride elimination are two fundamental transformations that are ubiquitous in metal-mediated processes. Consequently, significant effort has been directed toward understanding their mechanisms.[1] However, studies of these elimination reactions have largely focused on systems involving metal−carbon bonds; comparatively little is known about the related reactions with metal−heteroatom linkages. The fact that there are fewer studies of the mechanisms of fundamental reactions of late metal hydroxides and alkoxides relative to those of late metal alkyls may be attributable to there being fewer monomeric hydroxide and alkoxide complexes available for study.[2] Since theoretical and experimental studies have shown that late metal M−O bonds are at least as strong as their alkyl analogs,[3] it has been proposed that the relative scarcity of such species may in fact stem from their access to low energy decomposition pathways,[2a,c] including reductive elimination and *β*-hydride elimination. Thus, the elucidation of the mechanisms of these fundamental reactions for metal−heteroatom species is important. Recent contributions appear to indicate that the more polar nature of metal−heteroatom bonds and the presence of heteroatom electron lone pairs can result in significant differences in reaction mechanisms from those of their metal−carbon analogs. This contribution focuses on these differences in reductive elimination and *β*-hydride elimination pathways when hydroxide and alkoxide groups are involved.

In contrast to the large number of examples and mechanistic studies of C−C reductive elimination reactions,[4] there are relatively few reported direct observations of C−O reductive

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987; pp 322−353; 386−389. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2005; pp 55−60.

(2) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44. (c) Roesky, H. W.; Singh, S.; Yusuff, K. K. M.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **2006**, *106*, 3813.

(3) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (b) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *199*, 12800.

(4) Reference 1b, pp 170−175.

(5) (a) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (b) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2046, and references therein. (c) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (d) Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224. (e) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 10718. (f) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775.

(6) (a) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (b) Widenhoefer, R. A.; Buchwald, S. L *J. Am. Chem. Soc.* **1998**, *120*, 6504, and references therein.

(7) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

(8) (a) Matsunaga, P. T.; Mavropoulos, J. C.; Hillhouse, G. L. *Polyhedron* **1995**, *14*, 175. Note that the reductive elimination from Ni(II) is promoted by oxidants, and thus Ni(III) is likely involved in the reactions. (b) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 8135. (c) Koo, K.; Hillhouse, G. L. *Organometallics* **1998**, *17*, 2924.

(9) Haarman, H. F.; Kaagman, J.-W. F.; Smeets, W. J. J.; Spek, A. L.; Vrieze, K. *Inorg. Chim. Acta* **1998**, *270*, 34.

(10) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790.

(11) (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. (c) Canty, A. J.; Denney, M. C.; van Koten, G.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 5432.

(12) Thompson, J. S.; Randall, S. L.; Atwood, J. D. *Organometallics* **1991**, *10*, 3906. See ref 5a for more information on this reaction.

(13) Sanford, M. S.; Groves, J. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 588.

(14) (a) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82. (b) Khusnutdinova, J. R.; Zavalij, P. Y.; Vedernikov, A. N. *Organometallics* **2007**, *26*, 3466. (c) Khusnutdinova, J. R.; Newman, L. L.; Zavalij, P. Y.; Lam, Y.-F.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2008**, *130*, 2174.

(15) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576, and references therein.

(16) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75.

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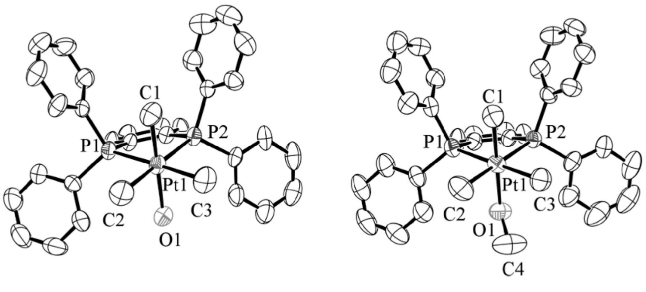
elimination.[5−16] Those cases involving alkyl and hydroxide groups to produce alcohols, a potentially highly valuable product release step in catalysis, are exceptionally rare.[14,16] Notably, several examples of C(sp^3)−O reductive elimination reactions to form methyl aryl ethers and methyl carboxylates have recently been reported.[15] In these reactions, which occur at Pt(IV) centers, a common two-step pathway involving dissociation of the anionic oxygen group followed by nucleophilic attack of the oxyanion on the cationic Pt(IV) alkyl intermediate has been proposed. A similar nucleophilic coupling has also been proposed as the product-forming step in platinum-catalyzed alkane oxidation reactions.[16,17] In contrast to these C−O reductive elimination reactions, C−C bond formation typically occurs via a concerted three-centered transition state.[4] Thus, the mechanisms of reductive elimination involving metal−oxygen bonds can be quite different than those involving metal−carbon bonds.

Whereas alkyl C−O reductive elimination is a relatively rare reaction, *β*-hydride elimination is accepted as a common and predictable decomposition pathway for transition metal alkoxides. Notably, the reaction of alcohols and bases with transition metal halides is a traditional method of preparing metal hydride complexes.[18] Such reactions are thought to proceed via metathesis of the halide for an alkoxide group followed by *β*-hydride elimination from the intermediate metal-alkoxide species. It has been generally assumed that the latter step proceeds by the same mechanism that has been established for metal alkyl complexes.[19] As described in organometallic textbooks, for metal alkyl complexes, the hydride moves from the *β*-carbon of the alkyl through a four-coordinate planar transition state to an open site on the metal that is *cis* to the alkyl ligand. This *cis* open site is a requirement for this mechanism, and the stability of many metal alkyls with *β*-hydrogens has been attributed to the lack of labile ancillary ligands or other access to a *cis* open site on the metal.[1] However, a few examples of *β*-hydride elimination from metal alkoxide complexes have been recently reported wherein a *cis* open site does not appear to be available,[20−23] suggesting that an alternative mechanism is needed in at least some cases to account for this fundamental reaction when metal−heteroatom bonds are involved.

In this contribution, we report the synthesis, characterization, and thermal reactivity of the monomeric platinum(IV) hydroxide and alkoxide complexes *fac*-(dppbz)PtMe$_3$(OR) (dppbz = *o*-bis-(diphenylphosphino)benzene; R = H (**1**), CH$_3$ (**2**)). C−O reductive elimination was observed upon thermolysis of the platinum(IV)-hydroxide complex **1** in C$_6$D$_6$. This is the first direct observation of carbon−oxygen reductive elimination involving an alkyl and hydroxide group to form alcohol in a nonaqueous solvent system. Studies of this reaction indicate that the mechanism is different than that of C−C reductive elimination. Despite hydroxide being a relatively poor leaving group and the reaction taking place in a nonpolar solvent, dissociation of the heteroatom group followed by nucleophilic C−O coupling, similar to the mechanism proposed for other C(sp^3)−O couplings from Pt(IV),[15] is indicated. Given the rarity of the formation of an alcohol by C(sp^3)−O reductive elimination from a metal center[14a,b] and the promise of this coupling as a product-forming step in catalysis, this mechanistic insight is relevant to rational catalyst design efforts.



1 **2**

Figure 1. ORTEP drawing of complexes **1** and **2**, with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

In contrast to the C−O reductive elimination reaction observed from the hydroxide complex **1**, thermolysis of the methoxide analog **2** leads primarily to products expected from formal *β*-hydride elimination followed by C−H reductive elimination. Notably, this *formal β-hydride elimination* occurs from a coordinatively saturated alkoxide complex without an easily accessible *cis* open site. Evidence of alkoxide dissociation is presented and a *dissociative β-hydride abstraction mechanism*, distinct from the traditional *β*-hydride elimination mechanism of metal alkyls, is proposed for this reaction. This dissociative *β*-hydride abstraction may be a general and unappreciated decomposition pathway for metal alkoxides and amide species. It is significant that both alkyl C−O reductive elimination and formal *β*-hydride elimination from the Pt(IV) complexes reported herein involve initial heterolytic cleavage of the Pt−O bond. A similar reaction step for a metal alkyl species (heterolytic M−C bond cleavage) would be unreasonable. Thus, entirely different mechanisms for these fundamental reactions of reductive elimination and *β*-hydride elimination, distinct from those of metal alkyls, are possible for metal alkoxides.

Results

Synthesis and Characterization of Platinum Complexes 1 and 2. The monomeric Pt(IV) hydroxide and methoxide complexes, *fac*-(dppbz)PtMe$_3$(OR) (R = H (**1**) and CH$_3$ (**2**)), were prepared via metathesis reactions of the appropriate potassium salts with the Pt(IV) trifluoroacetate and acetate complexes, respectively. Reaction of *fac*-(dppbz)PtMe$_3$(O$_2$CCF$_3$) with excess KOH proceeds in toluene at 35 °C to form the Pt(IV) hydroxide complex **1**, which was isolated in 95% yield. The analogous Pt(IV) methoxide complex **2** was prepared by reaction of *fac*-(dppbz)PtMe$_3$(O$_2$CCH$_3$) with excess KOMe in toluene at ambient temperature and was isolated in 75% yield. Both **1** and **2** have been characterized by X-ray crystallography, and the ORTEP diagrams appear in Figure 1. Selected bond lengths and angles are presented in Table 1. Complete details of the structures are given in Supporting Information.

Both species **1** and **2** exhibit the characteristic ^{1}H NMR signals for *fac*-L$_2$PtMe$_3$(X) species. In the ^{1}H NMR spectrum of each species, there are signals for two equivalent equatorial and one axial Pt(IV) methyl groups, with both signals exhibiting coupling to ^{195}Pt and ^{31}P. The ^{1}H NMR spectrum for **1** in C$_6$D$_6$ shows a Pt(IV) hydroxide signal at −2.39 ppm, which exhibits coupling to ^{195}Pt ($^2J_{\text{Pt−H}}$ = 13 Hz) as well as to two equivalent

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(17) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 10235.

(18) Reference 1a, p 90.

(19) Reference 1a, p 95.

(20) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582.

(21) Blum, O.; Milstein, D. *J. Organomet. Chem.* **2000**, *479*, 593–594.

(22) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6826.

(23) Fafard, C. M.; Ozerov, O. V. *Inorg. Chim. Acta* **2007**, *360*, 286.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Structures of 1 and 2

1		2	
Pt−C1	2.061(10)	Pt−C1	2.080(6)
Pt−C2	2.087(10)	Pt−C2	2.072(7)
Pt−C3	2.090(9)	Pt−C3	2.095(7)
Pt−P1	2.352(2)	Pt−P1	2.3559(17)
Pt−P2	2.356(2)	Pt−P2	2.3650(17)
Pt−O1	2.116(7)	Pt−O1	2.138(4)
		O1−C4	1.410(10)
		C4−O1−Pt	120.2(5)
P1−Pt−P2	83.98(8)	P1−Pt−P2	83.89(6)
C2−Pt−C3	86.4(4)	C2−Pt−C3	88.1(3)
O1−Pt−P1	88.77(19)	O1−Pt−P1	86.58(14)
O1−Pt−P2	90.0(2)	O1−Pt−P2	87.43(14)
O1−Pt−C2	88.3(4)	O1−Pt−C2	91.1(3)
O1−Pt−C3	88.5(4)	O1−Pt−C3	92.1(2)
O1−Pt−C1	175.7(4)	O1−Pt−C1	177.7(2)

^{31}P nuclei ($^3J_{P-H}$ = 2.7 Hz). In the ^{1}H NMR spectrum of **2** in C_6D_6, a methoxide signal is observed at 4.04 ppm with Pt satellites ($^3J_{Pt-H}$ = 24.4 Hz). Finally, in the ^{31}P{^{1}H} NMR spectra, both **1** and **2** display singlets with ^{195}Pt satellites at 15.3 and 18.2 ppm, with $^1J_{Pt-P}$ = 1161 and 1159 Hz, respectively.

The X-ray structures of **1** and **2** both show a distorted octahedral geometry around the Pt(IV) center with the two structures exhibiting similar angles and bond distances between the phosphorus and platinum atoms. Notably, the axial and equatorial platinum−methyl bond lengths are very similar in **1** (2.06 Å (ax) vs. 2.09 Å (eq)), and the same is observed for **2** (2.08 Å (ax) vs 2.07 and 2.10 Å (eq)), suggesting that the *trans* influence of hydroxide and methoxide are both reasonably similar to that of a triaryl substituted phosphine at a Pt(IV) center.

The Pt−O bond lengths of previously reported Pt(IV) hydroxide complexes range from 1.94 to 2.08 Å,[24] yet none of these contain a platinum(IV) hydroxide species wherein the hydroxo-group is *trans* to a methyl group. Similarly, in related structurally characterized platinum(IV) methoxide complexes in which the methoxide ligands are *trans* to hydroxide, hydroperoxide-, methoxide-, acetate-, or pyridine-derived ligands, the Pt(IV)−O bonds range in length from 1.88 to 2.05 Å.[14b,25] A Pt−O bond length of 2.116(7) Å is observed in the crystal structure of **1**, and the Pt−O bond length of **2** is 2.138(4) Å. These values are significantly longer than previously reported Pt−O bond lengths in Pt(IV) hydroxide and methoxide complexes, presumably due to the stronger *trans* influence of the axial methyl group relative to those of OH, OCH_3, Cl, or NR_3.

Equilibrium between 1 and 2. It has been shown that a hydroxide ligand can exchange with an alcohol at a transition metal center to generate a metal alkoxide species and water in a reversible reaction.[2a,3a] Similar reactivity was found for the hydroxide and methoxide complexes **1** and **2** which were observed to equilibrate with one another in the presence of methanol or water, respectively (Scheme 1). The equilibrium constant for this reaction was estimated by monitoring a solution prepared by the addition of water (ca. 2 equiv) to **2** in C_6D_6 (6.3 mM) over 3 days at ambient temperature. Examination of the solution by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed the formation of **1** and methanol as the concentration of **2** decreased. Equilibrium was reached after ca. 19 h at ambient temperature (Scheme 1, Figure 2).

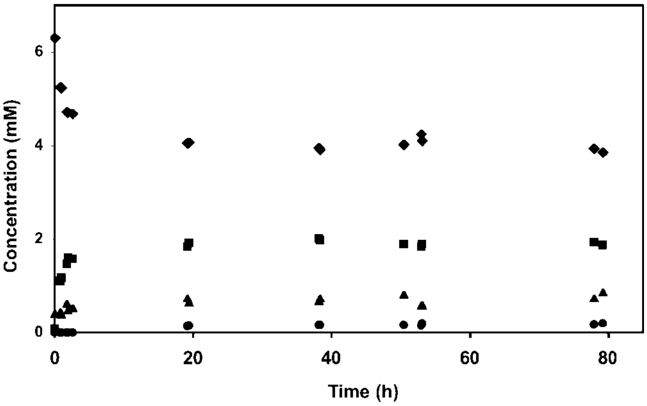

Figure 2. Reactant and product concentrations at 23 °C in C_6D_6 for reaction between **2** ($[\mathbf{2}]_0$ = 6.3 mM) and water ($[\text{water}]_0$ = 13 mM) to form **1** and methanol. Small amounts of **3** ($[\mathbf{3}]_0$ = 0.4 mM) and *fac*-(dppbz)$PtMe_3(OCH_2OCH_3)$ (**4**) also formed. (**1** = ■, **2** =◆, **3** =▲, **4** = ●).

The equilibrium constant (K_{eq} = ca. 0.3) for this reaction was calculated from eq 1 using the equilibrium concentrations measured by ^{1}H NMR spectroscopy for **1**, **2**, and methanol and calculated for water.[26]

$$K_{eq}=([\mathbf{1}][CH_3OH])/([\mathbf{2}][H_2O]) \qquad (1)$$

The Pt(II) species (dppbz)$PtMe_2$, **3**,[27] was detected as early as 10 h into the reaction and accounted for 5−10% of the total Pt species in solution at equilibrium. In addition, a small amount (ca. 2−3%) of *fac*-(dppbz)$PtMe_3(OCH_2OCH_3)$ (**4**, vide infra) was also observed. The presence of these other products limited the accuracy to which K_{eq} could be determined.[28]

In a separate experiment, the reverse reaction, that between methanol and **1**, was also demonstrated. A solution of methanol (700 mM) and **1** (14 mM) in THF-d_8 at ambient temperature was prepared, and formation of the methoxide complex **2** (ca. 50%) was observed by ^{31}P{^{1}H} NMR spectroscopy within 10 min. As with the reaction of **2** and water, formation of a small amount of the Pt(II) complex (dppbz)$PtMe_2$ (**3**) (<10%) was noted.

Thermolysis of 1. Thermolysis of **1** (4.8−9.5 mM) at 120 °C in C_6D_6 yielded the C−O reductive elimination products (dppbz)$PtMe_2$ (**3**) (74−93%) and methanol (34−68%), as the major organometallic and organic products, respectively (Scheme 2, Table 2). The C−C reductive elimination products (dppbz)-PtMe(OH) (**5**) (7−26%) and ethane (8−25%)[29] were also observed in these reactions. Thus, the thermolysis of **1** is similar to that of the related *fac*-$L_2PtMe_3(OR)$ complexes (L_2 = dppe

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[24] Based on a search of Pt(IV) hydroxide crystal structures in the Cambridge Structural Database using Conquest 1.8, Copyright CCDC 2006. Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389.

[25] (a) Lee, Y.-A.; Jung, O.-S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3868. (b) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608. (c) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2005**, *24*, 482.

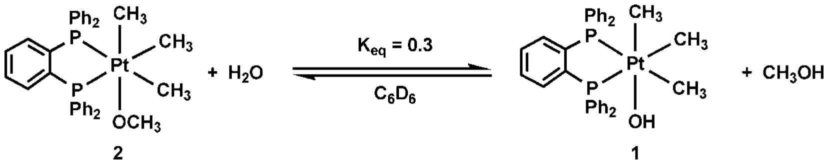
[26] The concentrations of complexes **1**−**3** and methanol were determined by integration of their respective ^{1}H NMR signals against an internal standard (toluene). The ^{1}H NMR signal for water was broad and overlapped with the axial methyl signals of **1** and **3** and therefore was not integrated. The concentration of water used in the calculation of the equilibrium constant was taken to be the initial concentration of water ($[H_2O]_0$) with the concentration of methanol formed ($[CH_3OH]_t$) deducted from it.

[27] (a) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962. (b) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442.

[28] Complex **3** is a product of decomposition reactions from both **1** and **2**. Methanol can also be generated in these reactions.

[29] As a result of the volatility of several of the organic species (methane, ethane, etc.), it is expected that some portion of these products is present in the headspace of the NMR tube, and therefore integrated yields are low estimates of the actual yields.

Scheme 1



Scheme 2

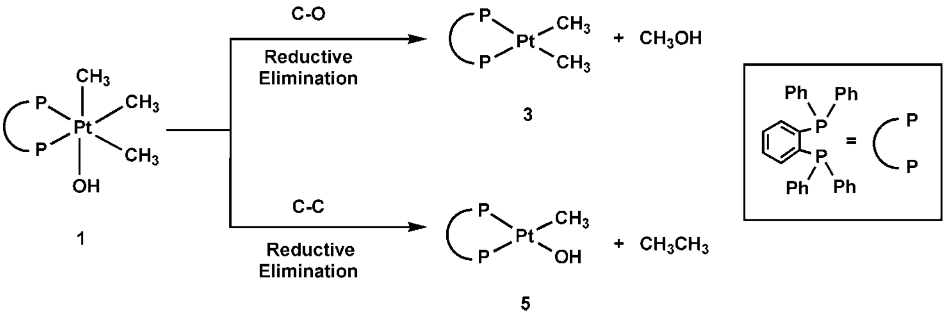


Table 2. Yields of Products from Thermolyses of 1 (4.8−9.5 mM) in C_6D_6 at 120 °C with and without Additives of H_2O (53 mM) and $CsOH \cdot H_2O$ (500 mM)

product	% yield	% yield (with H_2O)	% yield (with $CsOH \cdot H_2O$)
(dppbz)$PtMe_2$ (**3**)	74−93	87−90	93−97
CH_3OH	34−68	51−72	72−76
(dppbz)PtMe(OH) (**5**)	7−26	10−13	3−7
C_2H_6[29]	8−25	10−13	3−7

Table 3. Yields of Products in Thermolyses of 2 (6−7 mM) in C_6D_6 at 100 °C[32,33]

platinum product	% yield	organic product	% yield
(dppbz)$PtMe_2$ (**3**)	94−100	$(CH_3)_2O$	ca. 1
(dppbz)PtMe(OMe) (**7**)	0−6	C_2H_6[29]	3−7
		CH_2O	ca. 1
		CH_3OCHO	32−44
		$(CH_3O)_2CO$	21−33
		CH_4[29]	12−20
		CH_3OH	19−21

or dppbz, OR = carboxylate or aryloxide; dppe = 1,2-bis(diphenylphosphino)ethane) in which C−O and C−C reductive elimination reactions occurred competitively.[15] Notably, while the thermolyses of the related *fac*-(dppe)$PtMe_3$(OAc) and *fac*-(dppbz)$PtMe_3$(OAr) complexes exhibited reproducible first-order kinetics for the disappearance of the Pt(IV) complexes, the time required for complete conversion of different samples of **1** was observed to range from 5 h to more than 300 h at 120 °C.

In the thermolyses of **1**, although the Pt product of C−O coupling, **3**, was formed in high yield, the organic product, methanol, was observed in significantly lower yield. In addition, the ^{1}H NMR spectra of the samples upon completion of thermolysis showed the presence of other organic products: methyl formate (0−3%), methane (1−7%), and minor amounts of three unidentified organic products.[30] It is also of interest that other Pt(IV) species, *fac*-(dppbz)$PtMe_3$(OMe) (**2**), *fac*-(dppbz)$PtMe_3$(OCH_2OCH_3) (**4**), and an unidentified *fac*-(dppbz)$PtMe_3$(X) species (**6**),[31] were observed transiently during thermolysis of **1**. The maximum yields of **2**, **4**, and **6** detected at any point in the thermolysis were 12%, 5%, and 2%, respectively. No signals for these species remained visible in either the ^{1}H or ^{31}P NMR spectra at the conclusion of the thermolysis of **1**. Mass balance of the Pt was confirmed in the reaction as **3** and **5** were the only Pt-containing species in solution upon reaction completion and the sum of the concentrations of these complexes matched the starting concentration of **1**.

Thermolysis of 2. It was anticipated that if carbon−oxygen reductive elimination were to occur from **2**, (dppbz)$PtMe_2$ (**3**) and dimethyl ether would be formed. Similarly, C−C reductive elimination from **2** would generate (dppbz)PtMe(OMe) (**7**) and ethane. Thermolysis reactions of **2** at 100 °C in C_6D_6 proceeded to completion over 33−35 days and produced **3** as the major organometallic product (94−100%) (Table 3). However, less than 1% of the corresponding organic product from the C−O coupling reaction, dimethyl ether, was detected. Instead, a variety of other organic products, including methyl formate and dimethyl carbonate, were observed (Table 3).[32] The C−C reductive elimination products, (dppbz)PtMe(OMe) (**7**) (0−6%) and ethane (3−7%), were observed as very minor products in this thermolysis reaction.

As was the case in the thermolysis of **1**, transient organometallic species were observed during the reaction. Small amounts of *fac*-(dppbz)$PtMe_3$(OCH_2OCH_3) (**4**) (maximum of 7%) and *fac*-(dppbz)$PtMe_3$(OH) (**1**) (maximum of 5%) were detected at intermediate reaction times.

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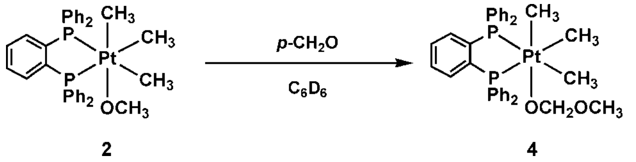
(30) The presence of three minor unidentified products was indicated by the observation of three small singlets at 3.49 ppm (ca. 1%), 4.68 ppm (0−5%), and 5.25 ppm (0−3%). Estimated yields of these unknown organic products (calculated on the assumption that the integral of each singlet represents three hydrogens) indicate that the contribution of these species to the overall product distribution is small.

(31) The coupling patterns observed in the ^{1}H NMR spectrum of complex **6** are similar to those observed for other *fac*-(dppbz)$PtMe_3$X complexes. The coupling constant ($^1J_{PtP}$ = 1114 Hz) associated with the phosphorus signal of this complex in the $^{31}P\{^1H\}$ NMR spectrum of this complex is comparable to those of other Pt(IV) (1080−1200 Hz), rather than Pt(II) (1700−1800 Hz), dppbz complexes, in which the phosphines are *trans* to methyl groups. No hydroxide signal was observed for **6**; see Experimental Section for NMR characterization of **6**.

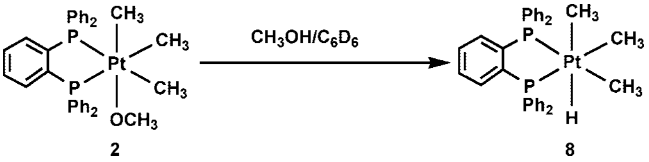
(32) In addition to the species listed in Table 3, two minor unidentified species showing singlets at 3.47 (0−3%) and 3.27 (ca.1%) ppm in the ^{1}H NMR spectrum were also evident. Estimated yields of these unknown organic products (calculated on the assumption that the integral of each singlet represents three hydrogens) indicate that the contribution of these species to the overall product distribution is small.

(33) Note that the total yield of organic products, including the estimates for the two unidentified species at 3.47 and 3.27, is 92 ± 9% (see refs 29 and 32). Methane is not included, as it is a byproduct of the formation of formaldehyde, methyl formate, and dimethyl carbonate (vide infra). The total Pt product yield is 100 ± 4%.

Scheme 3



Scheme 4



Reaction of 2 with Formaldehyde. The formation of species **4** in the thermolysis of **2** suggests a possible insertion reaction of CH_2O into a Pt(IV)−OCH_3 bond. To investigate this proposal, 10 equiv of paraformaldehyde (*p*-CH_2O) was added to **2** in C_6D_6 (7 mM). After only 15 min at ambient temperature, the platinum species identifiable by NMR spectroscopy were **2** and **4** in roughly equal amounts, and a trace amount of **3** (Scheme 3). The addition of an even greater excess of *p*-CH_2O (>33 equiv, not all of which initially dissolved) to **2** in C_6D_6 at ambient temperature resulted in the complete conversion of **2** to *fac*-(dppbz)$PtMe_3(OCH_2OCH_3)$ (**4**) and several unidentified *fac*-(dppbz)$PtMe_3(X)$[34] species within 15 min. The unidentified complexes are most likely the products of multiple insertions of CH_2O into a Pt−O bond based on the similarity of their ^1H and $^{31}P\{^1H\}$ NMR spectral data to those of **4**.

Species **4** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy but could not be successfully isolated from the other insertion products. In a similar fashion, the addition of excess *p*-CH_2O to **1** in C_6D_6 produced several new Pt species, which were assigned by NMR as *fac*-(dppbz)$PtMe_3(OCH_2)_xOH$ complexes. The insertion of formaldehyde into a Pt−O bond is an interesting reaction with very little precedent in the literature.[35]

Thermolysis of 1 in the Presence of H_2O. Thermolyses of **1** in C_6D_6 in the presence of 10 equiv of water (53 mM) at 120 °C in C_6D_6 produced consistently higher yields of C−O reductive elimination products, **3** (87−90%), and methanol (51−72%) than did thermolyses of **1** without added water (Table 2). The products of C−C reductive elimination, **5** and ethane, were observed as minor products (10−13%). These thermolyses of **1** demonstrated not only increased yields of methanol but also increased consistency in the yields of the different products. For example, the yield of **3** produced in the thermolyses samples of **1** to which no water was added ranged from 74−93%. With the addition of water, this range was narrowed to 87−90%. It should also be noted that in "anhydrous" samples, the heating time required for complete conversion of **1** (5.1−9.5 mM) varied from 5 to 300 h at 120 °C, while the reaction time for **1** at 120 °C in the presence of 10 equiv of water was consistently less than 18 h. Thus, variable amounts of adventitious water in the "anhydrous" samples may have contributed to the lack of uniformity in reaction time and product yields.

A maximum of 7% yield of the methoxide complex **2** was detected at intermediate reaction times during the thermolyses of **1** with added water, less than was observed in the anhydrous thermolyses (12%). Methane was still detected (3−6%), but methyl formate and the three other signals ascribed to minor organic products in the ^1H NMR spectrum (vide supra) were not observed.[36]

Thermolysis of 1 in the Presence of CsOH and H_2O. Thermolysis of **1** in the presence of an excess of CsOH·H_2O (ca. 10 equiv, 50 mM) at 120 °C in C_6D_6 produced much higher and more consistent yields of both **3** (93−97%) and methanol (72−76%) than were seen in the absence of added hydroxide (Table 2). These reactions were complete in ca. 60−70 h. C−C reductive elimination products, **5** and ethane, were evident in low yields (3−7%). No methyl formate was detected but very small amounts of methane (2−3%) were observed in the ^1H NMR spectra.[37]

Reaction of 2 with Methanol. Upon dissolution of 2 in a 50:50 mixture of CH_3OH/C_6D_6 at ambient temperature, *fac*-(dppbz)$PtMe_3H$ (**8**) was formed within a few minutes, as observed by ^1H NMR spectroscopy (Scheme 4).

Species **2** was completely consumed in under 20 min, but the product **8** was unstable in solution, slowly decomposing to form (dppbz)$PtMe_2$ (**3**) and methane as previously reported.[27] This reaction of **2** was significantly faster than the reaction of **2** in pure C_6D_6, in which complete consumption of the same concentration of **2** typically required over 33 days at 100 °C. Dissolution of **2** in a 50:50 mixture of CD_3OD/C_6D_6 formed *fac*-(dppbz)$PtMe_3D$ (**8**-d_1) within a few minutes by ^1H NMR spectroscopy. Compound **8**-d_1 then reacted to form CH_3D and **3** over time.

Thermolysis of *fac*-(dppbz)$PtMe_3(OCD_3)$ (2-d_3). In order to demonstrate that the source of hydride in **8** was the methoxide ligand in **2**, the partially deuterated complex *fac*-(dppbz)-$PtMe_3(OCD_3)$ (**2**-d_3) was prepared from *fac*-(dppbz)$PtMe_3(O_2CCH_3)$ and $KOCD_3$. Upon thermolysis of **2**-d_3, CH_3D and ethane were observed. No other organic products were observed in significant yield by ^1H NMR spectroscopy. The observation of CH_3D is consistent with the formation of *fac*-(dppbz)$PtMe_3D$ (**8**-d_1), followed by C-D reductive elimination.

Reaction of 2 with [18-crown-6-K][OCD_3]. When an excess of [18-crown-6-K][OCD_3] was added to a thermolysis reaction of **2** in C_6D_6, slow exchange of OCD_3 into the methoxide position of **2** was observed via ^1H NMR spectroscopy in competition with formation of the Pt(II) product (dppbz)$PtMe_2$ (**3**). After 2 h at 100 °C, ca. 10% of the methoxide complex **2** had been converted to **2**-d_3, while approximately 10% of the initial quantity of **2** had been converted to (dppbz)$PtMe_2$ (**3**).

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(34) The coupling patterns of the ^1H NMR spectra of these complexes are similar to those observed for other *fac*- (dppbz)$PtMe_3X$ complexes. The coupling constants ($^1J_{PtP}$ = 1140−1160 Hz) associated with the phosphorus signals of these complexes in the $^{31}P\{^1H\}$ NMR spectra of these complexes are comparable to other Pt(IV) (1080−1200 Hz), rather than Pt(II) (1700−1800 Hz), dppbz complexes, in which the phosphines are *trans* to methyl groups.

(35) (a) Litz, K. E.; Banaszak Holl, M. M.; Kampf, J. W.; Carpenter, G. B. *Inorg. Chem.* **1998**, *37*, 6461. (b) For a similar reaction at Ni(II) see ref 8b.

(36) The presence of excess water in the thermolyses of **1** also slightly increased the maximum observed yield of the unidentified transient Pt(IV) species (**6**) from 2% to 5%. Notably, it was shown in independent experiments that the addition of water to the Pt(IV) hydroxide complex **1** (5.7mM in C_6D_6) also resulted in the generation of species **6** at ambient temperature (80% conversion over 4 weeks).[31] However, pure samples of **6** could not be isolated, which inhibited further characterization. The very slow formation of **6** (weeks at ambient temperature) argues against characterization of **6** as a simple hydrogen-bonded species **1**·H_2O. A sample of **6** in THF was analyzed by ESI-MS and shows a signal at *m*/*z* = 1478 with an isotopic pattern indicative of two platinum atoms. The molar mass of a dimeric complex with the form of [(dppbz)$PtMe_3(OH)$·$H_2O]_2$ would be 1443 g/mol.

(37) In addition, two other trace organic products (4.68 ppm, 0−1%; 5.25 ppm, 3−4%)[30] were observed.

Discussion

Reductive Elimination from Pt(IV). A variety of Pt(IV) model complexes have been observed to exhibit sp^3 C−Y (Y = hydrogen, carbon, pnictogen, chalcogen, halogen) reductive elimination.[15,38−54] Many of these reactions have been studied in detail and their mechanisms elucidated. Reductive eliminations from Pt(IV) complexes can be categorized into two basic mechanisms: one involving concerted bond formation and one proceeding via nucleophilic attack. These two mechanism types generally, but not exclusively, correspond to C−C/C−H and C−heteroatom reductive elimination, respectively.

The concerted reductive elimination of a hydrocarbon from isolated octahedral Pt(IV) complexes via C−H or C−C reductive elimination has been shown to generally require preliminary ligand loss to form a five-coordinate intermediate.[27] Reductive elimination of the hydrocarbon then takes place in a concerted fashion through a three-centered (C-M-H or C-M-C) transition state.[54,55] Initial ligand loss from the six-coordinate compound can occur via ancillary neutral ligand dissociation,[51,54] dechelation of one "arm" of a polydentate ligand,[27,39] or dissociation of an anionic X$^-$ ligand to form a cationic five-coordinate species.[15,38,41] Recently, neutral five-coordinate Pt(IV) alkyl species have been isolated.[40] These five-coordinate complexes undergo thermally promoted C−C reductive elimination without preliminary ancillary ligand dissociation,[40] consistent with the idea that the formation of a five-coordinate species allows for direct C−C coupling.

There is one study in the literature that reports evidence for a direct C−H reductive elimination from an octahedral Pt(IV) complex.[27] In that investigation, *fac*-(dppbz)PtMe$_3$H, **8**, and the related complex *fac*-(dppe)PtMe$_3$H were proposed to directly eliminate methane from the six-coordinate geometry because of the very similar rates and activation parameters displayed by the two reactions, in spite of the difference in rigidity between the dppe and dppbz ligands.[56]

Bercaw and co-workers have demonstrated that in their Pt(IV) system sp^3 C−O bond formation proceeds via an S$_N$2 reaction, in which inversion of stereochemistry at carbon was observed.[17b] Similarly, Groves and Sanford have reported a Rh(III) system that undergoes sp^3 C−O reductive elimination reactions in which both S$_N$2 hallmarks of inversion of stereochemistry and higher reaction rates for primary than for secondary alkyl groups were observed.[13] Vedernikov et al. have also reported reductive elimination reactions to form sp^3 C−O bonds in aqueous solution which seem to proceed via nucleophilic attack.[14a,b] That the nucleophilic attack mechanism has been documented with a variety of metals and heteroatom groups speaks to its generality. However, a couple of recent examples indicate that C−heteroatom coupling from high valent d^6 late metals does not occur exclusively by this nucleophilic attack mechanism. Concerted reductive elimination of methyl iodide from a Rh(III) complex has recently been proposed by Milstein.[57] Notably, this elimination occurs from a five- rather than a six-coordinate species, perhaps indicating that the intimate mechanism of coupling bears some resemblance to that of C−C reductive elimination reactions from high valent d^6 metal centers. Furthermore, Vedernikov has recently reported a concerted C(sp^3)−O reductive elimination from Pt(IV) to form epoxides.[14c] Thus, evidently both concerted and nucleophilic attack mechanisms are possible for C(sp^3)−heteroatom bond formation from high valent d^6 metals. Overall, there are relatively few examples of C(sp^3)−heteroatom coupling reactions from d^6 metal centers and the nucleophilic attack pathway appears to be the more common mechanism of reaction.

Thermal reactions of a variety of *fac*-(L$_2$)PtMe$_3$X complexes with different X groups (L$_2$ = dppe, dppbz; X = I, O$_2$CR, OAr, N(R)SO$_2$Ar) have been found to yield alkyl C−heteroatom reductive elimination products.[15,38,41] Evidence has been presented indicating that all of these C−heteroatom couplings occur by a common mechanism as shown in Scheme 5. Following dissociation of X$^-$ and formation of a five-coordinate Pt(IV) cation, nucleophilic attack of the X$^-$ group on the axial methyl group of the Pt(IV) cation forms MeX and (L$_2$)PtMe$_2$. Notably, as a five-coordinate Pt(IV) intermediate bearing multiple methyl groups is formed in these systems, C−C reductive elimination to form ethane is also viable and observed.

Mechanism of Reductive Elimination from *fac*-(dppbz)PtMe$_3$(OH) (1). The Pt(IV) hydroxide complex **1** undergoes C−O reductive elimination in competition with C−C reductive elimination, behavior that is remarkably similar to that observed for the aryloxide and carboxylate analogues *fac*-(dppbz)PtMe$_3$(OR) (OR = *p*-XC$_6$H$_4$O, OAc, O$_2$CCF$_3$).[15] However, the organic products observed upon thermolysis of **1** are more varied than those observed in the thermolysis reactions of the related carboxylate and aryloxide compounds, wherein the products were limited to those resulting directly from competitive C−O and C−C reductive elimination reactions.[15]

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(38) Goldberg, K. I.; Yan, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

(39) Arthur, K. L.; Wang, Q. L.; Bregel, D. M.; Smythe, N. A.; O'Neill, B. A.; Goldberg, K. I.; Moloy, K. G. *Organometallics* **2005**, *24*, 4624.

(40) (a) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286. (c) Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 3460. (d) Luedtke, A. T.; Goldberg, K. I. *Inorg. Chem.* **2007**, *46*, 8496.

(41) Pawlikowski, A. V.; Getty, A. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 10382.

(42) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 9538.

(43) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Organometallics* **2006**, *25*, 3996.

(44) Wik, B. J.; Ivanovic-Burmazovic, I.; Tilset, M.; Van Eldik, R. *Inorg. Chem.* **2006**, *459*, 3613.

(45) Procelewska, J.; Zahl, A.; Liehr, G.; Van Eldik, R.; Smythe, N. A.; Williams, B. S.; Goldberg, K. I. *Inorg. Chem.* **2005**, *44*, 7732.

(46) Jenkins, H. A.; Klempner, M. J.; Prokopchuk, E. M.; Puddephatt, R. J. *Inorg. Chim. Acta* **2003**, *352*, 72.

(47) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614.

(48) Vedernikov, A. N.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4102.

(49) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854.

(50) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4256.

(51) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (b) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (c) Hill, G. S.; Redina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (d) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (e) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 4522. (f) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408.

(52) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.

(53) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275.

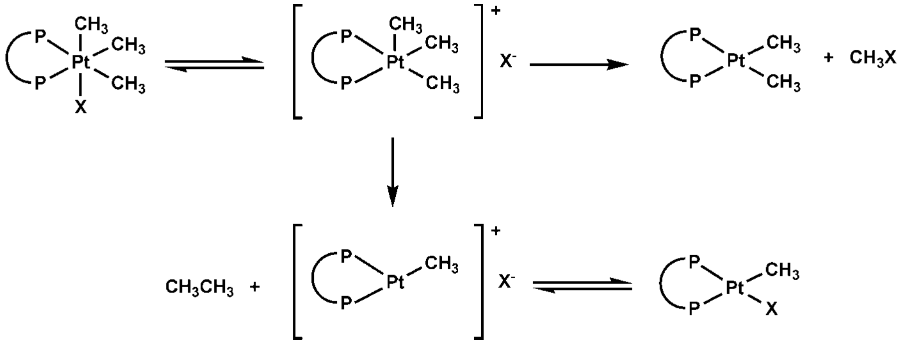
(54) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*, 157, and references therein.

(55) (a) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478. (b) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456.

(56) A computational study of models of **8** and the related dppe system with different substituents on the phosphorous atoms proposed that phosphine dissociation may occur concurrently with C-H reductive elimination. Michel, C.; Laio, A.; Mohamed, F.; Krack, M.; Parrinello, M.; Milet, A. *Organometallics* **2007**, *26*, 1241.

(57) Frech, C. M.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 12434.

Scheme 5



The presence of additional products indicates that other reactions occur concurrently with and/or subsequently to C—O and C—C reductive elimination. Notably, other Pt(IV) species were observed at intermediate times during the reaction. However, the only Pt products observed at the end of the reaction were (dppbz)PtMe$_2$ (**3**) and (dppbz)PtMe(OH) (**5**).

The reaction of methanol with **1** to produce **2** (Scheme 1) explains the observation of **2** (up to 12%) at intermediate times in the thermolysis of **1** in C_6D_6. On the basis of the equilibrium reaction shown in Scheme 1, it was anticipated that the formation of **2** could be suppressed by the addition of water to the thermolyses of **1**. Indeed, thermolysis of **1** in the presence of a large amount of water (ca. 10 equiv) led to a smaller amount of **2** (7%) observed during the reaction and higher yields of C—O reductive elimination products (dppbz)PtMe$_2$ (**3**) (from 74—93% to 87—90%) and methanol (from 34—68% to 51—72%).

If the C—O and C—C reductive eliminations from complex **1** proceed through a mechanism of initial dissociation of the hydroxide to form a five-coordinate ionic intermediate analogously to the aryloxide and carboxylate complexes *fac*-(dppbz)PtMe$_3$(OR) (Scheme 5, X = OR), then the addition of hydroxide would be expected to inhibit C—C coupling. Indeed, thermolysis of **1** in the presence of CsOH·H$_2$O shows a reduction in the yield of the C—C coupled products, **5** (3—7%) and ethane (3—7%) and produces a larger yield of C—O coupling products, **3** (93—97%) and methanol (72—76%), relative to thermolyses of **1** in the absence of hydroxide. Similar results were found when the thermolyses of *fac*-(dppbz)PtMe$_3$(OAc) and *fac*-(dppbz)PtMe$_3$(OAr) were carried out in the presence of added acetate and added aryloxides, respectively; C—C reductive elimination was inhibited and high yields of C—O coupled products were observed.[15]

The mechanism shown in Scheme 5 with X = OH is consistent with other observations as well. In the presence of water, the conjugate acid of hydroxide, both the C—O and C—C coupling reactions from **1** clearly proceeded faster, being complete in less than 18 h, compared to up to 300 h without added water. Similar behavior was observed in thermolysis of the analogous Pt(IV) carboxylate, aryloxide, and sulfonamide complexes, *fac*-(dppbz)PtMe$_3$X (X = O$_2$CR, OAr, NHSO$_2$Ar), with addition of the conjugate acids of the X$^-$ group, HO$_2$CR, HOAr and NH$_2$SO$_2$Ar, respectively.[15,41,58] Addition of the acid accelerates the formation of the five-coordinate intermediate cation by assisting initial X$^-$ dissociation through hydrogen bonding. Note that acceleration could be observed regardless of which mechanistic step in the two-step mechanism is rate-determining. If the first step were rate-limiting, hydrogen bonding would directly increase the rate of the reaction by increasing the rate of this dissociation step. The hydrogen bonding interaction would also be expected to decrease the nucleophilicity of the resulting anion and thus inhibit the second step of the reaction (C-X bond formation). However, an overall acceleration in the C-X reductive elimination could be explained on the basis of a larger influence of the hydrogen bonding on the dissociation step as was observed in the C—O reductive elimination reactions of the aryloxide analogs of **1** and **2**.[15]

Although this C(sp^3)—OH coupling from **1** may at first seem to be a logical extension of the mechanisms observed in these previous cases of C—O reductive elimination from Pt(IV),[15] it should be noted that dissociation of hydroxide in a nonpolar organic solvent such as benzene is expected to be significantly more unfavorable than dissociation of acetate or aryloxide. Notably, the only other example of directly observed C—O reductive elimination to produce an alcohol is a reaction in aqueous solution wherein hydrogen bonding to the water molecules would be expected to stabilize the hydroxide anion.[14,59]

While there seems to be a common mechanism for the reductive elimination reactions of **1** and those of the related carboxylate and aryloxide species, the C—O coupling reaction from **1** adds a new level of complexity, as the product, methanol, is not innocent in the reaction. Like water, methanol accelerates reductive elimination from **1** by assisting the dissociation of hydroxide through hydrogen bonding. As a consequence, the formation of the five-coordinate cationic intermediate is facilitated and both C—O and C—C coupling pathways accelerate as the reaction progresses.[15] This autoaccelerative effect was also observed in the thermolysis of *fac*-(dppbz)PtMe$_3$(NHSO$_2$Ar) species in which the product MeNHSO$_2$Ar can hydrogen bond and assist dissociation of the NHSO$_2$Ar$^-$ anion from the starting material.[41] The fact that the methanol product reacts with the platinum hydroxide **1** to generate water and the platinum methoxide complex **2** adds further complications, as the reaction pathways and products resulting from thermolysis of **2** become available (vide infra).

Reductive Elimination in the Thermolysis of *fac*-(dppbz)-PtMe$_3$(OMe) (2). Contrary to our initial expectations based on the observed reactivity of **1**, the organic products of C—O (dimethyl ether) and C—C (ethane) reductive elimination accounted for only a small portion of the products of thermolysis of **2** (1% and 3—7%, respectively, Table 3, vide supra). While

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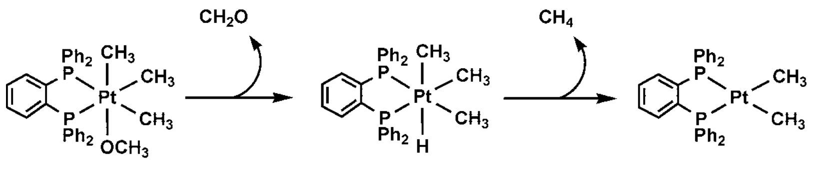
[58] Acceleration of an O-H reductive elimination from a Pd(II)(O$_2$CR)(H) complex by protic additives was recently reported by Stahl and co-workers. Konnick, M. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 5753.

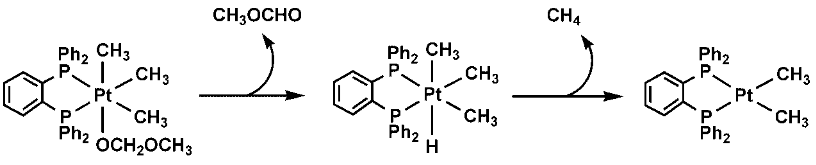
[59] Note that other examples (see ref 17b) are known in which water acts as the nucleophile. There is one other claim in the literature of direct C—O reductive elimination involving hydroxide,[12] but later experiments by Hartwig and Mann on a related system[5a] have suggested that the reaction proceeds via nucleophilic attack of the iridium hydroxide group on methyl iodide and not a reductive elimination step.

Scheme 6



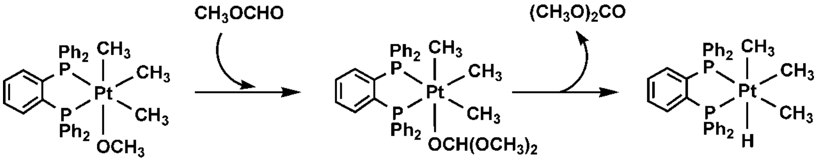
2 **8** **3**

Scheme 7



4 **8** **3**

Scheme 8



2 **8**

the small contribution from these processes prevented detailed mechanistic study of the reaction, these products are presumably generated by a mechanism similar to the one discussed for reductive elimination from **1,** with the substitution of methoxide for hydroxide as the nucleophile (Scheme 5, X = OMe).

Were C−O reductive elimination to occur from *fac*-(dppbz)PtMe$_3$(OCH$_2$OCH$_3$) (**4**, observed as an intermediate at concentrations of up to 7% of total Pt), it would yield (dppbz)PtMe$_2$ (**3**) and dimethoxymethane, the latter of which was observed by ^{1}H NMR spectroscopy (ca. 1%).[60] The lack of significant quantities of products resulting from C−O reductive elimination (dimethyl ether and dimethoxymethane) in the thermolysis of **2** points toward the existence of one or more lower energy pathways that lead to the other products observed in the reaction.

Formal β-Hydride Elimination from 2. In the thermolysis of **2**, products expected from formal β-hydride reactions, i.e., formaldehyde (and its further reaction products), methyl formate, dimethyl carbonate, and methane, were far more plentiful than those generated by C−C or C−O reductive elimination from **2**. The initial products expected for β-hydride elimination from **2** would be formaldehyde and *fac*-(dppbz)PtMe$_3$H (**8**) (Scheme 6).

Thermal studies of **8** have been reported in which **8** was observed to undergo direct C−H reductive elimination to form methane and (dppbz)PtMe$_2$ (**3**) at 25 °C.[27] Therefore, species **8** would not be stable at the 100 °C temperature of the thermolyses. Consistent with this analysis, along with a high yield of **3**, a significant amount of methane (12−20% in solution) was observed by ^{1}H NMR spectroscopy after the thermolysis of **2** in C_6D_6. When the thermolysis of **2**-d_3 was carried out under identical conditions, CH_3D was the only isotopomer of methane observed, indicating that the source of the hydride in **8** (and subsequently in methane) was the methoxy group of **2**. The actual amount of methane produced probably exceeded that measured by integration of the ^{1}H NMR signal (12−20%), as some of the methane would enter the headspace of the NMR tube.

Formaldehyde was detected only in trace amounts in the thermolyses of **2**.[61] However, *fac*-(dppbz)PtMe$_3$(OCH$_2$OCH$_3$), **4** was observed at intermediate reaction times during the thermolysis of **2** (maximum concentration of 7% of total Pt). It was shown in an independent experiment that *p*-formaldehyde reacts with **2** at room temperature to form **4**, suggesting that formaldehyde formed in the thermolysis of **2** could insert into the Pt−O bond of **2**, thereby reducing the concentration of formaldehyde. This product of formaldehyde trapping, **4**, can also undergo formal β-hydride elimination to generate *fac*-(dppbz)PtMe$_3$H (**8**) and methyl formate (Scheme 7). In contrast to formaldehyde, methyl formate does not autopolymerize and was quantified by ^{1}H NMR (32−44% yield).

A third organic product observed in the thermolysis of **2** is dimethyl carbonate (21−33% yield). In a process similar to the formation of methyl formate, the formation of dimethyl carbonate could involve the insertion of methyl formate into the Pt−O bond of **2** to form a new Pt(IV) species with a dimethoxymethoxide ligand. Subsequent β-hydride elimination would lead to **8** and dimethyl carbonate as illustrated in Scheme 8.

The Pt(IV) dimethoxymethoxide intermediate in Scheme 8 was not detected in the thermolysis of **2**. However, it should be noted that attempts to synthesize Pt(IV) species analogous to **2** with larger alkoxide ligands (e.g., ethoxide, isopropoxide) were unsuccessful, and only **3** and the organic products from formal β-hydride elimination were observed.[62]

Finally, methanol was detected in 19−21% yield in the thermolysis of **2**. It is possible that methanol was formed by the dehydrogenation of formaldehyde by the methoxide complex (**2**) to form CO, methanol and the hydride complex (**8**). The

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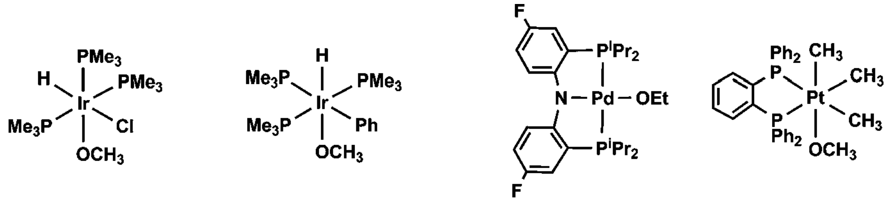
[60] Accurate integration of the signals for dimethoxymethane (δ 3.12 (s, 6H), δ 4.38 (s, 2H)) was not possible due to the very close proximity of other peaks.

[61] In organic solvents, formaldehyde autopolymerizes, and so large amounts would not be expected to be observable by ^{1}H NMR spectroscopy. Walker, J. F. *Formaldehyde*: Chapman & Hall: New York, 1964.

[62] Smythe, N. A. Reactivity Studies of Platinum(IV) Hydroxide and Methoxide Complexes and the Study of Pincer Palladium(II) Complexes as Potential Catalysts for Olefin Epoxidation. Ph.D. Thesis, University of Washington, Seattle, WA, 2004.



Blum and Milstein[20]
1995

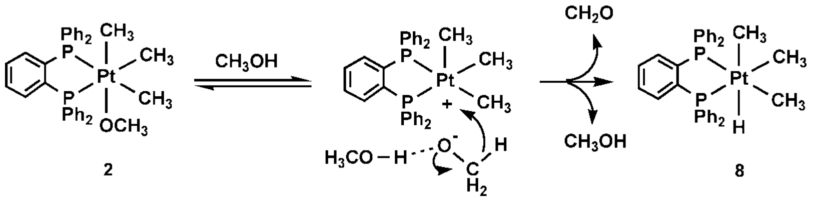
Blum and Milstein[21]
2000

Fafard and Ozerov[23]
2007

2

Figure 3. Complexes undergoing alcohol-promoted formal β-hydride elimination.

Scheme 9



Pt(IV) hydride **8** would then undergo C—H reductive elimination to form **3** and methane. Such reactivity has previously been reported from Pt(II) methoxide complexes.[63] Methanol could also be generated from reaction of **2** and adventitious water as shown in Scheme 1 (vide supra).

An Alcohol-Promoted Dissociative β-Hydride Abstraction Mechanism. The prevalence of products expected from a formal β-hydride elimination in the thermolysis of **2** is surprising for a coordinatively saturated, 18-electron complex. The accepted mechanism of β-hydride elimination, well-established for alkyl groups[1] and generally thought to be operative in similar reactions of alkoxides and amides,[64] requires an open site on the metal center *cis* to the β-hydrogen-bearing ligand. Complex **2** has no ligand that would easily dissociate to generate an open site *cis* to the methoxide. While dissociation of one arm of the bisphosphine chelate could generate such an open site, earlier studies of reductive elimination from a related complex, (dppbz)PtMe$_4$ suggest that phosphine dissociation is not kinetically accessible at 100 °C.[27] The fact that addition of methanol to a C_6D_6 solution of **2** rapidly generates the hydride complex **8** at room temperature, while the thermal reaction of **2** in C_6D_6 occurs over the course of hours to days at 100 °C, indicates that methanol dramatically accelerates this formal β-hydride elimination process. While this acceleration of β-hydride elimination in the presence of alcohol may seem unusual, we suspect that it is more widespread than is currently appreciated. Two similar examples of acceleration of formal β-hydride elimination of an alkoxide in the presence of alcohol at iridium have been reported,[20,21] as well as one at palladium.[23] A common feature of **2** and both iridium complexes is that the alkoxides from which the formal β-hydride elimination occurs are saturated, 18-electron d^6 metal compounds (Figure 3).

For the iridium chloro complex (Figure 3, far left), the reaction to form the analogous hydride complex was substantially accelerated by the presence of methanol. The authors also reported that added $P(CD_3)_3$ did not incorporate into the complex on the time scale of the reaction. Presumably to accommodate the traditional mechanism of β-hydride elimination previously established in alkyl systems, the authors proposed that the role of methanol was to assist in the dissociation of the chloride to generate an open site *cis* to the methoxide ligand.[20] For the phenyl complex (Figure 3, center left), the lack of dissociable ligands and the lack of $P(CD_3)_3$ incorporation caused Blum and Milstein to argue that methanol was assisting the dissociation of the *methoxide* ligand itself.[21] More recently, Fafard and Ozerov observed that β-hydride elimination from a Pd(II) ethoxide species was dramatically accelerated in the presence of ethanol and similarly proposed alcohol-assisted dissociation of the alkoxide.[23]

In light of these examples, we propose that a *dissociative β-hydride abstraction* mechanism may be an important and general pathway in formal β-hydride elimination reactions from late metal alkoxides. In such a process, initial dissociation, often promoted by hydrogen bonding from a Brønsted acid, precedes the abstraction by the metal of a β-hydride, which then resides in the coordination site vacated by the alkoxide. This second step of the proposed mechanism is very similar to the Canizzarro reaction in organic chemistry.[65] Scheme 9 depicts this mechanism for the conversion of methoxide **2** to hydride **8** and formaldehyde. While the previous examples from Ir and Pd involve alkoxide dissociation assisted by the alcohol, it is also possible that dissociative reactions could proceed without assistance, albeit under more forcing conditions, as was observed for the thermolysis of **2** in C_6D_6. In addition, this pathway should also be available for other anionic ligands that both are capable of dissociation and bear β-hydrogens. Indeed, this was proposed as a significant decomposition route of *fac*-(dppbz)PtMe$_3$(N(Me)SO$_2$Ar), in which products consistent with β-hydride elimination were observed.[41]

Thus, the dissociative β-hydride abstraction mechanism either with methanol assistance as shown in Scheme 9 or without methanol assistance under alcohol-free conditions is proposed as a primary reaction pathway for **2**. The results of our previous studies of the effect of conjugate acids, HX, on reaction pathways that proceed via preliminary dissociation of X^- (reductive elimination from *fac*-L_2PtMe_3X complexes (L_2 = dppe, dppbz, X = OH, O_2CR, OAr, $N(H)SO_2Ar$))[15,41] support the role of methanol in assisting methoxide dissociation from **2**. Notably, all of those reactions also proceed, albeit more slowly, in the absence of HX by a similar dissociative pathway. This is also expected to be in the case for dissociative β-hydride abstraction from **2**, which requires forcing thermal conditions in the absence of methanol. That the thermolysis of **2** at 100 °C in the presence of [18-crown-6-K][OCD$_3$] results in forma-

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(63) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(64) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, 7220.

(65) March, J. *Advanced Organic Chemistry*, 4th ed., John Wiley & Sons: New York, 1992; pp 1233−1235.

tion of **2**-d_3 on the same time scale as the β-hydrogen abstraction reaction to form **3** is consistent with the dissociation of methoxide being kinetically competent as a preliminary reaction step.

One other possible mechanism of formal β-hydride elimination from **2** involves dissociation of methoxide from **2** to form a cationic intermediate, which then can abstract a β-hydride from a second molecule of **2**, thereby generating **8**, formaldehyde, and the cation again. Ritter and Bergman have proposed a similar type of behavior in β-hydride elimination from Cp*(PMe_3)Ir(OCH_2R)Ph, in which the presence of iridium cations was observed to catalyze the formation of the corresponding iridium hydrides and aldehydes.[22] It is difficult to fully investigate a similar situation in this Pt(IV) system as the five-coordinate Pt(IV) cation is not stable. In addition, the rate of β-hydride elimination from **2** is irreproducible, likely due to adventitious water or a variable amount of another acid. Finally, it would be difficult to measure the rate dependence on the concentration of **2** since it is only sparingly soluble under the reaction conditions. Thus, a bimolecular β-hydride elimination mechanism cannot be ruled out for **2**, although it seems unlikely given the steric bulk of **2**.

Critical in the above discussion is that the Pt(IV) example described herein and the reported Ir(III) and Pd(II) examples all seem to involve an abstraction of an alkoxide β-hydride rather than a traditional β-hydride elimination to a *cis* open site. Since the mechanism involves preliminary dissociation of the alkoxide, the presence of alcohol accelerates the dissociation and therefore the overall reaction. Ozerov's results with a 16-electron Pd(II) ethoxide complex indicate that this alcohol-assisted pathway can even operate under conditions when an open *cis* site is nominally available.[23] Notably, a classical method for preparing metal-hydrides is the addition of base and excess alcohol to a metal halide complex. The presence of alcohol may be key to accelerating a similar dissociative β-hydride abstraction in these cases. In addition, the observation of an analogous type of dissociative β-hydride abstraction in the thermal reactions of sulfonamide complexes *fac*-(dppbz)PtMe_3(N(Me)SO_2Ar)[41] suggests that this reaction pathway is important for other heteroatomic groups as well. Indeed, it is likely that the mechanism depicted in Scheme 9 for **2** is representative of an underappreciated mechanism of formal β-hydride elimination available to both coordinatively saturated and unsaturated late metal complexes with β-hydrogen laden heteroatom ligands. Thus, unlike their metal alkyl counterparts, for metal alkoxides and metal amides, there are at least two viable modes for β-hydride elimination. In addition to the traditional route of transfer of the β-hydride to a *cis* open site, the β-hydride can be abstracted by an open site generated via dissociation of the heteroatom group itself.

Summary and Conclusions

Two fundamental organometallic reactions, reductive elimination and dissociative β-hydride abstraction, were observed as the primary reactions resulting from thermolysis of *fac*-(dppbz)PtMe_3(OH) (**1**) and *fac*-(dppbz)PtMe_3(OMe) (**2**), respectively. Thermolysis of **1** produces (dppbz)PtMe_2 (**3**) and methanol in good yield. The C−O reductive elimination reaction can be optimized by adding water and hydroxide to the thermolysis, resulting in high yields (72−76%) of methanol. This is a rare example of a directly observed alkyl C−O reductive elimination to yield an alcohol. Despite the expected poor leaving group ability of hydroxide in a nonpolar solvent, the mechanistic evidence implicates a C−O reductive elimination mechanism proceeding via hydroxide dissociation followed by nucleophilic attack on the Pt(IV) methyl group. Thus, the mechanism for C−O coupling is essentially identical to that demonstrated in other C−X couplings from similar *fac*-L_2Pt(IV)Me_3X (X = I, O_2CR, OAr, N(R)SO_2Ar) complexes in which the X anions are significantly better leaving group candidates.[15,38,41]

Formation of methanol as a product of the thermolysis of **1** has two important effects on the reaction. First, the hydrogen-bonding ability of methanol assists in dissociation of the hydroxide ligand, increasing the rate of both C−O and C−C elimination. Second, methanol can exchange with **1** to form the analogous methoxide, *fac*-(dppbz)PtMe_3(OMe) (**2**). This situation is similar to the behavior noted in reductive elimination to form sulfonamides from *fac*-(dppbz)PtMe_3(NHSO_2Ar),[41] in which the hydrogen-bonding capability of HN(Me)SO_2Ar resulted in both sulfonamide anion exchange and acceleration of elimination.

In contrast to the reactivity observed for **1**, C−O reductive elimination is a very minor reaction in the thermolysis of the Pt(IV) methoxide complex **2**. Instead, products resulting from formal β-hydride elimination are observed. Again, this behavior is similar to that observed for the sulfonamide complexes, in which products of formal β-hydrogen elimination resulted from the decomposition of *fac*-(dppbz)PtMe_3(N(Me)SO_2Ar) species.[41] Both of these systems lack ancillary ligands capable of facile dissociation. Thus, the standard textbook mechanism established for β-hydride elimination involving a concerted four-centered transition state seems implausible. Instead, we propose a dissociative β-hydride abstraction mechanism, in which dissociation of the methoxide or sulfonamide group is followed by hydride abstraction by the metal from the dissociated anion. The lack of appreciable amounts of C−O reductive elimination products in the thermolysis of **2** indicates that β-hydride abstraction from the dissociated methoxide is a lower energy pathway than nucleophilic attack by the methoxide on the methyl group. Thus, β-hydride abstraction may be a complication in reactions for which C-X reductive elimination reactions are desired if the X group bears β-hydrogens. As similar observations of alcohol-promoted formal β-hydride elimination of alkoxides with no accessible open *cis* coordination site have been reported in the past several years, it seems that this alternative mechanism of dissociative β-hydride abstraction may be quite general. Thus, just as multiple mechanisms are possible for reductive elimination reactions (e.g., "concerted" and two-step "dissociation and nucleophilic attack"), depending on the nature of the metal-bound atoms that are forming the bond, more than one common mechanism also appears viable for β-hydride elimination reactions. Depending on the type of metal-bound atom and the availability of a *cis* open site, the reaction can proceed via a traditional β-hydride elimination involving transfer of a hydride to a *cis* open site on the metal, as is seen with metal alkyls, or via a "dissociative β-hydride abstraction" wherein heterolytic metal−ligand cleavage is followed by abstraction of hydride from the dissociated ligand. Thus, our current long-held mechanistic understanding of this fundamental reaction, originally proposed and well-established for metal alkyl complexes, requires amendment when alkoxide or amide ligands are involved in which case a dissociative β-hydride abstraction pathway should also be considered.

Experimental Section

General Considerations. Unless otherwise noted, all transformations were carried out under a N_2 atmosphere in a drybox (O_2

< 1 ppm, H_2O < 0.5 ppm) or using standard Schlenk techniques. THF, benzene, and toluene were distilled under vacuum from sodium/benzophenone ketyl. Pentane was distilled from CaH_2. Methanol was triply distilled from sodium under vacuum. Deuterated solvents were dried by analogous methods and transferred under vacuum. KH was purchased as a suspension in mineral oil, isolated on a fritted glass funnel, washed multiple times with hexanes and pentane, dried under vacuum, and kept in the drybox. *o*-Bis(diphenylphosphino)benzene (dppbz) was purchased from Strem, treated with KH in THF, and recrystallized from THF/pentane. Other reagents, unless specified, were used as received from commercial suppliers. The complexes *fac*-(dppbz)Pt-$Me_3(O_2CCH_3)$ and *fac*-(dppbz)$PtMe_3(O_2CCF_3)$ were prepared by established literature procedures.[15] [18-crown-6-K][OCD_3] was synthesized according to an established literature procedure for the protio analog.[66] KOH was produced by the reaction of potassium metal with water (2 equiv) in toluene and left under vacuum for 3 days after removal of the toluene. Celite was dried for >48 h at >150 °C under vacuum. Thermolysis samples were heated in a Neslab Ex-250HT elevated temperature bath. NMR spectra were recorded on Bruker DPX200, AF300, or DRX499 spectrometers. All coupling constants are reported in Hz. ^1H NMR spectra were referenced by using residual solvent peaks and are reported in ppm downfield of tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 (0 ppm). GC/MS data was collected on a Hewlett-Packard 5971 GC-mass spectrometer. Electrospray MS data was collected on a Bruker Esquire ion trap LC-mass spectrometer.

Preparation of *fac*-(dppbz)$PtMe_3$(OH) (1). A Teflon-stoppered glass vessel was charged with *fac*-(dppbz)$PtMe_3(O_2CCF_3)$ (267 mg, 0.33 mmol), toluene (100 mL), and KOH (387 mg, 6.9 mmol). The reaction mixture was heated to 35 °C for 2 days. The solution was cooled, and excess KH was added to the reaction mixture, which was left to stir for 1 h at ambient temperature. This solution was filtered through a Teflon syringe filter, and the filtrate was reduced in volume to 30 mL in vacuo and left to crystallize. White crystals were harvested, and solvent was reduced under vacuum to 5 mL to yield a second crop of crystals. Combined yield from two crystallizations = 223 mg, 95%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.3 (s w/Pt satellites, $^1J_{PtP} = 1161$). ^1H NMR (C_6D_6): δ −2.39 (t w/Pt satellites, 1H, $^3J_{PH} = 2.7$, $^2J_{PtH} = 13.0$, Pt−O**H**), 0.02 (t w/Pt satellites, 3H, $^3J_{PH} = 6.6$, $^2J_{PtH} = 63.8$, Pt−C**H$_3$** *trans* to hydroxide), 1.68 (t w/Pt satellites, 6H, $^3J_{PH} = 7.4$, $^2J_{PtH} = 60.0$, Pt−C**H$_3$** *cis* to hydroxide), 6.7−7.4 (m, 20H, aryl protons on dppbz ligand), 8.67 (m, 4H, aryl protons on dppbz ligand). Anal. for $C_{33}H_{34}OP_2Pt$: Calcd C, 56.33; H, 4.87; Found C, 56.38; H, 4.90.

Preparation of *fac*-(dppbz)$PtMe_3(OCH_3)$ (2). Small pieces of potassium metal (880 mg, 22.5 mmol) and methanol (500 μL, 12.3 mmol) were added to toluene and left to stir for 1 day. The potassium metal was then removed and *fac*-(dppbz)$PtMe_3(O_2CCH_3)$ (130 mg, 0.160 mmol) was added. The solution was stirred for five days and then filtered through a medium porosity fritted glass funnel or a syringe equipped with a Teflon filter. The solvent was removed under vacuum and the product was recrystallized from toluene layered with pentane. Yield = 86.2 mg, 75%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.2 (s w/Pt satellites, $^1J_{PtP} = 1159$). ^1H NMR (C_6D_6): δ 0.01 (t w/Pt satellites, 3H, $^3J_{PH} = 6.6$, $^2J_{PtH} = 64.0$, Pt−C**H$_3$** *trans* to methoxide), 1.76 (t w/Pt satellites, 6H, $^3J_{PH} = 7.7$, $^2J_{PtH} = 60.0$, Pt−C**H$_3$** *cis* to methoxide), 4.04 (s w/Pt satellites, 3H, $^3J_{PtH} = 24.4$, Pt-OC**H$_3$**), 6.7−7.4 (m, 20H, aryl protons on dppbz ligand), 8.44 (m, 4H aryl protons on dppbz ligand). Anal. for $C_{34}H_{36}OP_2Pt$: Calcd.: C, 56.90; H, 5.06; Found: C, 57.11; H, 5.09. *fac*-(dppbz)$PtMe_3(OCD_3)$ was prepared similarly, except for the substitution of methanol-d_4 for methanol.

Treatment of Thermolysis Samples. In a typical set of experiments for thermolysis of **1** without additives, complex **1** (20.0 mg, 0.028 mmol) was added in a drybox to a Teflon-stoppered glass vessel and subsequently brought out of the drybox. C_6D_6 (10 mL) was added by vacuum transfer, and then 4.4 mL of this solution was removed in vacuo to concentrate the solution of **1**. In the drybox, toluene was added to the solution as an NMR standard. For each sample, 0.6 mL (0.003 mmol, 5 mM) of this solution was loaded into a medium-walled NMR tube (Wilmad 504-PP), which was subsequently sealed on a vacuum line. In the reactions involving additional H_2O, this reagent (0.035 mmol; 50 μL of 0.069 M H_2O in C_6D_6 solution) was also added to the NMR tube prior to sealing. For the thermolysis of **1** in the presence of cesium hydroxide, **1** (1.7 mg, 0.0024 mmol), CsOH•H_2O (4.2 mg, 0.025 mmol), toluene as a NMR standard, and C_6D_6 (0.5 mL) were loaded into a medium-walled NMR tube (Wilmad 504-PP) which was subsequently sealed on a vacuum line. For thermolysis of **2** or **2**-d_3, 0.5 mL of a solution of **2** or **2**-d_3 (0.003 mM) and toluene as a NMR standard in C_6D_6 were loaded into a medium-walled NMR tube (Wilmad 504-PP) that had been fitted with a 14/20 ground glass joint.

In all thermolyses, after loading the NMR tube, the sample was affixed to a stopcock adaptor, cooled in a liquid N_2 bath, and evacuated under high vacuum. The tube was then flame-sealed under active vacuum. The sealed NMR tubes were heated, and the reactions were quenched at various time intervals by rapidly cooling the tubes in ice water. Thermolysis tubes were stored in a laboratory freezer (−20 °C) or in liquid N_2 when not being heated or monitored by NMR spectroscopy. All ^1H and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker DRX499 spectrometer, averaging the integrals for three acquisitions at a given reaction time. For each aquisition, eight scans were collected with a 60 s recycle delay. Signals for all species were integrated relative to the internal standard (toluene, $T_1 = 11$ s). Mass balance of Pt complexes (>95%) was confirmed by integration of Pt−C**H$_3$** signals (*trans* to P) against the internal standard at the end of the reaction.

Reaction of 1 with CH_3OH. In a drybox, **1** (5.0 mg, 0.0071 mmol) and an internal NMR standard (toluene, 1 μL, 0.01 mmol) were loaded into a medium-walled J. Young NMR tube (Wilmad 504-PP). THF-d_8 (0.5 mL) was vacuum transferred into the sample. After initial ^1H and $^{31}P\{^1H\}$ NMR spectra were collected, this sample was brought back into the drybox, and methanol (0.014 mL, 0.35 mmol, ca. 48 equiv) was added. ^1H and $^{31}P\{^1H\}$ NMR spectra were collected within 10 min of adding methanol. The reaction was left to react at ambient temperature and was monitored for 3 days by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 2 with H_2O. In a drybox, **2** (2.4 mg, 0.0033 mmol) and an internal NMR standard (toluene, 0.5 μL, 0.005 mmol) were loaded into a medium-walled J. Young NMR tube (Wilmad 504-PP). C_6D_6 (0.5 mL) was vacuum-transferred into the sample. After initial ^1H and $^{31}P\{^1H\}$ NMR spectra were collected, this sample was brought back into the drybox, and water (0.035 mL of a 0.185 M solution in C_6D_6, 0.007 mmol) was added. ^1H and $^{31}P\{^1H\}$ NMR spectra were collected at least twice per hour for the first 6 h and then at least every 15 h for the next 75 h at ambient temperature. ^1H NMR spectra were integrated against the internal standard.

Reaction of 1 with H_2O. In a drybox, **1** (10.0 mg, 0.014 mmol) and an internal NMR standard (toluene, 3 μL, 0.03 mmol) were loaded into a 2 mL volumetric flask. The solution was diluted to 2 mL with C_6D_6; 0.4 mL of this solution was added to a medium-walled NMR tubes. Water (3.0 μL) was added to the sample, and the tube was frozen and flame-sealed under active vacuum. The sample was thawed and left at ambient temperature. The progress of the reactions was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at various time intervals for at least 4 weeks. ^1H NMR spectra were integrated against the internal standard. Complex **6** was observed to form over time, with a maximum of 80% yield after 4 weeks. NMR characterization of **6**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.0 (s w/Pt satellites, $^1J_{PtP} = 1114$). ^1H NMR: (C_6D_6): δ 0.14 (t w/Pt

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(66) Kurcok, P.; Jedlinski, Z.; Kowalczuk, M. *J. Org. Chem.* **1993**, *58*, 4219.

satellites, 3H, $^3J_{PH} = 7.7$, $^2J_{PtH} = 73.9$, Pt−C**H₃** *trans* to O), 1.75 (t w/Pt satellites, 6H, $^3J_{PH} = 6.9$, $^2J_{PtH} = 56.3$, Pt−C**H₃** *trans* to P), 6.7−8.8 (m, 24H, aryl protons on dppbz ligand).

Reaction of 2 with *p*-CH_2O. In a drybox, **2** (2.5 mg, 0.0035 mmol), *p*-CH_2O (1.0 mg, 0.033 mmol) and benzyl ether (ca. 0.01 mmol, internal standard) were loaded into a medium-walled NMR tube (Wilmad 504-PP). C_6D_6 (0.5 mL) was vacuum-transferred into the tube. The sample was kept frozen while the tube was flame-sealed under active vacuum. The sample was thawed and ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired within 15 min at ambient temperature. NMR characterization of *fac*-(dppbz)$PtMe_3(OCH_2OCH_3)$ (**4**): $^{31}P\{^1H\}$ NMR (C_6D_6): δ 20.1 (s w/ Pt satellites, $^1J_{PtP} = 1139$). ^1H NMR: δ 0.01 (3H, t w/ Pt satellites, $^3J_{PH} = 6.6$, $^2J_{PtH} = 68.4$, Pt−C**H₃** *trans* to O); 1.73 (6H, t w/ Pt satellites, $^3J_{PH} = 7.5$, $^2J_{PtH} = 58.0$, Pt−C**H₃** *trans* to P); 3.53 (s, Pt-OCH_2OC**H₃**); 5.56 (s w/ Pt satellites, $^3J_{PtH} = 18.7$, Pt-OC**H₂**OCH_3); 6.7−8.46 (m, 24H, aryl protons on dppbz ligand).

This procedure was also carried out with a larger excess of *p*-CH_2O (6.3 mg, 0.21 mmol) relative to **2** (4.5 mg, 0.0063 mmol) in C_6D_6 (0.8 mL). ^1H and $^{31}P\{^1H\}$ NMR spectra taken within 15 min at ambient temperature showed complete consumption of **2**. The ^1H NMR spectrum was complex and several singlets, including some with Pt satellites, were observed between 3−5 ppm. These signals are assumed to correspond to OC**H₂** units produced by the iterative insertion of formaldehyde into the Pt−O bond of **4** and those of subsequent insertion products. The $^{31}P\{^1H\}$ NMR spectrum displayed signals assigned to **4** (δ 20.13 ppm, $^1J_{PtP} = 1138$ Hz) and two other species: δ 20.44 ppm, $^1J_{PtP} = 1140$ Hz and δ 20.56 ppm, $^1J_{PtP} = 1134$ Hz. The approximate percentanges of total Pt of these species were 30%, 48%, and 22%, respectively, as estimated by $^{31}P\{^1H\}$ NMR peak heights.

Reaction of 2 with CH_3OH. In a drybox, **2** (2.5 mg, 0.0035 mmol), C_6D_6 (0.3 mL), methanol (0.3 mL), and an internal NMR standard (toluene, 1 μL, 0.01 mmol) were loaded into a medium-walled J. Young NMR tube (Wilmad 504-PP). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Signals for **2** disappeared within 20 min at ambient temperature and were replaced by those of **8**. Slow decomposition of **8** was observed with signals for **3** and methane appearing over time. The analogous experiment was also conducted with CD_3OD, in which **8**-d_1 was observed and CH_3D and **3** were observed to form over time.

Reaction of 2 with [18-crown-6-K][OCD_3]. In a drybox, **2** (2.8 mg, 0.0039 mmol), [18-crown-6-K][OCD_3] (32.9 mg, 0.097 mmol), and an internal NMR standard (hexamethylbenzene, 2.1 mg, 0.013 mmol) were loaded into a medium-walled J. Young NMR tube (Wilmad 504-PP). The tube was evacuated under high vacuum, and C_6D_6 (0.42 mL) was vacuum-transferred into the sample. Despite the use of the crown ether, [18-crown-6-K][OCD_3] did not completely dissolve and solid [18-crown-6-K][OCD_3] was observable in the reaction mixture. The reaction was monitored by ^1H NMR spectroscopy. The NMR tube was heated at 100 °C for varying amounts of time, and then the reaction was quenched by rapidly cooling the tube in ice water (0 °C). A direct comparison of the integrals for Pt−C**H₃** signals (*trans* to O) and Pt−OC**H₃** for **2** in the ^1H NMR spectra was used to determine how much of the methoxide ligand had exchanged with OCD_3. As the reaction progressed, signals for CH_4, CH_3D, and [18-crown-6-K][OCH_3] (OC**H₃** $\delta = 4.12$ in C_6D_6) were observed in the ^1H NMR spectra.

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Supporting Information Available: CIF files for *fac*-(dppbz)$PtMe_3(OH)$ (**1**) and *fac*-(dppbz)$PtMe_3(OMe)$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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