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β-Hydride Elimination from Methoxo vs. Ethyl Ligands: Thermolysis of $(DPPE)Pt(OCH_3)_2$, $(DPPE)Pt(CH_2CH_3)(OCH_3)$ and $(DPPE)Pt(CH_2CH_3)_2$[†]

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Abstract: Thermolysis of $(DPPE)Pt(OCH_3)_2$ (**1**) (DPPE = 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) at 25 °C leads to a mixture of methanol, formaldehyde oligomers, and small amounts of carbon monoxide (CO). Kinetics experiments, labeling studies, and solvent effects suggest this decomposition proceeds by initial preequilibrium β-hydride migration to the metal followed by rate-limiting release of organic products. While **1** decomposes at 25 °C and $(DPPE)Pt(CH_2CH_3)_2$ only slowly releases ethylene and ethane at 160 °C, $(DPPE)Pt(CH_2CH_3)(OCH_3)$ (**3**) decomposes to a mixture of ethylene, ethane, methanol, and formaldehyde oligomers at 100 °C. The predominance of ethylene over ethane suggests thermolysis proceeding by β-elimination from the ethyl ligand is energetically easier than the comparable process from the methoxo ligand by 0.3 kcal/mol. Labeling studies confirm the preequilibrium nature of this β-elimination. The relative M–C vs. M–O bond strengths are discussed in light of this information.

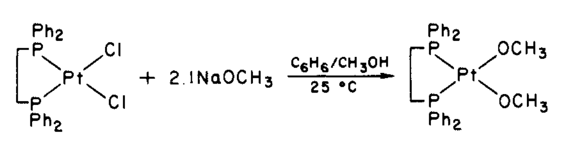
Background

It has been historically more difficult to prepare alkoxide and amide complexes of the group VIII (groups 8–10) metals than to prepare comparable alkyl species containing β-hydrogen substituents. In addition, the chemistry of late-metal alkoxides has only recently been explored[1] while reactions of metal alkyl complexes have been studied for many years.[2] The commonly held perception that such species have weak metal–oxygen bonds has been attributed to the suspected poor interaction of hard base ligands with relatively soft group VIII (groups 8–10) metal centers. The difficulty in isolating alkoxide complexes and the ease with which they decompose (presumably by β-hydride elimination) to metal hydrides[3] adds credence to these hypotheses; it has been assumed that weak M–O bonds lower the intrinsic barrier to β-hydride elimination reactions by raising the ground-state free energies of alkoxides relative to alkyls. Consistent with this interpretation, synthesis of platinum alkoxides containing β-hydrogen atoms has been accomplished most successfully in species containing electron-withdrawing substituents[4] and comparable hydroxide and phenoxide complexes are generally much more stable than alkoxide analogues.[5]

Whitesides, Yamamoto, and others have provided elegant labeling studies which show β-hydrogen elimination from platinum(II) alkyls most easily takes place by dissociation of phosphine ligands from P_2PtR_2 complexes followed by β-elimination and reductive coupling of alkyl and hydride ligands.[6] At high phosphine ligand concentrations or with chelating bis-phosphine ligands, a higher energy β-elimination from the 16-electron starting materials becomes competitive with the dissociative route.[6] We now report that analogous platinum alkoxides show the same behavior and provide interesting comparisons between the two classes of compounds.

Results and Discussion

Synthesis of Platinum Methoxo Complexes. $(DPPE)Pt(OCH_3)_2$ (1). Metathesis of $(DPPE)PtCl_2$ with 2.1 equiv of freshly prepared $NaOCH_3$ in mixed benzene/methanol solvent results in the formation of the bis-alkoxide complex **1** within 90 min (eq 1).



(1)

1, 80% yield

Minimal reduction is seen with the chelating phosphine complex

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(3) For leading references, see: (a) Muetterties, E. L. *Transition Metal Hydrides*; **1971**; Marcel Dekker: New York, 1971; pp 203–269 by R. A. Schunn. (b) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075. (c) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17. (d) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. Also see ref 1h,o.

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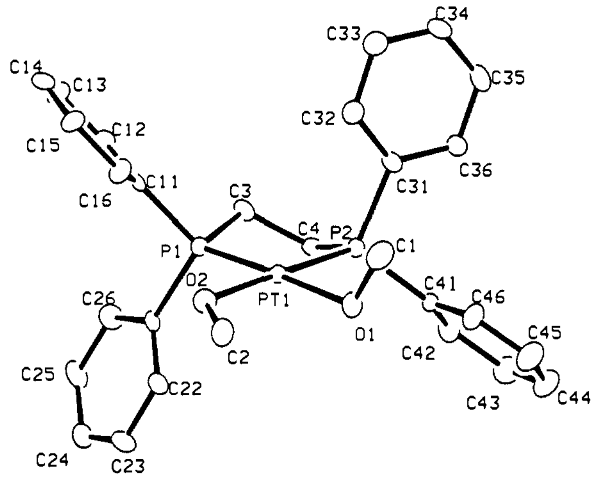

Figure 1. ORTEP drawing of complex **1** shown with 25% probability ellipsoids. Hydrogen atoms and CH_2Cl_2 of crystallization omitted for clarity.

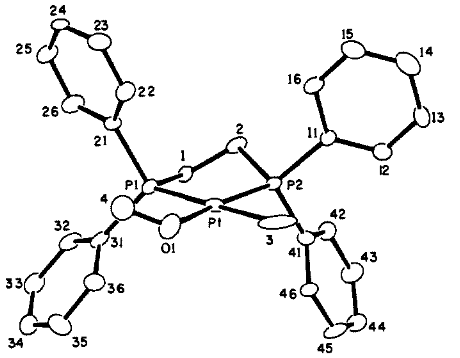

Figure 2. ORTEP drawing of complex **2** shown with 25% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table I. Selected Bond Lengths and Angles for $(DPPE)Pt(OMe)_2$ in Figure 1

	Interatomic Distances (Å)		
Pt(1)–P(1)	2.228 (3)	C(15)–C(16)	1.389 (15)
Pt(1)–P(2)	2.222 (3)	C(21)–C(22)	1.382 (15)
Pt(1)–O(1)	2.037 (7)	C(21)–C(26)	1.395 (14)
Pt(1)–O(2)	2.041 (7)	C(22)–C(23)	1.390 (15)
Cl(1)–C(5)	1.742 (19)	C(23)–C(24)	1.397 (17)
Cl(2)–C(5)	1.683 (16)	C(24)–C(25)	1.352 (18)
P(1)–C(3)	1.837 (11)	C(25)–C(26)	1.381 (15)
P(1)–C(11)	1.796 (12)	C(31)–C(32)	1.362 (16)
P(1)–C(21)	1.829 (9)	C(31)–C(36)	1.405 (13)
P(2)–C(4)	1.822 (10)	C(32)–C(33)	1.394 (17)
P(2)–C(31)	1.818 (10)	C(33)–C(34)	1.364 (17)
P(2)–C(41)	1.803 (10)	C(34)–C(35)	1.356 (18)
O(1)–C(1)	1.369 (14)	C(35)–C(36)	1.397 (16)
O(2)–C(2)	1.370 (13)	C(41)–C(42)	1.390 (14)
C(3)–C(4)	1.523 (17)	C(41)–C(46)	1.392 (14)
C(11)–C(12)	1.436 (16)	C(42)–C(43)	1.405 (19)
C(11)–C(16)	1.398 (16)	C(43)–C(44)	1.353 (18)
C(12)–C(13)	1.349 (17)	C(44)–C(45)	1.405 (17)
C(13)–C(14)	1.375 (17)	C(45)–C(46)	1.356 (18)
C(14)–C(15)	1.389 (18)		
	Intramolecular Angles (deg)		
P(1)–Pt(1)–P(2)	86.2 (1)	P(2)–C(31)–C(36)	121.5 (9)
P(1)–Pt(1)–O(1)	175.7 (3)	P(2)–C(41)–C(42)	121 (1)
P(1)–Pt(1)–O(2)	92.5 (2)	P(2)–C(41)–C(46)	120.7 (8)
P(2)–Pt(1)–O(1)	91.8 (2)	C(12)–C(11)–C(16)	117 (1)
P(2)–Pt(1)–O(2)	177.8 (2)	C(11)–C(12)–C(13)	121 (1)
O(1)–Pt(1)–O(2)	89.3 (3)	C(12)–C(13)–C(14)	121 (1)
Pt(1)–P(1)–C(3)	108.6 (4)	C(13)–C(14)–C(15)	120 (1)
Pt(1)–P(1)–C(11)	117.6 (4)	C(14)–C(15)–C(16)	120 (1)
Pt(1)–P(1)–C(21)	113.4 (4)	C(11)–C(16)–C(15)	121 (1)
Pt(1)–P(2)–C(4)	107.6 (3)	C(22)–C(21)–C(26)	119.3 (9)
Pt(1)–P(2)–C(31)	114.2 (3)	C(21)–C(22)–C(23)	120 (1)
Pt(1)–P(2)–C(41)	119.2 (3)	C(22)–C(23)–C(24)	119 (1)
C(3)–P(1)–C(11)	103.6 (6)	C(23)–C(24)–C(25)	120 (1)
C(3)–P(1)–C(21)	105.2 (4)	C(24)–C(25)–C(26)	121 (1)
C(11)–P(1)–C(21)	107.4 (5)	C(21)–C(26)–C(25)	120 (1)
C(4)–P(2)–C(31)	104.4 (4)	C(32)–C(31)–C(36)	119 (1)
C(4)–P(2)–C(41)	105.7 (5)	C(31)–C(32)–C(33)	122 (1)
C(31)–P(2)–C(41)	104.4 (5)	C(32)–C(33)–C(34)	118 (1)
Pt(1)–O(1)–C(1)	117.0 (8)	C(33)–C(34)–C(35)	122 (1)
Pt(1)–O(2)–C(2)	121.0 (7)	C(34)–C(35)–C(36)	120 (1)
Cl(1)–C(5)–Cl(2)	112.5 (8)	C(31)–C(36)–C(35)	119 (1)
P(1)–C(3)–C(4)	108.7 (8)	C(42)–C(41)–C(46)	118 (1)
P(2)–C(4)–C(3)	108.5 (7)	C(41)–C(42)–C(43)	121 (1)
P(1)–C(11)–C(12)	123 (1)	C(42)–C(43)–C(44)	119 (1)
P(1)–C(11)–C(16)	120 (1)	C(43)–C(44)–C(45)	121 (1)
P(1)–C(21)–C(22)	119.2 (7)	C(44)–C(45)–C(46)	119 (1)
P(1)–C(21)–C(26)	121.4 (8)	C(41)–C(46)–C(45)	122 (1)
P(2)–C(31)–C(32)	119.3 (8)		

perhaps due to the instability of (DPPE)Pt, the presumed product.[7] Concentration of the solution followed by precipitation of product (along with excess NaCl and $NaOCH_3$) gave a solid which was extracted with THF to generate a pale yellow solution of **1**. Concentration below ambient temperature followed by precipitation with pentane generates the THF adduct of **1** in 85% isolated yield. Diffusion–crystallization from cold CH_2Cl_2/diethyl ether gave small colorless crystals of the CH_2Cl_2 adduct suitable for X-ray crystallography[8] (Figure 1, Table I). As anticipated, the structure shows the complex to be monomeric with relatively open axial coordination sites above and below the square-planar ligand system. No interactions with CH_2Cl_2 of crystallization were noted. Interestingly, the O–C bonds in the methoxo ligands are shorter than expected (1.370 (14) vs. 1.43 Å found in diethyl ether) though

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(5) Martin Bennett (and others) have used this relative stability of hydroxides to alkoxide complexes to advantage in the synthesis of reactive metal hydrides from MOH complexes and methanol. See, for example, ref 1c and 3c,d.

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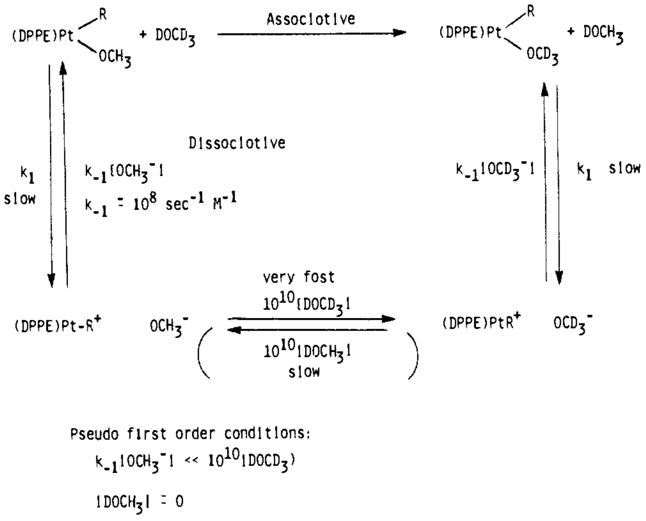
(7) For leading references and a recent summary of P_2Pt chemistry, see: Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.

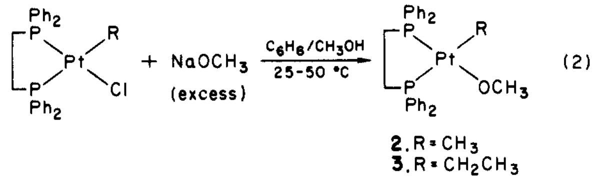
(8) Parameters for crystal structure of $(DPPE)Pt(OCH_3)_2$: (fw 740.52) colorless crystals obtained from CH_2Cl_2/Et_2O; orthorhombic, $P2_12_12_1$ (No. 19), a = 13.570 (4) Å, b = 19.639 (10) Å, c = 10.633 (3) Å, V = 2833.7 Å^3; temp = 0 °C; d(calcd) n = 1.735 g cm^{-3} for $Z = 4$; 2618 unique diffractometer reflections (Mo Kα) [$I < 3\sigma(I)$] corrected for adsorption (μ = 53.29 cm^{-1}, Gaussian grid 8 × 8 × 8); full-matrix anisotropic refinement on 329 variables yielded R = 0.035 and R_w = 0.032.

Scheme I



no obvious interaction of a methoxo proton with the metal center is evident.

(DPPE)PtR(OCH$_3$): R = CH$_3$ (2), CH$_2$CH$_3$ (3). Platinum alkyl methoxide complexes can be prepared by the same metathesis technique outlined for the bis-methoxide synthesis above. In this case, heating the mixture of platinum alkyl chloride and sodium methoxide (eq 2) for 2 h at 50 °C or stirring the mixture for 14 h at ambient temperature efficiently generates the desired alkyl methoxo complexes **2** and **3** in 90% and 77% yields, respectively. Isolation was accomplished by the same extraction procedure outlined for **1**. Recrystallization from toluene/pentane generated crystals of **2** suitable for X-ray crystallography (Figure 2, Table II) (communicated previously).[9] In this structure, as in the structure of **1**, the square-planar ligand environment is evident with the alkyl ligand proving to be a stronger trans-labilizer than the methoxo ligand. In this complex the C–O bond, at *1.258* (*19*) Å, is even shorter than that observed for **1**. While there are essentially no comparable structures of monomeric group VIII (groups 8–10) metal methoxide complexes reported, some reports of short O–C bonds in *trans*-(PPh$_3$)$_2$(CO)IrOPh[1p] and alkoxymetalloporphyrin complexes[1q–v] are published. C–O bond lengths in these porphyrin complexes average approximately 1.38 Å though values range from 1.358 (8)[1u] to 1.45 Å.[1v] Bond lengths of 1.38 Å are close to what we see in bis-methoxide **1** but still significantly longer than observed in **2**. As further structural determinations become available, it will be interesting to determine if short O–C bonds are a general feature of this class of compounds.



2, R = CH$_3$
3, R = CH$_2$CH$_3$

Methoxide Dissociation from Methoxo Complexes. While it is clear from the ^{195}Pt and ^{31}P couplings to the methoxide protons in **1**, **2**, and **3** that methoxide dissociation from these complexes is not fast on the NMR time scale, this does not preclude dissociation from assuming a kinetically significant role in the thermolysis of these complexes. In order to define the upper limit for the rate of methoxide dissociation, methanol-exchange experiments were conducted on **1** and **2**. As shown in Scheme I, if methoxide dissociation is important for methanol exchange in these complexes, the rate-limiting step will be methoxide dissociation since deuteron transfer from CD$_3$OD to methoxide anion

Table II. Selected Bond Lengths and Angles for (DPPE)PtMe(OMe) in Figure 2

Interatomic Distances (Å)			
Pt(1)–P(1)	2.281 (3)	C(21)–C(22)	1.371 (16)
Pt(1)–P(2)	2.211 (3)	C(21)–C(26)	1.417 (16)
Pt(1)–O(1)	1.990 (10)	C(22)–C(23)	1.394 (17)
Pt(1)–C(3)	2.145 (17)	C(23)–C(24)	1.352 (19)
P(1)–C(1)	1.860 (11)	C(24)–C(25)	1.388 (17)
P(1)–C(21)	1.829 (10)	C(25)–C(26)	1.401 (17)
P(1)–C(31)	1.833 (13)	C(31)–C(32)	1.370 (16)
P(2)–C(2)	1.848 (11)	C(31)–C(36)	1.402 (16)
P(2)–C(11)	1.822 (12)	C(32)–C(33)	1.373 (19)
P(2)–C(41)	1.821 (11)	C(33)–C(34)	1.358 (21)
O(1)–C(4)	1.258 (19)	C(34)–C(35)	1.387 (20)
C(1)–C(2)	1.484 (17)	C(35)–C(36)	1.386 (18)
C(11)–C(12)	1.384 (17)	C(41)–C(42)	1.390 (16)
C(11)–C(16)	1.420 (15)	C(41)–C(46)	1.394 (15)
C(12)–C(13)	1.372 (17)	C(42)–C(43)	1.384 (16)
C(13)–C(14)	1.410 (20)	C(43)–C(44)	1.370 (20)
C(14)–C(15)	1.401 (22)	C(44)–C(45)	1.367 (22)
C(15)–C(16)	1.353 (20)	C(45)–C(46)	1.414 (18)

Intramolecular Angles (deg)			
P(1)–Pt(1)–P(2)	86.0 (1)	P(2)–C(41)–C(42)	121 (1)
P(1)–Pt(1)–O(1)	101.7 (3)	P(2)–C(41)–C(46)	119 (1)
P(2)–Pt(1)–O(1)	172.3 (3)	C(12)–C(11)–C(16)	119 (1)
P(1)–Pt(1)–C(3)	177.9 (6)	C(11)–C(12)–C(13)	121 (1)
P(2)–Pt(1)–C(3)	92.1 (6)	C(12)–C(13)–C(14)	119 (1)
O(1)–Pt(1)–C(3)	80.2 (6)	C(13)–C(14)–C(15)	119 (1)
Pt(1)–P(1)–C(1)	107.5 (3)	C(14)–C(15)–C(16)	121 (1)
Pt(1)–P(1)–C(21)	114.1 (4)	C(11)–C(16)–C(15)	120 (1)
Pt(1)–P(1)–C(31)	118.8 (4)	C(22)–C(21)–C(26)	119 (1)
Pt(1)–P(2)–C(2)	106.9 (4)	C(21)–C(22)–C(23)	121 (1)
Pt(1)–P(2)–C(11)	116.5 (3)	C(22)–C(23)–C(24)	120 (1)
Pt(1)–P(2)–C(41)	117.5 (4)	C(23)–C(24)–C(25)	121 (1)
C(1)–P(1)–C(21)	102.6 (5)	C(24)–C(25)–C(26)	120 (1)
C(1)–P(1)–C(31)	104.3 (5)	C(21)–C(26)–C(25)	119 (1)
C(21)–P(1)–C(31)	107.8 (5)	C(32)–C(31)–C(36)	118 (1)
C(2)–P(2)–C(11)	104.7 (5)	C(31)–C(32)–C(33)	121 (1)
C(2)–P(2)–C(41)	104.4 (5)	C(32)–C(33)–C(34)	122 (1)
C(11)–P(2)–C(41)	105.5 (5)	C(33)–C(34)–C(35)	119 (1)
Pt(1)–D(1)–C(4)	119 (1)	C(34)–C(35)–C(36)	120 (1)
P(1)–C(1)–C(2)	108 (1)	C(31)–C(36)–C(35)	121 (1)
P(2)–C(2)–C(1)	110 (1)	C(42)–C(41)–C(46)	119 (1)
P(2)–C(11)–C(12)	123 (1)	C(41)–C(42)–C(43)	120 (1)
P(2)–C(11)–C(16)	117 (1)	C(42)–C(43)–C(44)	121 (1)
P(1)–C(21)–C(22)	119 (1)	C(43)–C(44)–C(45)	120 (1)
P(1)–C(21)–C(26)	122 (1)	C(44)–C(45)–C(46)	121 (1)
P(1)–C(31)–C(32)	125 (1)	C(41)–C(46)–C(45)	118 (1)
P(1)–C(31)–C(36)	117 (1)		

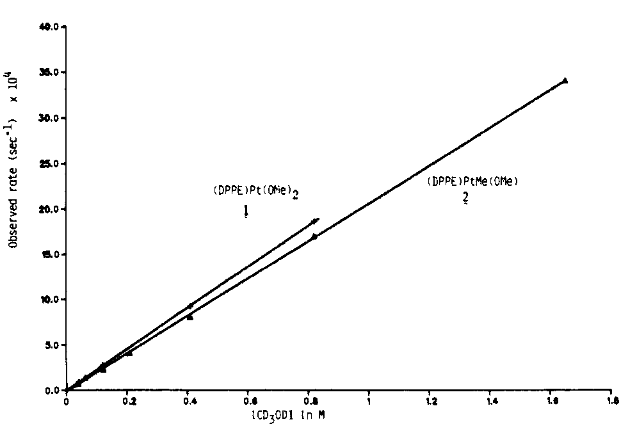


Figure 3. Methanol exchange kinetics. Observed rates of [PtOCH$_3$] loss vs. [CD$_3$OD] for (DPPE)Pt(OCH$_3$)$_2$ and (DPPE)PtCH$_3$(OCH$_3$) at 23 °C in THF-d_8. Initial [(DPPE)PtR(OCH$_3$)] = 0.08–0.025 M (R = CH$_3$, OCH$_3$).

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[9] A preliminary report of this structure has been included as supplementary material in ref 1j. A summary of pertinent parameters follows: (DPPE)PtMe(OMe) (fw 639.59), colorless crystals obtained from THF/pentane; monoclinic, $P2_1/c$, a = 11.547 (2) Å, b = 13.152 (6) Å, c = 16.658 (5) Å, β = 98.51 (2)°; V = 2502 Å^3; temp = −100 °C; d(calcd) n = 1.698 g cm^{-3} for Z = 4; 4071 diffractometer reflections (Mo Kα) [$I > 2\sigma(I)$] corrected for adsorption (μ = 58.095 cm^{-1}, Gaussian grid 8 × 8 × 8); full-matrix anisotropic refinement on 289 variables yielded R = 0.066 and R_w = 0.073.

Table III. Methanol Exchange Rates at 23 °C[a]

complex	solvent	rate/s^{-1}
(DPPE)Pt(OMe)$_2$ (**1**)	THF-d_8	9.20×10^{-4} ($\pm 0.05 \times 10^{-4}$)
	toluene-d_8	2.41×10^{-3} ($\pm 0.01 \times 10^{-3}$)
(DPPE)PtMe(OMe) (**2**)	THF-d_8	8.05×10^{-4} ($\pm 0.05 \times 10^{-4}$)
	toluene-d_8	2.30×10^{-3} ($\pm 0.01 \times 10^{-3}$)
(DPPE)PtEt(OMe) (**3**)	THF-d_8	6.55×10^{-4} ($\pm 0.05 \times 10^{-4}$)
	toluene-d_8	9.60×10^{-4} ($\pm 0.05 \times 10^{-4}$)

[a] [CH_3OH] = 0.41 M.

is known to proceed faster than diffusion-controlled rates.[10] If both associative and dissociative paths for methanol exchange are kinetically competitive, both zero and first-order methanol dependencies will be observed in a k_{obsd} vs. [CD_3OD] plot, with the nonzero intercept providing the rate of methoxide dissociation.

For both **1** and **2**, methanol exchange was found to be first order in the platinum methoxide complexes and first order in [CD_3OD] as shown in Figure 3. This result shows methanol exchange is an associative process with the "error" in the intercept of the k_{obsd} vs. [CD_3OD] plots representing the maximum rate of methoxide dissociation from these complexes. For both **1** and **2**, this corresponds to maximum rates of 10^{-6} s^{-1} at 25 °C. As previously reported, this rate is 3 orders of magnitude slower than insertions of CO[11] and fluoro olefins[12] into the Pt–O bonds of these methoxide complexes. While detectable methanol exchange is clearly associative, several discrete mechanistic possibilities might be involved. Since exchange is dramatically accelerated by the addition of traces of acids and bases (5% based on Pt) protonation/metathesis with CD_3OD and metathesis with OCD_3^- probably account for at least some of the associative exchange under "neutral" conditions. However, other studies of "σ-ligand metathesis" reactions involving other "less-dissociating" species suggest that a methanol coordination, proton transfer, methanol dissociation mechanism is also significant.[22]

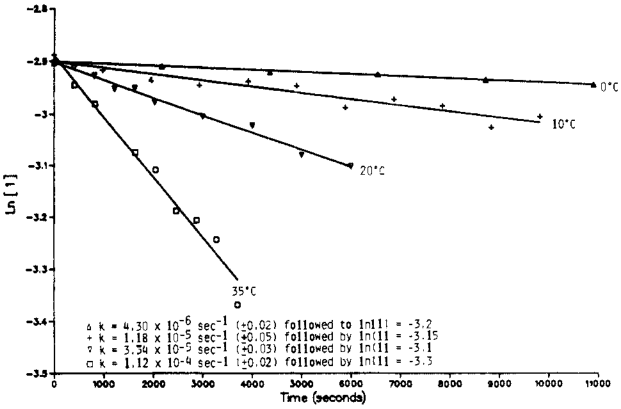

Figure 4. Thermolysis of (DPPE)Pt(OMe)$_2$ in CD_2Cl_2. ln [**1**] vs. time as measured between 0 and 35 °C. Least-squares lines fitted as listed, $[\mathbf{1}]_0$ = 0.055 M.

Interestingly, the rates of methanol exchange for **1** and **2** are surprisingly close to one another. This observation holds in THF-d_8 as well as toluene-d_8 solvents, though the associative exchange rate for both of these complexes in THF was found to be substantially slower than in toluene (Table III). Methoxide dissociation, on the other hand, would be faster in THF than in toluene so the dissociation rate in less polar solvents should be much slower than 10^{-7} s^{-1}. This inhibition of methanol exchange in THF relative to toluene suggests donor solvents may compete with methanol for the open coordination site on these platinum complexes which is necessary for methoxo ligand exchange to take place. While only two methanol exchange experiments have been conducted with ethyl methoxo complex **3**, the rates were again found to be similar to those found for **2** and **1**. This suggests these admittedly small changes in ligand environment do not significantly change either the sterics of the methanol exchange or the

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(10) A few leading references to this extremely important reaction follow: (a) Caldin, E. F., Gold, v., Eds. *Proton-Transfer Reactions*; Chapman and Hall: London, 1975. (b) Koch, H. F. *Acc. Chem. Res.* **1984**, *17*, 137. (c) Menger, F. M. *Tetrahedron* **1983**, *39*, 1013. (d) Bell, A. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980. (e) Chou, P.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 4596. (f) Rossetti, R.; Rayford, R.; Haddon, R. C.; Brus, L. E. *J. Am. Chem. Soc.* **1981**, *103*, 4303. (g) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185. (h) Engdahl, K.-A.; Bivehed, H.; Ahlberg, P.; Saunders, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 4767. (i) Grunwald, E. *J. Phys. Chem.* **1982**, *86*, 1302. (j) Scheiner, S. *Acc. Chem. Res.* **1985**, *18*, 174.

(11) (a) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686. (b) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A.* **1969**, 443. (c) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (d) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88. (e) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239.

(12) Bryndza, H. E. *Organometallics* **1985**, *4*, 406.

(13) Arnold, D. P.; Bennett, M. A.; Bilton, M. S.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1982**, 115.

(14) The complex *trans*-$(PEt_3)_2PtH(CH_3)$ has been prepared (along with other related trans methyl hydrido complexes of Pt(II)) as reported in: Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263. Many other analogous *trans*-$L_2PtR(H)$ complexes have been isolated by Bennett, as reported in ref 3c,d, by thermolyzing *trans*-$(PR_3)_2PtR'(OH)$ in methanol; in some cases the (presumably) intermediate methyl methoxide complexes were observed.

(15) (a) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uhlarte, R. J. *Organometallics* **1984**, *3*, 816. (b) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (c) Anton, D. R.; Crabtree, R. H. *Organometallics* **1982**, *2*, 855. (d) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(16) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637.

(17) No loss of ^{195}Pt couplings to phosphine ligands has been noted in any of these thermolyses. Similar studies with (DPPP)PtEt(OMe) (DPPP = 1,3-bis(diphenylphosphino)propane, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$) show very similar rates of decomposition, suggesting P ligand dissociation is not important for these processes.

(18) Specific information for the (DPPE)PtMe(X) series can be found in: (a) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738. Other references to trans effects in platinum(II) complexes include: (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335 and references therein. (c) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707. (d) Powell, J.; Shaw, B. L. *J. Chem. Soc.* **1965**, 3879. (e) Atkins, P. W.; Green, J. C.; Green, M. L. H. *J. Chem. Soc. A* **1968**, 2275. (f) Chatt, J.; Duncanson, L. A.; Shaw, B. L.; Venanzi, L. M. *Discuss. Faraday Soc.* **1958**, *26*, 131. (g) Chatt, J. *Proc. Chem. Soc. London* **1962**, 318. (h) Dean, R. R.; Green, J. C. *J. Chem. Soc. A* **1968**, 3047. (i) Keskinen, A. E.; Senoff, C. V. *J. Organomet. Chem.* **1972**, *37*, 201. (j) Toniolo, L.; Cavinato, G. *Inorg. Chim. Acta* **1978**, *26*, L5. (k) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2117. (l) Arnold, D. P.; Bennett, M. A.; Crisp, G. T.; Jefferey, J. C. *Adv. Chem. Ser.* **1982**, *196*, 195. (m) Church, M. J.; Mays, M. J. *J. Chem. Soc. A* **1968**, 3074.

(19) While we have not observed hydroxymethyl species (MCH_2OH) in any of our methoxo ($MOCH_3$) thermolyses, we have never seen significant deuterium kinetic isotope effects, either. While this does not rule out a thermolysis mechanism involving rate-limiting, rather than preequilibrium, β-elimination, it suggests this possibility is unlikely. The similarity of the activation barriers for the release of organic products through β-eliminations from ethyl and methoxo substituents also suggests the reaction profiles for the two processes might be similar. While our data suggest the relative thermodynamic stabilities of (DPPE)Pt(C_2H_4) and (DPPE)Pt(CH_2O) do not determine the ratio of ethylene to ethane formed, we cannot rule out major stability differences in (DPPE)Pt(H)(OCH_3)(C_2H_4) and (DPPE)Pt(H)(Et)(CH_2O) from determining the product ratios. We have evidence[22] that suggests these intermediates should be thermodynamically close in energy, and the similar activation barriers for the production of ethane and ethylene further suggests this possibility is likely. We acknowledge a referee for bringing this possibility to our attention.

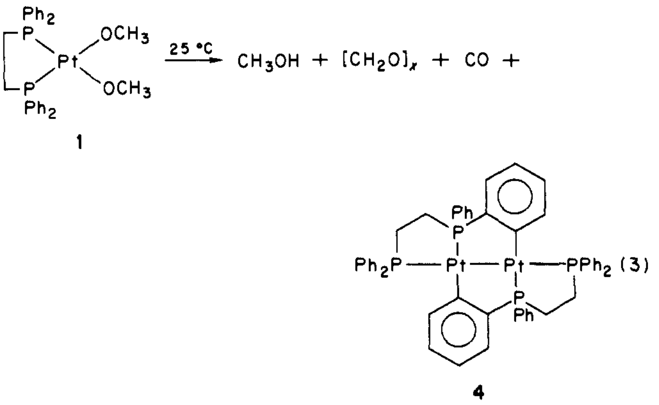
(20) A preliminary account of this approach using (COD)Pt($^*CH_2CH_3$)(X) complexes has been published: *J Chem. Soc., Chem. Commun.* **1985**, 1696.

(21) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735.

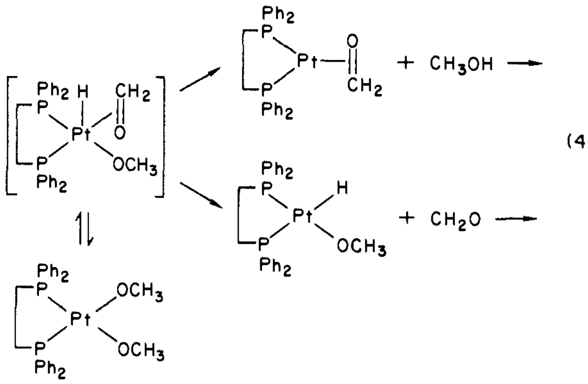
(22) An equilibrium technique outlined in Bryndza et al. (Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939) has been extended to evaluate both the (DPPE)PtMe(X) (X = OH, OCH_3, NPh_2, NMePh, CH_2COCH_3) and Cp*Ru(PMe_3)$_2$(Y) systems (Y = OH, NHPh, NPh_2, CH_2COCH_3, CCPh, H) for relative metal–ligand bond dissociation energies (Bryndza, H. E.; Paciello, R. A.; Fong, L. K.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.*, accepted for publication. The correlation of H–X to M–X bond strengths in both these systems shows M–O and M–C bond strengths are similar to one another and suggests this to be a general trend for group VIII (groups 8–10) metals.

electronic factors governing methanol binding to the metal center. It is worth mentioning that qualitative experiments on the addition of *tert*-butyl alcohol to **1** and **2** show markedly slower ligand interchange with this bulky alcohol.

Thermolysis of 1. While easy to prepare, complex **1** decomposes rapidly at room temperature in nondonor solvents such as CD_2Cl_2 or α,α'-dimethyl-THF to generate formaldehyde and its oligomers as well as methanol in approximately 1:1 ratios. Small amounts (less than 5% based on methoxo ligands) of carbon monoxide are also formed, especially at long reaction times, which probably arise by further dehydrogenation of formaldehyde. In CD_2Cl_2, the organometallic products include some orthometalated dimer **4** (25%) (eq 3) as identified by NMR techniques[13] along with about 5% each of (DPPE)Pt(OMe)(CO_2Me) and (DPPE)Pt(CO_2Me)$_2$. After 24 h about 30% of the original platinum can be isolated from methylene chloride solution as (DPPE)$PtCl_2$. In α,α'-dimethyl-THF the major identifiable organometallic product is **4**, present in 50% yield by NMR. When 2 equiv of free DPPE are added to **1** in α,α'-dimethyl-THF, thermolysis is quite slow. However, after 3 h at 50 °C, $(DPPE)_2Pt$ could be spectroscopically observed to account for 80% of the platinum in solution. Formaldehyde oligomers and methanol were again observed as organic products by NMR, GC/MS, and chromotropic acid analysis. In α,α'-dimethyl-THF the major identifiable organometallic product identified is **4**.



These observations suggest a decomposition mechanism involving initial β-hydride elimination from the 16-electron starting complex followed by rate-limiting release of organic products (eq 4). The following are consistent with this interpretation:



(1) Thermolysis kinetics (measured by ^1H and ^{31}P NMR techniques) in CD_2Cl_2 solvent show the decomposition is first order in **1** (Figures 4 and 5) from 0 to 35 °C.

(2) Thermolysis of (DPPE)Pt(OCD_3)$_2$ shows no kinetic deuterium isotope effect ($k_H/k_D = 0.9 \pm 0.2$). Products of this thermolysis in CH_2Cl_2 are CD_3OD and $[CD_2O]_x$ (x = 1, 3) as identified by ^2H NMR and GC/MS. No evidence of protic materials was noted. Decomposition of 1-d_6 in CD_2Cl_2 forms no detectable protic organic products by ^1H NMR and GC/MS. Together these results show the decomposition does not involve protons from either the solvent or the aromatic phosphine ligands. The lack of a large isotope effect is consistent with preequilibrium β-elimination and suggests thermolysis does not proceed by proton transfer from one methoxide ligand to the oxygen lone pair of the second methoxide ligand.

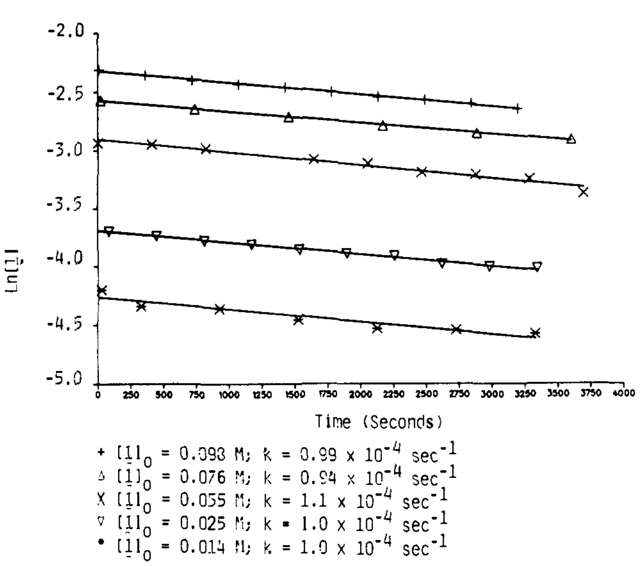


Figure 5. Thermolysis of (DPPE)Pt(OMe)$_2$ (**1**) at 35 °C.

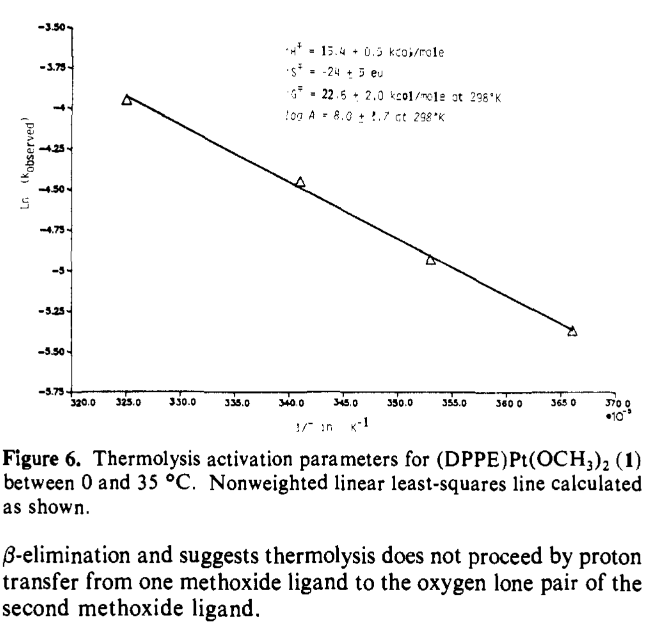


Figure 6. Thermolysis activation parameters for (DPPE)Pt(OCH_3)$_2$ (**1**) between 0 and 35 °C. Nonweighted linear least-squares line calculated as shown.

(3) Decomposition of (DPPE)$PtCH_3(OCH_3)$ (**2**), a model complex containing only one methoxide group, decomposes to generate methane, formaldehyde oligomers, and complex **4**.[13] This result demonstrates that an easily deprotonated second alkoxide ligand is not required to obtain similar reaction products.

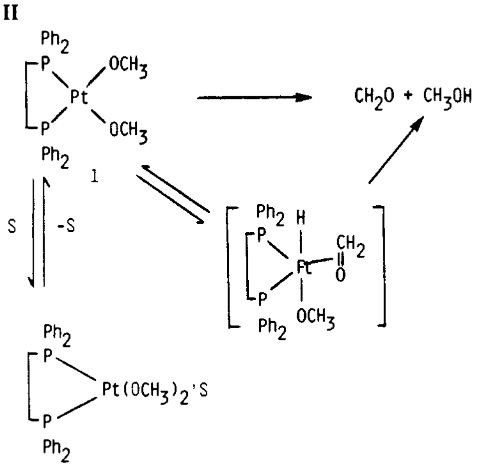
(4) Activation parameters for the thermolysis of **1** measured between 35 and 0 °C in CD_2Cl_2 show (Figure 6) $\Delta H^{\ddagger} = 15.4 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -24 \pm 5$ eu and are inconsistent with dissociative mechanisms.

(5) The rate of decomposition of **1** in CD_2Cl_2 is about the same as the rate in α,α'-dimethyl-THF. However, donor solvents such as THF stabilize the complex and slow the decomposition; the rate of thermolysis in THF solvent at 50 °C is about the same as that found in nondonor solvents at 20 °C. These results show methoxide dissociation is not involved in this thermolysis and suggest β-elimination can be inhibited by coordination of solvent which blocks the necessary open site for hydrogen atom migration.

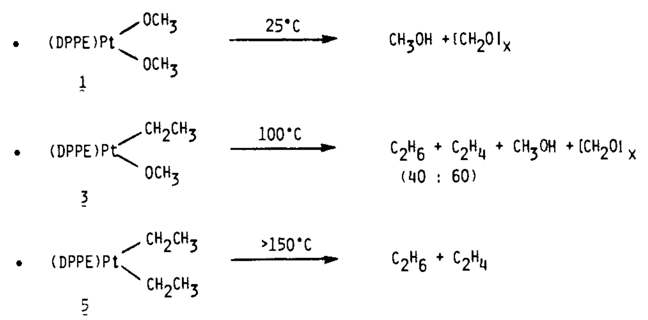
Significantly, this result also shows the intimate involvement of the metal in this process, as an intramolecular hydrogen atom transfer from one OCH_3 group to the other should not be affected by solvent coordination at the metal.

(6) Allowing *trans*-Pt(PEt_3)$_2$(CH_3)(OCH_3) to warm above 0 °C generates formaldehyde, trioxane, and *trans*-Pt(PEt_3)$_2$(H)(CH_3) as the only observed products. The organometallic product has been reported previously[14] as the isolated species formed on treating *trans*-(PEt_3)$_2$PtH(Cl) with MeMgBr. Other related *trans*-hydridoalkyl and -hydridoaryl complexes of this type have

Scheme II



Scheme III



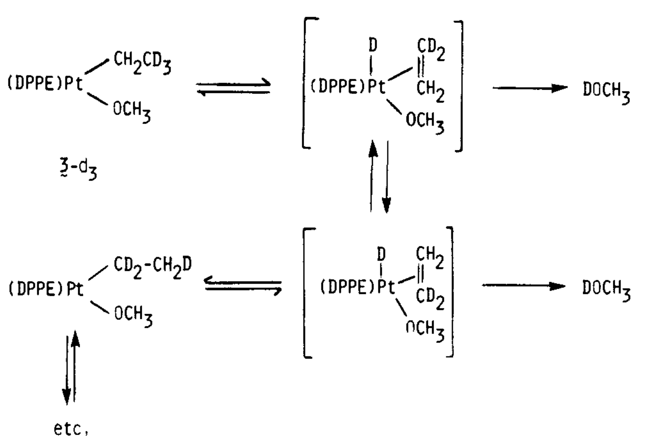
been prepared by Bennett through thermolysis of the corresponding *trans*-hydroxoalkyl and -hydroxoaryl complexes in methanol.[3c,d]

Together these results indicate that **1** decomposes by preequilibrium β-hydride elimination from a 16-electron complex which can be inhibited by the presence of donor solvents (Scheme II). Rate-limiting release of organic products follows. Additionally, mechanisms involving proton transfer between one methoxy ligand and a second oxygen must be deemed unlikely.

β-Elimination from Alkyl vs. Alkoxo Ligands. The above observations show β-eliminations from alkoxo ligands bear similarities to the analogous processes outlined by Whitesides, Yamamoto, and others for platinum(II) dialkyl species.[6] It is, however, interesting to note that while **1** decomposes at 25 °C to generate CH_2O and CH_3OH, the analogous diethyl complex **5** (Scheme III) requires temperatures in excess of 150 °C in *p*-xylene-d_{10} to slowly release C_2H_4 and C_2H_6 as the only observed organic products; in this case more ethane is produced than ethylene (the ratio $C_2H_4/C_2H_6 = 0.8 \pm 0.1$), suggesting that involvement of the aromatic phosphine ligands or solvent becomes competitive at these extreme temperatures. In this process, platinum metal is produced which can be effectively scavenged with mercury.[15] When thermolyses were carried out in vigorously stirred solutions in the presence of mercury, the solutions remained clear and the ratio of C_2H_4/C_2H_6 did not change. Interestingly, Yamamoto did not observe more alkanes formed than olefins in either the solid-phase pyrolysis of (DPPE)PtEt(Pr) or the solution-phase thermolysis of $(PPh_3)_2PtEt_2$ (in the presence of large excesses of PPh_3, to force nondissociative β-elimination to dominate the reaction).[6d] This suggests that solvent involvement, rather than aromatic phosphine ortho-metalation, is responsible for the slightly larger amounts of ethane observed (relative to ethylene) in our thermolysis of **5** in xylene.

Studies by Whitesides and Yamamoto show Pt–C bond homolysis in related species which have no β-hydrogen substituents takes place only to low conversion after several hours at 180 °C. Similarly, $(DPPE)PtMe_2$ does not decompose detectibly under these thermolysis conditions; not unexpectedly, the presence of β-hydrogen atoms provides a lower energy path for decomposition of **5**. Perhaps more importantly, complex **5**, with six β-hydrogen substituents, is significantly more robust toward decomposition

Scheme IV



by β-hydride elimination than bis-methoxide **1** which has six β-hydrogen substituents attached to platinum through an oxygen-containing framework.

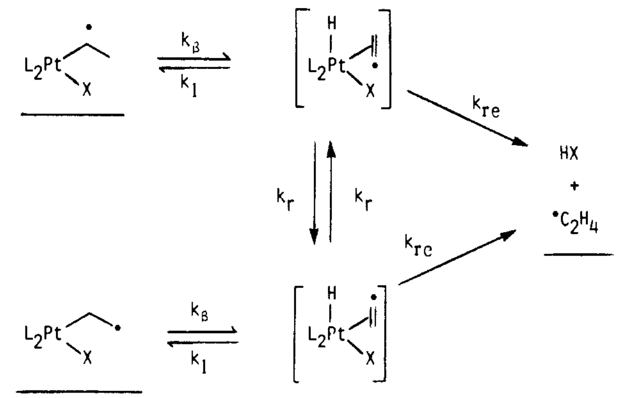
Given these dramatic differences in thermolysis conditions for **1** and **5**, we decided to directly compare β-elimination from ethyl and methoxo ligands. To do this, the thermolysis of (DPPE)-$Pt(CH_2CH_3)(OCH_3)$ (**3**), which has three hydrogen atoms bound to β-carbon positions on each type of ligand, has been studied.

Our initial hypothesis predicted that the presumably weak metal–oxygen bond in **3** would lead to intrinsically faster β-elimination from the methoxo ligand than from the ethyl substituent; this, in turn, was anticipated to lead to ethane and formaldehyde products. We were, therefore, surprised to find minor amounts of those products accompanied by larger quantities of ethylene and methanol formed when **3** was thermolyzed at 100 °C in toluene-d_8. As shown in Scheme III, the ratio of ethylene to ethane was 1.5, demonstrating that decomposition arising from initial β-elimination at the ethyl ligand is a lower activation energy process by about 0.3 kcal/mol than the analogous decomposition pathway from the methoxo ligand. Two possible thermolysis intermediates, $(DPPE)Pt(C_2H_4)$ and $(DPPE)Pt(CH_2O)$, previously described by Head,[16] have no measureable lifetimes at 100 °C. To determine if the C_2H_4 to C_2H_6 ratio is governed by the irreversibility of ethane addition to $(DPPE)Pt(CH_2O)$ vs. the reversibility of methanol addition to $(DPPE)Pt(C_2H_4)$ (i.e., to determine if the $\Delta G^‡$ values are coincidentally similar because the path involving β-elimination from the ethyl ligand is reversible and the path involving β-elimination from the methoxide substituent is not), the thermolysis of **3** was studied in the presence of both ethane and methanol. As expected, thermolysis of **3** in the presence of 4 equiv of ethane (pressure <2 atm, depending on the amount which dissolves at 100 °C) at 100 °C in toluene does not affect the amount of methanol formed. Interestingly, when **3** is heated at 100 °C in toluene-d_8 containing 4 equiv of methanol (in a sealed tube) the ratio of ethane to ethylene is unchanged. While these results suggest the relative stabilities of $(DPPE)Pt(C_2H_4)$ and $(DPPE)Pt(CH_2O)$ do not govern the ratios of ethylene to ethane formed in these thermolyses, they do not require isoenergetic decomposition mechanisms for the two types of ligands (see below).

It is worth emphasizing that complex **3**, which has one methoxo ligand, decomposes at 100 °C, while **1**, which has two electronegative methoxo substituents, decomposes at ambient temperature. No evidence for phosphine dissociation was noted[17] and, based on the trans-labilizing series established by Bennett[18] for $(DPPE)PtCH_3(X)$ complexes (which is also supported by the crystal structures mentioned above), if dissociation were important, the diethyl complex **5**, with two trans-labilizing ligands, would have been expected to decompose fastest of all.

In order to determine if this 0.3 kcal/mol energy-barrier difference reflects the barriers to the two β-eliminations (which would be the case only if that step is rate-limiting), we prepared $(DPPE)Pt(CH_2CD_3)(OCH_3)$ (**3**-d_3). This thermolysis was intended to determine if β-elimination is a preequilibrium step in

Scheme V[a]



[a] Observed rates: k_β = β-elimination, k_l = insertion, k_r = rotation, k_{re} = release of organics.

the thermolysis of **3** by providing diagnostic access to starting material which has undergone β-elimination, olefin rotation, and reinsertion of the resultant olefin hydride (Scheme IV) faster than organic products are released.

This labeled ethyl complex was thermolyzed at 100 °C in xylene in the ^{2}H probe of an NMR spectrometer, and spectra acquired showed that substantial deuterium scrambling from the methyl to the methylene position takes place in the starting material. That this scrambling is qualitatively 2–3 times faster than decomposition of **3**-d_3 shows the thermolysis of **3** proceeds by preequilibrium β-elimination followed by rate-limiting release of organic products. By analogy, the alkoxo ligand likely does the same thing, especially considering the similar activation barriers of the two decompositions.[19]

Scheme V outlines a useful extension of previous work on β-elimination. While kinetic deuterium isotope effects make quantitative analysis of the relative rates of β-elimination and reductive elimination in **3** complex (and make relative decomposition rates of **3**-d_0/**3**-d_3 meaningless), the use of ^{13}C-labeled ethyl complexes should allow the direct quantification of the rate of β-hydride elimination in this system, divorced from other complicating reaction steps. Such studies are in progress.[20]

The dramatic accelerating effect of an ancillary methoxide ligand on β-elimination from an ethyl substituent can be noted by comparing the thermolyses of **5** and **3**, while the same acceleration of β-elimination from a methoxo ligand can be seen by comparing the thermolyses of **3** and **1**. For both ethyl and methoxo ligands, therefore, β-elimination is accelerated by the presence of a "spectator" methoxo ligand. This may be due to ease of distorting the geometry of M–OR linkages or the increased positive character of the platinum center caused by addition of a polarizing ligand and suggests that electron-deficient character at a metal center might provide an energetic driving force for β-elimination comparable with providing coordinative unsaturation through ligand dissociation. Further studies of ancillary σ ligand effects on β-elimination energetics are in progress with use of the ^{13}C labeling scheme outlined above.

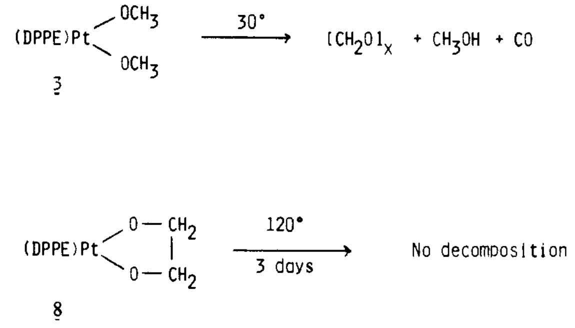
To further compare the thermolysis of alkyl complexes with that of analogous alkoxo species, we noted that while Whitesides found $(PEt_3)_2Pt(CH_2CH_3)_2$ (**6**) decomposes at 100 °C, the analogous metallacycle $(PEt_3)_2Pt(CH_2)_4$ (**7**) is considerably more stable due to the inability of the β-hydrogen substituents to access the metal center.[21]

Addition of ethylene glycol to a THF solution of **1** allows isolation of the analogous "heterometallacycle" **8**. While **1** decomposes at 25 °C, **8** did not detectably decompose after 3 days at 120 °C (Scheme VI).

Conclusions

The thermolysis of platinum(II) alkoxides to generate methanol and formaldehyde oligomers is obviously a low-energy process relative to other intermolecular types of C–H bond activation. Kinetics and labeling studies suggest thermolysis can best be explained by a mechanism involving preequilibrium β-hydride elimination followed by rate-limiting release of organic products. In complex **3**, where both ethyl and methoxo ligands are present, decomposition from ethyl ligand β-elimination predominates; this is inconsistent with the commonly held assumption that M–O bonds of the group VIII (groups 8–10) metals are characteristically weak and suggests they may have thermodynamic stability comparable to M–C bonds in alkyl complexes.[22] The presence of nondissociating polar ligands like methoxide can accelerate β-elimination from both alkyl and alkoxo substituents. This suggests systematic study of spectator ligand effects might lead to control of the energetic barriers to β-elimination from alkyl and alkoxo ligands through design of complexes. Chelating glycolate complex **8** shows striking stability relative to bis-methoxide **1**, again in complete analogy with findings in platinum(II) alkyl chemistry.

Scheme VI



Previous studies have shown that platinum alkoxides can insert CO[11] and fluoro olefins[12] by the same coordinative insertion mechanisms established for group VIII (groups 8–10) alkyls and hydride complexes. With our findings that β-elimination can apparently also take place by similar mechanisms in these complexes, we predict catalytic chemistry similar to that established for metal alkyls can be developed for metal alkoxides.[23]

Experimental Section

General. All operations were carried out in a Vacuum Atmospheres drybox equipped with nitrogen purge system and a Dry-Kool freezer or used standard Schlenk and high-vacuum techniques.

Platinum starting materials were prepared by published methods.[24] DPPE was used as obtained from Strem Chemicals while Grignard and lithium reagents were used as purchased from Aldrich. Trideuterioethyl iodide was obtained from Merck and was used as received for the synthesis of $(COD)Pt(CH_2CD_3)_2$ by standard methods.[25] Sodium was obtained as 2–4-mm balls in kerosene and was filtered, washed with pentane, and stored under nitrogen in the drybox.

Diethyl ether and tetrahydrofuran (THF) were obtained from MCB and were dried with activated (350 °C for 2 h) 4-Å molecular sieves before being degassed with an argon purge and distilled from a sodium

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(23) Some processes which employ metal hydroxides and alkoxides as added catalysts follow. In most of these cases the role of metal–oxygen bonds has not been clearly established: (a) Otsuka, S.; Yoshida, T. *Adv. Chem. Ser.* **1982**, *196*, 135 and references contained therein. (b) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1363. (c) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030. (d) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127. (e) Hirai, K.; Nutton, A.; Maitlis, P. M. *J. Mol. Catal.* **1981**, *10*, 203. (f) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1980**, 144. (g) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (h) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119. (i) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 2, p 82. (j) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Halsted Press: New York, 1973; p 172. (k) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 443.

(24) (DPPE)PtMeCl was prepared as outlined in ref 15a. (DPPE)PtEtCl was prepared by analogous methods using $(COD)PtEt_2$ which was, in turn, prepared by the method of Whitesides (ref 6j–s). Dialkyls were converted to the alkyl chlorides by the methods of: Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *5*, 411. $(DPPE)PtEt_2$ was prepared by the addition of DPPE to $(COD)PtEt_2$ as outlined in ref 6j–s to give the material reported previously in: (a) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 233. (b) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277. (c) Clocking, F.; McBride, T.; Pollock, R. J. I. *Inorg. Chim. Acta* **1974**, *8*, 81.

(25) See, for example, ref 6n.

benzophenone purple ketyl solution. Benzene and pentane were treated similarly except that sufficient tetraglyme was added to the ketyl solutions to maintain a purple color. Before drying, the pentane was first washed with 3 × 150 mL of mixed acids (15% concentrated reagent grade HNO_3 and 85% concentrated reagent grade sulfuric acid), 1 × 200 mL of distilled water, 2 × 200 mL of saturated aqueous $NaHCO_3$ solution, and 2 × 200 mL of distilled water and then dried with excess $MgSO_4$ before being stored over activated 4-Å moecular sieves. Toluene was dried over activated molecular sieves, degassed with an argon sparge, and distilled in an argon atmosphere from sodium. Methanol was degassed with a 20-min vigorous argon sparge and dried in the drybox with activated 3-Å molecular sieves. Methylene chloride was similarly degassed and distilled under argon from calcium hydride. Deuterated solvents were obtained from Aldrich and were treated as the protic analogues except that vacuum transfers were used in place of distillations. Water and D_2O were degassed with seven freeze–pump–thaw cycles on a high-vacuum line. In all cases (except water), purity of solvents was assayed by GC and found to contain less than 1% total impurities (not corrected for response factors).

All infrared spectra were recorded on a Perkin-Elmer Model 983G optical null spectrophotometer in 0.1-mm path length KBr solution cells. Satisfactory elemental analyses were obtained for all compounds, except as noted, from Galbraith Analytical Labs. NMR spectra were recorded on NT series GE spectrometers operating at either 300- or 360-MHz proton frequencies and were referenced to residual protic solvent peaks to obtain chemical shift information.

Spectra were recorded in standard pulsed FT mode at constant temperature on an instrument calibrated by methanol standards. Standard mass determinations were conducted in the drybox by using a calibrated Sartorius 1605 MP balance, while physical experiments were prepared by using standard dilution techniques in volumetric glassware and a Mettler Model AE160 (0.1 mg) balance, also maintained in the inert-atmosphere box. In some cases, volumetric solutions were prepared directly in no. 507-TR screw-capped NMR tubes, using the 0.1-mg balance and calculating the solution volume from the following relationship:

$$\text{volume } (\mu\text{L}) = \text{height (mm)} \times 14 + 5.55$$

The data used to determine this relationship can be inspected in the supplementary material.

Kinetics experiments were conducted by NMR in either 5- or 10-mm-o.d. Pyrex NMR tubes. Spin lattice relaxation times (T_1, s) were determined by standard spin inversion/recovery methods and spectra were recorded in standard pulsed FT mode, using 90° pulses and at least five T_1 periods between pulses to assure good quantitative results. Intensities were measured by integration and rates were determined by standard nonweighted least-squares procedures or on iterative multiple nonlinear regression programs based on HAVECHEM programs.[26]

Syntheses. (DPPE)Pt(OCH$_3$)$_2$. This preparation was conducted in the drybox by using oven-dried glassware throughout. (DPPE)$PtCl_2$ (2.00 g, 3.01 mmol) was weighed into a 500-mL round-bottom flask equipped with magnetic stir bar. Benzene (100 mL) was added and the slurry treated with 30 mL (6.15 mmol) of a freshly prepared solution of sodium methoxide in methanol. The resulting mixture was stirred at ambient temperatures for 2 h and then concentrated to 50 mL total volume without external heating. Pentane (100 mL) was added and the resulting solid was filtered and dried briefly in a stream of nitrogen gas. The solid was extracted with 150 mL of THF and that resulting solution was concentrated to 30 mL total volume, again without external heating. Pentane (150 mL) was added and the resulting solid collected and vacuum dried. The resulting solid was found to contain a THF of crystallization which could be removed by low-temperature recrystallization from CH_2Cl_2/pentane. While this material was too unstable to obtain satisfactory elemental analysis it has, by handling at low temperature, been crystallized and analyzed by single-crystal X-ray diffraction methods. Typical yields, 1.68 g (2.56 mmol, 85% yield); ^{1}H NMR ($CD_2Cl_2/CDHCl_2$) δ 7.4–8.2 (m, 20 H), 3.60 (dd with Pt satellites, $^4J_{PH} = 6.4$, $^4J_{P2H} = 0.7$, $^2J_{PtH} = 37.2$ Hz, 6 H), 1.9–2.5 (m, 4 H); ^{31}P NMR (THF-d_8/H_3PO_4 ext) δ 25.7 (s with Pt satellites, $^1J_{PtP} = 3287$ Hz) $T_1 = 3.59$, (CD_2Cl_2/H_3PO_4 ext) δ 28.5 (s with Pt satellites, $^1J_{PtP} = 3342$ Hz) $T_1 = 3.52$ s.

(DPPE)PtCH$_3$(OCH$_3$).[27] All steps were carried out in dry glassware in the drybox. In a 500-mL round-bottom flask 5.00 g (7.76 mmol) of (DPPE)PtMeCl was suspended in 300 mL of benzene with a magnetic stir bar. A freshly prepared 2.2 M solution of sodium methoxide in methanol (35 mL, 77.6 mmol) was added and the solution was stirred overnight at 25 °C. Alternately the solution could be heated at 50 °C for 2 h with only slight deterioration of the resulting platinum methoxide. The solution was then stripped to dryness and the resulting solid extracted with 5 × 100 mL of THF. The combined solutions were stirred to dryness and the resulting solid recrystallized in warm toluene/pentane. Typical yield, 4.5 g (7.04 mmol, 90%); ^{1}H NMR (THF-d_8/THF-d_7) δ 0.526 (dd with Pt satellites, $^3J_{PH} = 7.79$, $^3J_{P2H} = 3.11$, $^2J_{PtH} = 59.55$ Hz, 3 H), 2.3 (complex m, 4 H), 4.01 (d with Pt satellites, $^4J_{PH} = 5.33$, $^3J_{PtH} = 48.8$ Hz, 3 H), 7.4–8.3 (m, 20 H), ($CH_2Cl_2/CDHCl_2$) δ 0.425 (dd with Pt satellites, $^3J_{PH} = 7.72$, $^3J_{P2H} = 3.18$, $^2J_{PtH} = 57$ Hz, 3 H), 2.2 (m, 4 H), 3.91 (d with Pt satellites, $^4J_{PH} = 6.1$, $^3J_{PtH} = 47.5$ Hz, 3 H), 7.4–8.0 (multiplet, 20 H); ^{31}P NMR (THF-d_8/H_3PO_4 ext) δ 37.35 (s with Pt satellites, $^1J_{PPT} = 1852$ Hz), 36.00 (s with Pt satellites, $^1J_{PtP} = 3356$ Hz). Anal. Calcd for $C_{28}H_{30}OP_2Pt$: C, 52.58; H, 4.73. Found: C, 52.21; H, 4.73%.

(DPPE)PtEt(OMe). The same method used for the preparation of (DPPE)PtMe(OMe), above, was used to prepare the analogous ethyl methoxide in up to 77% yield. ^{1}H NMR (THF-d_8/THF-d_7) δ 7.2–8.1 (m, 20 H), 3.92 (d with Pt satellites, $^4J_{PH} = 5.57$, $^3J_{PtH} = 48.0$ Hz, 3 H), 2–2.4 (m, 4 H), 1.2 (br m, 2 H), 0.85 (br m, 3 H); ^{31}P NMR (CD_2Cl_2/H_3PO_4) δ 43.63 (d with Pt satellites, $^2J_{PP} = 8.20$, $^1J_{PtP} = 1614$ Hz, 1 P), 35.91 (d with satellites, $^2J_{PP} = 8.2$, $^1J_{PtP} = 3558$ Hz, 1 P). Anal. Calcd for $C_{29}H_{32}OP_2Pt$: C, 53.29; H, 4.94. Found: C, 53.28; H, 4.74.

(DPPE) Pt(CH$_2$**CD$_3$**)**(OMe).** The same method used to prepare (DPPE)PtMe(OMe), above, was used to prepare the trideuterioethyl methoxide **3**-d_3. NMR as for (DPPE)Pt(CH_2CH_3)(OCH_3) except the following: ^{2}H NMR (THF-d_0/THF-d_1) CH_3 at δ 0.88 (br m,), ($CH_2Cl_2/CDHCl_2$) δ 0.80 (br m); ^{1}H NMR (THF-d_8/THF-d_7) no methyl signal seen, Pt–CH_2 at δ 1.18 (br m, 2 H), ($CD_2Cl_2/CDHCl_2$) PtCH_2 at δ 1.10 (br m, 2 H).

$\mathbf{(DPPE)}\overline{\mathrm{Pt}(\mathbf{O}\mathrm{CH_2CH_2}\mathbf{O}}\mathbf{).}$ This procedure was conducted in the drybox by using oven-dried glassware. A 250-mL round-bottom flask was charged with 1.00 g (1.52 mmol) of (DPPE)Pt(OMe)$_2$ and a magnetic stir bar. The solid was dissolved in 50 mL of CH_2Cl_2 and treated with 1.0 mL of ethylene glycol. The solution was stirred for 2 h and concentrated to an oil. CH_2Cl_2, 10 mL, was added and solid was precipitated with pentane. The material was further purified by passing a methylene chloride solution through a Celite pad and then successively recrystallizing the material in CH_2Cl_2/pentane until no ethylene glycol remained. Typical yield, 0.450 g 0.69 mmol, 45% yield; ^{1}H NMR (THF-d_8/THF-d_7) δ 7.25–7.4 (m, 12 H), 8.1–8.2 (m, 8 H), 3.71 (d with Pt satellites, $^4J_{PH} = 3.71$, $^3J_{PtH} = 35.4$ Hz, 4 H), 2.45 (m, 4 H), ($CD_2Cl_2/CDHCl_2$) δ 7.9–8.0 (m, 8 H), 7.4–7.5 (m, 12 H), 3.09 (d with Pt satellites, $^4J_{PH} = 3.6$, $^3J_{PtH} = 31$ Hz, 4 H), 2.33 (m, 4 H); ^{31}P NMR (THF-d_8/H_3PO_4 ext) δ 28.15 (s with Pt satellites, $^1J_{PtP} = 3209$ Hz), (CD_2Cl_2/H_3PO_4 ext) δ 30.64 (s with Pt satellites, $^1J_{PtP} = 3256$ Hz). Anal. Calcd for $C_{28}H_{28}OP_2Pt$: C, 51.46; H, 4.32. Found: C, 51.45; H, 4.35 %.

Physical Experiments. Methanol Exchange. Volumetric solutions of the desired platinum methoxide complex in toluene were prepared as previously described. The solution was partitioned among several silylated and dried no. 507-TR screw-capped NMR tubes which had been soaked for 1 week in a pH 7 buffer and washed 10 times with distilled water. Additional deuterated solvent was added to bring the solution volume up to the desired level (at least 0.600 mL) and the tubes were capped and cooled to −40 °C in a drybox freezer. Prior to obtaining spectra a tube was warmed to ambient temperature, then CD_3OD was added and the tube immediately placed in a thermostated NMR probe, and spectra were recorded as already described.

Thermolysis of (DPPE)Pt(OMe)$_2$. As above, known-concentration solutions of **1** were prepared in a drybox and kept cold until used. Spectra were obtained as described and rate constants obtained by the method outlined above. Initial rates were used (one half-life or less) in these cases as at longer reaction times dehydrogenation of formaldehyde generates (presumably) platinum hydrides, which react with **1** to form methanol. To ensure the same reaction order in **1** holds from 0.08 to 0.01 M concentrations, several thermolyses were carried out at 35 °C in CD_2Cl_2. The consistency of the slopes (Figure 5) found in the ln ([**1**]) vs. time plots shows the reaction order in **1** does not change with concentration over a range which, if layed "end-to end" would correspond to better than three half-lives of first-order dependence. Carbon monoxide, also formed by dehydrogenation of formaldehyde, reacts with **1** to form (DPPE)Pt(CO_2Me)(OMe). Initial rates were therefore used as obtained early in the thermolyses.

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[26] An iterative version of HAVECHEM, as reported in Stabler et al. (Stabler, R. N.; Chesnick, J. P. *Int. J. Chem. Kinet.* **1978**, *10*, 461–469) and developed at Du Pont by Dr. F. J. Weigert was used for numerical integrations.

[27] (DPPE)PtMeOMe has been prepared, in situ, by another method as reported by Bennett in ref 13.

Products were analyzed by a combination of wet chemical,[28] spiking, and GC/MS analysis and Toepler pump collection of volatiles followed by GC/MS analysis. In a typical thermolysis experiment, 700 μL of a 0.055 M solution of **1** in a screw-capped NMR tube was heated in CD_2Cl_2 at 35 °C. The initially colorless solution turned orange without showing any evidence of metal deposition. Concentrations of methanol were evaluated after 50 min by NMR and GC, using benzene as an internal standard, while total formaldehyde was analyzed by quantitative chromotropic acid test.[28] The ratio of total formaldehyde to methanol was found to be 0.8 ± 0.2 (the total formaldehyde determination accounts for the high uncertainty) while ^1H NMR integrations show that, to the accuracy of integration methods, one equivalent of methanol was produced for every equivalent of bis-methoxide **1** which decomposed. At these early reaction times, only traces of CO (less than 1%) could be detected by Toepler pump/GC/MS techniques though after 3 h at 35 °C reaction solutions contained about 5% each of (DPPE)Pt(CO_2Me) [^1H NMR ($CD_2Cl_2/CHDCl_2$) δ 3.80 (d, $^4J_{PH} = 6.0$, $^3J_{PtH} = 35$ Hz, 3 H) relative to 3.26 (s, $^4J_{PtH} = 4.5$ Hz, 3 H), with PCH_2 and aromatic resonances obscured by other signals; ^1H-decoupled ^{31}P NMR (CD_2Cl_2/H_3PO_4 external) δ 37.8 (d, $^2J_{PP} = 7.6$, $^1J_{PtP} = 4119$ Hz, 1 P), 33.3 (d, $^2J_{PP} = 7.6$, $^1J_{PtP} = 2977$ Hz, 1 P)] and (DPPE)Pt$(CO_2Me)_2$ [^1H NMR ($CD_2Cl_2/CHDCl_2$) δ 3.21 (s, $^4J_{PtH} = 4.9$ Hz); ^1H-decoupled ^{31}P NMR (CD_2Cl_2/H_3PO_4 external) δ 39.45 (s, $^1J_{PtP} = 1849$ Hz)] as spectroscopically observed. Addition of an authentic sample of (DPPE)Pt$(CO_2Me)_2$ confirmed the identity of this product. Larger amounts of **4** (25%) were identified based on addition of an authentic sample prepared by the method of Bennett.[13] After 24 h a white solid precipitated from solution. Filtration, pentane washing, and vacuum drying gave about 30% (DPPE)$PtCl_2$; the identity was confirmed by NMR comparison with an authentic sample.

In the presence of 2 equiv of DPPE in α,α′-dimethyl THF, $(DPPE)_2Pt$ was identified as the major product by NMR. Spiking the solution with an authentic sample of $(DPPE)_2Pt$ confirmed the identity of this component.

In CD_2Cl_2, THF, and α,α′-dimethyl-THF solutions the early ratio of formaldehyde to methanol was the same within experimental uncertainty. Similarly, the amount of methanol was found to be 1.0 + 0.1 equiv, on the basis of conversion of **1**. In CH_2Cl_2 ^2H NMR showed trioxane, paraformaldehyde, and methanol were the only deuterium-containing products formed on thermolysis of **1**-d_6 at 35 °C for 50 min; no evidence of any aromatic or $CDHCl_2$ resonances were noted. GC/MS analysis of the trioxane and methanol showed, to the 5% uncertainty of the method, no incorporation of protons from the phosphine ligands or solvent. Similarly, no protic organic products were noted by ^1H NMR when **1**-d_6 was thermolyzed in CD_2Cl_2.

Thermolysis of *trans*-$(PEt_3)_2$MePt(OMe). The title complex was generated in situ and the results described are essentially the same as those published independently by Bennett. Halide abstraction from 1.00 g (2.08 mmol) of *trans*-$(PEt_3)_2$MePtCl using 1 equiv (426 mg, 2.18 mmol) of $AgBF_4$ in 15 mL of 0 °C methanol generated a slurry which was filtered into a 50-mL round-bottom flask. The solution was cooled in the drybox freezer to −20 °C and was then treated with a −20 °C solution of 150 mg (2.78 mmol) of NaOMe in 5 mL of methanol. The resulting solution was quickly filtered and then stripped to dryness below −20 °C (cooling maintained with a Neslab Model RTE-8 circulating refrigerated bath) on a high-vacuum line. The solid which remained was extracted in the drybox with 3 × 15 mL of cold THF. Solvent removal below −20 °C gave 402 mg (0.84 mmol) of crude product which could be further purified by extracting the resulting pale yellow oil with 3 × 20 mL of cold pentane. The resulting solution was filtered and stripped to dryness at −20 °C to generate a waxy pale yellow solid, which is unstable above 0 °C. ^1H NMR (in agreement with previous reports) (THF-d_8/THF-d_7 at −20 °C) δ 0.071 (3 H t, $^3J_{PH} = 5.87$, $^2J_{PtH} = 73.58$ Hz), 1.21 (18 H, dt, $J_{PH} = 15.77$, $^3J_{HH} = 7.7$ Hz), 1.87 (12 H, complex m), 3.55 (3 H, s, $^3J_{PtH} = 27.41$ Hz).

Allowing a THF-d_8 solution to warm above 0 °C generated *trans*-$(PEt_3)_2$MePt(H) as indicated by ^1H NMR signals as follows (in agreement with those reported by Halpern[14]): δ 0.06 (3 H, dt, $^3J_{HH} = 2.20$, $^3J_{PH} = 5.37$, $^2J_{PtH} = 52.25$ Hz), −5.53 (1 H, tq, $^2J_{PH} = 19.3$, $^3J_{HH} = 2.1$, $^1J_{PtH} = 674$ Hz), 1.7 (approximately 12 H though partially obscured by residual solvent peak, complex multiplet), 1.05 (18 H, complex multiplet). The presence of methanol and trioxane were noted by ^1H NMR and confirmed by GC/MS. Removal of volatiles leaves *trans*-$(PEt_3)_2$MePt(H) as an orange oil. This species has been prepared previously.[14]

Thermolysis of (DPPE)$PtEt_2$. A 0.05 M solution of (DPPE)$PtEt_2$ in *p*-xylene-d_{10} was heated in a 5-mL carius tube at 150 °C for 3 and 6 h, with gaseous products being removed by Toepler pump at both times. GC analysis (Porapak Q column calibrated with a synthetic mixture of ethylene and ethane) showed the ratio of ethylene to ethane was 0.8 (±0.1) for both samples. As thermolysis proceeds, deposition of a metal mirror was observed, which could be prevented when the reaction was carried out in the presence of mercury (which did, after the reaction, have a grey film on it). Analysis of the gaseous products showed, within experimental error, the same ratio of ethylene to ethane produced. ^1H NMR of the filtered solution showed some starting material remained after 3 h though no evidence of any platinum hydrides was noted at either 3 or 6 h.

Thermolysis of (DPPE)PtEt(OMe). Complex **3** was thermolyzed in toluene-d_8 solvent at 100 °C and found to generate methanol, ethylene, ethane, and formaldehyde oligomers which were analyzed as previously described. The ratio of ethylene to ethane was found to be 1.5 ± 0.1 and the ratio of methanol to total formaldehyde was found to be, within experimental error, the same (1.6 ± 0.4). No difference in the ratios of the products was noted in samples thermolyzed for 3 and 6 h. Thermolysis solutions turned red and showed small amounts of deposited metal which could be scavenged when reactions were run in the presence of mercury (which did not change the ratio of organic products formed). Thermolysis kinetics were acquired by the same method of initial rates from [**5**] = 0.08–0.02 M in toluene-d_8 and were found to be first order in **3** (though, as shown by deuterium-labeling studies and the various products observed, this clearly represents the rates of several competing reactions) with $-d[\mathbf{3}]/dt = 2.3 \times 10^{-4}\ s^{-1}$ at 100 °C.

Thermolysis of a 0.055 M toluene solution of **3** in the presence of 2 atm of ethane (4 equiv) in a sealed NMR tube showed no detectible increase in the amount of methanol produced as analyzed by GC (relative to solvent as internal standard). When 4 equiv of methanol was added, the ratio of ethylene to ethane was similarly unaffected.

Thermolysis of **3**-d_3 was carried out in a broad-band 10-mm NMR probe tuned for ^2H and thermally equilibrated prior to use. The instrument was shimmed by computer (analysis of the FID), using a 5-mm tube containing toluene-d_8 in toluene prior to use, and spectra were acquired on the thermolysis solution as quickly as possible (2 min or less) to prevent field drift from broadening the signals acquired. While the solution was heated the broad resonance at 0.88 ppm broadened further and a new resonance at 1.2 ppm grew into the spectra. Within 30 min the final 3:2 ratio of the signals was seen and isolation of the scrambled starting material was accomplished by filtering the solution and adding pentane until cloudy. Cooling at −40 °C and filtering the resulting off-white solid gave material which showed broad resonances in the proton NMR (THF-d_8) at 0.9 and 1.2 ppm along with the apparently unchanged methoxide doublet at 3.9 ppm. Only when **3**-d_3 was thermolyzed at 100 °C for longer periods of time (hours) did ethane (0.6 ppm), ethylene (5.3 ppm), and methanol (2.9 ppm) signals become evident, though reduced sensitivity of this method (quickly acquired spectra which contained fairly broad peaks) makes this qualitative information a fairly insensitive means of assessing relative rates of deuterium scrambling and organic product formation. No meaningful k_H/k_D data could be acquired, as once deuterium scrambling takes place intramolecular kinetic isotope effects become important within the $PtCD_2CDH_2$ ligand.

Acknowledgment. The technical assistance of Barry Johnson and Michael Stepro is acknowledged. Valuable discussions with Drs. Steven D. Ittel, David Milstein, and Andrew H. Janowicz are appreciated.

Registry No. 1, 102781-76-0; **2**, 82405-05-8; **3**, 102781-77-1; **4**, 82405-04-7; (DPPE)$PtEt_2$, 52621-10-0; (DPPE)$PtCl_2$, 14647-25-7; (DPPE)PtMeCl, 27711-50-8; (DPPE)Pt(CH_2CD_3)(OMe), 102781-78-2; (DPPE)$\overline{Pt(OCH_2CH_2O}$), 102781-79-3; *trans*-$(PEt_3)_2$MePt(OMe), 102781-80-6; *trans*-$(PEt_3)_2$MePt(H), 79452-66-7; (DPPE)Pt(OMe)(CO_2Me), 97295-83-5; (DPPE)Pt$(CO_2Me)_2$, 97295-82-4; (DPPE)PtEtCl, 65098-10-4; (DPPE)Pt(CH_2CD_3)Cl, 102781-81-7; ethylene glycol, 107-21-1.

Supplementary Material Available: Tables and additional information on the crystal structures of (DPPE)PtMe(OMe) and (DPPE)Pt$(OMe)_2\cdot(CH_2Cl_2)$ and height–volume calibration of Wilmad no. 507-TR screw-capped NMR tubes (16 page). Ordering information is given on any current masthead page.

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(28) Total formaldehyde was identified by a spectrophotometric version of the standard chromotropic acid test for formaldehyde as developed at Du Pont by Dr. David Milstein. Samples were treated with pentane, filtered, and treated with chromotropic acid and sulfuric acid aqueous solutions. After heating (sealed) at 100 °C with vigorous stirring for 30 min, the aqueous solutions were diluted with water in a 50–mL volumetric flask and the absorbance at 570 μm was noted and compared against standards prepared from paraformaldehyde. Control experiments in which paraformaldehyde was added to thermolysis solutions (which were analyzed independently) suggest the accuracy of this method is within ±20%.