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Water-Promoted Reaction of a Platinum(II) Oxo Complex with Ethylene[†]

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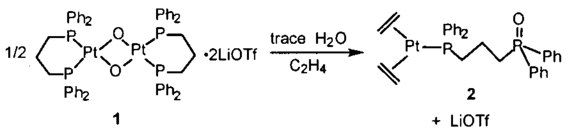
Summary: Treatment of [(dppp)Pt(μ-O)]$_2$(LiOTf)$_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$) with ethylene in the presence of trace amounts of water results in oxygen atom transfer to one arm of the bidentate phosphine ligand and formation of (dpppO)Pt(η^2-CH_2═CH_2)$_2$ (dpppO = $Ph_2P(CH_2)_3P(O)$-Ph_2). Further investigation reveals that the reaction of [L_2Pt(μ-O)]$_2$(LiOTf)$_2$ with water forms (dppp)Pt(OH)$_2$, which acts as a catalyst for the oxygen atom transfer reaction. The analogous oxo complex [$(PPh_3)_2$Pt(μ-O)]$_2$-($LiBF_4$)$_2$ does not react with ethylene under similar conditions. These results indicate that hydroxo complex intermediates should be considered in oxygen atom transfer reactions.

Introduction

The chemistry of transition-metal oxo complexes has been of interest to chemists for many years.[1] Chemical industries use late-transition-metal catalysts in a variety of processes.[2] Many of these processes involve the reaction of molecules with a metal surface, where oxygen atoms (oxo groups) are formed and transferred to other species. The chemistry occurring at the surface is poorly understood and is more easily studied through the use of soluble model complexes. Of particular interest to us is the synthesis and reactivity of late-transition-metal oxo complexes with small molecules.[1c,d] In this paper we report studies of the reactivity of dimeric [(dppp)Pt(μ-O)]$_2$(LiOTf)$_2$ (dppp = $Ph_2P(CH_2)_3$-PPh_2, OTf = CF_3SO_3) and the discovery of its reaction with ethylene in THF that contains trace amounts of water. This ability of water contamination to activate the platinum oxo complex toward alkenes is remarkable. Furthermore, to our surprise, oxygen atom transfer to the phosphine ligand occurs rather than oxidation[3] of the alkene or insertion[4] of the alkene into the Pt−O bond. Oxygen atom transfers from transition metal oxo complexes to phosphines are not uncommon;[5] however, in our system, a hydroxo complex produced from the water catalyzes the process, suggesting the involvement of a hydroxo group in the oxygen atom transfer.

Results

In dry THF, [(dppp)Pt(μ-O)]$_2$(LiOTf)$_2$ (**1**) displays no measurable reactivity toward ethylene. However, upon addition of trace amounts of water (0.03 equiv), **1** reacts readily with ethylene to form (dpppO)Pt(η^2-CH_2═CH_2)$_2$ **2** (eq 1).



(1)

The reaction mixture containing complex **2** and LiOTf reduces to an orange oil in vacuo, and **2** cannot be isolated in crystalline form. Efforts to isolate solid **2** by trituration and column chromatography were unsuccessful. Similar diphosphine oxide complexes have been reported[6] in which crystallization and purification have posed problems. However, the NMR spectroscopic data clearly establish (dpppO)Pt(CH_2═CH_2)$_2$ (**2**) as a member of the known class of complexes of formula LPt(CH_2═CH_2)$_2$ (L = a phosphine).[7] With the exception of the signals from the “dangling” $OPPh_2$ end of the dpppO ligand, all spectroscopic data closely resemble that for (Ph_2PMe)Pt(CH_2═CH_2)$_2$.[7] The ^{31}P NMR spectrum of **2** in the THF reaction mixture shows a singlet at 16.7 ppm with Pt satellites for the Ph_2P end of the dpppO group bonded to Pt(0) and a singlet at 31 ppm without satellites for the “dangling” $OPPh_2$ end of the dpppO ligand. The shift of 31 ppm is similar to that of other reported diphosphine oxides.[6,8] The ^{1}H NMR spectrum

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[†] Taken in part from the Ph.D. thesis of Jian-Jun Li (1996).

[1] (a) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459−517. (b) Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996**, *25*(1), 1−13. (c) Sharp, P. R. *Comments Inorg. Chem.* **1999**, *21*(1−3), 85−114. (d) Sharp, P. R. *J. Chem. Soc. Dalton Trans.* **2000**, *16*, 2647−2884. (e) West, B. *Polyhedron* **1989**, 219−274. (f) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339−387.

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[3] For a rare example of alkene oxidation by an isolated late-transition-metal oxo complex see: Hosokawa, T.; Takano, M.; Murahashi, S. I. *J. Am. Chem. Soc.* **1996**, *118*, 3990−3991.

[4] For examples of alkene or alkyne insertion into late-transition-metal−oxygen bonds see: (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603−1604. (b) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*(17), 7888−7889.

[5] For examples of phosphine oxidation by late-transition-metal oxo complexes see: (a) Brownlee, G. S.; Carty, P.; Cash, D. N.; Walker, A. *Inorg. Chem.* **1975**, *14*, 323−327. (b) Vilmer, M. C. M.S. Thesis, University of Missouri, Columbia, MO, 1986. (c) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543. (d) Dobbs, D. A.; Bergman, R. G. *Organometallics* **1994**, *13*, 4594−4605. (e) Shan, H.; James, A. J.; Sharp, P. R. *Inorg. Chem.* **1998**, *37*, 5727−5732. (f) Obias, H. V.; Lin, Y.; Murthy, N. N.; Pidcock, E.; Solomon, E. I.; Ralle, M.; Blackburn, N. J.; Neuhold, Y. M.; Zuberbuhler, A. D.; Karlin, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 12960−12961. For other transition-metal systems see: Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325−332 and references therein.

[6] Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285−292.

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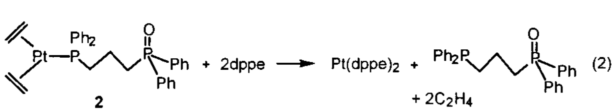
10.1021/om010868d CCC: $22.00

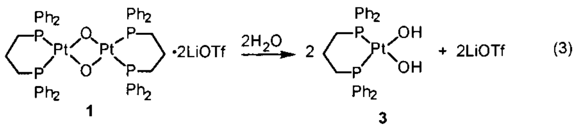
of **2** in CD_2Cl_2 shows the ethylene ligands as a broad singlet at 2.3 ppm with $^1H-^{195}Pt$ coupling of 58 Hz. The broadness of the peak is due to rotation of the ethylene ligands, common to this class of complexes.[7] This was confirmed by a low-temperature ^1H NMR study, which showed collapse of this peak ($T_c \approx -40$ °C) as the temperature was lowered and emergence of two broad peaks on each side of the original peak position. The ^{13}C NMR spectrum shows an ethylene peak at 39 ppm with $^{13}C-^{195}Pt$ coupling of 141 Hz. The ^{31}P NMR spectrum of **2** in CD_2Cl_2 is similar to that in THF, with the exception that the $OPPh_2$ peak at 31 ppm is notably broadened. This broadness is most likely due to hemilabile[9] activity of the phosphine oxide ligand (a weak interaction of the phosphine oxide portion of the dpppO ligand with the platinum metal center) in the poor donor solvent CD_2Cl_2. Confirmation of the presence of the dpppO ligand is obtained by the addition of dppe to a THF solution of **2,** which yields $Pt^0(dppe)_2$,[10] free dpppO[11] (by ^{31}P NMR spectroscopy), and presumably ethylene (eq 2).



(2)

Mass spectral analysis also shows the presence of dpppO.

Careful examination of the eq 1 reaction mixture by ^{31}P NMR spectroscopy reveals trace amounts of another platinum-containing product, **3**. This same complex is formed in high yield from the reaction of **1** in THF with 2 molar equiv of H_2O (eq 3).



(3)

Yellow crystals are deposited from the reaction solution. X-ray crystallography shows the crystalline material to be the hydroxo complex $[(dppp)Pt(OH)_2(Li)(THF)]_2[OTf]_2$ (**3′**) (Figure 1). An abbreviated summary of the crystal data collection and processing is given in Table 1. Selected distances and angles are listed in Table 2. The Pt portion of the structure consists of two square-planar $(dppp)Pt(OH)_2$ units bridged through the hydroxo groups by two $Li(THF)^+$ units. The average Pt−O distance (2.05 Å) falls in the low end of the range (2.02−2.19 Å) for the few structurally characterized Pt(II) terminal hydroxo complexes[12] and is slightly longer than the Pt−O distance found in the only structurally characterized Pt(II) complex with a terminal hydroxo group trans to a phosphine center (2.03 Å).[12e] The Pt−O distances in **3′** are shorter than those found in $[(dppp)Pt(OH)]_2^{2+}$, where the hydroxo groups bridge the two Pt centers (Pt−O = 2.10 Å).[13] The interaction of the hydroxo groups with the Li ions in **3** evidently does not greatly perturb the Pt−O distances from that of a terminal hydroxo group. For simplicity in the following considerations, dimeric **3′** is assumed to behave as the monomer $(dppp)Pt(OH)_2$ (**3**) in solution.

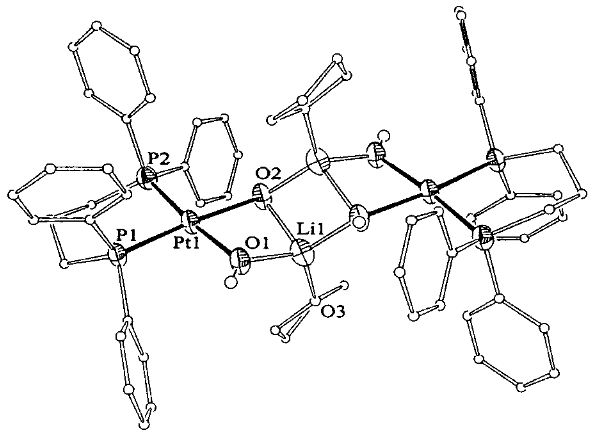


Figure 1. ORTEP drawing of the cationic portion of $[(dppp)Pt(OH)_2(Li)(THF)]_2[OTf]_2$ (**3′**), showing two $(dppp)Pt(OH)_2$ units bridged by two $Li(THF)^+$ units.

Table 1. Selected Distances (Å) and Angles (deg) for $[(dppp)Pt(OH)_2(Li)(THF)]_2[OTf]_2$ (3′)

Pt1−O1	2.039(4)	O1−Li1	1.890(10)
Pt1−O2	2.070(4)	O2−Li1	1.912(10)
Pt1−P1	2.2157(13)	Li1−O3	1.932(11)
Pt1−P2	2.2267(14)		
O1−Pt1−O2	79.48(16)	Li1−O1−Pt1	97.5(3)
O1−Pt1−P1	93.65(12)	Li1−O2−Pt1	92.4(3)
O1−Pt1−P2	173.72(11)	O1−Li1−O2	115.2(5)
O2−Pt1−P2	173.72(12)	O2−Li1−O3	119.9(5)
O2−Pt1−P2	91.28(12)	O1−Li1−O3	118.3(5)
P1−Pt1−P2	92.57(5)		

Table 2. Crystal Data and Structure Refinement Details for $[(dppp)Pt(OH)_2(Li)(THF)]_2[OTf]_2$ (3′)

empirical formula	$C_{28}H_{28}F_3LiO_5P_2PtS$
fw	797.55
temp (K)	173
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.507(2)
b (Å)	13.627(3)
c (Å)	15.891(3)
α (deg)	100.512(3)
β (deg)	106.577(3)
γ (deg)	111.330(3)
V (Å^3)	1924.0(7)
Z	2
D_{calcd} (g/cm^3)	1.63
λ (Å)	0.7107
μ (mm^{-1})	3.844
R1,[a] wR2[b]	0.0498, 0.0111

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [(\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{1/2}$ with weight $= 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 15.9835P]$; $P = (F_o^2 + 2F_c^2)/3$.

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(8) Appleton, T. G.; Bryiel, K. A.; Hall, J. R.; Kennard, C. H. L.; Lynch, D. E.; Sinkinson, J. A.; Smith, G. *Inorg. Chem.* **1994**, *33*, 444−455.

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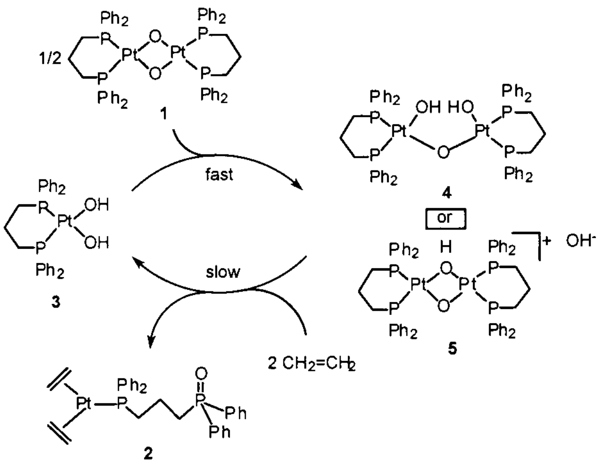
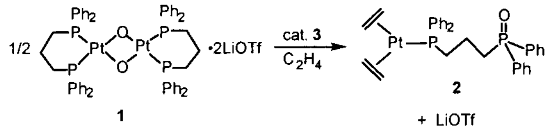
Scheme 1



Complex **3** does not react with ethylene in THF or CH_2Cl_2. However, small amounts of **3** (0.1 equiv) induce a reaction of **1** with ethylene in dry THF, where the product is again **2** with **3** remaining at the end of the reaction. Thus, **3** is a catalyst for the reaction of **1** with ethylene (eq 4).

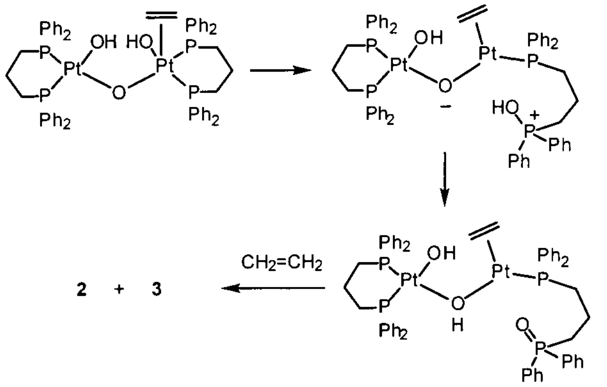


(4)

To further investigate the role of **3** in the reaction, solid **3′** was added to a solution of **1** (2:1 molar ratio) in d_8-THF. (Solid **3′** only partially dissolved.) The ^{31}P NMR spectrum of the mixture showed **1**, **3**, and what is believed to be $[(dppp)Pt(OH)]_2(\mu\text{-}O)$ (**4**) or $[(dppp)_2Pt_2(\mu\text{-}O)(\mu\text{-}OH)][OH]$ (**5**) (Scheme 1), which appears as two doublets ($J_{P-P} = 27$ Hz). The ^{195}Pt$-^{31}$P coupling constants are consistent with one P center trans to a strong donor oxo ligand (−4.5 ppm, $J_{Pt-P} = 2571$ Hz) and another P center trans to a weaker donor hydroxo ligand (−11.0 ppm, $J_{Pt-P} = 3774$ Hz).[14] These same peaks are observed in the catalyzed reactions of **1** with ethylene (eqs 1 and 4) but are absent at the end of the reactions; only **3** remains.

To test the phosphine ligand requirements, $[(PPh_3)_2Pt(\mu\text{-}O)]_2(LiBF_4)$ was pressurized with ethylene in the presence and in the absence of traces of water. No reaction occurred in either case. Treatment of $[(Ph_3P)_2Pt(\mu\text{-}O)]_2(LiBF_4)$ with 1 molar equiv of water yields a product that appears to be similar to **4** or **5** (^{31}P NMR, 250 MHz, THF: 8 ppm (d, $J_{P-P} = 17$ Hz, $J_{Pt-P} = 4462$ Hz) and 15 ppm (d, $J_{Pt-P} = 2761$ Hz)), but this species apparently does not catalyze the reaction of the oxo complex with ethylene. The dppp oxo complex $[(dppb)Pt(\mu\text{-}O)]_2(LiOTf)_2$ (dppb = $Ph_2PCH_2CH_2CH_2CH_2PPh_2$) was also examined. Like the dppp complex **1**, trace amounts of water are required to observe a reaction with ethylene. The reaction appears to be analogous to that of **1** with ethylene (eq 1).

Scheme 2



Discussion

The catalysis of the oxygen atom transfer reaction of the oxo complex **1** by the hydroxo complex **3** is noteworthy. Oxygen atom transfers to phosphines from transition-metal oxo complexes, including late-transition-metal oxo complexes, have been reported previously but apparently do not involve hydroxo species.[5] If we had not noticed the need for traces of water in the reaction of **1**, we would not have been aware of the involvement of hydroxo complexes in this system. A possible pathway for the catalytic reaction of oxo complex **1** is given in Scheme 1 and begins with the reaction of **1** with the catalyst **3** to produce the detected complex formulated as **4** or **5**. Complex **4** or **5** is given as the species that undergoes reaction with ethylene. This follows from the observation that neither **1** nor **3** reacts with ethylene by itself and that the intermediate **4** or **5**, produced from the reaction of **1** and **3**, is observed in the ethylene reaction mixtures up until the end of the reaction. Since no other species are observed during the reaction, the slow step is assigned to the reaction of ethylene with **4** or **5**. It is possible that another low-concentration, undetected species is responsible for the ethylene reaction; however, lacking any further evidence, **4** and **5** are the best candidates.

The details of the ethylene reaction step are unknown but may involve ethylene-induced reductive elimination of a phosphine center and a hydroxo ligand, as illustrated for **4** in Scheme 2. Similar reductive eliminations of a hydroxo group or an acetate group and a phosphine ligand have been suggested by Amatore and co-workers in the reduction of Pd(II) to Pd(0).[15] π-Acid-ligand-induced reductive eliminations are known,[16] consistent with the ethylene-induced elimination proposed here. Proton transfer from the P−OH group to the oxo group and reaction with another ethylene would give the observed product **2** and re-form the catalyst **3**. A similar process may be involved in the Pd-catalyzed synthesis of bis-phosphine monoxides from diphosphines, NaOH, and $BrCH_2CH_2Br$.[17]

Finally, in the above discussion we have neglected possible solution-phase Li ion interactions with the oxo

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[14] Li, J. J.; Li, W.; Sharp, P. R. *Inorg. Chem.* **1996**, *35*, 604−613. Recent observations in our laboratories suggest that mixed hydroxo/oxo cores such as in **5** are distorted such that the oxo ligand is a stronger donor and the hydroxo ligand is a weaker donor than in the unmixed dioxo and dihydroxo complexes. This results in more extreme values of J_{P-Pt} than expected from the dioxo and dihydroxo complexes.

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and hydroxo ligands of the complexes, such as the interactions observed in the solid-state structure of the dihydroxo complex **3** and the dioxo complex $[(Ph_3P)_2Pt(\mu\text{-}O)]_2(LiBF_4)$.[14] Such Li ion interaction may play a role in the solution chemistry by stabilizing complexes and ionic species such as the hydroxide ion in proposed **5**. That such interactions are important is shown by the reaction of the Li-free dioxo complex $[L_2Pt(\mu\text{-}O)]_2(NaOTf)_x$ (L_2 = dppp) with ethylene in the presence of ca. 0.1 equiv of water. Only a very slow reaction occurs, giving the ethylene complex **2**, suggesting that the weaker Na ion interactions with the oxo and hydroxo ligands are not as effective at stabilizing key species. Consistent with this, the ^{31}P NMR spectrum of the mixture shows the presence of the dioxo complex and $L_2Pt(OH)_2$ (**3**) but no signals for the proposed reaction intermediate, **4** or **5**, could be detected.

Conclusions

An oxygen atom transfer reaction of $[L_2Pt(\mu\text{-}O)]_2(LiOTf)_2$ (L_2 = dppp, dppb; OTf = CF_3SO_3) is catalyzed by the hydroxo complex $L_2Pt(OH)_2$ (**3**). Observations on the reaction are consistent with mediation of the oxygen atom transfer by a hydroxo group. These results indicate that oxygen atom transfer reactions of basic oxo complexes may occur through hydroxo species generated by trace amounts of water or other protic species. By analogy, nitrene transfers from imido complexes may also occur through amido species.

Experimental Section

Unless stated otherwise, all experiments were performed under a dinitrogen atmosphere using a VAC drybox or by Schlenk techniques. Degassed THF and Et_2O were passed through activated alumina solvent drying columns before use.[18] The complexes $[(dppp)Pt(\mu\text{-}O)]_2(LiOTf)_2$ (**1**), $[(dppb)Pt(\mu\text{-}O)]_2(LiOTf)_2$, and $[(PPh_3)_2Pt(\mu\text{-}O)]_2(LiBF_4)$ were prepared as previously reported.[14] The bidentate phosphine ligands dppp and dppe were purchased from Aldrich Chemical Co. CP grade ethylene was purchased from Scott Specialty Gases. Experiments involving ethylene were performed in either a Parr pressure vessel or a Fisher-Porter pressure bottle. NMR spectra were recorded on a Bruker ARX-250 NMR instrument at ambient temperatures. Mass spectra were recorded on a Laser Desorption (ToF) instrument in the linear mode using 2,5-dihydroxybenzoic acid as an external reference. Infrared spectra were obtained with a Nicolet Magna-550 spectrometer. ^1H and ^{31}P NMR chemical shifts are reported in parts per million and are referenced to TMS (internal) and 85% H_3PO_4 (external) standards, respectively. Desert Analytics performed the elemental analyses.

$[(dppp)Pt(OH)_2(Li)(THF)]_2[OTf]_2$ (3′). Water (24 μL, 0.013 mmol) was added by syringe to a solution of $[(dppp)Pt(\mu\text{-}O)]_2(LiOTf)_2$ (0.020 g, 0.013 mmol) in 1.0 mL of THF. The initially pale yellow solution immediately darkened slightly. After 1 h, crystals began to form and the solution was chilled to 0 °C overnight. The yellow crystals were collected, washed with diethyl ether, and dried in vacuo. The crystals are unstable to solvent loss and become a powder in vacuo. Yield: 12 mg (60%). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): −9.0 (J_{Pt-P} = 3262 Hz). ^{31}P NMR (101 MHz, THF): −7.7 (J_{Pt-P} = 3246 Hz). ^1H NMR (250 MHz, CD_2Cl_2): 7.55−7.28 (m, 20H, Ph), 2.59 (broad, 4H), 1.88 (broad, 2H), −0.44 (s, 2H, OH). Anal. Calcd (found) for $PtP_2C_{28}H_{28}LiF_3SO_5\cdot 0.4C_4H_8O$: C, 43.02 (43.12); H, 3.81 (3.86).

$(dpppO)Pt(\eta^2\text{-}CH_2{=}CH_2)_2$ (2). A solution of $[(dppp)Pt(\mu\text{-}O)]_2(LiOTf)_2$ (0.050 g, 0.032 mmol) and $(dppp)Pt(OH)_2(LiOTf)$ (ca. 1 mg) in 2 mL of THF was treated with ethylene gas (12 atm) in a Parr pressure vessel for 24 h. The resulting solution was evaporated under a stream of ethylene, and the oily residue was redissolved in CD_2Cl_2 for NMR measurements. ^{31}P NMR (101 MHz, CD_2Cl_2): 35.2, 15.6 (J_{Pt-P} = 3330 Hz). ^1H NMR (250 MHz, CD_2Cl_2): 7.3−7.7 (m, 20H, Ph), 2.6 (broad, 4H, $PCH_2CH_2CH_2P$), 2.3 (broad, 8H, J_{H-Pt} = 58 Hz, $CH_2{=}CH_2$), 1.7 (broad, 2H, $PCH_2CH_2CH_2P$). ^{31}P NMR (101 MHz, THF): 32.9 (s, 1P), 16.7 (s, 1P, J_{Pt-P} = 3349 Hz). ^{13}C NMR (250 MHz, THF/C_6D_6): 127−135 (m, 30C, Ph), 39 (s, 2C, J_{C-Pt} = 141 Hz, $CH_2{=}CH_2$), 33 (broad, 2C, $PCH_2CH_2CH_2P$), 19 (broad, 1C, $PCH_2CH_2CH_2P$). LD(ToF) MS: *m/z* 201 ($[P(O)Ph_2]^+$), 243 ($[P(O)Ph_2CH_2CH_2CH_2]^+$), 249 ($[P(C_2H_4)_2]^+$), 451 ($[CH_2P(Ph)_2Pt(C_2H_4)_2]^+$), 605 ($[Pt(PPh_2CH_2CH_2CH_2PPh_2)]^+$), 621 ($[Pt(PPh_2CH_2CH_2CH_2P(O)Ph_2]^+$).

Crystal Structure Analysis. Crystal data, reflection collection, and processing parameters and solution and refinement data are summarized in Table 2 and as a CIF file in the Supporting Information. The crystal was grown as described above and is sensitive to solvent loss. The crystal was mounted by pipetting a sample of crystals and mother liquor into a pool of heavy oil. A crystal was selected and removed from the oil with a glass fiber. With the oil-covered crystal adhering to the end of the glass fiber, the sample was transferred to an N_2 cold stream on the diffractometer.

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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