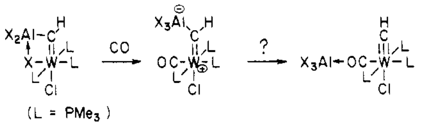
2.571 (1) Å). Cis angles about the octahedral tungsten range from ∠P(2)–W–Cl (4) = 81.06 (4)° through ∠P(1)–W–Ac = 98.9°. (Ac represents the midpoint of the acetylenic C(2)–C(3) bond and the acetylene ligand is considered monodentate.)

One of the more interesting questions concerns the role of the aluminum reagent. Since W(CH)(Cl)L_4 reacts with AlX_3 reagents (2 equiv) to give W(CH)(Cl)L_3(AlX_3) and Me_3PAlX_3,[3] it is reasonable to propose this as the first step, followed by coordination of CO in the position of the ligand bridging between Al and W (eq 1). The question then reduces to whether the two carbon atoms couple at this point or later. Since activation of carbonyl ligands by interaction of the carbonyl oxygen atom with a Lewis acid is well documented,[13] it might seem more necessary for AlX_3 to activate the carbon monoxide toward coupling than the methylidyne ligand. On the other hand, it is also attractive to postulate that the two carbenoid ligands (CO and C(H)(AlX_3)) couple first and that AlX_3 (probably from outside the coordination sphere) subsequently coordinates to the carbonyl oxygen atom. In either case, AlX_3 plays an intimate role in the coupling reaction. Preliminary experiments suggest that removing $AlCl_3$ from W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl with a strong base (in order to generate W(CH)(CO)(PMe$_3$)$_3$Cl) is not facile.



(1)

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE80-23446 (M.R.C.) and by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A002 (R.R.S.).

Supplementary Material Available: Positional parameters, anisotropic thermal parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(13) Shriver, D. F. *ACS Symp. Ser.* **1981**, *No. 152*, 1.

Photochemical Generation of Bis(triethylphosphine)platinum(0) and Synthesis of Ethylenebis(triethylphosphine)platinum(0)

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Summary: UV irradiation of the platinum(II) oxalate complex Pt(PEt$_3$)$_2$(C$_2$O$_4$) in the presence of coordinating ligands L or oxidative addition substrates X-Y produces, respectively, Pt(PEt$_3$)$_2$L$_n$ (n = 1, 2) and Pt(PEt$_3$)$_2$XY, with release of two equivalents of CO$_2$. When L = ethylene, Pt(PEt$_3$)$_2$(C$_2$H$_4$) can be prepared; its reactions are described.

Zerovalent, 14-electron complexes consisting of platinum and two tertiary phosphine ligands, PtL$_2$, are stable only if L is so sterically demanding that approach to the metal center is hindered.[1,2] The steric bulk of the ligands, however, attenuates the reactivity of these compounds. The crowded complex Pt[P(t-Bu)$_3$]$_2$ does not react with dioxygen, molecular hydrogen, or methanol; as L becomes smaller [e.g., L = P(t-Bu)$_2$Ph, P(c-Hx)$_3$, P(i-Pr)$_3$], the reactivity of PtL$_2$ toward small molecules increases.[3,4] Relatively unhindered PtL$_2$ complexes, where L is a small phosphine ligand, have not been observed and should be highly reactive. For example, one phosphine can dissociate from Pt(PEt$_3$)$_4$ to give the 16-electron species Pt(PEt$_3$)$_3$, but further dissociation to produce spectroscopically observable quantities of Pt(PEt$_3$)$_2$ does not occur.[5-8] The oxalate complex Pt(PPh$_3$)$_2$(C$_2$O$_4$) loses 2 equiv of carbon dioxide upon UV irradiation to produce platinum(0) compounds, presumably via Pt(PPh$_3$)$_2$.[9] This suggested the Pt(PEt$_3$)$_2$ fragment could be generated in situ photochemically from Pt(PEt$_3$)$_2$(C$_2$O$_4$), 1, and its reactions studied *under mild conditions*. Because triethylphosphine is both sterically undemanding and electron-rich, Pt(PEt$_3$)$_2$ should be highly reactive.[10] Furthermore, this photochemical procedure could provide a convenient route to platinum(0) and platinum(II) complexes containing two triethylphosphine ligands; the only side product of the synthesis would be carbon dioxide.

Complex 1 can be prepared[11] from *cis*-Pt(PEt$_3$)$_2$Cl$_2$ and K$_2$C$_2$O$_4$·H$_2$O as white crystals, soluble in polar solvents; it is air-stable and unreactive in the absence of UV light, both as a solid and in solution, but it is photochemically reactive. The ^{31}P{^{1}H} NMR and IR spectra of 1 are consistent[12] with the square planar geometry shown in Scheme I. Several experimental facts support the hypothesis that UV irradiation of 1 generates Pt(PEt$_3$)$_2$. Irradiation of solutions of 1 in the presence of donor and acceptor ligands, L, leads to formation of zerovalent complexes Pt(PEt$_3$)$_2$L$_n$ (Scheme I). If 1 is irradiated in the presence of substrates XY that can undergo oxidative addition, platinum(II) complexes Pt(PEt$_3$)$_2$XY form.[13] Two

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(1) (a) Green, M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 3. (b) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006–1009.

(2) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850–5857.

(3) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134–2140.

(4) Abbreviations: Me = methyl; Et = ethyl; Ph = phenyl; i-Pr = isopropyl; c-Hx = cyclohexyl; t-Bu = *tert*-butyl.

(5) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–3544.

(6) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *14*, 107–110.

(7) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776–785.

(8) The species Pt(PEt$_3$)$_2$ is not seen spectroscopically, e.g., by ^{31}P NMR spectroscopy. Kinetically significant quantities of Pt(PEt$_3$)$_2$ could, however, be present in solutions of Pt(PEt$_3$)$_3$. For example, the results of variable-temperature NMR line-shape analysis suggest that Pt(PEt$_3$)$_3$ exchanges with free PEt$_3$ by both associative and dissociative pathways.[7]

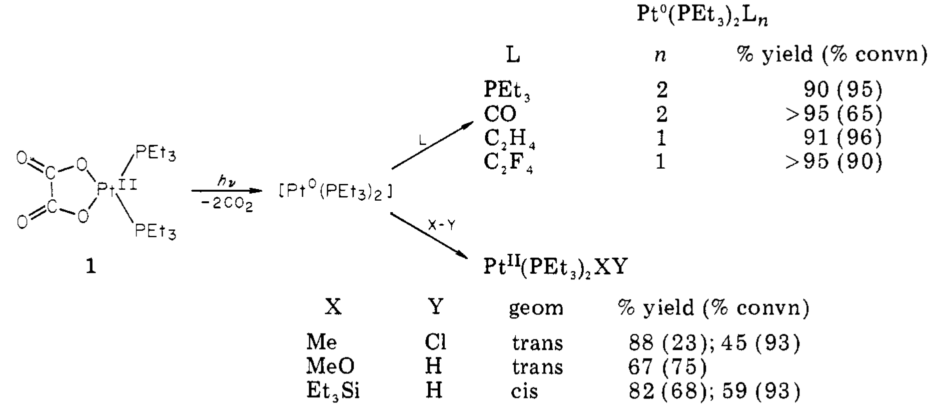
(9) Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5359–5364.

(10) Trialkylphosphines are known to greatly increase the nucleophilic reactivity of platinum(0) complexes compared with that of triarylphosphine analogues; see ref 5.

(11) Metathesis of *cis*-Pt(PEt$_3$)$_2$Cl$_2$ (Parshall, G. W. *Inorg. Synth.* **1970**, *12*, 26–33) with K$_2$C$_2$O$_4$·H$_2$O in equal volumes of hot methanol and water, followed by reduction of the liquid volume and cooling, produces off-white crystals of 1. Recrystallization from dichloromethane/diethyl ether produces pure white crystals of 1 in 85% yield. Anal. Calcd: C, 32.37; H, 5.82; P, 11.93; Pt, 37.56. Found: C, 32.38; H, 5.76; P, 11.98; Pt, 37.80. Ir (CH$_2$Cl$_2$): 1704 (vs), 1681 (s), 1670 (m), 1458 (w), 1366 (s), 1042 (sh), 1036 (m), 792 (m) cm^{-1}. UV-Vis (CH$_3$CN): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 206 (2.3 × 10^4), 236 (8.3 × 10^3), 258 (3.1 × 10^3), 286 (7.5 × 10^2).

(12) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd Ed.; Wiley: New York, 1978; pp 233–236.

Scheme I



1

$Pt^0(PEt_3)_2L_n$

L	*n*	% yield (% convn)
PEt_3	2	90 (95)
CO	2	>95 (65)
C_2H_4	1	91 (96)
C_2F_4	1	>95 (90)

$Pt^{II}(PEt_3)_2XY$

X	Y	geom	% yield (% convn)
Me	Cl	trans	88 (23); 45 (93)
MeO	H	trans	67 (75)
Et_3Si	H	cis	82 (68); 59 (93)

equivalents of carbon dioxide are evolved in these reactions. In each case the product contains the $Pt(PEt_3)_2$ moiety. To monitor the course of these reactions, we irradiated solutions in NMR tubes and recorded the $^{31}P\{^1H\}$ NMR spectra at successive stages of the photolysis (Figure 1). These spectra showed the gradual conversion of 1 to the products described; yields are described below. The reactions stopped in the absence of UV irradiation. The course of these reactions is most easily explained by assuming UV light triggers intramolecular reduction of Pt(II) to Pt(0) by the "built-in" two-electron reductant $C_2O_4^{2-}$. The reactive platinum species is probably $Pt(PEt_3)_2$ or a weak complex with solvent.[14] Further evidence of the formation of $Pt(PEt_3)_2$ from 1 comes from the observation that, in the absence of substrates to scavenge the reactive $Pt(PEt_3)_2$ fragment, disproportionation produces $Pt(PEt_3)_3$ and platinum metal (reaction 1). An analogous reaction

$$3Pt(PEt_3)_2 \rightarrow 2Pt(PEt_3)_3 + Pt \qquad (1)$$

occurs when $Pt(PPh_3)_2$ is generated in situ by reductive elimination of methane from *cis*-$Pt(PPh_3)_2MeH$.[15] When degassed solutions of 1 in acetonitrile are irradiated in the absence of added substrates, a complex mixture of products forms, along with finely divided platinum metal. If the solvent is removed under vacuum and the residue extracted into toluene-d_8, $Pt(PEt_3)_3$ is seen from the $^{31}P\{^1H\}$ NMR spectrum to be the major product. Thus, disproportionation of $Pt(PEt_3)_2$ occurs in competition with other unidentified decomposition pathways.

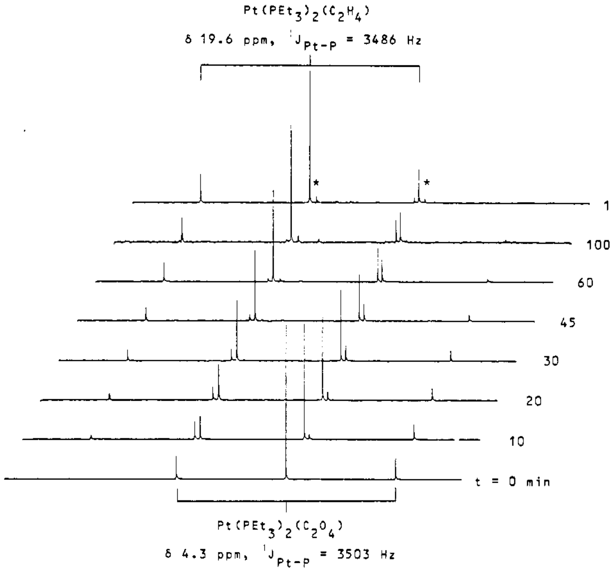


Figure 1. Successive $^{31}P\{^1H\}$ NMR spectra (109 MHz) showing the photochemical conversion under 1 atm ethylene of $Pt(PEt_3)_2(C_2O_4)$ (1) to $Pt(PEt_3)_2(C_2H_4)$ (2). Irradiation times are shown at right. The symmetrically disposed satellite peaks result from those molecules that contain ^{195}Pt (33.8% abundance, $I = 1/2$). The rate of conversion decreases steadily as the concentration of 2 increases, because 2 absorbs an increasingly greater fraction of the incident irradiation. The signals marked by an asterisk in the final spectrum are unidentified side products which form at long irradiation times.

The reactions of photogenerated $Pt(PEt_3)_2$ can be compared with those of more hindered, thermally stable PtL_2 complexes. For example, $Pt[P(t\text{-}Bu)_2Ph]_2$ reacts immediately with CO to form $Pt_3(CO)_3[P(t\text{-}Bu)_2Ph]_3$, accompanied by the loss of one phosphine ligand per platinum;[3] however, the photoreaction of 1 with CO yields the mononuclear complex $Pt(PEt_3)_2(CO)_2$. Facile loss of the $P(t\text{-}Bu)_2Ph$ ligand is no doubt driven by release of steric strain. The formation of *trans*-$Pt(PEt_3)_2H(OMe)$, 3, when 1 is irradiated in methanol, is particularly significant. Bulkier PtL_2 complexes [L = $P(i\text{-}Pr)_3$, P(c-Hx)$_3$, P(*t*-

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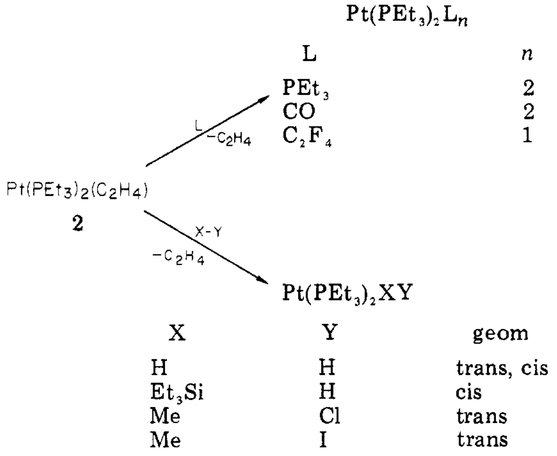
(13) (a) Irradiations were performed by using a Hanovia 450-W medium-pressure mercury arc lamp or an Oriel 450-W focused Xenon arc lamp. Light output was filtered through cooled water (to removed IR radiation). Reactions followed by $^{31}P\{^1H\}$ NMR were carried out in 10-mm Pyrex NMR tubes by irradiating solutions of 1 (0.04 mmol) in CH_3CN (1 mL)/C_6D_6 (0.5 mL) (freeze–pump–thaw degassed or nitrogen-purged) that contained excess substrate (gases at 1 atm); the reaction with MeOH was carried out in MeOH/C_6D_6. Products were identified by comparison of NMR and IR spectra with those of authentic samples or by NMR spectroscopy for the following new compounds. $Pt(PEt_3)_2(C_2F_4)$: $^{31}P\{^1H\}$ NMR δ 15.4 (m, A part of $AA'X_2X_2'$ multiplet, $^1J_{PtP}$ = 2425 Hz); ^{19}F NMR δ 2.7 (relative to C_2F_4 at 0 ppm, m, X part of $AA'X_2X_2'$ multiplet, $^2J_{PtF}$ = 279). Anal. Calcd: C, 31.64; H, 5.69; F, 14.30; P, 11.66. Found: C, 31.72; H, 5.61; F, 14.16; P, 11.87. *trans*-$Pt(PEt_3)_2H(OMe)$: $^{31}P\{^1H\}$ NMR δ 24.8 (s, $^1J_{PtP}$ = 2804 Hz); ^1H NMR PtH δ −23.76 (t, $^2J_{PH}$ = 15.4 Hz, $^1J_{PtH}$ = 1309 Hz), $PtOCH_3$ δ 2.87 (br, $^3J_{PtH}$ = 56 Hz); $^{13}C\{^1H\}$ NMR $PtOCH_3$ δ 53.0 (br). *cis*-$Pt(PEt_3)_2H(SiEt_3)$: $^{31}P\{^1H\}$ NMR P_A (trans to Si) δ 22.8 (d, $^2J_{P_AP_B}$ = 16.4 Hz, $^1J_{PtP_A}$ = 1432 Hz), P_B (trans to H) δ 19.1 (d, $^2J_{P_AP_B}$ = 16.4 Hz; $^1J_{PtP_B}$ = 2392 Hz); ^1H NMR PtH δ −2.29 (dd, $^2J_{P_AH}$ = 23 Hz, $^2J_{P_BH}$ = 154 Hz, $^1J_{PtH}$ = 942 Hz). Preparation and spectra of the following compounds were previously reported: $Pt(PEt_3)_3$;[5,6] $Pt(PEt_3)_4$;[5,6] **2**[13b,c] $Pt(PEt_3)_2(CO)_2$;[13d] *trans*-$Pt(PEt_3)_2MeX$, X = Cl, I.[13e,f] (b) Nuzzo, R. G., McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* **1981**, *20*, 1312–1314. (c) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318–325. (d) Chini, P.; Longoni, G. *J. Chem. Soc. A* **1970**, 1542–1546. (e) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716. (f) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700–2704.

(14) The solvent mixture affects the photoreactions of 1 in a way we do not fully understand. The photoreaction of 1 with ethylene in acetonitrile/benzene cleanly yields 2, while the same reaction in acetonitrile yields 2 and a mixture of unidentified side products. The solubility of ethylene is the same in each solvent and in mixtures of the two. It is possible that benzene suppresses formation of side products by weakly coordinating to $Pt(PEt_3)_2$, thereby stabilizing it until it reacts with C_2H_4. A stable, fluxional complex of $Pt(PEt_3)_2$ with perfluorohexamethylbenzene, $Pt(PEt_3)_2[\eta^2\text{-}C_6(CF_3)_6]$, is known: Browning, J.; Green, M.; Penforld, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31–32.

(15) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

Scheme II



Bu)$_2$Ph] react with methanol to yield *trans*-PtL$_2$H$_2$, presumably via β-hydrogen elimination from an intermediate PtL$_2$H(OMe) complex and release of formaldehyde.[3] Complex **3** is the first example of a PtL$_2$H(OMe) complex that is directly observed. The formation of **3** exemplifies the ability of **1** to produce the Pt(PEt$_3$)$_2$ species *in the absence of strongly competing ligands*. In contrast, Pt(PEt$_3$)$_3$ reacts with methanol to yield [Pt(PEt$_3$)$_3$H][MeO],[5] while Pt(PEt$_3$)$_2$(C$_2$H$_4$) is inert to methanol (see below).

The yields of the photoreactions in Scheme I, as measured by NMR spectroscopy, are affected by the absorption characteristics, photosensitivity, and thermal stability of the products. The conversion yield (% of **1** consumed) is a function of irradiation time and light intensity and generally approaches 80–100% upon prolonged irradiation.[16] The product yield, which we define as the yield based on the amount of **1** reacted, is highest for those products which are photochemically and thermally stable under the photolysis conditions, and decreases otherwise. For example, *trans*-Pt(PEt$_3$)$_2$MeCl is photosensitive; although it forms cleanly in the early stages of the reaction, UV irradiation gradually converts it to other products. The previously unreported complex Pt(PEt$_3$)$_2$(C$_2$F$_4$) was prepared photochemically from **1** and isolated as an analytically pure solid[13a] in 55% yield.

We have found complex **1** to be convenient for the preparation of the labile ethylene complex Pt(PEt$_3$)$_2$(C$_2$H$_4$), **2**. This reaction traps the reactive Pt(PEt$_3$)$_2$ fragment in a stable adduct which can be isolated and from which ethylene is readily displaced to yield compounds containing the Pt(PEt$_3$)$_2$ moiety. This procedure circumvents the problem of product photodecomposition. Furthermore, reactions of the highly soluble ethylene complex can be carried out in a range of solvents. In a typical preparation of **2**, an ethylene-saturated solution of **1** in equal volumes of deaerated acetonitrile and benzene is irradiated in a quartz Schlenk tube for 8 h, after which time approximately 80–90% conversion of **1** to **2** is observed. (Further conversion of **1** is very slow at this point, because **2** now absorbs almost all the UV irradiation.) Complex **2** is an air-sensitive liquid (mp <−20 °C), and we have been unable to isolate analytically pure samples; however, for many purposes, isolation of **2** is not necessary. For example, addition of RX (e.g., RX = MeCl, MeI) cleanly produces *trans*-Pt(PEt$_3$)$_2$MeX, which can then be isolated. Alternatively, because **2** reacts reversibly with hydrogen to form Pt(PEt$_3$)$_2$H$_2$, **4**, we have found it convenient to convert **2** to **4** under a stream of hydrogen in *n*-hexane solution, from which **4** can be isolated as an analytically pure crystalline solid.[17] Complex **2** can then be regenerated quantitatively in situ by simply treating solutions of **4** with a stream of ethylene.[18] Reactions of **2** are summarized in Scheme II; spectroscopic yields are quantitative based on **2**.

Although **1** and **2** are both precursors to compounds containing the Pt(PEt$_3$)$_2$ fragment, their reactions can be quite different, and the choice of which reagent to use to prepare a particular complex will vary. As described above, use of **2** circumvents the problem of secondary photolysis and allows a wider range of solvents to be employed. Complex **1**, however, provides the more reactive, "ligand-free" source of Pt(PEt$_3$)$_2$. Thus, for example, methanol readily adds to the highly reactive Pt(PEt$_3$)$_2$ species formed photochemically from **1**, whereas **2** is inert to alcohols.

Acknowledgment. We thank the National Science Foundation (Grants CHE78-01615 and 81-050698) for support of this work and Johnson Matthey, Inc., for a generous loan of platinum.

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[16] The rate of conversion of **1** decreases with increasing irradiation time (at constant incident light intensity) as the products formed compete with **1** for absorption of the incident irradiation. This behavior can be seen, for example, in Figure 1.

[17] Although **2** is very soluble in *n*-hexane, the oily residue of impure **2** that forms after removal of solvent only partially dissolves in *n*-hexane. The impurities are probably acetonitrile and traces of water. We have found that stirring this residue in *n*-hexane under ethylene in the presence of lithium aluminum hydride for 4–8 h leads to complete extraction of **2** into solution, presumably as LiAlH$_4$ scavenges the impurities. This solution is then filtered through Celite. Hydrogen is bubbled through the solution for 0.5 h to produce **4**, which can be obtained as crystals by cooling to −30 °C. Pure complex **4** can be recrystallized in 35% yield (based on **1**) from *n*-hexane and is stable under hydrogen.[18]

[18] The preparation and properties of *cis*- and *trans*-Pt(PEt$_3$)$_2$H$_2$ have been described: Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–1140.