Insight into the Selective Room-Temperature Platinum(II) Catalytic Hydration of Alkynes in Water

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Three platinum complexes of water-soluble, bidentate phosphine ligands have been prepared and characterized. The complexes, $PtCl_2(P-P)$ (P−P = (*m*-$NaSO_3C_6H_4)_2PCH_2CH_2P$-(*m*-$C_6H_4SO_3Na)_2$, DPPETS, (*m*-$NaSO_3C_6H_4)_2PCH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPPTS, (*m*-$NaSO_3C_6H_4)_2PCH_2CH_2CH_2CH_2P$(*m*-$C_6H_4SO_3Na)_2$, DPPBTS), catalyze the hydration of 3-pentyn-1-ol and 4-pentyn-1-ol. 2-Pentyn-1-ol is slowly polymerized, allowing characterization of the intermediate η^1-allenyl complexes. For $PtCl_2$(DPPBTS) the η^1-allenyl complex Pt(C(Et)CCH_2)-(X)(DPPBTS), where X is either OH^-, OH_2, or Cl^-, is formed. However for $PtCl_2$(DPPPTS) and $PtCl_2$(DPPETS) the extent of formation of the coordinated complex is much less. The stability of the coordinated Pt(η^1-allenyl)(X)(P−P) complexes shows a significant effect on chelate ring size, with DPPBTS > DPPPTS > DPPETS being the order of decreasing stability. Catalytic hydrations of 4-pentyn-1-ol with $PtCl_2$(P−P) show a major effect of chelate ring size in the opposite direction, DPPETS > DPPPTS > DPPBTS. For 3-pentyn-1-ol catalytic hydration is less affected by the chelate ring size. The effect of excess Cl^- is also examined. A mechanism is proposed for the catalytic hydration involving coordination, cyclic attack by the alcohol according to Baldwin's rules, and rearrangement to 5-hydroxypentan-2-one.

Introduction

Homogeneous catalysis plays an important role as atom efficiency becomes increasingly important for both financial and environmental reasons. Homogeneous catalysis using water as a solvent and reactant has enormous potential for the same reasons.[1] This potential has, thus far, only been realized in the Rhone-Polenc/Rurhchemie process for hydroformylation of propene,[2] although water-soluble transition metal complexes have been reported to catalyze hydroformylation,[2,3] hydrogenation,[4] alkylation,[5] allylic substitution,[6] isomerization,[7] carbonylation,[8] chlorination,[9] oxidation,[10] and hydration.[11−15]

Bidentate ligands offer some advantages, especially for stability and asymmetric catalysis. A recent review summarizes the effect of bidentate ligand bite angle on structures and reaction rates,[16] following up on a molecular mechanics calculation of bite angles.[17] Casey and colleagues examined rhodium complexes of BISBI ligands, correlating structures and regioselectivity of hydroformylation with natural bite angle and the effects of substitution in equatorial positions.[18] van Leeuwen and co-workers examined the effect of large bite angle xantphos ligands on rhodium hydroformylation selectivity.[19] The effect of bidentate ligands complexed to nickel on hydrocyanation has also been examined.[20] Of special importance to this article, the ligands dppe ($Ph_2PCH_2CH_2PPh_2$), dppp ($Ph_2PCH_2CH_2CH_2PPh_2$), and dppb ($Ph_2PCH_2CH_2CH_2CH_2PPh_2$) were examined for methyl migration on Pd(LL)MeY complexes.[21] The reactivity of the complexes depends on the bidentate ligand in the

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order dppb ≥ dppp ≫ dppe, attributed to a flexible backbone of the bidentate ligand.[21]

The direct hydration of alkynes has been realized by Jennings et al.,[13] Katoaka et al.,[14] and recently by Wakatsuki et al.[15] Jennings et al. used $PtCl_4^{2-}$ as the catalyst and did not clearly resolve the mechanism for the Markovnikov hydration.[13] Using $PtCl_2(L_2)$, where L_2 is 2 PPh_3, 2 PPh_2Me, diphos, and 1,5-bis(diphenylphosphino)pentane in a CH_2Cl_2/MeOH system, Katoaka et al.[14] observed the Markovnikov hydration of alkynes. They did not, however, propose a mechanism. Wakatsuki et al. recently demonstrated the effectiveness of a Ru(II)−phosphine system as a catalyst for the anti-Markovnikov hydration of terminal alkynes in an H_2O/2-propanol system.[15] They found that the use of bidentate phosphorus ligands with small bite angles increased the selectivity and yields of the isolated aldehyde products.[15b] Specifically, they found that the order of reactivity of complexes made from bidentate ligands was the following:

DPPM > DPPE > DPPBTS > DPPB ≥ DPPP ≫ DEPE ≥ DMPM

where DPPM is bis(diphenylphosphino)methane, DMPM is bis(dimethylphosphino)methane, and DEPE is 1,2-bis(diethylphosphino)ethane. The conclusions state that the direct protonation of an η^2-coordinated alkyne by water is the cause of the unusual anti-Markovnikov regioselection. This mode of attack is predicted to be dominant because of the steric characteristics of the resulting vinyl complex,[15b,c] which leads to this order of reactivity. The smaller bite angle bidentate ligand causes more steric congestion (bulk) at the metal center.

We recently reported that $PtCl_2(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) functions as a hydration catalyst for 3-pentyn-1-ol and 4-pentyn-1-ol.[12] This article examines the synthesis, characterization, and catalytic activity for hydration of 3- and 4-pentyn-1-ol with $PtCl_2$(DPPETS), $PtCl_2$(DPPPTS), and $PtCl_2$(DPPBTS). Mechanisms of these hydrations are considered.

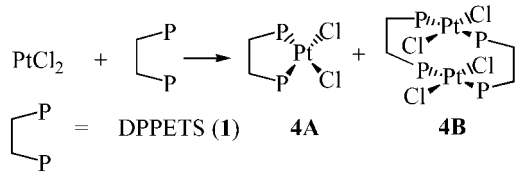

Figure 1. Reaction of $PtCl_2$ with DPPETS.

Results and Discussion

Synthesis of Bidentate Water-Soluble Ligands (1−3). The sulfonation of diphosphines was carried out in the same manner as described for DPPE,[22] Binas,[23] (*S*,*S*)-cyclobutanediop, (*S*,*S*)-BDPP, (*S*,*S*)-Chiraphos, and (*R*)-Prophos.[24] Attempts to sulfonate these diphosphines in a manner similar to that described by Herrmann et al.[25] and Vespui et al.[26] were unsuccessful. Experimentally, the best reaction conditions consisted of 12 mmol of organic substrate (DPPE, DPPP, or DPPB) in 65 mL of 30% SO_3 in H_2SO_4 for 48 h at ambient temperature. Further reaction time led to oxidation of the phosphines. This trend was also noted by Amrani et al.[23] in the synthesis of the asymmetric water-soluble diphosphines.

The workup of the diphosphine ligands is very important to product purity. DPPETS (**1**) requires workup in an inert atmosphere, whereas DPPPTS (**2**) and DPPBTS (**3**) could be worked up in air. The best results were obtained by neutralizing the solution to a pH of 2.2−2.4. Then, after complete evaporation and subsequent redissolving in a minimum amount of triply distilled water, the solution is adjusted to basic pH. Na_2SO_4 impurities can be eliminated by recrystallization from water and acetone.

These ligands were characterized by ^{31}P and ^1H NMR analyses in both D_2O and dimethyl sulfoxide-d_6 (DMSO) and by elemental analysis. All NMR spectral results were in complete agreement with the literature (DPPETS[22] and DPPPTS[26]). The elemental analyses were also in good agreement with the calculated values. These ligands were then used in the synthesis of $PtCl_2$(P−P) complexes.

Synthesis of $PtCl_2$(P−P) Complexes (4−6). Complexes **4**−**6** are prepared by addition of 1.0 equiv of **1**−**3** to a dissolved solution of $PtCl_2$ in DMSO. In the synthesis of **4**, if the $PtCl_2$/DMSO solution was allowed to cool to room temperature before addition of **1**, the *trans* dimer (Figure 1: **4B**) was formed. This species was characterized by a ^{31}P NMR resonance at 52.8 ppm with $^1J_{(Pt-P)} = 2310$. By heating this complex in D_2O or in DMSO-d_6 to 70 °C, complete conversion to the *cis*-monomer (Figure 1: **4A**) occurred.

Bartik et al.[22] reported the synthesis of $PtCl_2$-(DPPETS) (**4A**) from the reaction of H_2^{2+}DPPETS in

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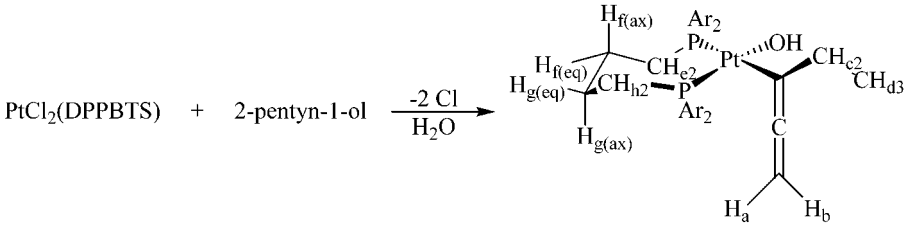
Table 1. Selected $^{31}P\{^1H\}$ and ^{195}Pt NMR Data for Complexes 1−6, *cis*-$PtCl_2(TPPTS)_2$, and *trans*-$PtCl_2(TPPTS)_2$

	^{31}P NMR (D_2O)[a]		^{195}Pt NMR (D_2O)[a]		^{31}P NMR (DMSO-d_6)[a]	
complex	δ(P)	$^1J_{(Pt-P)}$[b]	δ(Pt)[c]	$^1J_{(Pt-P)}$[b]	δ(P)	$^1J_{(Pt-P)}$[b]
DPPETS (**1**)	−13.1				−11.1	
DPPPTS (**2**)	−16.2				−16.4	
DPPBTS (**3**)	−15				−15.4	
DPPETS[19]	−12.45					
DPPPTS[23]	−16.3					
$PtCl_2$(DPPETS)[19]	52.97	2310				
$PtCl_2$(DPPETS) (**4a**)	46	3670	−4610	3670	44.7	3610
trans-[$PtCl_2$(DPPETS)]$_2$ (**4b**)	52.8	2310				
$PtCl_2$(DPPE)	45.3[26]	3618	−4572[27]	3631		
$PtCl_2$(DPPPTS) (**5**)	−4.5	3420	−4510	3420	−1.5	3420
$PtCl_2$(DPPP)	−5.6[26]	3420	−4498[27]	3412		
$PtCl_2$(DPPBTS) (**6**)	13.0	3580	−4501	3580	13.0	3550
$PtCl_2$(DPPB)	13.4[26]		−4485[27]	3533		
cis-$PtCl_2$(TPPTS)[12]	14.3	3720	−4437	3720	15.5	3720
trans-$PtCl_2$(TPPTS)[12]	22.3	2600	−4072	2600		

[a] Chemical shifts (δ) are recorded in ppm, and coupling constants (J) are recorded in Hz. [b] Coupling constants refer to platinum satellites. [c] Referenced to 0.2 M K_2PtCl_6 in H_2O.

Scheme 1. Reaction of $PtCl_2$(DPPBTS) (6) with 2-Pentyn-1-ol in Water



H_2O and $Pt(PhCN)_2Cl_2$ in CH_2Cl_2. However the only characterization data were ^{31}P NMR and ^1H NMR spectra. Their ^{31}P data report only one resonance at 52.97 ppm in D_2O with a $^1J_{(Pt-P)} = 2310$ Hz. This is not consistent with a Pt(II) complex that has a phosphine *trans* to a halide.[27] *cis*-$PtCl_2L_2$ complexes have significantly larger coupling constants than *trans* complexes, with the chemical shift of the *cis* isomer for a particular tertiary phosphine always upfield from that of the *trans* isomer. The range of $^1J_{(Pt-P)}$ found by Grim et al. for tertiary phosphines of the type *cis*-$PtCl_2L_2$ was 3500−3641 Hz.[27] For *trans*-$PtCl_2L_2$ complexes of the same type, Grim et al. found that the $^1J_{(Pt-P)}$ ranged from 2385 to 2531 Hz. Thus, it is likely that Bartik et al.[22] actually prepared the bis-diphosphine dimer shown in Figure 1, **4B**. The coupling constant is very similar to that of *trans*-$PtCl_2(TPPTS)_2$, which has a $^1J_{(Pt-P)}$ of 2580.[12] The *cis* monomer $PtCl_2$(DPPE) has a chemical shift of 45.3 ppm and a $^1J_{(Pt-P)}$ of 3618 Hz relative to an external standard of 85% H_3PO_4,[28] consistent with the complex synthesized in our lab, **4**, which has a ^{31}P chemical shift of 44.7 ppm with a $^1J_{(Pt-P)}$ of 3610 Hz. This is consistent with the monomer shown in Figure 1, **4A**.

The effect of chemical shift relative to the chelating ligand ring size for organic derivatives of $PtCl_2(P'-P')$ and $PtMe_2(P'-P')$ has been discussed in detail by Garrou.[29] From this report, the chemical shift of **5** is expected to be deshielded compared to **4** and **6**. The chemical shift of **5** is −4.5 ppm with $^1J_{(Pt-P)} = 3420$ Hz. The chemical shift of its organic analogue ($PtCl_2$(DPPP)) is −5.6 ppm with $^1J_{(Pt-P)} = 3420$ Hz.[29] **6** is expected to have a chemical shift very close to that of the tertiary phosphine analogue closest to it. *cis*-$PtCl_2(TPPTS)_2$ has a chemical shift of 14.3 ppm.[12] The chemical shift of **6** is 13.0 ppm with $^1J_{(Pt-P)} = 3420$ Hz, in good agreement with its organic analogue ($PtCl_2$(DPPB)), which has a chemical shift of 13.4 ppm.[29] The ^{195}Pt NMR showed triplets for each complex that were very similar to those of their organic analogues as shown in Table 1.

Reactions of $PtCl_2(P-P)$ with 2-Pentyn-1-ol. Reacting **4**−**6** with an alkyne such as 2-pentyn-1-ol, which is not readily hydrated, allows other reaction chemistry to be examined. When 1 equiv of 2-pentyn-1-ol was reacted with **6** in D_2O, a new Pt(II) complex was formed (Scheme 1). The ^{31}P NMR spectrum of this intermediate after 1 h (**7**) contains two species, characterized by two doublets at 16.7 and 11.7 ppm with $^2J_{(P-P)} = 18.6$ Hz flanked with ^{195}Pt satellites of 4312 and 1761 Hz, respectively, and 21.9% of the starting $PtCl_2$(DPPBTS) (**6**). The phosphine *trans* to the stronger *trans* influence ligand will have the smallest $^1J_{(Pt-P)}$ and the longest Pt−P bond;[31] therefore, the resonance at 11.2 ppm is assigned to the phosphine that is *trans* to the allenyl ligand. The ^{31}P NMR spectrum of this complex is very similar to PtMe(Cl)(DPPP), which is characterized by two doublets at 3.0 and 5.1 ppm with $^2J_{(P-P)}$ of 21 Hz flanked with ^{195}Pt satellites of 1644 and 4116 Hz, respectively.[28b] The coupling constants are expected to

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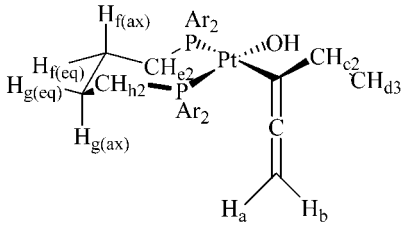

Figure 2. Pt(OH)(C(Et)CCH_2)(DPPBTS) (**7**).

be similar because both Me^- and the proposed η^1-allenyl ligand have a strong *trans* influence.[32] As far as we know, there is no characterization of an η^1-allenyl Pt(II) complex containing two *cis* phosphines, making direct comparisons impossible. However, there are a few examples of η^1-allenyl Pt(II) complexes containing two *trans* phosphines.[33−35]

The NOESY and COSY NMR experiments gave valuable structural information. Utilizing NOESY experiments it was possible to determine, due to a buildup of NOE on the methyl protons when the methylene protons are pulsed and vice versa, that the ethyl group of the bound η^1-allenyl ligand has restricted rotation about the ethyl−C bond. When NOESY NMR experiments are conducted on free 2-pentyn-1-ol, there is no NOE buildup on the methyl group when the α-methylene group is pulsed. Also, when H_a (see Figure 2 for lettering scheme) is pulsed, a small NOE buildup occurs at H_e, which is an indication of H_a being in a fixed position less than 5 Å from H_e.[36] This suggests that H_a and H_b do not interconvert on the NMR time scale. If they did interconvert on the NMR time scale, pulsing H_b would be expected to also build up a small NOE on H_e by first interconverting to H_a, which is close to H_e. This means that there is restricted rotation about the double bonds of the η^1-allenyl carbons. Wouters et al.[33] noted this restricted rotation in (η^1-allenyl)(Br)Pd(II) complexes containing two *cis* phosphines. When the two methylene substituents of the η^1-allenyl are inequivalent, atropisomerism shown in Figure 3 results. In this situation the two R groups are both hydrogens, making it so that the two atropisomers are not seen. However, this shows that there are two distinctly different hydrogens, one that is *cis* to the phosphine ligand and one *cis* to the hydroxide ligand, causing them to be magnetically and chemically inequivalent in the ^1H NMR spectrum.

COSY NMR experiments helped to determine the connectivity of the phosphine backbone. Also the selective ^{31}P decoupling experiments helped to further elucidate what is causing the coupling to protons H_a and H_b. The ^{31}P resonance at 11.7 ppm is *trans* to the alkyne

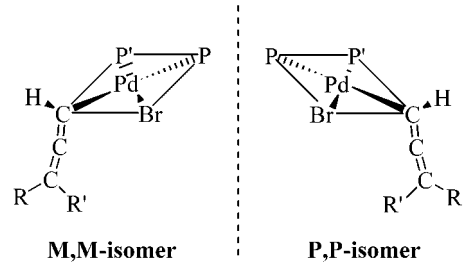

Figure 3. Atropisomeric enantiomers (M,M/P,P-isomers) when P and P′ are PPh_3 and R > R′.[33]

because as this resonance was decoupled with the ^1H NMR spectrum being recorded, loss of all $^5J_{(P-H)}$ of H_a and H_b results. Also from this experiment, it was found that $H_{f(ax)}$ and $H_{f(eq)}$ were closer to the phosphine *trans* to the alkyne than $H_{g(ax)}$ and $H_{g(eq)}$ because the energy that was used to decouple the ^{31}P resonance at 11.7 ppm caused $H_{f(ax)}$ and $H_{f(eq)}$ to interconvert or to become equivalent. The ^{31}P resonance at 16.7 ppm was selectively decoupled to verify the previous result. When the ^{31}P resonance at 16.7 ppm was decoupled and the ^1H NMR spectrum recorded, all $^5J_{(P-H)}$ was maintained. Also during this experiment, $H_{g(eq)}$ and $H_{g(ax)}$ began to interchange. This again means that these two hydrogens ($H_{g(eq)}$ and $H_{g(ax)}$) are closer to the phosphine, whose resonance appears at 16.7 ppm.

This complex was stable, providing this detailed characterization. However, this reaction slowly leads to polymerization of 2-pentyn-1-ol. After 7 days the ^{31}P NMR is characterized as 46.3% $PtCl_2$(DPPBTS) (**6**) and 53.7% η^1-allenyl complex (**7**).

By addition of 1 equiv of 2-pentyn-1-ol to **5**, it was possible to characterize the intermediate formed in D_2O, using $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The ^{31}P NMR spectrum after 45 min was very similar to that of **7** containing two species, characterized by two doublets at 1.1 and −2.1 ppm with $^2J_{(P-P)}$ of 26.7 Hz flanked with platinum satellites of 1711 and 4057 Hz, respectively, and 58.6% of the starting material (**5**). As with **7**, the use of COSY NMR experiments led to determination of the protons in the carbon backbone of the diphosphine ligand. The characterization is very similar to that of **7**, leading to the same interpretation of the NMR spectral data.

The lifetime of this intermediate was much shorter than that of **7**. It was found that 2-pentyn-1-ol does not get hydrated under these conditions. In fact 2-pentyn-1-ol polymerizes through the alkyne probably in a manner similar to the polymerization of dimethyl acetylene described by Chisholm and Clark.[37]

By addition of 2-pentyn-1-ol to **4** it is not possible to characterize the intermediate being formed in D_2O using ^1H NMR spectroscopy. However, from the ^{31}P NMR it is possible to determine that 2-pentyn-1-ol reacts with **4**. The ^{31}P NMR is characterized by resonances at 39.2 and 46.1 ppm, making up a new complex (11.6%) and 88.4% of the starting $PtCl_2$(DPPETS) complex (**4**). The ^{195}Pt satellites were not distinguishable, since only 11.6% of the η^1-allenyl complex (**9**) is formed. The ^{31}P coupling constants are not expected to be very large in this type of complex. Within a chelate ring, P−P coupling can be divided into through-the-

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(33) Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Haming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586−4593.

(34) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657−3663.

(35) (a) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993−1995. (b) Ackermann, M. N.; Ajmera, R. K.; Barned, H. E.; Gallucci, J. C.; Wojcicki, W. *Organometallics* **1999**, *18*, 787−792. (c) Blosser, P. W.; Calligaris, M.; Schimpff, D. G.; Wojcicki, A. *Inorg. Chim. Acta* **2001**, *320*, 110−116.

(36) "NOE can only be detected if the distance between the dipolar-coupled nuclei is less than 5 Å, and ideally it should be less than 3 Å." Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed.; Translated by Becconsall, J. K.; Wiley-VCH: New York, 1998; p 295.

(37) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 2−209.

backbone and through-the-metal contributions $J_{(P-P)} = {}^{B}J_{(P-P)} + {}^{M}J_{(P-P)}$. In five-membered rings these contributions are nearly equal but of opposite signs.[38] For example, the $^{2}J_{(P-P)}$ were not observable for Pt(DPPE)-PhCl[39] or Pt(DPPE)MeCl.[28b] Thus the resonance at 39.2 is assigned to the P *trans* to the alkyne while the resonance at 46.1 is *trans* to the Cl, if the ^{31}P NMR follows the same trend as **7** and **8**.

The formation of an η^1-allenyl complex from addition of 2-pentyn-1-ol to $PtCl_2$(P−P) shows a definite dependence on the bidentate ligand. The stability of the complexes (**7**−**9**) is as follows:

$$\text{P−P} = \text{DPPBTS} > \text{DPPPTS} > \text{DPPETS}$$

Two factors may contribute to the enhanced stability: (1) Structural determinations have shown that the butyl backbone provides considerable flexibility such that the aryl rings may rotate away, creating less steric interaction with the bound allenyl ligand. The propyl backbone has some flexibility, but the ethyl backbone is rigid. (2) The ethyl backbone is close to planar, but the propyl and butyl backbones have geometries where the hydrocarbon backbone may enhance the hydrophobicity near the platinum center and enhance reactivity of the alkyne. Both effects support the increased reactivity of 2-pentyn-1-ol to the platinum center for longer chelate ligand backbones.

Hydration of Water-Soluble Alkynes. $PtCl_2$(P−P) (**4**−**6**) are all effective catalysts for the room-temperature hydration of the water-soluble alkynes 3-pentyn-1-ol and 4-pentyn-1-ol. Dissolving 10−11 mg of $PtCl_2$(P−P) (**4**−**6**) in ∼1 mL water gives a nearly colorless solution of pH = 5. Upon addition of ∼480 equiv of substrate, the solution turns pale yellow and the pH drops to 3 from the acidity of the substrate. As the reaction proceeds, the solution becomes bright yellow. The reaction is monitored by ^{1}H NMR spectroscopy. The ^{31}P NMR was taken after 30 min and then after reaction completion.

Hydrations of both 3-pentyn-1-ol and 4-pentyn-1-ol cleanly produce 5-hydroxypentan-2-one. Over the course of the reaction, the disappearance of resonances corresponding to 3- and 4-pentyn-1-ol and the appearance of resonances corresponding to 5-hydroxypentan-2-one are evident. These reactions are very clean, and no other products are observed.

Complete conversion of 4-pentyn-1-ol occurs in as little as 50 min to more than 27 days for one half-life depending on the catalyst and conditions. Table 2 shows data for the turnover frequency (h^{-1}) and the amount of time it takes to get to 50% conversion for reactions with 4-pentyn-1-ol.

Comparing the time required for 50% conversion to the metal complexes **4**−**6**, the difference between hydration of 4-pentyn-1-ol without added NaCl is evident. Using **6** with no added NaCl the conversion is only 47.6% after 21 days, leading to a turnover frequency of less than 0.5 turnovers per hour. Using **4** with no added NaCl provides 50% conversion before the first NMR spectrum was taken. At that first spectrum, 10 min into the reaction, this reaction is already at 78.9% conversion, more than two half-lives. Thus through this first 10 min this reaction has actually progressed through a little over two half-lives.

Table 2. Catalytic Results for Reactions of 4.2−4.3 mmol of 4-Pentyn-1-ol + 0.21 mol % $PtCl_2$(P−P) in H_2O with *x* mol % NaCl

DPPBTS	50% conversion	
mol % NaCl	TOF (h^{-1})	time
0	<0.5	47.62% @ 21 days
4.9	∼9.6	24.4 h
10	14.3	17.0 h
16	221.3	68 min
21	222.2	65 min
DPPPTS	**50% conversion**	
mol % NaCl	TOF (h^{-1})	time (min)
0	69.2	210
16	129.5	110
21	212.6	70
DPPETS	**50% conversion**	
mol % NaCl	TOF (h^{-1})	time (min)
0	>2272.3	<10
16	291.9	50
21	310.1	50

The ^{31}P NMR spectra of the reaction mixtures throughout the catalytic cycle gave insight into the species that formed before the slow step. In all cases when a large excess of NaCl was added, the ^{31}P NMR spectrum throughout the catalytic cycle was composed solely of the starting materials (**4**−**6**). However, when there was no added NaCl, the ^{31}P NMR of the reaction mixture varied. The reaction of 4-pentyn-1-ol with **6** led to doublets at 13.5 and 13.3 with $^{2}J_{(P-P)}$ of 17.6, flanked with ^{195}Pt satellites of 3575 and 3730 Hz, respectively. This intermediate is characteristic of an η^3-allenyl-Pt(II) bis-phosphine complex.[34,40]

Baize et al. synthesized $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$, which is characterized by a ^{31}P NMR spectrum composed of doublets at 15.4 and 10.5 ppm with $^{2}J_{(P-P)}$ of 18.7 Hz and $^{1}J_{(Pt-P)}$ of 3785 and 4285 Hz, respectively.[40] $[(PPh_3)_2Pt(CH_2CCMe)]^+$ is characterized by a ^{31}P NMR spectrum containing doublets at 18.8 and 12.6 ppm with $^{2}J_{(P-P)}$ of 17.4 Hz and $^{1}J_{(Pt-P)}$ of 4240 and 3754 Hz, respectively.[40] Huang et al. synthesized $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH)]^+$, which is characterized by a ^{31}P NMR spectrum containing doublets at 13.0 and 11.5 ppm with $^{2}J_{(P-P)}$ of 20.0 Hz and $^{1}J_{(Pt-P)}$ of 3810 and 4179 Hz, respectively.[34] Thus our spectral results are consistent with intermediate **B** (Scheme 2) being formed throughout the hydration reaction of $PtCl_2$(DPPBTS) with 4-pentyn-1-ol with no added NaCl.

When NaCl was added to the reaction of $PtCl_2$-(DPPBTS) with 4-pentyn-1-ol, the presence of a new platinum species was evident from the ^{31}P NMR spectrum. This new species was characterized by two doublets at 15.7 and 15.4 with $^{2}J_{(P-P)}$ of 25.9 Hz. The $^{1}J_{(Pt-P)}$ for this intermediate was not distinguishable. This complex could be of type **D** or **G** (Scheme 2.)

The reactions with 4-pentyn-1-ol proceed through a 5-exo-dig mechanism[41] as shown in Scheme 2. The first

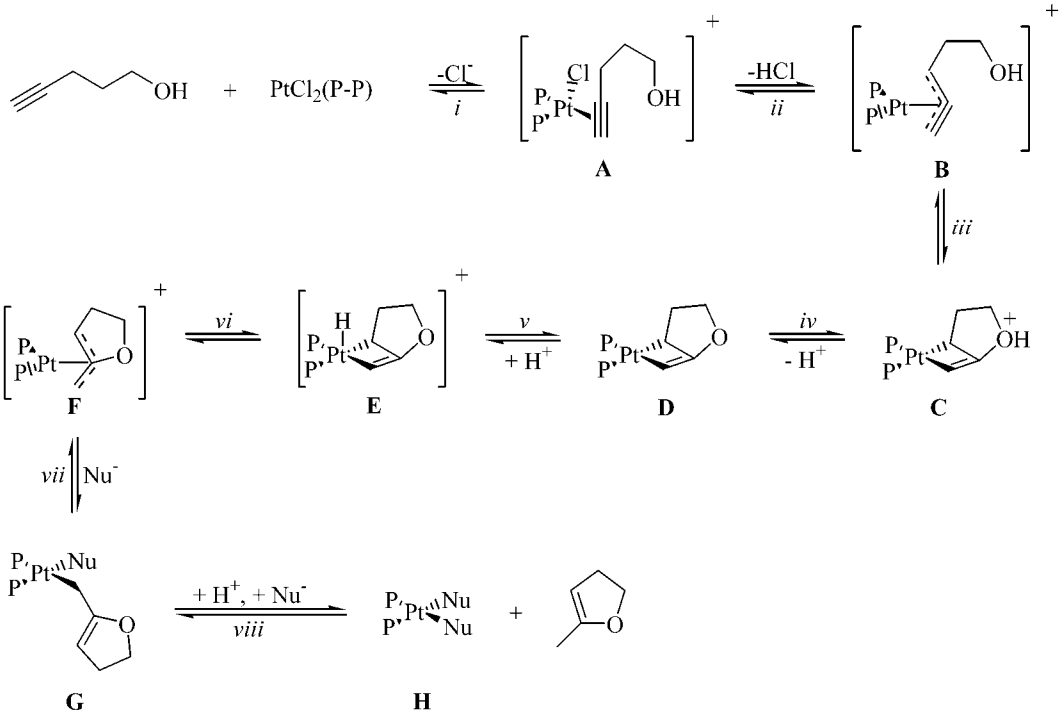
(38) Grim, S. O.; Barth, R. C.; Mitchell, J. D.; DelGaudio, J. *Inorg. Chem.* **1977**, *16*, 1776−1779. Also see: Grim, S. O.; Mitchell, J. D. *Inorg. Chem.* **1977**, *16*, 1770−1777.

(39) Anderson, G. K.; Lumetta, G. J. *Organometallics* **1985**, *4*, 1542−1545.

(40) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164−173.

(41) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734−736.

Scheme 2. Proposed Mechanism for 4-Pentyn-1-ol Hydration in Water



step (i) is substitution of 4-pentyn-1-ol for a halide. Since 4-pentyn-1-ol is a terminal alkyne with no electron-withdrawing group β to the alkyne, it undergoes β-hydride elimination and loss of HCl (ii) to form an η^3-allenyl complex (**B**). This Pt(II) η^3-allenyl intermediate is subject to intramolecular nucleophillic attack by the alcohol as described by Baldwin's rules.[41] Baize et al. and Huang et al. found that when NuH was added to this type of η^3-allenyl Pt(II) complex, addition to the central carbon was followed by deprotonation/protonation of the resultant intermediate to form an η^3-allyl intermediate which was isolable.[34,40] This has led to our interpretation of the deprotonation followed by protonation of the metal center to form the Pt(IV)-H intermediate, **E**, which would rapidly form the η^3-allyl intermediate shown, **F**. In the presence of a nucleophile, this would be converted rapidly into the corresponding η^1-allyl Pt(II) intermediate. Metal-assisted or solvent-assisted protonation of the η^1-allyl Pt(II) would lead to **H** and 5-methyl-2,3-dihydrofuran. This furan would become protonated under the reaction conditions, subjecting it to nucleophillic attack of water to form 5-hydroxypentan-2-one. Similar reactions were studied with 4-pentyn-1-ol that support the proposed mechanism. The reaction of 4-yn-1-ols with 1 mol % PdI_2 and 2 mol % KI for 18 h at room temperature in MeOH has led to 2-methyl-2-alkyl-4-ynyloxytetrahydrofuran products.[42] Also Arcadi et al. found that 3-yne-1-carboxylates undergo the same type of cyclization reactions under anhydrous conditions with $Pd(OAc)_2(PPh_3)_2$ and ROTf, forming (*E*)-δ-vinyl-γ-methylene-γ-butyrolactones.[43]

Complete hydration of 3-pentyn-1-ol occurs between 2 and 14 h depending on the specific catalytic conditions. Table 3 shows data for the turnover frequency (h^{-1}) and the amount of time it takes to get to 50% conversion for reactions with 3-pentyn-1-ol.

Table 3. Catalytic Results for Reactions of 4.2−4.3 mmol of 3-Pentyn-1-ol + 0.21 mol % $PtCl_2$(P−P) in H_2O with *x* mol % NaCl

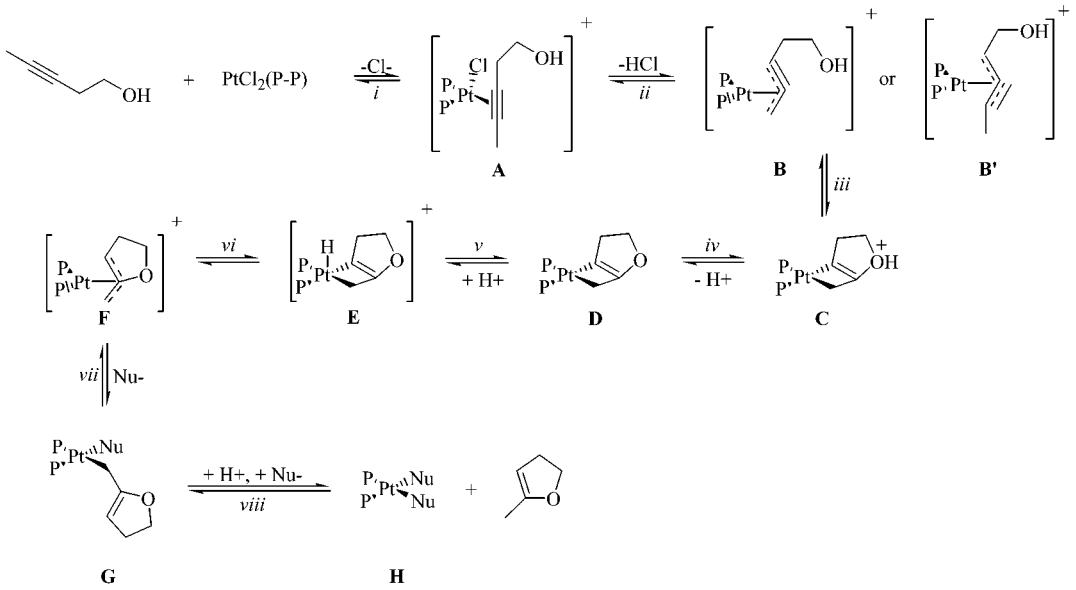
DPPBTS	50% conversion	
mol % NaCl	TOF (h^{-1})	time (min)
0	40.1	360
4.9	125.1	120
21	162.5	90
DPPPTS	**50% conversion**	
mol % NaCl	TOF (h^{-1})	time (min)
0	347.3	40
16	236.9	60
21	216.6	70
DPPETS	**50% conversion**	
mol % NaCl	TOF (h^{-1})	time (min)
0	103.3	140
16	100.4	150
21	116.9	120

The mechanism for this hydration is believed to be very similar in the steps to that of the 4-pentyn-1-ol hydration. The major difference is that this proceeds through a 5-endo-dig mechanism. Scheme 3 is a proposed mechanism for this hydration reaction. The first step in this mechanism is assumed to be the substitution of 3-pentyn-1-ol for Cl^-. The next step, (ii) is the loss of HCl to form an η^3-allenyl intermediate **B** or **B′**. The proton can be lost from either a terminal carbon or an internal carbon. This must proceed through loss from the terminal carbon since the final product is 5-hydroxypentan-2-one. The remaining steps are exactly the same as described for 4-pentyn-1-ol.

Previous reports on 3-yn-1-ols support the proposed mechanism. In reacting 3-yn-1-ols in THF under anhydrous conditions with $PdCl_2$ (20 mol %) at room temperature for 3.5 h, Saito et al. synthesized 5-alkyl-2,3-

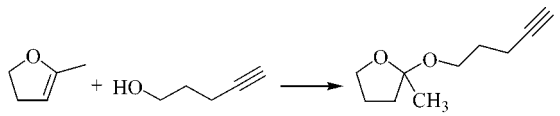
(42) Gabriele, B.; Salerno, G.; de Pascali, F.; Costa, M.; Chiusoli, G. P. *J. Organomet. Chem.* **2000**, *593−594*, 409−415.
(43) Arcadi, A.; Burini, A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietroni, B. R. *J. Org. Chem.* **1992**, *33*, 3915−3918.

Scheme 3. Proposed Mechanism for 3-Pentyn-1-ol Hydration in Water



dihydrofurans.[44] This was first done by Utimoto, where he used $PdCl_2(PhCN)_2$ (1−3 mol %) in anhydrous ether at room temperature for 5−10 h to form 5-alkyl-2,3-dihydrofurans.[45] Under aqueous conditions using aqueous CH_3CN and $PdCl_2$ at reflux for 30 min Utimoto showed the formation of 4-keton-1-ols.[45] Subsequently, Arcadi et al. showed that utilizing $PdCl_2$ (5 mol %), 10 mol % n-$Bu_4NCl{\cdot}H_2O$, 5 mL of 3 N HCl, and 5 mL of CH_2Cl_2 also formed 4-keton-1-ol.[46] Finally, House showed that using $Hg(OAc)_2$ with a catalytic amount of H_2SO_4 in 90% CH_3COOH formed 4-keton-1-ol products after 2 h at reflux.[47]

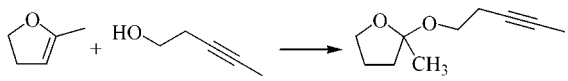
Reactions of 6 in DMSO. $Pt(DPPBTS)Cl_2$ is not an effective catalyst for the room-temperature hydration of 4-pentyn-1-ol in DMSO. However, when the temperature is raised to 70 °C, **6** is an effective hydration catalyst using adventitious water. When 4-pentyn-1-ol is added to **6** at room temperature, no reaction occurs, as determined by ^{31}P and ^1H NMR spectroscopy. Next, the temperature was raised to 70 °C for 30 min; after this cooled to room temperature, the ^{31}P NMR showed only the starting material and the ^1H NMR spectrum showed only the presence of 5-hydroxypentan-2-one. After this additional 4-pentyn-1-ol was added, which again showed no reaction at room temperature. However once the temperature was raised, this again began to hydrate until all the water was used up. At this point, 2-methyl-2-pent-4-ynyloxytetrahydrofuran, **10**, began to appear (eq 1).



(1)

10

Gabriele et al. observed this same product when they used 100 equiv of 4-pentyn-1-ol as both the solvent and reactant using 1 equiv of PdI_2 and 2 equiv of KI with no solvent.[41] If excess 4-pentyn-1-ol is reacted with **11** at room temperature, this reaction continues to form 5-hydroxypentan-2-one and its ring tautomer until all of the water is used up. The tautomer, 2-methyltetrahydrofuran-2-ol, is expected in DMSO as described by Whiting and Edward.[48] When 3-pentyn-1-ol was reacted with **11**, there was formation of 5-hydroxypentan-2-one until no traces of water remained. Then, **12** (2-methyl-2-pent-3-ynyloxytetrahydrofuran) was formed (eq 2). This is very similar to **10**; however, the attacking nucleophile in this case is 3-pentyn-1-ol.



(2)

12

Effect of Bidentate Ligand. For hydration of 4-pentyn-1-ol with $PtCl_2(P-P)$ the rate is fastest for P−P = DPPETS and slowest for P−P = DPPBTS. The magnitude of the effect is best shown by the time for 50% conversion of the 4-pentyn-1-ol to 5-hydroxypentan-2-one, DPPETS, t < 10 min; DPPPTS, t = 210 min; DPPBTS, t = 21 days. For comparison $PtCl_2(TPPTS)_2$ is a bit faster than $PtCl_2$(DPPBTS) but much slower than $PtCl_2$(DPPETS). Thus for hydration of 4-pentyn-1-ol a significant enhancement is observed for the smaller bite angle ligand.

For hydration of 3-pentyn-1-ol (Table 3) the trend is a bit different with DPPBTS, still the slowest but in this case the effects are much less, and DPPPTS is the most rapid. The times for 50% conversion (DPPETS, 140 min; DPPPTS, 40 min; DPPBTS, 360 min) show the diminished effect and altered order.

The effect of excess Cl^- negates the effect of the bidentate ligand, inhibiting hydration with $PtCl_2$-(DPPETS) and speeding hydration with $PtCl_2$(DPPBTS),

(44) Saito, T.; Suzuki, T.; Morimoto, M.; Akiyama, C.; Ochiai, T.; Takeuchi, K.; Matsumoto, T.; Suzuki, K. *J. Am. Chem. Soc.* **1998**, *120*, 11633−11644.

(45) Utimoto, K. *Pure Appl. Chem.* **1983**, *55* (11), 1845−1852.

(46) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* **1993**, *49* (22), 4955−4964.

(47) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; The Organic Chemistry Monograph Series; Breslow, R., Benjamin, W. A., Eds.; Menlow Park, CA, 1972; pp 387−390.

(48) Whiting, J. E.; Edward, J. T. *Can. J. Chem.* **1971**, *49*, 3799−3806.

suggesting a change in rate-determining step. For DPPETS the addition of 2-pentyn-1-ol gives a less stable product than for the other two bidentate ligands. If this trend continues for 4-pentyn-1-ol, it is likely that stability of the η^3-allenyl Pt(II) complex, **B** in Scheme 2, limits the catalytic reaction. Certainly $PtCl_2$(DPPETS) is the only species characterized during the catalytic reaction; the presence of excess Cl^- would drive the equilibrium away from **A** and slow the reaction, as observed. The hydration using $PtCl_2$(DPPETS) shows a significant effect on the alkyne (4-pentyn-1-ol is faster than 3-pentyn-1-ol), consistent with rate-determining binding of the alkyne. For both DPPPTS and DPPBTS the initial rates show very little dependence on the nature of the alkyne. For DPPBTS the platinum species shows two doublets in the ^{31}P NMR, indicating a Pt(P−P)(X)(Y) complex. From chemical shifts and coupling constants complex **B** (Scheme 2) is most likely. For $PtCl_2$(DPPBTS) the presence of excess Cl^- enhances the catalytic reaction.

Conclusions

The synthesis of $PtCl_2$(P−P) allows the reactivity of these complexes with 2-, 3-, and 4-pentyn-1-ol to be examined. 2-Pentyn-1-ol reacts with these complexes to form a stable, characterizable intermediate when (P−P) is DPPBTS. However, when DPPETS is the ligand, the intermediate is much less stable and polymerization of 2-pentyn-1-ol occurs. The order of 2-pentyn-1-ol polymerization is opposite the order of stability of the intermediate, η^1-allenyl complex, as a function of the bidentate ligand. The flexibility of the butyl backbone of DPPBTS allows the aryl groups to conform to a geometry that does not block the opposite face of the square-planar complex; the ethyl backbone of the DPPETS complex is much less flexible, thus forcing the aryl substituents into blocking the opposite face of the square-planar complex, destabilizing the formation of an η^1-allenyl complex and promoting polymerization of the alkyne.

3-Pentyn-1-ol is hydrated under the reaction conditions. This hydration proceeds through a 5-endo-diganol mechanism in accordance to Baldwin's rules. There is not a direct dependence on ligand size for this reaction and very little effect of added Cl^-.

4-Pentyn-1-ol is hydrated to 5-hydroxypentan-2-one under the reaction conditions. This reaction proceeds through a 5-exo-diganol mechanism in accordance to Baldwin's rules. The rate of this reaction has a direct dependence on the size of the bidentate ligand used, with the DPPETS complex reacting fastest (50% conversion in about 5 min), while the largest bidentate ligand, DPPBTS, reacts slowest (50% conversion in about 20 days). For a given complex, this reaction has been shown to have a direct dependence on added salt. Added NaCl to the reaction of $PtCl_2$(DPPBTS) with 4-pentyn-1-ol speeds up the reaction dramatically, influencing cyclization of the intermediate. Added NaCl to the reaction of $PtCl_2$(DPPETS) with 4-pentyn-1-ol slows hydration. These observations are consistent with differing rate-determining steps for $PtCl_2$(DPPBTS) and $PtCl_2$(DPPETS).

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Water was triply distilled, deionized, and purged with nitrogen prior to use. All other solvents were purged with nitrogen and used without further purification. Deuterium oxide was purchased from Isotec, Inc. DMSO-d_6 and methanol-d_4 were obtained from Aldrich. $H_2PtCl_6 \cdot 6H_2O$ was purchased from Strem Chemicals and used as received. $PtCl_2$ was prepared using literature procedures.[49] All other reagents were obtained from commercial sources and used without further purification.

^1H NMR (400 MHz), $^{31}P\{^1H\}$ NMR, and ^{195}Pt NMR spectra were recorded on a Varian XL 400 spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR 500 MHz NMR spectrometer. All ^{31}P NMR spectra were measured at 161.9 MHz, proton decoupled, and referenced to an external sample of 85% H_3PO_4 in D_2O set to 0.00 ppm. ^{195}Pt NMR spectra were measured at 85.97 MHz and referenced using an internal standard of 0.2 M K_2PtCl_4 in 0.4 M KCl/D_2O set to −1627.0 ppm (vs 0.2 M K_2PtCl_6 in H_2O).[50] Analyses were conducted by E & R Microanalytical Laboratory in Parsipanny, NJ. pH measurements were performed using a Fischer Scientific Accumet pH meter with a glass pH electrode with a silver/silver chloride reference electrode, referenced to three buffers (pH = 4, 7, 10).

Synthesis of Bidentate Water-Soluble Ligands. A 500 mL three-neck, round-bottom flask equipped with a stir bar, a gas adapter, a thermometer, and a pressure-equalizing addition funnel was charged with 65 mL of 30% fuming sulfuric acid. This was placed on an ice bath and flushed thoroughly with N_2(g). A solution of 12 mmol of the bidentate ligand (DPPE, DPPP, or DPPB) in 15 mL of cold concentrated sulfuric acid was prepared. The dissolved ligand was then added via the pressure-equalizing addition funnel to the fuming sulfuric solution while a temperature of less than 5 °C was maintained. Upon complete addition, an additional 20 mL of 30% fuming sulfuric acid was added directly to the reaction flask via the pressure-equalizing addition funnel. Utilizing a DMSO-d_6 or D_2O insert, the progress of the reaction was followed by ^{31}P NMR analysis. When the reaction mixture reached 95% conversion (48 h for all ligands), workup was done.

The reaction mixture was slowly added to 500 mL of triply distilled H_2O while keeping the temperature below 10 °C. The addition occurred over 45 min to 1.5 h (for DPPETS this was done under N_2(g) purge). The resulting solution was neutralized with 25−50% NaOH (w/w%) to a pH of 2.2−2.3 while maintaining a temperature below 10 °C. To facilitate the precipitation of Na_2SO_4, 350 mL of MeOH was added. The mixture was filtered using a Buchner funnel. The filtrate was place into a 1 L three-neck flask that is equipped with a stir bar, gas adapter, and two rubber septa. The solvent was removed by distillation in vacuo to a N_2(l) cooled trap to afford a beige solid. The product was immediately redissolved in a minimum amount of triply distilled water. Then the pH was adjusted to approximately 7. An additional 250 mL of MeOH was added to facilitate the precipitation of any remaining Na_2SO_4. This mixture was filtered and the filtrate was again distilled to dryness under vacuum to give a crude yield of ∼50%.

The crude product was placed into a Schlenk flask under N_2(g) and dissolved in a minimum amount of triply distilled H_2O. Once dissolved, acetone was added until a precipitate began to form. This flask was then cooled to 5 °C for 3−5 h. The solid was collected by filtration, and additional acetone was added to the filtrate until a precipitate began to form. The solution was cooled to 5 °C for 8−10 h. The solid was

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(50) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3494−3503.

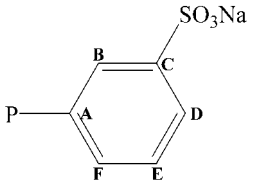

Figure 4. Figure of the aryl group to show labeling scheme for C and H atoms.

collected on a frit; this was determined to be clean product (90−95%). If interested in the oxide product, add additional acetone to the resultant solution until a total of 6−7 equiv of acetone to water is added or a precipitate starts to form. Repeated recrystalization of the crude product gives decent elemental analysis. The ligand was used in further synthesis if it was greater than 94% pure as determined by ^{31}P NMR analysis.

DPPETS (1) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): −13.1 (s). $^{31}P\{^1H\}$ NMR (DMSO-d_6): −11.1 (s). ^{1}H NMR(D_2O): 7.68 (br, 4H, **D**), 7.61 (br/m, 4H, **B**), 7.31 (br, 4H, **E**), 7.30 (br, 4H, **F**), 2.15 (t, $^2J_{(P-H)}$ = 4.80, 4H, PCH_2). ^{1}H NMR (DMSO-d_6): 7.65 (br, 4H, **D**), 7.58 (d, J = 7.60, 4H, **B**), 7.35 (t, J = 7.60, 4H, **E**), 7.24 (br, 4H, **F**), 2.03 (br/t, 4H, PCH_2) Anal. Calcd for $C_{26}H_{24}Na_4O_{14}P_2S_4$ or DPPETS·$2H_2O$: C, 37.06; H, 2.87; Na, 10.91; P, 7.35. Found: C, 37.13; H, 2.94; Na, 11.05; P, 7.18.

DPPPTS (2) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): −16.2 (s). $^{31}P\{^1H\}$ NMR (DMSO-d_6): −16.4 (s). ^{13}C NMR (D_2O/DMSO): 145.0 (d, $^3J_{(P-C)}$ = 7.3, **C**), 139.8 (d, $^2J_{(P-C)}$ = 13.7, **B**), 136.5 (d, $^2J_{(P-C)}$ = 17.2, **F**), 131.0 (d, **E**), 130.9 (d, $^1J_{(P-C)}$ = 26.90, **A**), 127.9 (s, **D**), 29.0 (t, $^2J_{(P-C)}$ = 10.39, PCH$_2$$CH_2$), 23.1 (t, $^1J_{(P-C)}$ = 16.2, PCH_2). ^{1}H NMR (D_2O): 7.70 (d, $^3J_{(H-H)}$ = 6.80, 4H, **D**), 7.65 (d, $^3J_{(P-H)}$ = 6.80, 4H, **B**), 7.37 (m, 8H, **E** + **F**), 2.22 (m, $^3J_{(P-H)}$ = 7.20 and $^3J_{(H-H)}$ = 6.80, 4H, PCH_2), 1.42 (br, 2H, PCH$_2$$CH_2$). ^{1}H NMR (DMSO-$d_6$): 7.66 (d, $^3J_{(H-H)}$ = 7.60, 4H, **D**), 7.58 (d, $^3J_{(P-H)}$ = 7.60, 4H, **B**), 7.34 (m, 8H, **E** + **F**), 2.26 (t, $^3J_{(H-H)}$ = 7.20, 4H, PCH_2), 1.42 (m, 2H, PCH$_2$$CH_2$). Anal. Calcd for $C_{27}H_{26}Na_4O_{14}P_2S_4$ or DPPPTS·$2H_2O$: C, 37.86; H, 3.06; P, 7.23. Found: C, 37.62; H, 2.88; P, 7.18.

DPPBTS (3) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): −15.0 (s). ^{31}P $\{^1H\}$ NMR (DMSO-d_6): −15.4 (s). $^{13}C\{^1H\}$ NMR (D_2O/DMSO): 144.9 (d, $^3J_{(P-C)}$ = 6.79, **C**), 140.1 (d, $^2J_{(P-C)}$ = 14.08, **B**), 136.6 (d, $^2J_{(P-C)}$ = 16.97, **F**), 131.0 (d, $^3J_{(P-C)}$ = 6.79, **E**), 130.9 (d, $^1J_{(P-C)}$ = 30.04, **A**), 127.8 (s, **D**), 27.9 (t, $^1J_{(P-C)}$ = 13.83, PCH_2), 27.5 (d, $^2J_{(P-C)}$ = 8.42, PCH$_2$$CH_2$). ^{1}H NMR ($D_2O$): 7.71 (d, $^3J_{(H-H)}$ = 7.20, 4H, **D**), 7.65 (d, $^3J_{(P-H)}$ = 7.20, 4H, **B**), 7.40 (t, $^3J_{(H-H)}$ = 7.20, 4H, **E**), 7.35 (t, $^3J_{(P-H)}$ = 7.20 and $^3J_{(H-H)}$ = 7.40, 4H, **F**), 2.03 (br, 4H, PCH_2), 1.40 (br, 4H, PCH$_2$$CH_2$). ^{1}H NMR (DMSO-$d_6$): 7.65 (d, $^3J_{(H-H)}$ = 8.00, 4H, **D**), 7.56 (d, $^3J_{(P-H)}$ = 4.40, 4H, **B**), 7.34−7.32 (br, m, 8H, **E** + **F**), 2.06 (br, 4H, PCH_2), 1.47 (br, 4H, PCH$_2$$CH_2$). Anal. Calcd for $C_{28}H_{28}Na_4O_{14}P_2S_4$ or DPPBTS·$2H_2O$: C, 38.63; H, 3.24; P, 7.12; Na, 10.56; S, 14.73. Found #1: C, 38.75; H, 3.26; P, 7.12; Na, 9.83; S, 12.00. Found #2: C, 38.92; H, 3.07; P, 7.15.

Synthesis of $PtCl_2$(P−P) (P−P = DPPETS, DPPPTS, DPPBTS) (4−6). Into a Schlenk flask 0.15 g of $PtCl_2$ was suspended in 3 mL of DMSO. The suspension was heated to 75−80 °C. When the $PtCl_2$ dissolved to give a yellow solution, the heat was removed and 1 molar equiv of the ligand was added. The solution lightens to pale yellow upon addition of the ligand. After the mixture reached room temperature, an excess of methylene chloride (75 mL) was added to precipitate the product. The product was collected by filtration and washed with 2 × 50 mL of CH_2Cl_2 followed by 2 × 50 mL of diethyl ether. The product was then placed under vacuum for 12 h, giving 95% crude product. Purification was effected by placing the crude product into a test tube containing 15 mL of MeOH. The mixture is allowed to stir for 10−15 min, then the mixture was centrifuged. The solution containing the desired Pt(II) complex is then added to 1 equiv of nitromethane to facilitate precipitation. Finally the pure complex is filtered, washed with 2 × 50 mL $MeNO_2$, dried under vacuum at 90 °C, and stored in the glovebox.

$PtCl_2$(DPPETS) (4) (refer to Figure 4 for labeling scheme). This complex is very slightly soluble in MeOH, so recrystalization was done from water with isopropyl alcohol (58.83% yield). $^{31}P\{^1H\}$ NMR (D_2O): 46.0 (s, $^1J_{(Pt-P)}$ = 3670) $^{31}P\{^1H\}$ NMR (DMSO-d_6): 44.7 (s, $^1J_{(Pt-P)}$ = 3610). ^{1}H NMR (D_2O): 8.03 (d, $^3J_{(H-H)}$ = 12.0, 4H, **D**), 7.94 (t, $^3J_{(H-H)}$ = 8.00, 4H, **B**), 7.91 (d, $^3J_{(H-H)}$ = 7.20, 4H, **E**), 7.61 (dd, $^3J_{(H-H)}$ = 8.00 and 1.60, 4H, **F**), 2.65 (d, $^2J_{(P-H)}$ = 20.00, 4H, PCH_2). ^{1}H NMR (DMSO-d_6): 7.94 (d, $^3J_{(H-H)}$ = 11.6, 4H, **D**), 7.86 (dd, $^3J_{(H-H)}$ = 4.40 and 7.60, 4H, **B**), 7.80 (d, $^3J_{(H-H)}$ = 8.00, 4H, **E**), 7.54 (dd, $^3J_{(H-H)}$ = 5.80 and 1.60, 4H, **F**), 2.42 (d, $^2J_{(P-H)}$ = 20.00, 4H, PCH_2). ^{195}Pt NMR (D_2O): −4610 (t, $^1J_{(Pt-P)}$ = 3670). Anal. Calcd for $C_{26}H_{22}Cl_2Na_4O_{13}P_2PtS_4$ or $PtCl_2$(DPPETS)·H_2O: C, 28.63; H, 2.03; Cl, 6.50; Na, 8.43; P, 5.68. Found: C, 28.95; H, 2.01; Cl, 6.54; Na, 8.67; P, 5.39.

$PtCl_2$(DPPPTS) (5) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): −4.5 (s, $^1J_{(Pt-P)}$ = 3420). $^{31}P\{^1H\}$ NMR (DMSO-d_6): −1.5 (s, $^1J_{(Pt-P)}$ = 3420). ^{1}H NMR (D_2O): 7.90 (br, 4H, **D**), 7.77 (br, d, $^3J_{(H-H)}$ = 10, 4H, **B**), 7.71 (br, 4H, **E**), 7.45 (br, t, $^3J_{(H-H)}$ = 7.60 and 7.20, 4H, **F**), 2.78 (br, 4H, PCH_2), 2.05 (br, 2H, PCH$_2$$CH_2$). ^{1}H NMR (DMSO-$d_6$): 7.95 (br, 4H, **D**), 7.75 (br, 4H, **B**), 7.71 (br, d $^3J_{(H-H)}$ = 7.60, 4H, **E**), 7.44 (br, t, $^3J_{(H-H)}$ = 7.20, 4H, **F**), 2.73 (br, 4H, PCH_2), 1.65 (br, 2H, PCH$_2$$CH_2$). ^{195}Pt NMR ($D_2O$): −4501 (t, $^1J_{(Pt-P)}$ = 3420). Anal. Calcd for $C_{27}H_{22}Cl_2Na_4O_{12}P_2PtS_4$ or $PtCl_2$(DPPPTS): C, 29.84; H, 2.04; Cl, 6.53; Na, 8.46; P, 5.70. Found: C, 29.68; H, 2.13; Cl, 6.38; Na, 8.26; P, 5.48.

$PtCl_2$(DPPBTS) (6) (refer to Figure 4 for labeling scheme). $^{31}P\{^1H\}$ NMR (D_2O): 13.0 (s, $^1J_{(Pt-P)}$ = 3580). $^{31}P\{^1H\}$ NMR (DMSO-d_6): 13.0 (s, $^1J_{(Pt-P)}$ = 3550). $^{13}C\{^1H\}$ NMR (D_2O/DMSO): 145.1 (s, **C**), 137.8 (s, **B**), 131.6 (s, **A**), 131.3 (br, **D** + **E**), 130.4 (s, **F**), 27.7 (d, $^1J_{(P-C)}$ = 40.22, PCH_2), 23.2 (s, PCH$_2$$CH_2$). ^{1}H NMR ($D_2O$): 8.00 (br, 4H, **D**), 7.88 (br, 4H, **B**), 7.77 (br, 4H, **E**), 7.52 (br, 4H, **F**), 2.70 (br, 4H, PCH_2), 2.53 (s, 9H, DMSO), 1.64 (br, 2H, PCH$_2$$CH_2$), 1.61 (br, 2H, PCH$_2$-CH$_2$$CH_2$). ^{1}H NMR (DMSO-$d_6$): 7.95 (d, $^3J_{(H-H)}$ = 10, 4H, **D**), 7.81 (t, $^3J_{(P-H)}$ = 8 and $^3J_{(H-H)}$ = 8, 4H, **B**), 7.75 (d, $^3J_{(P-H)}$ = 8, 4H, **E**), 7.51 (t, $^3J_{(H-H)}$ = 7, 4H, **F**), 2.68 (br, 4H, PCH_2), 1.44 (br, 4H, PCH$_2$$CH_2$). ^{195}Pt NMR ($D_2O$): −4510 (t, $^1J_{(Pt-P)}$ = 3580). Anal. Calcd for $C_{31}H_{33}Na_4O_{13.5}P_2PtS_{5.5}$ or $PtCl_2$(DPPBTS)·1.5DMSO: C, 30.58; H, 2.73; P, 5.09. Found: C, 30.41; H, 2.92; P, 5.04. Thermogravimetric analysis: 10.35 wt %; midpoint 327.91 °C.

In Situ Formation of Pt(C(Et)CCH$_2$)(OH)(DPPBTS) (7). An NMR tube was charged with 58 μmol (71 mg) of $PtCl_2$(DPPBTS). To this was added 0.50 mL of D_2O. The ^{31}P and ^{1}H NMR spectra were recorded. One equivalent of 2-pentyn-1-ol was then added (∼5.0−5.5 μL), and the ^{31}P, ^{1}H, and ^{195}Pt NMR spectra were recorded immediately. The ^{31}P NMR was followed over a period of 7 days. $^{31}P\{^1H\}$ NMR (D_2O) (refer to Figure 2 for labeling scheme): 16.7 (d, $^2J_{(P-P)}$ = 18.6, $^1J_{(Pt-P)}$ = 4312, P *trans* to Cl^-), 11.7 (d, $^2J_{(P-P)}$ = 18.6, $^1J_{(Pt-P)}$ = 1761, P *trans* to alkyne) and 13.0 (s, $^1J_{(Pt-P)}$ = 3580, 21.9%, starting $PtCl_2$(DPPBTS)). ^{1}H NMR (D_2O) ignoring starting $PtCl_2$-(DPPBTS): Varian VXR 500 MHz 6.28 (d, $^4J_{(P-H)}$ = 19.50, a), 5.37 (d, $^4J_{(P-H)}$ = 9.50, b), 2.73 (br, s, h), 2.38 (br, s, e), 2.25 (q, $^3J_{(H-H)}$ = 7.0, c), 1.79 (s, g_{ax}), 1.73 (s, g_{eq}), 1.40 (s, f_{ax}), 1.36 (s, f_{eq}), 0.550 (t, $^3J_{(H-H)}$ = 7.0, d). Selective decoupling experiment: Varian 400 MHz: decouple ^{31}P resonance at 11.7, record ^{1}H NMR: 6.28 (s, a), 5.37 (s, b), 1.79 (s, g_{ax}), 1.73 (s, g_{eq}), 1.40 (br, s, f_{ax} and f_{eq}); decouple ^{31}P resonance at 16.7, record ^{1}H NMR: 6.28 (d, $^4J_{(P-H)}$ = 19.50, a), 5.37 (d, $^4J_{(P-H)}$ = 9.50, b), 1.76 (br, s, g_{ax} and g_{eq}), 1.40 (br, s, f_{ax} and f_{eq}). ^{195}Pt NMR: −4490 (dd, $^1J_{(Pt-P)}$ = 4312 and 1761). $^{31}P\{^1H\}$ NMR (D_2O) after 7 days: 16.7 (d, $^2J_{(P-P)}$ = 18.6, $^1J_{(Pt-P)}$ = 4312, P *trans* to Cl^-),

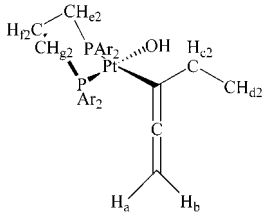

Figure 5. Pt(OH)(C(Et)CCH$_2$)(DPPPTS) (**8**).

11.7 (d, $^2J_{(P-P)}$ = 18.6, $^1J_{(P-P)}$ = 1761, P *trans* to alkyne), and 13.0 (s, $^1J_{(Pt-P)}$=3580, 46.3%, starting $PtCl_2$(DPPBTS)).

In Situ Formation of Pt(C(Et)CCH$_2$)(OH)(DPPPTS) (8). An NMR tube was charged with 92 μmol (111.0 mg) of $PtCl_2$(DPPPTS). To this was added 0.50 mL of D_2O. The ^{31}P and ^1H NMR spectra of the solution were recorded. One equivalent of 2-pentyn-1-ol was then added (5.0 μL), and the ^{31}P and ^1H NMR spectra were recorded. The ^{31}P was followed over time. $^{31}P\{^1H\}$ NMR (D_2O) after 45 min (refer to Figure 5 for labeling scheme): 1.1 (d, $^2J_{(P-P)}$ = 26.7, $^1J_{(Pt-P)}$ = 1711, P *trans* to alkyne) −2.1 (d, $^2J_{(P-P)}$ = 26.7, $^1J_{(P-P)}$ = 4057, P *trans* to Cl^-), and −4.5 (s, $^1J_{(Pt-P)}$ = 3420, 58.6%, starting $PtCl_2$(DPPPTS)). ^1H NMR (D_2O) ignoring starting $PtCl_2$(DPPPTS): Varian VXR 500 MHz 6.32 (d, $^4J_{(P-H)}$ = 19.50, a), 5.51 (d, $^4J_{(P-H)}$ = 10.00, b), 2.85 (t, $^3J_{(H-H)}$ = 15, g), 2.61 (t, $^3J_{(H-H)}$ = 15, e), 2.30 (q, $^3J_{(H-H)}$ = 10, c), 1.77 (m, f) and 0.587 (t, $^3J_{(H-H)}$ = 10, d). $^{31}P\{^1H\}$ NMR (D_2O) after 14 h: 1.1 (d, $^2J_{(P-P)}$ = 26.7, $^1J_{(Pt-P)}$ = 1711, P *trans* to alkyne) −2.1 (d, $^2J_{(P-P)}$ = 26.7, $^1J_{(P-P)}$ = 4057, P *trans* to Cl^-), and −4.5 (s, $^1J_{(Pt-P)}$ = 3420, 87.7%, starting $PtCl_2$(DPPPTS)).

In Situ Formation of Pt(C(Et)CCH$_2$)(OH)(DPPETS) (9). An NMR tube was charged with 29.5 μmol (32.2 mg) of $PtCl_2$(DPPETS). To this was added 0.45 mL of D_2O. The ^{31}P and ^1H NMR spectra of the solution were recorded. One equivalent of 2-pentyn-1-ol was then added (3.0 μL), and the ^{31}P and ^1H NMR spectra were recorded. The ^{31}P was followed over time. $^{31}P\{^1H\}$ NMR (D_2O) after 30 min: 46.6 (s, $^2J_{(P-P)}$ = ND, $^1J_{(Pt-P)}$ = ND, P *trans* to alkyne) 39.2 (s, $^2J_{(P-P)}$ = ND, $^1J_{(P-P)}$ = ND, P *trans* to Cl^-), and 46.0 (s, $^1J_{(Pt-P)}$ = 3670, 88.4%, starting $PtCl_2$(DPPETS)). ^1H NMR (D_2O): mainly free 2-pentyn-1-ol.

Reaction of 50 equiv of 2-Pentyn-1-ol with PtCl$_2$(DPPPTS) (5). A 10 mL Schlenk flask was loaded with 28.2 μmol (33.9 mg) of $PtCl_2$(DPPPTS) (**5**) and a stir bar and backfilled with N_2(g) three time. Then 2.0 mL of triply distilled water was added. Finally to start the reaction, 1.40 mmol (130 μL) of 2-pentyn-1-ol was added. This reaction was then followed by ^{31}P and ^1H NMR over a period of 150 h. After that time, the organic materials were separated by addition of 2.0 mL of $CHCl_3$ to the mixture, vigorous stirring, separation, and finally evaporation of the volatile components of each layer. $^{31}P\{^1H\}$ NMR (D_2O insert) after 18 h: 0.68 (d,$^2J_{(P-P)}$ = 22.6 Hz) and −0.98 (d, $^2J_{(P-P)}$ = 22.6) 49.0%, −0.71 (d, $^2J_{(P-P)}$ = 23.6 Hz), and −4.20 (d, $^2J_{(P-P)}$ = 23.6 Hz) 20.4%, −1.53 (d, $^2J_{(P-P)}$ = 22.5 Hz) and −4.13 (d, $^2J_{(P-P)}$ = 22.5 Hz) 18.1%, −1.17 (d, $^2J_{(P-P)}$ = 21.4 Hz) and −2.99 (d, $^2J_{(P-P)}$ = 21.4 Hz) 12.4%. ^1H NMR (D_2O insert) after 18 h: mainly 2-pentyn-1-ol. $^{31}P\{^1H\}$ NMR (D_2O insert) after 150 h: −4.5 (s, $^1J_{(Pt-P)}$ = 3420, 22.8%) and many other resonances. ^1H NMR (D_2O insert) after 18 h: no clearly resolved resonances for 2-pentyn-1-ol. $^{31}P\{^1H\}$ NMR (D_2O insert) aqueous layer after separation, but before evaporation: −4.5 (s, $^1J_{(Pt-P)}$ = 3420, > 80%) and two other sets of doublets that were not well resolved. ^1H NMR ($CDCl_3$) of nonvolatile aqueous components: 4.8 (br, br), 2.1 (br, br), 0.98 (br, br), 0.50 (br, br). All resonances are very broad, and there is no distinct coupling. This is believed to be a polymer that has slow rotation or tumbling about C−C bonds, causing the broading of ^1H resonances (spectrum in Supporting Information). ^1H NMR (D_2O insert) of volatile aqueous components: 2-pentyn-1-ol.

Preparation of [PtCl(DPPBTS)(DMSO)]$^+$·[BF$_4$]$^-$ (11). Into a 13 × 100 mm test tube 115.8 mg (95.0 μmol) $PtCl_2$(DPPBTS) was placed. To this a stir bar and 1.0 mL of 95.1 mM $AgBF_4$ (95.1 μmol of $AgBF_4$) were added. This was allowed to react for 1 h in the absence of light. By syringe, 0.5 mL of this mixture was withdrawn, and the precipitated AgCl was filtered using a 0.2 μm NYLON valuprep syringe filter. The resulting solution was analyzed by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (DMSO-d_6 insert): 13.3 (s, 4.3%) $^1J_{(Pt-P)}$ = 3691 Hz, 17.7 (d) $^2J_{(P-P)}$ = 23.3 Hz $^1J_{(Pt-P)}$ = 3591 Hz, 5.3 (d) $^2J_{(P-P)}$ = 23.3 Hz $^1J_{(Pt-P)}$ = 3777 Hz. ^1H NMR (DMSO-d_6 insert): 8.0−7.5 (m, 16H, Ar), 1.68 (br, s, 2H), 1.62 (br, s, 2H), 1.48 (br, s, 2H), 1.42 (br, s, 2H).

Preparation of [PtCl(DPPBTS)(H$_2$O)]$^+$[BF$_4$]$^-$ (13). 13 was prepared in same manner as **11** utilizing H_2O as solvent in place of DMSO. ^{31}P NMR (D_2O insert): 19.1 (d) $^2J_{(P-P)}$ = 23.8 Hz, $^1J_{(Pt-P)}$ = 3576 Hz, 1.0 (d) $^2J_{(P-P)}$ = 23.8 Hz, $^1J_{(Pt-P)}$ = 3755 Hz. ^1H NMR (D_2O insert): 8.0−7.5 (m, 16H, Ar), 1.96 (br, s, 2H), 1.90 (br, s, 2H), 1.63 (br, s, 2H), 1.59 (br, s, 2H).

Catalytic Reactions of PtCl$_2$(P−P) (4−6) with Alkynes. Into the NMR apparatus, 8.6−8.7 μmol of $PtCl_2$(P−P) was added. Then 0.97−1.0 mL of a NaCl solution in triply distilled water was added. The NaCl concentration was varied depending on the equivalents of NaCl (relative to Pt(P−P)Cl_2) needed to obtain the ratios of 0:1, 25:1, 50:1, 75:1, and 100:1 for NaCl:$PtCl_2$(P−P). This mixture was then freeze−pump−thaw degassed three times. The apparatus was backfilled with N_2(g). Using an airtight syringe, 4.1−4.3 mmol of substrate (3-pentyn-1-ol or 4-pentyn-1-ol) was added. The apparatus was placed under vacuum, and the NMR-O-matic was removed from the Schlenk line. The frozen reaction mixture was thawed in a hot water bath. This was considered time = 0. In all cases the first ^1H NMR was recorded after 10 min and the reaction was followed to 90% conversion.

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