ORGANOMETALLICS

Facile Styrene Formation from Ethylene and a Phenylplatinum(II) Complex Leading to an Observable Platinum(II) Hydride

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Supporting Information

ABSTRACT: A new 2-(di-*tert*-butylphosphanyl)benzenesulfonate-supported phenylplatinum(II) complex instantaneously but reversibly binds ethylene at room temperature. Direct and rapid styrene formation at room temperature via insertion of the Pt^{II}-bound ethylene into the Pt^{II}-Ph fragment followed by β -hydride elimination results in the formation of a



solution-stable Pt^{II} -H complex. The Pt^{II} -H fragment is resistant toward protonolysis by acetic acid. Oxidation of the Pt^{II} -H fragment by excess $Cu^{II}(OTf)_2$ leads to an inorganic Pt^{II} complex incapable of C-H activation.

C onventional energy-inefficient technologies for the production of styrene, the monomer for the synthesis of the ubiquitous polystyrene, involve arene alkylation followed by subsequent dehydrogenation.¹ The Pd-catalyzed Fujiwara-Moritani reaction² (Scheme 1), considerable improvements³⁻⁵

Scheme 1. Fujiwara–Moritani Reaction for Oxidative Coupling of Benzene and Ethylene



of which have been made in recent years, is a lucrative alternative strategy for styrene production via oxidative coupling of benzene and ethylene. The proposed mechanism^{6,7} involves C–H activation of benzene by 1 (step i) to form a phenylpalladium complex (2), which undergoes migratory insertion (step ii) of ethylene to form the phenethylpalladium complex (3). β -Hydride elimination (step iii) from 3 leads to the formation of styrene and a hydridopalladium complex (4), which directly undergoes formation of a Pd⁰ species (5). The

role of the oxidant (e.g., Cu^{II}) is to regenerate the Pd^{II} catalyst (step v) by oxidation of 5.

Given the demonstrated ability of Pt^{II} complexes to activate C–H bonds,⁸ attempts to catalytically produce styrene from ethylene and benzene have also been made; however, the decomposition of Pt^{II}–H species, presumably via disproportionation, has been suggested to limit turnover.^{9–12} Thus, by using Rh^I, for which the thermodynamics of disproportionation are unfavorable, an efficient catalytic cycle for styrene production has been realized.¹³ However, to the best of our knowledge, the purported hydride complexes have never been isolated in related catalytic transformations.¹⁴

We rationalized that by using a mixed-donor ligand such as 2-(di-*tert*-butylphosphanyl)benzenesulfonate (L), the supported $Pt^{II}-H$ complexes might allow isolation. The soft P donor would disfavor formation of Pt^{IV} , while the hard O donor would disfavor formation of Pt^{0} . Indeed, the intermediacy of $LPd^{II}-H$ complexes in olefin polymerization¹⁵ has been confirmed by isolation.¹⁶ Thus, we chose to explore the reactivity of the derived phenylplatinum(II) complexes toward olefins.¹⁷

As shown in Scheme 2, reaction of KL with 1 equiv of $Ph_2Pt^{II}(SMe_2)_2$ resulted in clean formation of the K[LPt^{II}Ph_2] complex 6 (see section 1.3 in the Supporting Information). Careful protonolysis of one Pt—Ph fragment of 6 in THF with HBF₄·OEt₂ leads to the formation of 7-THF. The air-stable complex 7-SMe₂, featuring SMe₂ as an ancillary ligand, was synthesized by reacting the Ph_2Pt^{II}(SMe_2)_2 precursor with HL. Single crystals of complexes 6, 7-THF, and 7-SMe₂ were analyzed by single-crystal X-ray diffraction (see the Supporting Information for details). The molecular structures of complexes 7-THF and 7-SMe₂, as shown in Figure 1, feature THF and SMe₂ (respectively) bound to the Pt^{II} center trans to the phosphine fragment. Consistent with a highly trans influencing

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Received: December 1, 2016
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Figure 1. ORTEP representation of complexes 7-THF (top) and 7-SMe₂ (bottom) at the 50% probability level. Hydrogen atoms are omitted for clarity.

Pt-bound phenyl fragment in complex 6, and weakly trans influencing Pt-bound THF and SMe₂ fragment in complexes 7-**THF** and 7-**SMe₂**, respectively, a substantial increase in ${}^{31}P{-}^{195}Pt$ coupling is observed by ${}^{31}P$ NMR spectroscopy in going from complex 6 (${}^{1}J_{P-Pt} = 1874$ Hz) to 7-**THF** (${}^{1}J_{P-Pt} = 5439$ Hz) or 7-**SMe₂** (${}^{1}J_{P-Pt} = 4195$ Hz).

First we explored the reactivity of complex 7-THF with ethylene. Immediate coordination of ethylene, indicated by the observation of a doublet at 4.92 ppm (${}^{3}J_{H-P} = 3.3 \text{ Hz}$) with corresponding ${}^{195}\text{Pt}$ satellites (${}^{2}J_{H-Pt} = 53 \text{ Hz}$), as shown in Scheme 3 (inset a for ¹H NMR and inset b for ¹H{ ${}^{31}\text{P}$ } NMR resonances) was observed upon exposure of a THF- d_{8} solution of 7-THF to 1 atm. of ethylene. In THF- d_{8} solution, both 7-THF and 7-C₂H₄ (in 1:2.5 ratio) were observed by ¹H NMR spectroscopy, while in C₆D₆, only 7-C₂H₄ was observed (see Figures S2.5 and S2.6 in the Supporting Information). When the THF- d_{8} solution was exposed to dynamic vacuum, complex 7-THF was recovered completely, which indicated that coordination of ethylene is reversible. Although both steric congestion and electron-donating ability have been implicated

Scheme 3. Reversible Coordination of Ethylene to Form an Observable $Pt-(\eta^2-C_2H_4)$ Intermediate (Top) and ¹H (Inset a) and ¹H{³¹P} (Inset b) NMR Resonances of the $Pt-(\eta^2-C_2H_4)$ Fragment in THF- d_8

Communication



in stabilizing η^2 -ethylene bound five-coordinated Pt^{II} complexes,^{18–20} the intermediate observed upon coordination of ethylene (7-C₂H₄) was identified as a four-coordinated Pt^{II} complex.²¹ Interestingly, no coordination of styrene was observed when 10 equiv of styrene was added to a THF-*d*₈ solution of 7-THF (see section 1.7 and Figure S2.8 in the Supporting Information).

When it is kept under 1 atm of ethylene, over the course of \sim 4 h at room temperature, the purported ethylene complex 7-C₂H₄ underwent direct formation of the hydridoplatinum(II) complex (8-THF) and styrene (Scheme 4) in 83% yield, as

Scheme 4. Facile Formation of Styrene from 7-THF



indicated by NMR spectroscopy. Additionally, the formation of styrene was confirmed by GCMS. The ¹H and ³¹P{¹H} NMR resonances corresponding to the Pt–H fragment and Pt–P fragments of **8-THF** are shown in parts a and b of Figure 2, respectively. The olefinic protons of styrene are shown in Figure 2c. Since no Pt^{II}-bound olefin fragment was seen in the ¹H NMR spectrum (see Figure S2.9 in the Supporting Information), we assigned the doublet (with corresponding ¹⁹⁵Pt satellites) at –25.6 ppm (¹J_{H–Pt} = 1305 Hz, ²J_{H–P(cis)} = 8.3 Hz) to the hydridoplatinum(II)–THF-*d*₈ adduct **8-THF** rather than styrene or ethylene adducts. Although isolation attempts resulted in progressive decomposition, complex **8-THF** could be unambiguously characterized in THF-*d*₈ solution by ¹H and ³¹P NMR spectroscopy (see Figure S2.9).

Since 8-THF could not be isolated cleanly, we rationalized that the SMe₂ analogue might be sufficiently stable to allow isolation, especially since 7-SMe₂ was found to be much more robust than 7-THF. Upon treatment of 7-SMe₂ with ethylene, no visible coordination of ethylene to form 7-C₂H₄ was observed at 298 K (see Figure S2.10 in the Supporting Information), presumably because the substitution of SMe₂ by ethylene was much less favorable than the substitution of 7-SMe₂ under 1 atm of ethylene at 333 K for 48 h led to the



Figure 2. (a) ¹H NMR resonance of the Pt–H fragment of 8-THF and (b) ${}^{31}P{}^{1}H{}$ NMR spectrum of 8-THF and (c) olefinic protons (*) of styrene.

formation of **8-SMe**₂, as shown in Scheme 5(see section 1.9 and Figure S2.11 in the Supporting Information). Single crystals of

Scheme 5. Synthesis and Molecular Structure of a Stable $Pt^{II}-H$ Complex (8-SMe₂)^{*a*}



^{*a*}Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms other than the Pt–H are omitted for clarity.

8-SMe₂ were analyzed by X-ray diffraction (see the Supporting Information for details), and the molecular structure is shown in Scheme 5.

We monitored the evolution of styrene and complex 8-THF in THF- d_8 at room temperature by ¹H NMR spectroscopy, paying particular attention to the aliphatic region of the ¹H NMR spectra of the reaction mixture. However, no evidence of the 2-phenylethylplatinum(II) intermediate (9-THF; Scheme 6) was observed. Indirect but conclusive evidence for the concurrent formation of 8-THF and 9-THF is obtained from the following experiment. Upon exposure of complex 7-THF to higher pressures of ethylene, in addition to styrene, olefin oligomers with and without phenyl substituents, as shown in Scheme 6, were observed by GCMS (see section 1.10 in the Scheme 6. Formation of Olefin Oligomers with Ethylene Pressurized at 4 MPa



Supporting Information). While the aliphatic oligomers (n = 2-6) arise from complex 8-THF via ethylene insertion and subsequent β -hydride elimination (reaction i, Scheme 6), phenylbutene isomers arise from the 2-phenylethylplatinum(II) intermediate 9-THF (reaction ii, Scheme 6).

Finally, in order to realize the catalytic cycle similar to that presented in Scheme 1, the Pt-H fragment in 8-THF must be oxidized rapidly. We found that the Pt^{II} -H fragment could not be protonated by acetic acid. Indeed, formation of both styrene and $Pt^{II}-H$ was also observed in acetic acid- d_4 . However, treatment of the THF- d_8 solution containing complex 8-THF with 5 equiv of Cu^{II}(OTf)₂ resulted in immediate obliteration of the Pt^{II}-H signal (see section 1.11 and Figure S2.12 in the Supporting Information). Analysis of the reaction mixture by ESI-MS reveals a signal at 496.06 amu corresponding to the cationic LPt^{II} fragment.²² Attempts at catalytically converting benzene and ethylene in the presence of excess Cu^{II}(OAc)₂ produced only a substoichiometric amount of styrene (see section 1.12 in the Supporting Information). We presume that C-H activation of benzene at the 2-(di-tert-butylphosphanyl)benzenesulfonato-Pt^{II} center is a high-energy process and prevents turnover under the current conditions. In order to indirectly probe a model C-H activation step, complex 7-THF was heated in C_6D_6 (Scheme 7). No scrambling of the Pt- C_6H_5 fragment for C_6D_5 was observed at 100 °C.



In conclusion, we have synthesized new 2-(di-*tert*butylphosphanyl)benzenesulfonatoplatinum representatives of this popular (nickel, palladium) platform for catalytic olefin polymerization.¹⁵ The supported monophenylplatinum(II)– THF complex reacts with ethylene at room temperature to directly produce styrene and a hydridoplatinum(II) complex, the latter being stable toward disproportionation or protonolysis. The molecular structures of these new complexes were characterized by X-ray diffraction. To the best of our knowledge, formation of styrene from a phenylplatinum(II) complex at room temperature has never been reported. Efforts are being undertaken to investigate the potential of this phosphine-sulfonate platinum platform toward catalytic styrene formation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00892.

Synthetic procedures, ¹H, ¹³C, and ³¹P NMR spectra, details of attempted catalysis, GC traces, and X-ray characterization of complexes **6**, **7-THF**, **7-SMe**₂, and **8-SMe**₂ (PDF)

Crystallographic data for complexes 6, 7-THF, 7-SMe₂, and 8-SMe₂ (ZIP)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the JSPS KAKENHI (Grant Number JP15K21707 and JP15H05796) in "Precisely Designed Catalysts with Customized Scaffolding" for financial support of this work.

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(22) This signal was not observed for any of the other Pt complexes, implying a new "inorganic" Pt complex as its origin.

(23) At temperatures higher than 100 $^\circ$ C, formation of Pt black was observed.