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Immobilized Platinum Hydride Species as Catalysts for Olefin Isomerizations and Enyne Cycloisomerizations

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making them somewhat unsustainable. We have synthesized surfaceimmobilized Pt–H species via oxidative addition of surface OH groups to Pt(PⁱBu₃)₂ (1), a rarely used immobilization technique in surface organometallic chemistry. The hydride species thus made were characterized by infrared, magic-angle spinning nuclear magnetic resonance, and X-ray absorption spectroscopies and catalyzed both olefin isomerization and cycloisomerization of a 1,6 enyne (5) with a high selectivity and low Pt loading.

INTRODUCTION

Platinum hydrides are useful catalysts for both olefin isomerizations¹ and enyne cycloisomerizations (Figure 1).² These



Figure 1. Enyne cycloisomerization catalyzed by group 10 metal hydrides.

reactions are widely used in the fine chemical and pharmaceutical industries due to their excellent atom economy, 1c,3 low waste production, and their ability to make and break multiple C–C bonds in a single synthetic step. 2c,4 However, these reactions require relatively high catalyst loadings and are difficult to recycle. Pt–H complexes can easily be made by the addition of Brønsted acids to Pt(0) complexes.⁵ Deactivation of

the catalyst can occur by dimerization of hydrides, necessitating higher catalyst loadings (usually 5 mol %). $^{4b,6}_{}$

t Bus

P^tBu₃

Metal Oxide

k (A⁻¹)

OH

Metal Oxide

Pt(P^tBu₃)₂

hexane

Immobilizing catalysts on metal oxide surfaces using surface organometallic chemistry (SOMC) can prevent dimerization and often reduce metal loadings through site isolation of the active sites on a metal oxide surface.⁷ Immobilization has the added bonus of making the recycling of the catalyst material simpler. In SOMC, OH groups on metal oxide surfaces typically act as acids to protonolyze basic ligands and create new M–O bonds. However, Bergman and Kaplan showed that surface OH groups can also oxidatively add to Ru(0) complexes.⁸ Analogous oxidative addition of surface OHs to Pt(0) complexes would form immobilized Pt hydride species, as shown in Figure 1.

Here, we immobilize Pt–H species on metal oxides by oxidative addition of surface OHs to $Pt(P^tBu_3)_2$ (1) and characterize them by nuclear magnetic resonance (NMR), infrared (IR), elemental analysis, X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), and comparison with molecular models. Oxidative addition of surface OH groups to Pt(0) (as opposed to the protonolysis reactions typical of SOMC) is analogous to the reactions of $Pt(P^tBu_3)_2$ with Brønsted acids. The reactivity of Pt(0) model species with OH groups is related to their pK_a , and immobilization is only possible

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on supports with stronger Brønsted acids. These immobilized Pt-H species are selective catalysts for enyne cycloisomerizations. Oxidative additions of surface OH groups to M(0) complexes are uncommon in SOMC and represent a novel immobilization method in the toolkit of surface organometallic chemists.

EXPERIMENTAL SECTION

All experiments were carried out under an inert atmosphere using standard Schlenk and glovebox techniques. Hexane, THF, toluene, deuterated benzene, and chloroform were purified by standard methods. P^tBu₃, K₂PtCl₄, KOH, Zn, alcohols **2a**–**d**, 1-hexene, dimethyl propargylmalonate, sodium hydride, and 4-bromo-2-methyl-2-butene were purchased and used as received. SiO₂ (Degussa Aerosil-200, 209 m² g⁻¹), γ -Al₂O₃ (Gobain, 260 m² g⁻¹), and SiO₂/Al₂O₃ (Gobain, Si:Al ratio, 5.87:1, 351 m² g⁻¹) were compacted by drying of a water suspension and then sieved to a particle size between 100 and 300 μ m before being dehydroxylated under a flow of synthetic air at 500 °C and stored in a glovebox. Pt(P^tBu₃)₂ (**1**) and substrate **6** were synthesized by known literature procedures.⁹ Pt/SiO₂ was synthesized by a known procedure¹⁰ with a Pt loading of 1 wt % and a Pt dispersion of 80%, as measured by H₂ chemisorption.

Liquid-state 1 H and ${}^{31}P{}^{1}H$ NMR spectra were measured on a 300 MHz Bruker Avance III spectrometer. ¹³C NMR spectra were measured on a 400 MHz Bruker AVIII spectrometer. Solid-state NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer in 4 mm zirconia rotors. ¹H and ³¹P CPMAS NMR spectra were recorded at 8-11 kHz at resonance frequencies of 400.1 or 161.9 MHz, respectively. The contact time of ³¹P CPMAS was 2 ms and a 70 100 ramp was applied during the Hartmann-Hahn contact period and spinal64 decoupling during acquisition. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis of Pt was measured in the Institute of Technical Chemistry using a Perkin-Elmer Avio 200 optical emission spectrometer calibrated to standard Pt solutions. IR spectra were measured under an inert atmosphere with a Nicolet 6700 IR spectrometer in transmission mode with the sample diluted in KBr (for surfaces) or with a Diamond ATR attachment (for 3). TEM and energy-dispersive X-ray (EDX) spectra were measured using a Philips CM200-FEG electron microscope operated at 200 kV.

Pt L3-edge XAS spectra were collected as pure solid samples in transmission mode on the P65 beamline at the PETRA III extension at DESY.¹¹ The experiments were performed using ionization chambers with partial pressures of 800 mbar or Ar plus 200 mbar Kr (15.5% of absorption) and 1000 mbar Kr (49.5% absorption) for detection of the I_0 and I_1 signals, respectively. Energy selection was performed with a Si(311) double-crystal monochromator (DCM), and Pt-coated mirrors were used for higher harmonic rejection and beam focusing. The DCM resolving power was between 0.6×10^4 and 1.4×10^4 , resulting in an experimental resolution of 1.2 eV at the Pt L3-edge. The spectra were measured to 1000 eV over the edge energy. The reported edge energies here correspond to the first inflection points of the absorption spectra. No indications of radiation damage were observed. Samples 4a and 4b were not measured due to their low loading. Modeling of the k and Rspace data was performed using the Artemis program of the Demeter software package.¹² All spectra were modeled with satisfactory χ^2 and R values. The fitted values of $R + \Delta R$, N, and σ_0^2 are given in Table 1.

Synthesis and Characterization of HPt(P^tBu₃)₂[H(OC(CF₃)₃)₂] (3). In a Schlenk flask, Pt[P^tBu₃]₂ (0.083 mmol, 50 mg) and alcohol 2d (1.79 mmol, 0.25 mL) were suspended in *n*-hexane (1.5 mL) under an inert atmosphere with vigorous stirring. A yellow precipitate formed after 1 min. The supernatant was filtered away, and the solvent was removed from the product by flushing it with an argon stream to yield a yellow solid. Treatment of this solid under vacuum resulted in loss of alcohol and reproduced the starting material Pt[P(^tBu₃)₂. NMR was measured in the presence of an excess of 2d. ¹H NMR (300 MHz, C₆D₆, δ) 1.13 (t ($J_{PH} = 5.7$ Hz), -CH₃, 54H), -36.34 (s, $J_{Pt-H} = 2577$ Hz, H–Pt). ³¹P{¹H} NMR (121.5 MHz, C₆D₆, δ) 120.03 (quartet, -CF₃), 76.60 (multiplet, -C-CF₃), 39.69 (t, P-C-), 31.20 (t, -CH₃). ¹⁹F NMR (400 MHz, C_6D_6 , δ) –75.38 (s, –CF₃). IR (ATR Diamond Crystal) 2987, 2963, 2937, 2892, 1470, 1383, 1353, 1269, 1245, 1214, 1173, 1021, 969, 808, 725. Elemental analysis ($C_{32}H_{56}F_{18}O_2P_2Pt$): Calc: 35.86% C, 5.27% H. Found: 36.16% C, 4.89% H.

Equilibrium Measurements. Stock solutions of 1 and 2d in C₆D₆ were mixed in J-young NMR tubes to achieve the desired concentrations of 1 (fixed at 0.0274 M initial concentration) and 2d (between 0.060 and 0.6 M initial concentrations). These solutions were then allowed to equilibrate for 10 min (after this amount of time, no further change to the NMR spectrum was seen), and ¹H NMR was measured with a recycle delay of 10 s (enough for all the protons to fully relax). The Pt species in the solution were quantified using their signature ^tBu resonances at 1.52 ppm (1) and 1.13 ppm (3). The fluorinated alcohol concentration was corrected from the initial concentration based on the amount of ${\bf 3}$ that had formed in the sample. The results are shown in Figure 2 in the text. For the temperature-dependent samples, two separate samples with $[1]_0$ and [2d]₀ of 0.02 and 0.73 M and 0.015 and 0.31 M, respectively, were heated in an NMR spectrometer until equilibrium was achieved and no solid was present. The equilibrium constants were determined as above.

Synthesis and Characterization of Surface Species 4a–c. The desired solid support $(SiO_2, Al_2O_3, or SiO_2-Al_2O_3, 1 g)$ was suspended in pentane (5 mL) under an inert atmosphere. A solution of 1 (0.1 mmol, 60 mg) dissolved in 5 mL of pentane was filtered into this suspension and stirred overnight under Ar. The supernatant was then filtered away, and the support was washed with toluene $(1 \times 5 \text{ mL})$ and $3 \times 5 \text{ mL}$ of pentane and dried under vacuum. Loadings of Pt on the surface were determined by Pt ICP-OES to be 0.04, 0.02, and 0.09 mmol of Pt g⁻¹ for SiO₂, γ -Al₂O₃, and SiO₂-Al₂O₃ (4a–c), respectively. TEM, IR, magic-angle spinning (MAS) NMR, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) spectra are shown in Figure 3 and Figures S7–S21 for each surface complex. XAS spectra were only measured for 4c due to the low Pt loadings of 4a and 4b.

Catalytic Olefin Isomerization. 1-Hexene (0.1 mL, 0.81 mmol) was added to the Pt catalyst (4 μ mol, 0.5 mol %) suspended in 0.9 mL of C₆D₆ under inert gas. This mixture was heated for 18 h at 80 °C, and the conversion was measured by ¹H NMR. The peaks of each product were confirmed vs authentic samples. Product peaks are labeled in Figure S22.

Catalytic Cyclization of Substrate 5. Substrate 5 (50 mg, 0.21 mmol) was mixed with the desired loading of the Pt catalyst and internal standard and dissolved in C_6D_6 (0.5 mL). The reaction was then heated at 80 °C for the reported time and monitored periodically by ¹H NMR. The reaction conversion and yield of the product were determined by ¹H NMR versus internal standard. The peaks corresponding to 6a matched what was known in the literature.^{9b} Higher catalyst loadings and longer reaction times led to the formation of another product 6b. Although we were not able to isolate 6b, we can tentatively assign a structure based on its ¹H NMR spectra, as shown in Figures S27 and S28. Cyclized product 6b: ¹H NMR (CDCl₃, 300 MHz, d) 5.64 ppm (s, 1H, $-CH=CCH_3$), 3.68 ppm (s, 6H, $-CO_2CH_3$), 3.04 (s, 2H, CH₂-C=C, overlapping with the peak from 6a), 1.98 (s, 3H, Me), 1.83 (s, 3H, Me), 1.66 (s, 3H, Me).

Hot Filtration Tests. Hot filtration experiments were performed for both the isomerization of 1-hexene and the cyclization of substrate 5 to test whether the catalytically active species was present in the solution. In a typical hot filtration experiment, a catalytic reaction was performed at 80 °C for a typical amount of time (0.5 mol % 4b for 1-hexene and 5 mol % 4c for cyclization of substrate 5). While keeping the solution at 80 °C, half of the supernatant was extracted with a preheated glass syringe and needle (80 °C) and filtered using a syringe filter into a new vessel with half as much fresh substrate and solvent as for the initial reaction preheated to 80 °C and allowed to react for the same amount of time as for the initial reaction. The Pt leaching was determined by removing the solvent in vacuo, dissolving the residue in aqua regia, and measuring the Pt content by ICP-OES. The remaining 50% of the initial supernatant was removed and analyzed by ¹H NMR. During the hot filtration experiment of 5, twice as much solvent was added to the initial reaction to ease the extraction of the supernatant.

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Recycling Experiments. Recycling experiments of the isomerization of 1-hexene (with 4b) and cyclization of substrate 5 (with 4c) were performed at 80 °C with 0.5 and 5 mol % catalyst for 18 and 36 h, respectively. For 1-hexene, reactions were filtered by filter canula, washed successively with toluene and pentane, and dried in vacuo after which fresh substrate and solvent were added to the dry catalyst. This process was repeated to perform three total cycles and the results of each cycle analyzed by ¹H NMR. For substrate 5, the reaction (performed in toluene solvent) was filtered and washed with toluene (3 $\times 2$ mL) into a pre-weighed vial and these washings were dried in vacuo to weigh the isolated product. Ferrocene as the internal standard was weighed into this mixture, and the quantities of different products were measured by ¹H NMR. The data for the recycling experiments are shown in Figures S32 and S33.

RESULTS

 $Pt(P^tBu_3)_2(1)$ reacts with alcohols to produce complexes of the type HPt(OR)(P^tBu_3)_2.^{5d} We started by reacting 1 with the molecular silanol HOSi(O^tBu)₃ (a good model for isolated silanols) as well as heptaisobutyryl-POSS-trisilanol (a good model for vicinal silanol groups). Neither of these reacted with complex 1. Next, we reacted 1 with fluorinated alcohols HOC(CH₃)_{3-x}(CF₃)_x (x = 0, 1, 2, and 3 denoted as 2a-d, respectively) as models of surface OH groups (SiOH groups on SiO_2 are thought to have similar electronic properties to 2b and 2c).¹³ Complex 1 did not react with 2a-c. However, mixing 1 with an excess of alcohol 2d in pentane gave a yellow precipitate whose elemental analysis showed two equivalents of 2d reacting with every Pt. We were not able to grow crystals of suitable quality for X-ray diffraction. However, NMR spectroscopy showed new peaks in the 1 H (1.13 ppm (54H) and -36.3 ppm (1H) $J_{H-Pt} = 2577$ Hz; Figure S1) and ${}^{31}P{}^{1}H{}$ spectra (88.4 ppm J_{P-Pt} = 2614 Hz; Figure S2). These data are similar to platinum hydrides such as [HPt(P^tBu₃)₂][BF₄].^{5a,c} In particular, chemical shifts of ca. -32 to -36 ppm and J_{H-Pt} of 2500–2600 Hz are diagnostic of such three coordinate Pt-H species, whereas the addition of a fourth ligand results in higher chemical shifts of -10 to -27 ppm and a much lower $J_{\text{H-Pt}}$ of 665–1450 Hz.^{5b,c} This suggests the structure [HPt(P^tBu₃)₂][H(OC- $(CF_3)_3)_2$ for 3 in which the charge of the cationic Pt-H is balanced by the perfluorinated alkoxide hydrogen bonding to a second alcohol. This assignment is supported by the Pt L3-edge EXAFS data of 3, which does not show a Pt-O scattering path in the first coordination sphere (vide infra). Full characterization data can be found in the Supporting Information (Figures S1-S5).

The reaction of 1 with 2d is fully reversible. Treating solid 3 under vacuum for several hours reproduces 1. We measured the equilibrium between 1 and 3 by varying [2d] (Figure 1). The equilibrium varies with $[2d]^2$ (as prescribed by the equilibrium in eq 1) and has $K_{eq} = 107(4)$ at 23 °C. Since some catalytic reactions of 3 require elevated temperatures, we tested the temperature dependence of this equilibrium up to 75 °C (Figure S6). While [2d] = 0.73 M gave nearly quantitative conversion of 1 to 3 at room temperature, between 65 and 75 °C, the 3:1 ratio was between 0.3 and 0.15. We estimate ΔH and ΔS of this reaction to be -23(1) kcal mol⁻¹ and -68(4) cal mol⁻¹ K⁻¹ respectively. More acidic OH groups may be necessary to prevent catalyst leaching and Pt nanoparticle formation at higher temperatures, both of which are common for late transition metal surface organometallic species.¹⁴ Therefore, only surfaces containing OH groups with pK_a values lower than those of alcohol **2d** (20.55 in MeCN¹⁵ or 5.33 in H₂O¹⁶) will immobilize 1 as 3. SiO₂ (with estimated pK_a values of 4.5 and 8.9 in H₂O)¹⁷

and Al_2O_3 (estimated pK_a as low as 4.9 in H_2O)¹⁸ are good candidates.

Pt(P^tBu₃)₂ + 2 HOC(CF₃)₃
$$\xrightarrow{K_{eq}}$$
 [HPt(P^tBu₃)₂][H(OC(CF₃)₃)₂]
1 2d C_eD₆ **3**



Figure 2. Measurement of the equilibrium between **1** and **3** at 23 °C by varying [**2d**].

Reaction of 1 with SiO₂, Al₂O₃, and SiO₂-Al₂O₃ (all dehydroxylated at 500 °C) made materials 4a-c, respectively. These were characterized by ICP-OES, IR, ¹H MAS, ³¹P CPMAS NMR, TEM, and Pt L3-edge X-ray absorption spectroscopies (of 4c). ICP-OES shows relatively low Pt loadings of 0.04, 0.02, and 0.09 mmol of Pt g⁻¹ (0.8, 0.4, 1.8 wt % Pt) for 4a-c, respectively. These are lower than typical for protonolysis reactions in SOMC. We saw above that more acidic OH groups are more reactive toward Pt-H formation. The low loadings may be the result of only a small percentage of all OH groups being reactive enough to add to the Pt(0) complex. Silica-alumina immobilized two to four times as much Pt as the other supports. This is due to both its higher surface area and its higher acidity than either silica or alumina (likely due to the formation of bridging and pseudo-bridging Si-OH-Al groups).¹⁹ TEM of all three samples (Figures S7–S9) confirmed that no Pt nanoparticles were formed during the synthesis. IR (Figures S10-12) shows C-H stretching and bending modes of ^tBu groups, with a higher intensity for a higher Pt loading. No Pt-H stretching band (expected around 2850 cm⁻¹) is seen in the IR spectra of 3 or 4a-c. This is likely due to its low intensity, low loading, and overlap with C-H stretches, similar to $HPt(P^{t}Bu_{3})_{2}BF_{4}$.

Immobilized species 4a has two ³¹P CPMAS NMR signals at 78 and 75 ppm having visible $J_{Pt-P} = ca. 3.0(3)$ kHz (Figure S14) that are similar to other HPt(PR₃)₂X.^{5d} This doubling is also seen in ¹H MAS NMR of the ¹Bu protons, indicating that there are two different Pt species present on the surface of SiO₂ (Figure S13). The presence of multiple chemically similar Pt–P species suggests that these are Pt–H species that are interacting with two different Si–O sites (e.g., isolated and vicinal) on the surface. No hydride signals were observed in ¹H MAS NMR of 4a. However, this is not unusual given the extremely large chemical shift anisotropy of transition metal hydrides²⁰ and the low loading of the complex on SiO₂. There is also a signal around 62 ppm in ³¹P CPMAS NMR most likely due to adsorbed $\mathsf{OP}^t\mathsf{Bu}_3$, indicating that some phosphines were oxidized on the metal oxide surface. 21

The ³¹P CPMAS NMR (Figure S16) spectrum of 4b showed two signals, one at 77 ppm ($J_{Pt-P} = 2.0(3)$ kHz) consistent with a HPt species and a separate signal at -19 ppm ($J_{Pt-P} = 3.9(3)$ kHz) with a very large anisotropy. These Pt–P coupling constants suggest that the signal at 77 ppm is a Pt(II)–H species, while the signal at -19 ppm is due to an unknown Pt(0) species. This unknown Pt(0) species does not match the spectrum of 1 (isotropic chemical shift of 100.8 ppm) but could potentially be a surface-stabilized Pt(PR₃) fragment.

Immobilization of 1 on SiO₂-Al₂O₃ was the cleanest. The ³¹P CPMAS NMR spectrum of **4c** (Figure S18) shows only one peak at 84 ppm having a full width at half max larger than our expected J_{Pt-P} . However, due to the higher loading of Pt on **4c**, we were able to observe a broad Pt-H resonance at -35 ppm in ¹H MAS NMR (Figure S17) with $J_{Pt-H} = 2.6(3)$ kHz, very similar to the molecular model **3**. This suggests that the immobilized complex on **4c** has a similar structure to that of **3**. A small peak at 54 ppm in the ³¹P CPMAS spectrum corresponds to a small amount of HP^tBu₃⁺ on the surface.²²

Pt L3-edge X-ray absorption spectroscopy was measured for species 1, 3, and 4c. Their XANES spectra (Figure 3) all have similar edge energies (within the spectral resolution of 1.2 eV). Based purely on the oxidation state, the expected edge energy of 1 should be lower than that of 3 or 4c. The L3-edge is dominated by the allowed $2p \rightarrow 5d$ electronic transition. Since 1 has a filled 5d shell, this transition will be of low intensity.²³ However, protonation of 1 to give 3 or 4c creates empty states in the 5d shell, resulting in a larger contribution of the $2p \rightarrow 5d$ transition to the overall edge intensity, counteracting the oxidation state effect and leaving the edge energy unchanged.

The parameters obtained from modeling the EXAFS spectra are shown in Table 1 (full data shown in Figures S19–S21).



Figure 3. XANES spectra for Pt complexes 1, 3, and 4c.

Both 1 and 3 have first coordination shells with only two P atoms. The Pt–P distances modeled for 1 and 3 (2.26(3) and 2.27(3) Å, respectively) are within the error of known crystallographic data for complex 1 (2.25 Å) and similar Pt(II)–H species (2.28 Å).²⁴ The EXAFS of 4c also showed two P scatterers as well as an additional O scattering path in the first coordination sphere, without which the data could not be modeled. The Debye–Waller factors of 4c are consistent with a previous report of immobilized catalysts on amorphous supports.²⁵ The Pt–P distance of 2.29(3) Å is similar to other four coordinate Pt(II) hydride complexes (e.g., 2.33 Å for HPt(PtBu₃)₂Cl).²⁴ The modeled Pt–O distance of 2.01(3) Å is

Table 1. Edge Energies and Fitted Parameters of the EXAFS Spectra of 1, 3, and 4c

	edge (eV)	atom	Ν	$R+\Delta R~(\rm{\AA})$	σ_0^2 (Å ²)
1	11566.3	Р	2.0(1)	2.26(3)	0.0032(4)
		С	4.2(4)	3.39(3)	0.0046(6)
		С	2.7(7)	3.93(3)	0.0054(7)
		С	5.4(1.6)	5.05(4)	0.0066(9)
3	11565.9	Р	2.1(2)	2.27(3)	0.0042(8)
		С	4.2(4)	3.38(3)	0.006(1)
		С	1.9(6)	3.81(3)	0.007(1)
		С	4.3(7)	3.94(3)	0.006(1)
		С	4.8(8)	4.13(3)	0.007(1)
4c	11565.2	Р	1.8(1)	2.29(3)	0.0070(2)
		0	1.0(1)	2.01(3)	0.0073(5)
		Si	2.1(3)	3.11(5)	0.012(1)
		С	4.1(4)	3.17(4)	0.0103(3)
		С	2.6(2)	3.47(5)	0.0105(3)
		Si	0.9(2)	3.87(6)	0.0142(9)
		С	6.3(6)	4.80(6)	0.0145(4)

within the range of other Pt(II)–O distances in the literature (between 1.95 and 2.06 Å) but 0.06 Å longer than other Pt—(OSi \equiv) distances.^{14b,26} Given that the NMR data of 4c (especially the Pt–H chemical shift and J_{Pt-H}) were consistent with a cationic three-coordinate platinum hydride, this would suggest a structure intermediate between a Pt–O bond and a true ion pair as in 3.

Complexes 3 and 4a-c catalyze the isomerization of 1-hexene at 80 °C to form mixtures of 2-hexene and 3-hexene (Table 2

Table 2. Activity and Selectivity of 1-Hexene Isomerization Using 3 and 4a-c as Catalysts

catalyst ^a catalyst ^a	% conv	% 2-hexene (cis:trans)	TON	TOF (h^{-1})
3	4.7%	100% (0.4)	9	0.5
Pt/SiO ₂	0%			
4a	5.1%	100% (0.6)	10	0.6
4b	78.6%	96.2% (0.7)	142	4.4 ^b
4c	7.0%	100% (0.5)	14	0.8

^{*a*}Standard conditions: 0.5 mol % (4 μ mol of Pt), with 0.8 mmol of 1hexene (0.1 mL), in a total volume of 1 mL, heated at 80 °C for 18 h with stirring. ^{*b*}Since the conversion of 1-hexene in this case was so high, the TOF listed in this table is a lower limit. The real value could be as high as 17.4 h⁻¹.

and Figure S22). Species 3 and 4a–c all had lower activity for olefin isomerization than the commonly used H_2PtCl_6 but higher activity than the similar complex HPtCl(PEt₃)₂ (only active at 180 °C).^{1a} This matches a previous report in which the olefin insertion into similar Pt–H complexes is slow.^{5c}

$$\begin{array}{c} \text{HPt}(\text{PtBu}_{3})_{2}X \\ & \overbrace{3,4a-c \ (0.5 \ \text{mol}\%)}^{3,4a-c \ (0.5 \ \text{mol}\%)} \\ & \overbrace{80 \ ^{\circ}\text{C}, \ C_{6}D_{6}}^{\ast} \end{array}$$

Catalyst **4b** is 10 times more active than the other catalysts and also gives the highest selectivity for the cis-product and even gives a small percentage of 3-hexene. Control reactions showed that the supports were inactive for catalysis, and therefore, the higher activity of **4b** is not due to the Al_2O_3 support. Attempts at isomerization of 1-hexene using platinum nanoparticles supported on silica (denoted Pt/SiO_2) under the same conditions resulted in no detectable isomerization. Complex **1** was also inactive for olefin isomerization. Hot filtration showed

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that the supernatant from 1-hexene isomerization with 4b was not catalytically active. Recycling experiments for 4b-catalyzed 1-hexene isomerization gave 78, 9, and 13 turnovers of isomerized products (Figure S31), showing deactivation after the first cycle (with some losses of the product due to the recycling procedure). TEM of 4a and 4c after isomerization showed no signs of Pt particles, while 4b showed some signs of Pt particle formation after catalysis (Figures S23-S25). As shown by NMR, catalyst 4b contains both Pt-H species and unidentified $Pt(0)-P^tBu_3$ complexes. These experiments suggest that the Pt(0) centers are likely more active for olefin isomerization but agglomerate to Pt particles during the first cycle of catalysis, which are inactive under these conditions. After the first cycle, the activity of **4b** is comparable to those of 4a and 4c, suggesting that the nanoparticles do not play a role in catalysis.

Finally, we tested 4a-c as catalysts for enyne cycloisomerization activity using the test substrate 5. The results are shown in Table 3. Complex 1 did not react with 5, while 3 and 4a-c were all active catalysts. The cyclization reactions are relatively slow, consistent with other Pt-catalyzed enyne reactions.²⁷ Reaction of 5 with 4a-c (0.5 mol %) at 80 °C gave 78% (4b), 35% (4a), and 82% (4c) conversions and 76, 10, and 81% yields of 6a, respectively, after 336 h (97 and 99% selectivity for 4a and 4c, respectively). The time profiles of the reactions at 0.5 mol % loading are shown in Figure 4. Catalysts



Figure 4. Time profile of cycloisomerizations using 4a-c.

4a and 4c both give time profiles that showed no induction period and fit to a simple first-order expression with essentially the same initial TOF of 2 h^{-1} . The activity and selectivity of 4b are both much lower than either 4a or 4c; therefore, it was not used further. Both 4a and 4c were about 40 times slower than the homogeneous complex 3 (with a TOF of >84 h^{-1}). Such slowing of catalysts upon immobilization is common for heterogenized catalyst systems^{13,28} and may be the result of the additional Pt-O bond to the surface, inhibiting the catalytic activity. Using a higher loading (5 mol %) of catalysts 4a and 4c required only 35 h to come to full conversion. At a higher catalyst loading, an unidentified isomer 6b was also made along with the desired product, which was inseparable from 6a. Monitoring the reaction over time showed that 6b is a secondary product due to further reaction of initial product 6a (Figure S27). One advantage of the heterogeneous over the homogeneous catalyst

is that it produces less of this side product **6b**. A tentative assignment of the structure of **6b** is given below, which is likely the result of isomerization of the terminal olefins of **6a** to internal positions.



Table 3. Cycloisomerizations Using Catalysts 3 and 4a-c

	catalyst	loading	temp, time	% 6a (% 6b) ^a
	1	5 mol %	80 °C, 22 h	n.o.
	3	0.5 mol %	80 °C, 2 h	82% (6%)
	4a ^b	5 mol %	80 °C, 35 h	62% (27%)
	4c	5 mol %	80 °C, 35 h	56% (32%)
	Pt/SiO_2	5 mol %	80 °C, 35 h	6%(—)
	4a	0.5 mol %	80 °C, 336 h	76% (—)
	4b	0.5 mol %	80 °C, 336 h	10% (—)
	4c	0.5 mol %	80 °C, 336 h	81% (—)
² N	lossurad	hy NMP we internal	standard ^b Solvent	(0.0 mT) was

"Measured by NMR vs internal standard. "Solvent (0.8 mL) was necessary to wet all the catalysts.

The activity of 4a-c was much higher than Pt/SiO_2 , which gave only 5.8% yield under the same conditions. In addition, TEM of the catalysts after cyclization of substrate 5 (Figures S28-S30) showed no signs of Pt particle formation. Both of these results suggest that the Pt particle formation does not play a role in enyne cycloisomerization. The bare supports were also not active for cyclization of 5. Hot filtration of the 5 mol % reactions at 80 °C showed roughly 11% Pt leaching into the supernatant, suggesting that Pt mostly remains on the surface. The hot filtration test also showed that the solution was not catalytically active. Recycling tests of 5 mol % 4c for cyclization of substrate 5 (Figure S32) gave 74% (15 TON), 76% (15 TON), and 62% (12 TON) yields over three cycles, showing that the catalyst can be reused without significant loss of activity (the minimal loss of activity here is due to loss of catalyst during filtration).

Based on these results, we can draw some conclusions about catalysis. Complex 1 does not react with substrate 5, while 3, 4a, and 4c all catalyze the cycloisomerization to product 6a with high selectivities. Based on the hot filtration and recycling experiments, the catalytic reactions likely occur at the supported Pt-H species on the catalyst surface and not in solution. The high selectivity for the 1,4-diene product suggests the mechanism shown in Figure 5, involving the insertion of alkyne into the Pt-H bond, insertion of pendant alkene into the Ptvinyl bond, and finally β -hydride elimination to reform the Pt-H bond.^{2c} The minor product **6b** may form by isomerization of the terminal olefins in **6a** to their more stable internal positions. Catalyst 4b is the most active for olefin isomerization but the least active for cycloisomerization of 5. This can be attributed to the presence of both Pt-H and Pt(0) species on its surface, which are known to be active for olefin isomerization²⁹ but do not catalyze cycloisomerization of enynes, as shown for complex 1 above. Therefore, the Pt(0) species has a much higher activity for isomerization of 1-hexene but does not contribute to the overall activity for cycloisomerization. Indeed, if we consider the fact that only ca. 40% of the Pt sites are in the form of Pt-H on 4b, then a conversion of 35% is comparable to the results with 4a



Figure 5. Proposed mechanism of the Pt-catalyzed cyclization of 5 to 6a.

and 4c. The reduced selectivity of 4b in the cycloisomerization reaction is probably due to the high activity for the Pt(0) sites in 4b to isomerize the desired terminal olefin product.

In conclusion, we have shown that $Pt(P^tBu_3)_2$ reacts with surface OH groups on SiO₂ and SiO₂-Al₂O₃ by oxidative addition to form immobilized SiO–Pt–H species. This method represents a seldom used immobilization paradigm in SOMC and should be possible for other M(0) complexes. We also showed that the Pt–H species thus synthesized were catalysts for olefin isomerization and for the selective cycloisomerization of a 1,6-enyne. This immobilization strategy should open up new possibilities for future studies of late transition metal complexes on surfaces by SOMC.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00216.

Experimental details, synthesis and characterization data of 3 and 4a-c, equilibrium reactions, details of catalytic reactions, XAS data, and modeling (PDF)

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Notes

The authors declare no competing financial interest.

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