7238 *Inorg. Chem.* **2010**, *49*, 7238–7240
DOI: 10.1021/ic101025h

Inorganic Chemistry
Communication

Reversible Hydrogen Activation by the Pt Complex $Pt(Sn^tBu_3)_2(CN^tBu)_2$

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Received May 20, 2010

The new platinum complex $Pt(Sn^tBu_3)_2(CN^tBu)_2(H)_2$, **1**, was obtained in 32% yield from the reaction of $Pt(COD)_2$ with $^tBu_3SnH$ and CN^tBu at room temperature. Compound **1** is a mononuclear 18 electron platinum complex in an octahedral geometry which contains two Sn^tBu_3's, two CN^tBu's, and two hydride ligands. The two hydride ligands in **1** can be eliminated, both in solution and in the solid state, to yield the 16 electron complex $Pt(Sn^tBu_3)_2(CN^tBu)_2$, **2**. Compound **2** reacts with hydrogen at room temperature in solution and in the solid state to regenerate **1**.

Transition metal complexes have and always will play a vital role in the chemistry of hydrogen in the rapidly approaching and inevitable hydrogen economy which remains a scientific area of national importance.[1] Today, catalytic hydrogenations constitute the largest set of reactions in the chemical industry.[2] Thus, there has been considerable interest in the reversible activation of hydrogen by materials and molecules—especially transition metal complexes.[3] It was with the discovery of Vaska's square planar Ir(I) complex $Ir(PPh_3)_2(CO)Cl$ and its ability to reversibly activate molecular hydrogen[4] and undergo a range of oxidative-addition reactions[5] that stimulated the growing field of homogeneous catalysis in the 1960s.[6] Over the years, a number of unsaturated transition metal complexes have been prepared and were shown to undergo H_2 activation reactions.[7] For instance, the unsaturated ML_2 ($M = Pd, Pt$; $L = PR_3$) species containing bulky phosphine groups react with hydrogen at room temperature,[8] and then in the 1980s it was shown that the H_2 molecule could coordinate to a metal center in the complex $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$[9] via reversible addition of H_2. The most common feature of these metal complexes that activate hydrogen is that they contain bulky phosphine ligands.[3,10] A number of years ago, Eaborn and co-workers provided evidence based on in situ spectroscopic data in solution for the reversible elimination of H_2 from the Pt−Sn phosphine complexes of the type $Pt(SnR_3)_2(PMe_2Ph)_2(H)_2$ ($R = Ph, PhCH_2$, *o*-, *m*-, or *p*-MeC_6H_4), but these complexes were not structurally characterized.[11] Recently bulky carbene ligands have been used in place of the bulky phosphine ligands.[12] Herein, we present a new example of a metal complex system that reversibly activates hydrogen, but contains neither phosphine nor carbene ligands.

The complex $Pt(Sn^tBu_3)_2(CN^tBu)_2(H)_2$, **1**,[13] was obtained in 32% yield from the reaction of $Pt(COD)_2$ (COD = cyclooctadiene) and tri-*tert*-butylstannane, $^tBu_3SnH$,[14] followed by the addition of *tert*-butylisocyanide, CN^tBu, at

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(13) In a glovebox (Ar atmosphere), 49.5 mg of $^tBu_3SnH$ (0.170 mmol) dissolved in 5 mL of hexane was added to 35.0 mg of $Pt(COD)_2$ (0.085 mmol). The reaction mixture was stirred at room temperature for 5 min, after which 14.0 mg of CN^tBu (0.170 mmol) was added, and the reaction mixture was stirred at room temperature for an additional 10 min. The solution was then filtered, and the filtrate was placed in a −20 °C freezer overnight, which gave crystalline $Pt(Sn^tBu_3)_2(CN^tBu)_2(H)_2$, **1**. After washing the crystalline product with approximately 2 mL of acetonitrile, 26 mg (32% yield) of **1** was obtained. Spectral data for **1**: ^1H NMR (C_6D_6 in ppm): δ 1.57 (s, 54 H, Sn^tBu_3, $^2J_{Sn-H} = 51$ Hz), 0.96 (s, 18H, ^tBu); −13.52 (s, 2H, hydride, $^1J_{Pt-H} = 697$ Hz, $^2J_{Sn-H} = 34$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6 in ppm): δ 81.50 (s, 2 Sn, $^1J_{Pt-Sn} = 3604$ Hz). Mass Spec. EI/MS *m*/*z* calcd. for M^+: 942. Found: 942.

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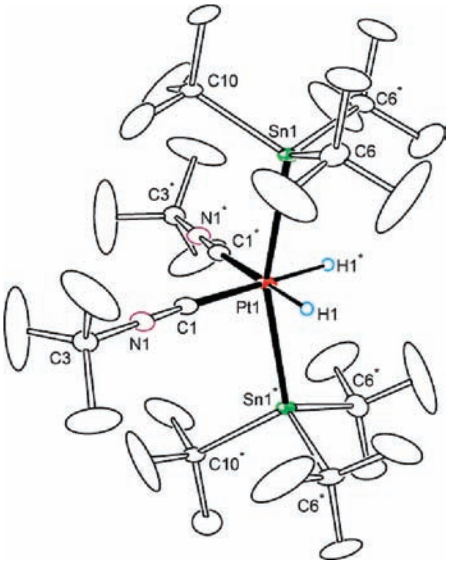

Figure 1. An ORTEP of the molecular structure of $\mathrm{Pt(Sn^tBu_3)_2(CN^tBu)_2(H)_2}$, **1**, showing 30% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)−Sn(1) = 2.6718(5); Pt(1)−C(1) = 2.014(8); Pt(1)−H(1) = 1.65(9); Sn(1)−Pt(1)−Sn(1*) = 161.35(3); C(1)−Pt(1)−C(1*) = 102.5(4); C(1)−Pt(1)−Sn(1) = 95.82(3); Sn(1)−Pt(1)−H(1) = 84.2(4).

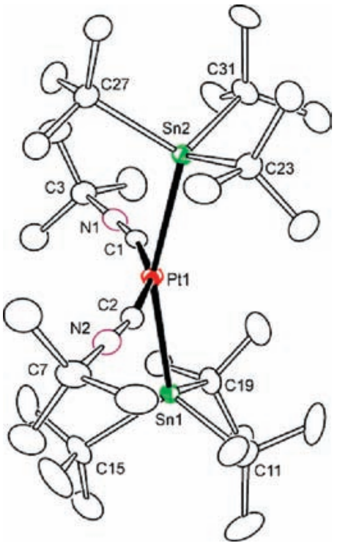

Figure 2. An ORTEP of the molecular structure of $\mathrm{Pt(Sn^tBu_3)_2(CN^tBu)_2}$, **2**, showing 50% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)−Sn(1) = 2.6765(3); Pt(1)−Sn(2) = 2.6851(3); Pt(1)−C(1) = 1.932(3); Pt(1)−C(2) = 1.929(3); Sn(1)−Pt(1)−Sn(2) = 159.539(8); C(1)−Pt(1)−C(2) = 158.69(13).

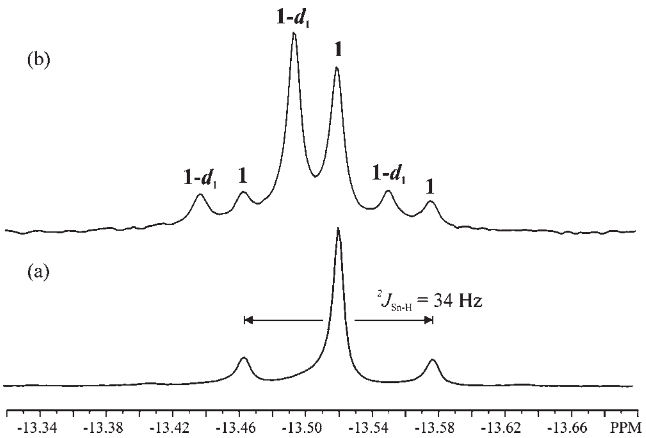

Figure 3. ^{1}H NMR spectra of the hydride region (a) for **1** from the addition of H_2 to **2** and (b) for the addition of HD to **2**. Pt−H one-bond coupling not shown.

room temperature. The compound was characterized by single-crystal X-ray diffraction, and its structure in the solid state is shown in Figure 1.[15]

Complex **1** is a mononuclear platinum complex having a slightly distorted octahedral geometry. The two $\mathrm{Sn^tBu_3}$ groups are *trans* with respect to each other, while the $\mathrm{CN^tBu}$ groups and the hydride ligands are in *cis* positions, such that the molecule has C_{2v} symmetry. The hydride ligand was located and refined in the structural analysis performed at 100 K. Appropriately, the ^{1}H NMR shows one resonance for the two equivalent hydrides, $\delta = -13.52$ (s, $^1J_{\mathrm{Pt-H}} = 697$ Hz, $^2J_{\mathrm{Sn-H}} = 34$ Hz).[16] Compound **1** contains 18 electrons, and the oxidation state on the Pt can be considered to be formally $\mathrm{Pt^{IV}}$.

Interestingly, when solutions of **1** were purged with argon gas at room temperature for approximately 20 h, H_2 gas was eliminated to afford the new complex $\mathrm{Pt(Sn^tBu_3)_2(CN^tBu)_2}$, **2**, in 89% yield.[17] Compound **2** was also characterized crystallographically, see Figure 2.[18]

Compound **2** is formally a 16 electron $\mathrm{Pt^{II}}$ species. As expected for platinum complexes in a d^8 configuration, the molecular geometry should be square planar. However, as seen in Figure 2, the structure of **2** is distorted from planarity due to steric crowding from the bulky $\mathrm{Sn^tBu_3}$ ligands, giving the complex approximate C_{2v} symmetry. Indeed when hydrogen gas (1 atm) is passed through solutions of **2** at room temperature, complex **1** is regenerated in 94% yield.

The complex **1**-d_1 was prepared by the reaction of **2** with HD gas, to test for the existence of direct H−H interactions in **1**. The ^{1}H NMR spectrum of **1**-d_1 did not show any H−D coupling, suggesting that there is no significant H−D interaction, which is consistent with the crystal structure analysis of **1**. In addition to the resonance of **1**-d_1, the hydride resonance for **1** was also present in the ^{1}H NMR spectrum, see Figure 3. The small shift difference in the spectrum in Figure 3b is due to isotope shift effects.

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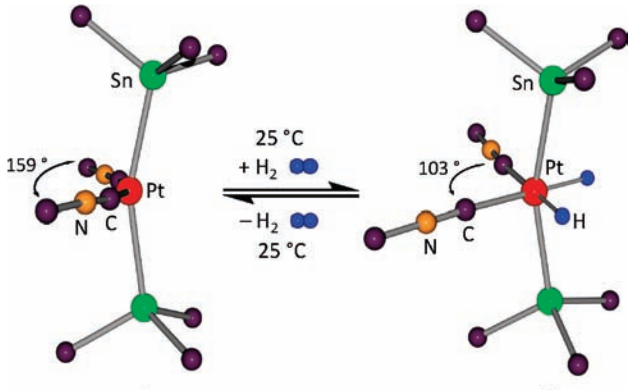
(15) Crystal data for **1**: $\mathrm{PtSn_2N_2C_{34}H_{74}\cdot Et_2O}$, M_r = 1017.54, orthorhombic, space group *Pmmn*, a = 13.1534(7) Å, b = 19.3120(10) Å, c = 9.2366(5) Å, V = 2346.3(2) Å^3, Z = 2, T = 100 K, Mo Kα = 0.71073 Å. GOF = 1.080, no. parameters = 120, $2\Theta_{\max}$ = 60°. The final R1(F^2) was 0.0437 for 2959 reflections $I > 2\sigma(I)$.

(16) In the ^{1}H NMR spectrum of $\mathrm{^tBu_3SnH}$ (in $CDCl_3$), the hydride resonance shows large one-bond coupling to tin (δ = 5.68, $^1J_{^{119}\mathrm{Sn-H}}$ = 1389 Hz and $^1J_{^{117}\mathrm{Sn-H}}$ = 1327 Hz), while the $\mathrm{^tBu_3}$ protons show small Sn−H coupling (δ = 1.40, $^3J_{\mathrm{Sn-H}}$ = 60 Hz). The value of 34 Hz for the Sn−H coupling in **1** indicates that the hydride ligand is not bonded to tin. Furthermore, the coupling assignments in **1** for the hydride resonance in the ^{1}H NMR were confirmed by ^{119}Sn decoupling experiments.

(17) Argon gas was purged through a solution of 15.0 mg of **1** (0.016 mmol) in 50 mL of hexane at 25 °C for ~20 h. ^{1}H NMR showed complete conversion of the starting **1** to **2**. The solvent was removed *in vacuo*, and the purple color residue was crystallized from a benzene/acetonitrile solvent mixture to yield 13.2 mg (89%) of **2**. Spectral data for **2**: ^{1}H NMR (C_6D_6 in ppm): δ 1.60 (s, 54 H, $\mathrm{Sn^tBu_3}$, $^2J_{\mathrm{Sn-H}}$ = 49 Hz), 1.15 (s, 18H, ^{t}Bu). Mass Spec. EI/MS *m*/*z*. calcd. for M^+: 940. Found: 940.

(18) Crystal data for **2**: $\mathrm{PtSn_2N_2C_{34}H_{72}}$, M_r = 941.41, monoclinic, space group $P2_1/n$, a = 13.6893(6) Å, b = 15.7758(7) Å, c = 19.1337(8) Å, β = 91.0532(7)°, V = 4131.4(3) Å^3, Z = 4, T = 100 K, Mo Kα = 0.71073 Å. GOF = 1.015, no. parameters = 376, $2\Theta_{\max}$ = 60°. The final R1(F^2) was 0.0293 for 9231 reflections $I > 2\sigma(I)$.

Scheme 1. Reversible Hydrogen Activation by **2**[a]



2 **1**

[a] Depiction of the crystal structures were created with Persistence of Vision Raytracer (POV-Ray). The methyl groups on the ^{t}Bu groups have been omitted for clarity.

In solution, complex **2** catalyzes H_2−D_2 exchange to give HD at room temperature. The addition of an equimolar mixture of H_2 and D_2 to solutions of **2** resulted in the rapid formation of HD, which was detected by ^{1}H NMR.[19] The mechanism of exchange is currently under examination.

The hydride ligands in **1** eliminate as H_2 to yield **2**. Even in the solid state, compound **1** converts to **2** slowly (∼ 24 h) under an atmosphere of argon gas at room temperature in quantitative yield. The introduction of hydrogen gas reverses the process in the solid state to yield **1** in quantitative yield at room temperature in 15 min. An analysis of the X-ray structures reveals how the ligands in **2** rearrange to accommodate the hydride ligands upon the addition of H_2, see Scheme 1. The addition of H_2 to **2** results in only a very slight perturbation of the Sn−Pt−Sn angle, 159.539(8)° in **2** versus 161.35(3)° in **1**, while the C−Pt−C bond angle between the CN^{t}Bu groups in **2** reduces significantly from 158.69(13)° to 102.5(4)° in **1**, to accommodate the two hydride ligands at the Pt metal center.

Further studies are currently underway to establish the role that the bulky stannyl and isocyanide ligands might play for the reversible activation of hydrogen, and also to investigate whether this compound can serve as a viable hydrogenation catalyst.

Acknowledgment. We thank the University of Miami (Start-up Funds) for financial support and Perry J. Pellechia at the University of South Carolina for help with the Sn decoupled ^{1}H NMR experiments.

Supporting Information Available: Experimental details for the syntheses and CIF files for the structural analyses are available for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) In a NMR tube, 4 mg of **2** was dissolved in 0.6 mL of C_6D_6 solvent. The NMR tube was evacuated under a vacuum, and an equimolar mixture of H_2 and D_2 gas was injected into the NMR tube using a syringe, at which time the violet colored solution turned colorless. The ^{1}H NMR spectrum of the reaction mixture after approximately 15 min showed formation of HD gas (δ = 4.44, $^1J_{D-H}$ = 43 Hz) along with formation of the corresponding HD complex **1**-d_1. H_2 gas was also present (δ = 4.47) as well as the H_2 complex **1**. Integration of the hydride region indicated that the HD complex **1**-d_1 and the H_2 complex **1** were present in approximately a 4:1 ratio. There was no indication of any unreacted **2**.