Tris(pyrazolyl)methane Sulfonate Complexes of Iridium: Catalytic Hydrogenation of 3,3-Dimethyl-1-butene

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The synthesis and characterization of three new iridium complexes bearing a tris(pyrazolyl)methane sulfonate ligand of the type $[Ir(Tpms)(LL')_2]$ (L, L′ = C_2H_4 **1**; L = C_2H_4, L′ = PPh_3 **2**; L = $(H)_2$, L′ = PPh_3 **3**; Tpms = tris(pyrazolyl)methane sulfonate) have been carried out. Complex **3** catalyzes the hydrogenation of the sterically crowded 3,3-dimethyl-1-butene to 2,2-dimethylbutane under mild conditions. The mechanism of the hydrogenation reaction has been studied using the model complex $[Ir(H)_2(Tpms)(PH_3)]$ (**3a**) by computational methods at the B3LYP/LANL2DZ level. Hydrogenation of ethylene to ethane by the model complex is exothermic by −27.1 kcal/mol.

Introduction

Ever since the introduction of the tris(pyrazolyl)borate anion (Tp) as a ligand,[1] it has been extensively used for the synthesis of coordination and organometallic compounds.[2] The synthesis and characterization of different families of Tp complexes bearing, for example, olefins or hydride co-ligands and the ability of these derivatives to bring about the C−H bond activation have been well established.[3] Tanke and Crabtree found the $[Ir(Tp)(C_2H_4)_2]$ complex to be a useful synthetic intermediate.[3] The synthesis and characterization of $[Ir(Tp)(PPh_3)(C_2H_4)]$ and its reactivity toward H_2 have been reported by Oldham and Heinekey.[4a] Gutiérrez-Puebla et al. reported that complexes of the type $[Ir(Tp/Tp')(C_2H_4)(L)]$ (Tp′ = substituted Tp; L = phosphine or CO) undergo facile ligand exchange (with soft bases) and bring about hydrogenation reactions via undetected 16-electron intermediates that are formed by transient unanchoring of one of the pyrazolyl arms.[4b] In comparison, the chemistry of isosteric and isoelectronic tris(pyrazolyl)methane (Tpm) and its substituted derivatives (Tpm′) has not experienced growth to the same extent as that of the Tp and Tp′ complexes.[5] The difficult syntheses of the Tpm and Tpm′ ligands in addition to their low yields have contributed to the slow progress of the chemistry of these interesting ligands. The tris(pyrazolyl)methane sulfonate (Tpms) ligand was shown to be a versatile alternative to Tp and, in fact, outweighs the Tp ligand in certain respects.[6] The Tpms ligand, in addition to being anionic like Tp, is hydrolytically stable and shows greater solubility in polar solvents.

Among the well-known iridium hydrogenation catalysts, the cationic square-planar Ir(I) complexes were found to be efficient for the hydrogenation of a variety of substituted olefins, e.g., Crabtree's catalyst $[Ir(PCy_3)(py)(COD)][PF_6]$ (py = pyridine; COD = 1,5-cyclooctadiene).[7] These catalysts often require highly polar solvents. In addition, their catalytic activity is influenced by the nature of the counterions and the solvents, being severely inhibited by coordinating solvents.[8] Recently, Stradiotto and co-workers reported a neutral Ir(I) alkene hydrogenation catalyst, [Ir(κ^2-*P*,*O*-phosphinoenolate)(COD)].[9a] The hydrotris(pyrazolyl)borate (Tp) and the substituted Tp hydrotris(3,5-dimethylpyrazolyl)borate-ligand-stabilized $[Ir(COD)Cl]_2$ complex catalyzes the regioselective hydrogenation of olefinic fuctional groups of α,β-unsaturated substrates.[9b,c] Prompted by the stability of Tpms toward hydrolysis and its greater solubility in lipophilic solvents, we began exploring the synthesis of Tpms complexes of iridium in the hope of realizing a neutral derivative that exhibits olefin hydrogenation catalytic behavior. Herein, we report the synthesis, characterization, and catalytic activity of certain Tpms complexes of iridium.

Experimental Section

General Procedures. All the reactions were carried out under an atmosphere of dry and oxygen-free N_2 at room temperature using standard Schlenk and inert atmosphere techniques unless otherwise specified.[10] The ^1H, ^{31}P, and inverse-gated decoupled ^{13}C NMR spectral data were obtained using an Avance Bruker 400 MHz instrument. The shift of the residual protons of the deuterated solvents (CD_2Cl_2: δ 5.32; C_6D_6: δ 7.15) was used as an internal reference in the case of ^1H NMR spectral measurements. The ^{31}P NMR spectra were recorded with respect to 85% H_3PO_4 (aqueous solution) as an external standard. The NOESY spectrum was recorded at 223 K (CD_2Cl_2) using the pulse program *noesyph* with a mixing time period of 250 ms. Li tris(pyrazolyl)methane sulfonate

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(LiTpms) and the complex $[IrCl(COE)_2]_2$ (COE = cyclooctene) were prepared using literature procedures.[11,12]

Preparation of $[Ir(C_2H_4)_2(Tpms)]$, 1. A suspension of $[IrCl(COE)_2]_2$ (0.200 g, 0.220 mmol) in THF (5 mL) was freeze−pump−thaw degassed. Ethylene gas was bubbled through this yellow suspension at 253 K until it became colorless. The LiTpms (0.128 g, 0.440 mmol) dissolved in a THF−absolute EtOH mixture (3 mL + 2 mL) was cannula-transferred into the Schlenk tube containing the iridium complex. The yellow reaction mixture was stirred for ca. 1 h at 253 K, during which time it became pale yellow. The volatiles were removed in vacuo, and to the solid was added CH_2Cl_2 (10 mL); the solution was filtered through a filter frit. The solvent from the filtrate was removed in vacuo, and the cream-colored product $[Ir(C_2H_4)_2(Tpms)]$ (**1**) was isolated and dried. Yield: 0.180 g (75%). Anal. Calcd for $C_{14}H_{17}N_6O_3SIr\cdot H_2O$: C, 29.99; H, 3.41. Found: C, 29.68; C, 4.15. ^{1}H NMR (CD_2Cl_2, 300 K): δ 2.16 (br s, 8H, C_2H_4), 6.44 (t, 3H, *4-pz*), 7.96 (d, 3H, *5-pz*), 9.02 (d, 3H, *3-pz*). ^{1}H NMR (CD_2Cl_2, 203 K): δ 1.77, 2.39 (d each, 4H each, C_2H_4, J = 9.8 Hz), 6.43 (t, 3H, *4-pz*), 7.93 (d, 3H, *5-pz*), 8.88 (d, 3H, *3-pz*). ^{13}C NMR (CD_2Cl_2, 300 K, inverse-gated decoupled): δ 30.7 (s, C_2H_4), 89.9 (s, CSO_3), 105.8 (s, *4-pz*), 135.0 (s, *3-pz*), 140.4 (s, *5-pz*).

Preparation of $[Ir(C_2H_4)(PPh_3)(Tpms)]$, 2. To a THF solution (5 mL) of complex **1** (0.100 g, 0.180 mmol) held at 273 K was added a THF solution (2 mL) of PPh_3 (0.048 g, 0.180 mmol). The mixture was stirred for 30 min and allowed to warm to room temperature during that period. The solvent was removed in vacuo, and the cream-colored product $[Ir(C_2H_4)(PPh_3)(Tpms)]$ (**2**) was dried in vacuo. Yield: 0.110 g (78.5%). Anal. Calcd for $C_{30}H_{28}N_6O_3PSIr\cdot H_2O$: C, 45.33; H, 3.80. Found: C, 45.16; H, 3.84. ^{1}H NMR (CD_2Cl_2, 300 K): δ 0.94, 1.02 (m each, 2H each, C_2H_4), 6.27 (t, 2H, *4-pz*$_{eq}$), 6.03 (br s, 1H, *4-pz*$_{ax}$), 7.24 (m, 15H, P*Ph*$_3$), 8.98, 7.28 (d each, 2H each, *3,5-pz*$_{eq}$), 8.97, 7.32 (d and m, 1H each, *3,5-pz*$_{ax}$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K): δ 8.5 (s, PPh_3). ^{13}C NMR (CD_2Cl_2, 213 K, inverse-gated decoupled): δ 4.0 (s, 2C, C_2H_4), 90.2 (s, 1C, CSO_3), 105.6 (s, 1C, *4-pz*$_{ax}$), 105.9 (s, 2C, *4-pz*$_{eq}$), 143.7, 134.1 (s each, 2C each, *3,5-pz*$_{eq}$), 135.5, 134.9 (s each, 1C each, *3,5-pz*$_{ax}$), 127.9, 132.9, 134.1 (m, 18C, P*Ph*$_3$).

Preparation of $[Ir(H)_2(PPh_3)(Tpms)]$, 3. A THF solution (5 mL) of complex **2** (0.100 g, 0.130 mmol) in a Schlenk tube was freeze−pump−thaw degassed. Then H_2(g) (1 atm) was introduced into this solution at 253 K. The tube was sealed off and shaken on a rotary shaker overnight. During this period, the yellow-colored solution became colorless. Solvent was removed in vacuo, and the colorless powder of $[Ir(H)_2(PPh_3)(Tpms)]$ (**3**) was isolated and dried in vacuo. Yield: 0.125 g (89.1%). The sample was crystallized via slow evaporation of CD_2Cl_2 from the solution of **3** in an NMR tube. Anal. Calcd for $C_{28}H_{26}N_6O_3PSIr\cdot H_2O$: C, 43.79; H, 3.67; N, 10.94. Found: C, 43.71; H, 3.34; N, 10.49. ^{1}H NMR (CD_2Cl_2, 300 K): δ −20.45 (d, 2H, J(H,P$_{cis}$) = 23.5 Hz, Ir-*H*), 6.56 (t, 2H, *4-pz*$_{eq}$), 6.25 (br t, 1H, *4-pz*$_{ax}$), 8.87, 6.56 (d and m respectively, 2H each, *3,5-pz*$_{eq}$), 7.19, 7.40 (m, 15H, P*Ph*$_3$), 8.84, 7.94 (d and m respectively, 1H each, *3,5-pz*$_{ax}$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K): δ 15.4 (s, PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K): δ 93.9 (s, 1C, CSO_3), 108.2 (s, 2C, *4-pz*$_{eq}$), 105.8 (d, 1C, *4-pz*$_{ax}$), 149.7, 137.1 (s each, 1C each, *3,5-pz*$_{ax}$), 146.3, 137.3 (s each, 2C each, *3,5-pz*$_{eq}$).

Catalytic Hydrogenation of 3,3-Dimethyl-1-butene. Complex **3** (0.020 g, 0.002 mmol) was dissolved in 0.6 mL of C_6D_6 in a septum-capped 5 mm NMR tube. The solution was freeze−pump−thaw degassed in three cycles. Then 1 equiv of 3,3-dimethyl-1-butene (3.4 μL, 0.002 mmol) was added. Next, H_2(g) (1 atm) was introduced into the tube, and the tube was sealed. It was continuously shaken on a rotary shaker, and the progress of the reaction was monitored using NMR spectroscopy.

The bomb catalysis was carried out using a Parr-hydrogenation apparatus with 0.25 mol % of catalyst with respect to olefin, which was dissolved in 6 mL of C_6H_6 in a 250 mL Pyrex reaction bottle. The bottle was flushed three times with hydrogen gas and refilled with 1 atm of H_2(g). The mixture was shaken, and the progress of the reaction was monitored by recording the ^{1}H NMR spectra of aliquots taken at 3, 8, and 12 h. At 12 h, the ^{1}H NMR spectrum showed the complete hydrogenation of the olefin. The experiment was repeated at a pressure of 2 atm of H_2(g), and the time required was only 5 h.

Crystal Structure of $[Ir(H)_2(PPh_3)(Tpms)]$, 3. Good quality crystals of complex **3** suitable for X-ray diffraction study were carefully selected after examination under an optical microscope and mounted on the Goniometer head with a paraffin oil coating. The unit cell parameters and intensity data were collected at room temperature using a Bruker SMART APEX CCD diffractometer equipped with a fine focus Mo Kα X-ray source (50 kV, 40 mA). The data acquisition was done using SMART software, and SAINT software was used for data reduction.[13] The empirical absorption corrections were made using the SADABS program.[14] The structure was solved and refined using the SHELXL-97 program.[15] The iridium atom was located from the Patterson map, and the non-hydrogen atoms and the hydrides were located from the difference Fourier map and refined anisotropically. All other hydrogen atoms were fixed in idealized positions and refined in a riding model. Crystal data for **3**: $C_{28}H_{26}N_6O_3P_1S_1Ir$, fw = 749.78, triclinic, $P\bar{1}$, a = 8.970(10) Å, b = 13.109(15) Å, c = 13.788(15) Å, α = 108.367(15)°, β = 97.054(16)°, γ = 109.366(15)°, V = 1404(3) Å^3, D_{calcd} = 1.773 g/cm^3, T = 293(2) K, λ = 0.71073 Å, μ = 4.928 mm^{-1}, R = 0.034, R_w = 0.082.

Computational Details. All the calculations were performed using the Gaussian03 program[16] at the B3LYP level of theory,[17] which consists of a hybrid Becke+Hartree−Fock exchange and Lee−Yang−Parr correlation functional with nonlocal correlations. The basis set used was LANL2DZ.[18] All the molecules were optimized without any symmetry restrictions and were identified by the number of imaginary vibrational frequencies. The model complex used for the calculation was $[Ir(H)_2(Tpms)(PH_3)]$ (**3a**), wherein the three phenyl groups in complex **3** were replaced by hydrogens, to minimize the computation time.

Results and Discussion

Preparation and Characterization of Tpms Complexes of Iridium. (a) $[Ir(Tpms)(C_2H_4)_2]$, 1. Reaction of the iridium dimer $[IrCl(COE)_2]_2$ with 2 equiv of LiTpms under an atmosphere of ethylene led to the isolation of a cream-colored product of the ethylene complex $[Ir(C_2H_4)_2(Tpms)]$ (**1**) (eq 1). The

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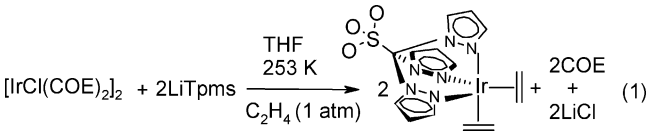
synthetic procedure follows the method of Tanke and Crabtree for the preparation of the Tp analogue.[3]

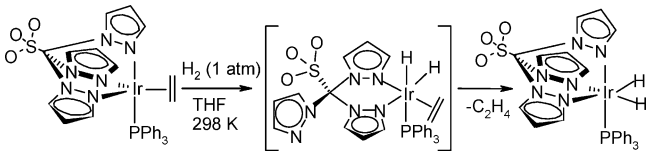


(1)

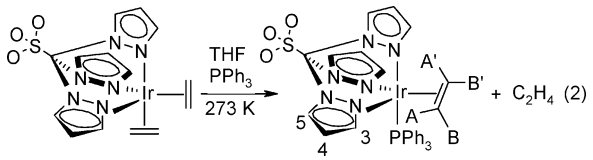
The ^{1}H NMR spectrum (see the Supporting Information) of **1** at room temperature consists of a set of three signals (δ 6.44, 7.96, and 9.02) for the pyrazolyl moieties, which remain invariant down to 203 K, and a broad singlet at δ 2.16 integrating to eight hydrogens for the metal-bound C_2H_4 ligands. The related Tp complex, [Ir(Tp)$(C_2H_4)_2$], similarly shows only one set of three pyrazolyl resonances down to 190 K in the ^{1}H NMR spectrum.[3] Venanzi and co-workers studied the dynamics of the pyrazolyl groups that renders them equivalent involving a trigonal bipyramidal (tbp) (κ^3) $\leftrightarrow$ square-planar (sp) (κ^2) equilibrium in a series of rhodium complexes of the type [RhTp^{3R,4R,5R}(LL)] (LL = 2CO, norbornadiene (NBD), 1,5-cyclooctadiene (COD)).[19] Trofimenko and co-workers also reported earlier such equilibria between the tbp and sp structures in certain Tp rhodium carbonyl complexes.[20] Kläui et al. found that the Tpms rhodium carbonyl complex [Rh(Tpms)$(CO)_2$] shows only a single set of peaks for all three pyrazolyl groups.[6] The ground state structure of the [Ir(Tp)$(C_2H_4)_2$] complex is not known with certainty since at all accessible temperatures the pyrazolyl groups were found to be dynamic.[3] A 2:1 spectral pattern is expected in the ^{1}H NMR spectrum for a static structure. The appearance of only one set of three resonances each integrating to three hydrogens for the pyrazolyl groups in the case of **1** is indicative of either a nonrigid tridentate structure or a bidentate geometry with a dynamic exchange that is faster than the NMR time scale. No static structure was accessible in our experiments. On the other hand, the broad singlet for C_2H_4 ligands decoalesces at ca. 243 K into two new doublets at δ 1.77 and 2.39. Using the free energy relationships,[21] the $\Delta G^{\ddagger}$ calculated for ethylene rotation is 11.5 kcal/mol.

(b) [Ir(Tpms)(C_2H_4)(PPh$_3$)], 2. Substitution of one of the C_2H_4 ligands in **1** with PPh_3 in THF solvent at 273 K gave in a clean reaction the phosphine derivative [Ir(Tpms)(C_2H_4)-(PPh_3)], **2** (eq 2). It is interesting to note that there is a parallel for this reaction in the chemistry of Tp complexes of iridium.[4b] The ^{31}P{^{1}H} NMR spectrum of **2** at 300 K shows a singlet at δ 8.5 for the bound PPh_3. The ^{1}H NMR spectrum at room temperature is composed of two sets of peaks integrating to 2:1 for the pyrazolyl groups, indicating that they are rigid, which is in contrast to that in **1** and the Tp analogue [Ir(Tp)(C_2H_4)-(PPh_3)].[4a] The [Ir(Tp)$(C_2H_4)(PPh_3)$] complex is dynamic at room temperature; however, it exhibits a rigid structure at low temperatures; the spectral characteristics of **2** are similar to the low-temperature spectral behavior of the Tp analogue. On the other hand, the metal-bound ethylene ligand exhibits two multiplets as an AA′BB′ pattern at δ 1.02 and 0.94, respectively, integrating to 2 H each. This indicates that there is no rotation

Scheme 1. Preparation of [Ir(H)$_2$(Tpms)(PPh$_3$)] (3) from [Ir(Tpms)(C_2H_4)(PPh$_3$)] (2) and H_2



of the ethylene ligand around the M$-C_2H_4$ bond. These spectral features are comparable to those of the Tp analogue.[4a]



Further insight into the structure was obtained from a low-temperature ^{1}H$-^1$H NOESY (CD_2Cl_2, 223 K) experiment. The NOESY spectrum (see the Supporting Information) showed cross-peaks between the hydrogens on the equatorial pyrazolyl groups and the phenyl hydrogens of PPh_3. This suggests that the PPh_3 ligand must be in the axial position and in close proximity to the equatorial pyrazolyl groups. As in the case of the Tp analogue,[4a] the ethylene ligand in complex **2** exhibits only a single resonance in the ^{13}C NMR spectrum at high field (δ 4.0, free C_2H_4 ca. δ 124); therefore, it must be occupying the equatorial plane with a mirror plane bisecting the C=C bond. Thus, the structure can be described as a tbp with one axial pyrazole trans to PPh_3 and two equatorial pyrazoles trans to ethylene. The ^{1}H NMR spectral features of the pyrazolyl region are consistent with this proposition.

(c) [Ir(Tpms)$(H)_2$(PPh$_3$)], 3. Exposure of a THF solution of **2** to H_2(g) (1 atm) in a sealed tube for 10$-$15 h led to the formation of a cis-dihydride complex, [Ir(Tpms)$(H)_2(PPh_3)$] (**3**), indicating that H_2 underwent oxidative addition at the iridium center (Scheme 1). The ^{1}H NMR spectrum in the hydride region shows a doublet at δ $-$20.45 integrating to two hydrogens for the metal-bound hydrides with $J(H,P_{cis})$ = 23.5 Hz. The pyrazolyl region of the ^{1}H NMR spectrum consists of two sets of peaks integrating to 2:1 for the equatorial and the axial pyrazole groups of an octahedral structure. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 15.4 for the PPh_3 ligand. Similar ethylene substitution reactions have been observed earlier.[4a,22] Gutiérrez-Puebla et al. proposed an associative mechanism involving a change in the coordination mode from κ^3 to κ^2 of the Tp ligand of [Ir(Tp)$(C_2H_4)(PPh_3)$], resulting in a 16-electron reactive intermediate that is trapped by H_2 to give the dihydride [Ir(κ^2-Tp)$(H)_2(C_2H_4)(PPh_3)$]. The C_2H_4 ligand is then extruded from this intermediate, and the κ^2-Tp reverts back to the κ^3-binding mode.[4a] Our theoretical calculations (see later) on the hydrogenation of ethylene using the model complex [Ir$(H)_2$-(Tpms)(PH_3)] as a catalyst predicts an associative process involving a change in the binding mode of the Tpms ligand from κ^3 to κ^2 followed by the binding of C_2H_4 to the iridium center. Although we have not been able to observe this process spectroscopically, we do not rule out a similar associative mechanism in the hydrogenation reaction of **2**. The dihydride complex shows good thermal stability and solubility in common organic solvents. Crystals suitable for X-ray crystallographic studies were obtained via slow evaporation of solvent from a CD_2Cl_2 solution of the sample.

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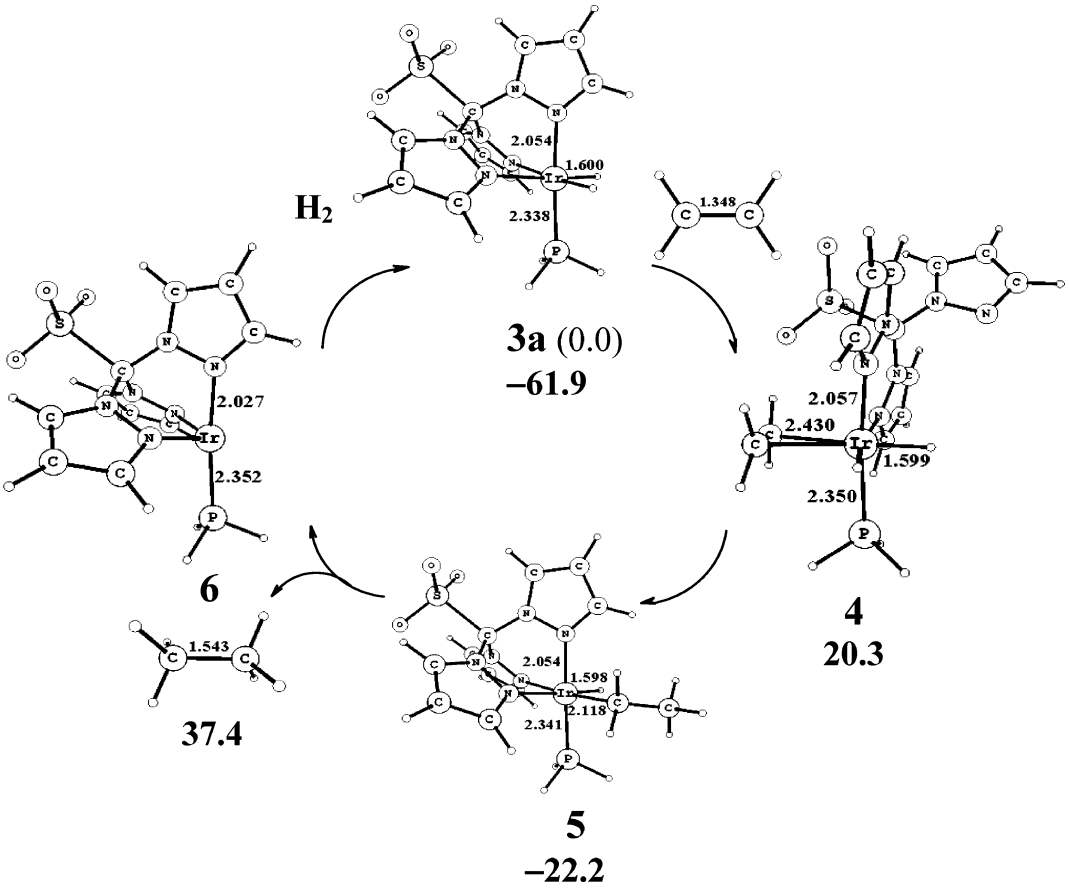
Scheme 2. B3LYP/LANL2DZ-Optimized Structures (bond lengths in Å) of the Reactant 3a, Intermediates (4−6), and the Product (ethane) in the Hydrogenation of Ethylene Using [Ir(H)$_2$(Tpms)(PH$_3$)], 3a, as a Catalyst; the Free Energies (kcal/mol) Are Also Given



Crystal Structure of [Ir(Tpms)(H)$_2$(PPh$_3$)], 3. The ORTEP diagram of **3** is shown in Figure 1. The structure consists of the Tpms ligand bound to the iridium center in a κ^3 fashion with two pyrazole rings occupying the equatorial positions and the third ring and the PPh_3 ligand in the axial positions of a distorted octahedron. The Ir(1)−N bond distances are in the range 2.099(5)−2.152(5) Å. These distances are comparable to those found in a related Tp complex, [Ir(Tp)(H)(η^2-H$_2$)(PMe$_3$)], which are in the range 2.070(8)−2.161(8) Å.[23] The hydride ligands were located from the successive difference Fourier maps. The sulfonate group orients away from the metal center and does not possess any bonding interaction with the metal. This is in contrast to the Tpms complexes of the type [M(Tpms^{iPr})$_2$ (M = Zn, Cu, Ni, Co, Fe)[24] and [Zn(Tpms^{tBu})-ZnBr],[25] in which the Tpms ligand acts as a N, N, O-donor.

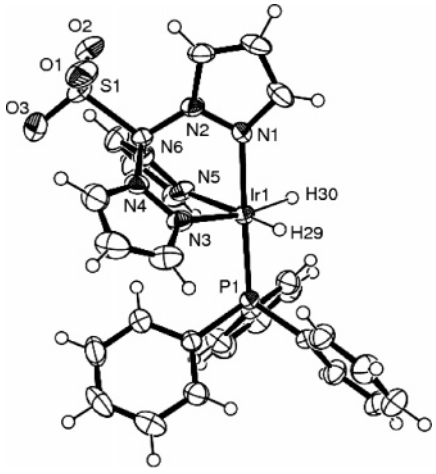


Figure 1. ORTEP view of [Ir(H)$_2$(Tpms)(PPh$_3$)] (**3**) at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ir(1)−H(29), 1.28(6); Ir(1)−H(30), 1.61(6); Ir(1)−P(1), 2.234(3); Ir(1)−N(1), 2.099(5); Ir(1)−N(3), 2.151(5); Ir(1)−N(5), 2.152(5); N(1)−Ir(1)−N(3), 82.59(17); N(1)−Ir(1)−N(5), 81.97-(16); N(3)−Ir(1)−N(5), 84.46(18); N(1)−Ir(1)−P(1), 178.37(11); N(5)−Ir(1)−P(1), 98.99(12).

Catalytic Hydrogenation of 3,3-Dimethyl-1-butene. The hydrogenation of 3,3-dimethyl-1-butene was performed by taking together a mixture of complex **3**, olefin, and H_2 gas (1 atm) in a sealed NMR tube (eq 3). The ^{1}H NMR (C_6D_6, 298 K) after ca. 8 h showed a decrease in the peak intensities of the olefin and the appearance of three new signals that can be assigned to 2,2-dimethylbutane (δ 0.80 (t, 3H), 0.85 (s, 9H), 1.18 (q, 2H)) (Figure S3, Supporting Information). After 20 h of reaction, the hydrogenation was complete. Further evidence of the formation of 2,2-dimethylbutane was obtained from the inverse-gated decoupled ^{13}C NMR spectroscopy (δ 8.0 (s, 1C), 27.9 (s, 1C), 35.6 (s, 4C)). These spectral features match with those of 2,2-dimethylbutane.[26] The same reaction was carried out in a Parr hydrogenation apparatus with a catalyst:olefin ratio of 0.25 mol % in C_6H_6 under 1 and 2 atm pressure of H_2.

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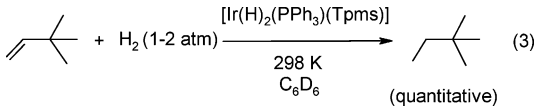
(26) NMR spectral data for 2,2-dimethylbutane were compared with the data given in the catalog of NMR spectra, Sigma-Aldrich.

Whereas 12 h was required for the hydrogenation to be complete in the experiment with 1 atm of H_2, complete hydrogenation of the olefin needed only 5 h when the pressure of H_2 was 2 atm. It is interesting to note that complex **3** is a neutral species with no charge on the complex. Examples of neutral iridium complexes that bring about the hydrogenation of olefins are very few.[9a,27] Werner and co-workers reported the catalytic hydrogenation of ethylene and propene using the cationic Ir(III) dihydride complex $[Ir(H)_2(P^iPr_3)(CH_3CN)_3][BF_4]$.[28]



We propose a mechanism involving the coordination of the olefin on a vacant site of the iridium center to form an Ir−olefin complex; the creation of the vacant site on the metal is facilitated by a change in the binding mode of the tris(pyrazolyl)-methane sulfonate ligand from κ^3 to κ^2, which is commonly observed in many catalytic reactions involving tris(pyrazolyl)-borate complexes.[29] Our efforts to observe this species at low temperatures failed. Migratory insertion of a hydride to the bound olefin resulting in an Ir−alkyl complex followed by the reductive elimination of the alkane 2,2-dimethylbutane generates a reactive 16-electron species. The migratory insertion is accompanied by the reversal of the κ^2 to κ^3 binding of the tris-(pyrazolyl)methane sulfonate. The 16-electron complex then facilitates the oxidative addition of H_2 to regenerate the iridium starting complex, thus completing the catalytic cycle.

Although we do not have any experimental evidence for the proposed mechanism, our theoretical studies support the above proposition. The optimized structures using the density functional theory at the B3LYP/LANL2DZ level are shown in Scheme 2. We performed calculations for the hydrogenation of ethylene using the model complex $[Ir(H)_2(Tpms)(PH_3)]$, **3a**. Binding of ethylene to the model complex **3a** is facilitated via a change in the coordination mode of the Tpms ligand from κ^3 to κ^2 that opens up a vacant site on the metal. The optimized structure of the intermediate **4** shows that two of the pyrazolyl groups are bound to the Ir center at Ir−N bond distances of 2.057 and 2.164 Å, whereas the third one is away from the metal at a nonbonded distance of 4.965 Å. Ethylene is bound in an η^2-C_2H_4 fashion with Ir−C distances of 2.430 and 2.404 Å. The free energy change (ΔG) calculated for the formation of **4** relative to **3a** is 20.3 kcal/mol. This energy is required for the rearrangement of the tris(pyrazolyl)methane sulfonate ligand. The next step involves the formation of the Ir−ethyl species **5**, which is favored by $\Delta G = -22.2$ kcal/mol. The reductive elimination of ethane requires 37.4 kcal/mol, resulting in the generation of the 16-electron species **6**. The energy requirement of this step is more than compensated for by the oxidative addition of H_2 to **6** by way of release of −61.9 kcal/mol to regenerate **3a**. The overall free energy change (ΔG) for the catalytic hydrogenation of ethylene using the model complex **3a** is favored by −27.1 kcal/mol. Scheme 2 summarizes this catalytic cycle.

Conclusions

A tris(pyrazolyl)methane sulfonate complex of iridium bearing an ethylene ligand of the type $[Ir(Tpms)(C_2H_4)_2]$ has been synthesized and characterized. The ethylene ligand undergoes facile substitution with PPh_3 to give the phosphine derivative $[Ir(Tpms)(C_2H_4)(PPh_3)]$. Hydrogenation of the phosphine complex results in the dihydride $[Ir(Tpms)(H)_2(PPh_3)]$ via extrusion of the C_2H_4 ligand. The $[Ir(Tpms)(H)_2(PPh_3)]$ complex catalyzes the hydrogenation of the sterically hindered 3,3-dimethyl-1-butene to 2,2-dimethylbutane under mild conditions. The DFT calculations carried out at the B3LYP/LANL2DZ level of theory using the model complex $[Ir(H)_2(Tpms)(PH_3)]$ suggest that the hydrogenation reaction proceeds through the intermediacy of $[Ir(H)_2(\kappa^2\text{-Tpms})(PPh_3)(C_2H_4)]$.[30]

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Supporting Information Available: Variable-temperature ^1H NMR spectral stack plot of $[Ir(Tpms)(C_2H_4)_2]$, **1**, $^1H-^1H$ NOESY spectrum of $[Ir(Tpms)(C_2H_4)(PPh_3)]$, **2**, at 223 K, ^1H NMR spectral stack plot for the hydrogenation of 3,3-dimethyl-1-butene using $[Ir(H)_2(Tpms)(PPh_3)]$, **3**, as a catalyst, optimized geometry of intermediate **6a** at the B3LYP/LANL2DZ level of theory, total energy (*E*, in au) and Cartesian coordinates of all the molecules at the B3LYP/LANL2DZ level of theory, and the X-ray crystallographic data for $[Ir(H)_2(Tpms)(PPh_3)]$, **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700515N

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(30) We found another isomer, **6a** (see Supporting Information), that is stable by −6.9 kcal/mol over intermediate **6**. This isomer, however, is unlikely in our catalytic cycle since it is a three-coordinate, 14-electron complex in which the Tpms ligand is κ^2-bound to the iridium center.