# Trapping of Tricyclo[3.3.1.0³,⁷]non-3(7)-ene with (Ph₃P)₂Pt. Structure of the (Ph₃P)₂Pt Complex of a Highly Pyramidalized Alkene

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Received February 20, 1990

Evidence has been presented for the formation of tricyclo-[3.3.1.0³,⁷]non-3(7)-ene (**2**),[1] a highly pyramidalized alkene,[2] when diiodide **1** is allowed to react with butyllithium. There have been several reports of stabilization of various types of strained alkenes[3–8] and alkynes[9] by complexation to Pt(0). However, to our knowledge, this type of stabilization of a pyramidalized olefin has not been reported. Herein we report the synthesis, spectroscopic characterization, and X-ray structure of the (Ph₃P)₂Pt complex (**3**) of **2**.
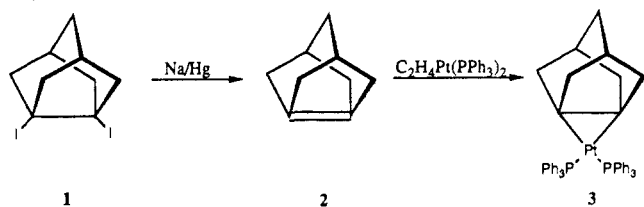
Diiodide **1** (100 mg, 0.27 mmol) and (PPh₃)₂Pt(C₂H₄)[10] (200 mg, 0.27 mmol) were placed in a flame-dried, two-necked, round-bottomed flask. The flask was evacuated, 15 mL of dry THF was distilled into it, the flask was filled with argon, and 8 g of Na/Hg (0.4% by weight Na) was added in one portion via a dropping funnel. The contents of the flask were stirred for 36 h, after which time the reaction mixture was filtered through Celite, and the solids were washed with 20 mL of THF. The THF solutions were combined and evaporated under reduced pressure to give a brown oil, which, on trituration with ethanol, gave a beige-colored powder (120 mg, 54%). The powder was recrystallized from THF–ethanol to give needle-like crystals, mp 192–194 °C. The crystals were indefinitely stable to air, but in solution they decomposed over several weeks.

The FAB mass spectrum showed the parent ion at $(M + H)/e$ = 840 (exact mass calculated for $C_{45}H_{43}P_2Pt$ 840.2486, found 840.2497), with peaks at 839 and 841 for the two other abundant isotopes of Pt. ¹H NMR (500 MHz, C_6D_6): δ 2.06 (s, 2 H), 2.20 (d, J = 10.3 Hz, 4 H), 2.37 (td, J_{PtH} = 52.2 Hz, J_{HH} = 10.3 Hz, 4 H), 3.46 (t, J_{PtH} = 60.3 Hz, 2 H), 7.12 (m, 18 H), 7.22 (m, 12 H). ¹³C NMR (75.4 MHz, proton decoupled, C_6D_6): δ 138.2 (m), 134.8 (m), 129.6 (s), 66.9 (t of m, J_{PtC} = 407.4 Hz), 61.2 (t, J_{PtC} = 106.7 Hz), 52.5 (s), 39.3 (s). ³¹P NMR (121 MHz, proton decoupled, C_6D_6): δ 30.5 (t of m, J_{PtP} = 2960 Hz).

Long-range coupling to Pt was observed for the bridgehead methine protons, the carbons to which they are attached, and for one of the two sets of four equivalent methylene protons in **3**. The coupling constant of 407.4 Hz between Pt and the two carbons to which it is directly bonded is twice as large as that (194 Hz)
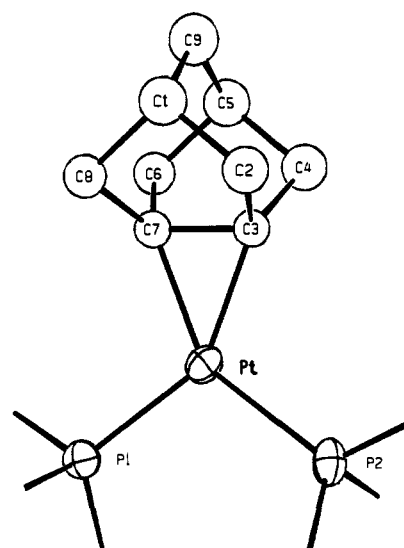
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Figure 1. ORTEP drawing of the crystal structure of **3**. The phenyl rings and the hydrogens have been omitted for clarity.

measured by us for the (Ph₃P)₂Pt complex of ethylene and larger than either of those reported for the (Ph₃P)₂Pt complex of bicyclo[3.3.1]non-1-ene (320 Hz and 220 Hz).[6] Since the Pt–C coupling constant would be expected to increase with increasing carbon s character in the Pt–C bonds,[11] the large Pt–C coupling constant is indicative of a high degree of pyramidalization at the carbons bonded to Pt in **3**.

In addition to being coupled to Pt, these carbons are each coupled to the two phosphorus atoms in an AXY fashion. This additional coupling splits each component of the triplet for these carbons into a five-line multiplet. The multiplet was simulated by using PANIC,[12] and the coupling constants that gave the best simulation were $J_{PtransC}$ = 67 Hz, J_{PcisC} = –10 Hz, and J_{PP} = –27 Hz. A similar simulation of the ¹³C NMR spectrum of the (Ph₃P)₂Pt complex of ethylene gave $J_{PtransC}$ = 27 Hz, J_{PcisC} = –3 Hz, and J_{PP} = –58 Hz. The coupling constants reported for the (Ph₃P)₂Pt complex of bicyclo[3.3.1]non-1-ene[6] are intermediate between those measured by us for **3** and for the (Ph₃P)₂Pt complex of ethylene. The larger magnitudes of the phosphorus–carbon coupling constants in **3** are again suggestive of a greater amount of carbon s character in the bonds to the (Ph₃P)₂Pt moiety in **3** and, hence, of a more highly pyramidalized geometry at carbon.

These indications from the NMR coupling constants in **3** of a highly pyramidalized geometry at the carbons coordinated to Pt were confirmed by X-ray crystallography.[13] With the platinum and phosphorus atoms anisotropic and all carbon atoms isotropic, final structure refinement converged to R_f = 0.059. An ORTEP drawing of the crystal structure of **3** is shown in Figure 1, with the phenyl rings of the two PPh₃ groups and the hydrogens omitted for clarity.

The important bond lengths in **3** (in Å) are C(3)–C(7) = 1.48 (3), Pt–C(3) = 2.07 (2), Pt–C(7) = 2.07 (2), Pt–P(1) = 2.30 (1), and Pt–P(2) = 2.29 (1). These distances fall well within the range of those found in other (Ph₃P)₂Pt complexes of alkenes.[14] The pyramidalization angles at C(3) and C(7), that is, the angles between the extensions of the C(3)–C(7) bond and the planes containing C(2)–C(3)–C(4) and C(6)–C(7)–C(8), are 60° ± 3°. These angles in **3** are midway in size between the pyramidalization angles of 53° and 66° that have been computed at the 3-21G SCF level for, respectively, **2** and its hydrogenation product.[15] The

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pyramidalization angles in 3 are significantly larger than the pyramidalization angles found in the $(Ph_3P)_2Pt$ complexes of other alkenes,[14] except for the $(Ph_3P)_2Pt$ complex of bicyclo[2.2.0]-hex-1(4)-ene.[4]

In the latter complex the bond angles within the four-membered rings are constrained to be close to 90°, which causes small amounts of nonplanarity at the carbons bonded to platinum to result in very large pyramidalization angles.[16] A better indicator of the degree of pyramidalization at these carbons in the $(Ph_3P)_2Pt$ complex of bicyclo[2.2.0]hex-1(4)-ene is the flap angle between the two four-membered rings, which has been found to be 123°.[4] This flap angle is considerably less than the 180° that is calculated for the equilibrium geometry of the free alkene,[15,17,18] but significantly larger than the corresponding flap angle in 3, which is found to be 114° ± 4°. Unlike bicyclo[2.2.0]hex-1(4)-ene, which is calculated to be planar, albeit with a small force constant for pyramidalization at the doubly bonded carbons,[17] 2 is computed to have a highly pyramidalized equilibrium geometry.[15]

Acknowledgment. We thank the National Science Foundation and the Department of Energy for support of this work and Professors James M. Mayer and Nancy M. Doherty for helpful discussions.

Supplementary Material Available: Details of data collection and refinement and tables of crystal parameters, bond lengths and angles, torsional angles, and least-squares planes for 3 (10 pages); tables of observed and calculated structure factors for 3 (10 pages). Ordering information is given on any current masthead page.

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Detection of an Alkyl Ethylene Complex during Ethylene Polymerization by a Co(III) Catalyst. Energetics of the β-Migratory Insertion Reaction

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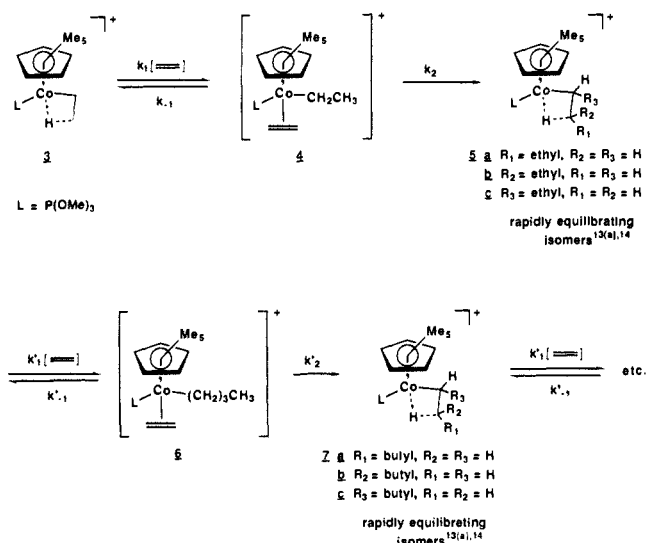Annandale, New Jersey 08801*

The mechanism of carbon–carbon bond formation in transition-metal-catalyzed olefin polymerization reactions is thought to be a β-migratory insertion reaction occuring via an intermediate alkyl olefin complex, 1 → 2 → 1′ (the Cossee–Arlman mechanism).[1-11] Although the stepwise polymerization of ethylene (and
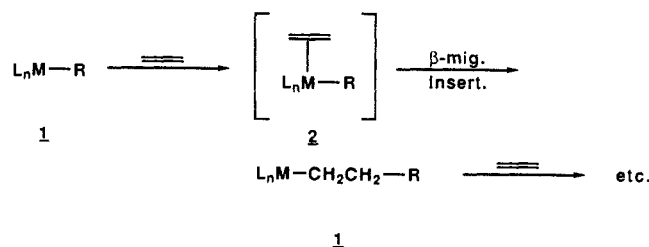
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Scheme I

L = P(OMe)₃

5 a R₁ = ethyl, R₂ = R₃ = H
  b R₂ = ethyl, R₁ = R₃ = H
  c R₃ = ethyl, R₁ = R₂ = H

rapidly equilibrating isomers[13(a),14]

7 a R₁ = butyl, R₂ = R₃ = H
  b R₂ = butyl, R₁ = R₃ = H
  c R₃ = butyl, R₁ = R₂ = H

rapidly equilibrating isomers[13(a),14]

other alkenes) in homogeneous systems has been studied spectroscopically,[3-6,8b,12] intermediate alkyl ethylene complexes have not been detected. Thus, activation energies for the β-migratory insertion reactions of alkyl olefin complexes in polymerizing systems are unknown. We report here spectroscopic detection of an intermediate cobalt alkyl ethylene complex during ethylene polymerization by a Co(III) catalyst together with a kinetic study which allows estimation of $\Delta G^{\ddagger}$ for the β-migratory insertion reaction.

The Co(III) complex $C_5Me_5(P(OMe)_3)CoCH_2CH_2$-μ-$H^+$ (3), has been previously shown to function as an ethylene polymerization catalyst.[13] On the basis of low-temperature ^1H and ^{13}C NMR studies of the polymerization, the mechanism shown in Scheme I was proposed. Agostic species 3, 5a–c, 7a–c, etc. are the "resting state" of the catalyst and were the only species that

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