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Evidence for the Formation of the $(Ph_3P)_2Pt$ Complex of 3,7-Dimethyltricyclo[3.3.0.$0^{3,7}$]oct-1(5)-ene, the Most Highly Pyramidalized Alkene in a Homologous Series. Isolation and X-ray Structure of the Product of the Ethanol Addition to the Complex

Fanitsa A. Theophanous,[†] Anastasios J. Tasiopoulos,[†] Athanassios Nicolaides,*[,†] Xin Zhou,[‡] William T. G. Johnson,[§] and Weston Thatcher Borden[‡,§]

Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus, Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203-5070, and Department of Chemistry, University of Washington, P.O. Box 351700, Seattle, Washington 98195-1700

athan@ucy.ac.cy

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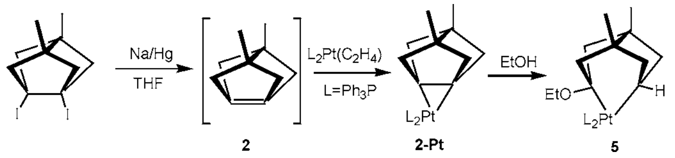
ABSTRACT



Attempts to isolate the $(Ph_3P)_2Pt$ complex of the highly pyramidalized olefin 3,7-dimethyltricyclo[3.3.0.$0^{3,7}$]oct-1(5)-ene 2 by generation of 2 in the presence of $(Ph_3P)_2PtC_2H_4$, followed by crystallization of the complex (2-Pt) from THF–ethanol, resulted in the isolation of the adduct of 2-Pt with ethanol (5). Calculations confirm that addition of alcohol across the C1–C5 bond is more favorable in 2-Pt than in the corresponding $(Ph_3P)_2Pt$ complexes of less pyramidalized olefins, despite the stronger Pt–C bonds in 2-Pt.

During the past 40 years, the synthesis and study of pyramidalized alkenes has been pursued in many different laboratories.[1] At the University of Washington, we focused on the preparation and investigation of the homologous series of pyramidalized alkenes **1** because this series offers a systematic way of increasing the pyramidalization of the C=C double bond by decreasing the number, *n*, of CH_2 groups in the methylene chain.[1,2] As the pyramidalization increases, so does the reactivity of the π bond.

For example, olefin **1**, $n = 3$, although very sensitive to oxygen, is isolable at room temperature.[3] However, the olefins with $n = 1$ and 2 could only be matrix isolated.[4a,d]

[†] University of Cyprus.

[‡] University of North Texas.

[§] University of Washington.

(1) Reviews: (a) Borden W. T. *Chem. Rev.* **1989**, *89*, 1095−1109. (b) Vázquez, S.; Camps, P. *Tetrahedron* **2005**, *61*, 5147−5208.

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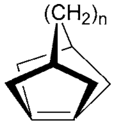
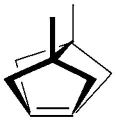
10.1021/ol060994j CCC: $33.50

Derivatives **2**−**4** of **1**, $n = 0$, have not even been matrix isolated, and their successful generation had to be inferred from isolation of dimers and products of chemical trapping by Diels−Alder reactions with dienes.[4e,h]



1



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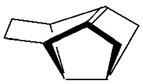

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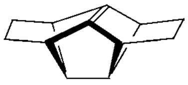


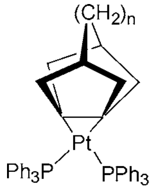
4

Molecules containing highly reactive π bonds can be stabilized by complexation with $(Ph_3P)_2Pt$.[5] Indeed, $(Ph_3P)_2$-Pt complexes of pyramidalized alkenes **1**, $n = 1-3$, have been isolated, and these complexes (**1-Pt**, $n = 1-3$) proved stable enough to be characterized by NMR spectroscopy and by X-ray crystallography.[6] The nature of the bonding between the alkenes and platinum in **1-Pt**, $n = 1-3$, has been studied computationally.[7] The calculations found that as pyramidalization of the uncomplexed alkene increases, so does the exothermicity of complex formation.

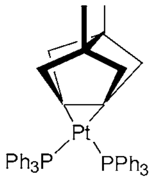
The computed strengthening of the Pt−C bonds in the complex with increasing olefin pyramidalization was shown to be largely due to better back-bonding between the metal and the alkene. The major electronic effect of double bond pyramidalization is to lower the energy of the π^* LUMO,[1,3] thus making it a better acceptor of electron density from the metal fragment.[7] The experimental results from the spectroscopic and X-ray studies of complexes **1-Pt**, $n = 1-3$, were found to support this theoretical picture.[6]

Since alkene **1**, $n = 0$, is the most highly pyramidalized member of the homologous series **1**, $n = 0-3$, it has the lowest LUMO in the series. Therefore, **1-Pt**, $n = 0$, is predicted to have the largest alkene−$Pt(Ph_3P)_2$ binding energy. However, although complexes **1-Pt**, $n = 1-3$, have been prepared and studied,[6] neither **1-Pt**, $n = 0$, nor the $(Ph_3P)_2Pt$ complexes of olefins **2**−**4** are known. In fact, attempts in two different laboratories to isolate **2-Pt**, the $(Ph_3P)_2Pt$ complex of the 3,7-dimethyl derivative of **1**, $n = 0$, have been unsuccessful.[1b,8]

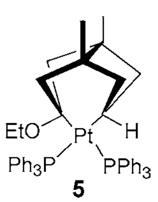
In this paper, we describe another attempt to isolate **2-Pt**. Although this attempt was also unsuccessful, our experiments did lead to the spectroscopic detection of **2-Pt** and to the isolation of **5**, the product of ethanol addition across the C3−C7 bond of complex **2-Pt**. We provide computational results which rationalize our findings that, although the Pt−C bonds in **1-Pt**, $n = 1-3$, are calculated to be weaker than the Pt−C bonds in **2-Pt**, the former complexes are isolable,[6] whereas the latter complex is not.



1-Pt



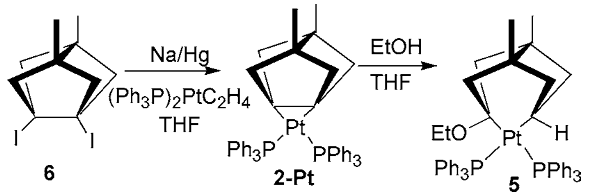
2-Pt



5

The diiodide precursor (**6**) of **2** was prepared following literature procedures.[9] Using the same reaction conditions that had led previously to the isolation of **1-Pt**, $n = 1-3$,[6] a THF solution of diiodide **6** was reduced with sodium amalgam in the presence of $(Ph_3P)_2PtC_2H_4$ (Scheme 1).[10]

Scheme 1. Reduction of **6** in the Presence of $(Ph_3P)_2PtC_2H_4$



The ^{31}P NMR spectrum of the crude product showed a peak at δ 32.40 ppm with two satellites, due to the ^{195}Pt isotope ($^1J_{Pt-P} = 2850$ Hz). The ^{195}Pt NMR showed a peak at −4956.6 ppm with essentially the same (2847 Hz) coupling constant to ^{31}P.[11,12] The observed chemical shifts are in the right range for the formation of **2-Pt**, as indicated by the ^{31}P and ^{195}Pt chemical shifts of the **1-Pt**, $n = 1-3$ complexes.[6] In addition, a least-squares fit between the computed pyramidalization angles[13] and the observed Pt−P coupling constants in the corresponding $(Ph_3P)_2Pt$ complexes (**1-Pt**, $n = 1-3$) predicts $^1J_{Pt-P} = 2745$ Hz for **1-Pt**, $n = 0$. This extrapolated value is within 4% of the one actually measured in **2-Pt**, and the two values agree to within 0.5% if the calculated pyramidalization angles in the free alkenes are used in obtaining the extrapolated value.

Camps, P.; Luque, F. J.; Orozco, M.; Pérez, F.; Vázquez, S. *Tetrahedron Lett.* **1996**, *37*, 8605−8608. **3**: (g) Camps, P.; Font-Bardia, M.; Méndez, N.; Pérez, F.; Pujol, X.; Solans, X.; Vázquez, S.; Vilalta, M. *Tetrahedron* **1998**, *54*, 4679−4696. **4**: (h) Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 774−776.

(5) (a) Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 685−686. (b) Godleski, S. A.; Gundlach, K. B.; Valpey, R. S. *Organometallics* **1985**, *4*, 296−302. (c) Bennett, M. A. *Pure Appl. Chem.* **1989**, *61*, 1695−1700. (d) Jason, M. E.; McGinnety, J. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1974**, *96*, 6532−6533.

(6) (a) Kumar, A.; Lichtenhan, J. D.; Critchlow, S. C.; Eichinger, B. E.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 5633−5634. (b) Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhardt, D. M.; Borden, W. T. *Organometallics* **1995**, *14*, 3475−3485.

(7) (a) Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 1912−1914. (b) Yates, B. F. *J. Organometallic Chem.* **2001**, *635*, 142−145.

(8) Johnson, W. T. G. Ph.D. Thesis, University of Washington, 1999.

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(10) Computational and experimental details, including those of the X-ray crystallography, are included in the Supporting Information.

(11) On our spectrometer, the observed ^{195}Pt chemical shift is given with reference to K_2PtCl_4. On the same instrument, the ^{195}Pt chemical shift of $(Ph_3P)_2PtC_2H_4$ is measured as δ −5146.5 ppm. With this reference, the ^{195}Pt chemical shifts of complexes **1**, $n = 1-3$,[6] become δ −5058.5, −5105.5, and −5092.5 ppm, respectively. Similarly our observed ^{31}Pt chemical shift of $(Ph_3P)_2PtC_2H_4$ is δ 35.83 ppm.

(12) The ^1H and ^{13}C NMR spectra of the crude product are not easily amenable to interpretation, presumably due to the presence of impurities. However, in the ^1H NMR spectrum the resonances at δ2.26 (d of d, $J = 26.0$ and 7.8 Hz) and 1.88 ($J = 7.8$ Hz) can almost certainly be assigned to the methylene protons of **2-Pt**.[6, 8] The splitting of 26.0 Hz in the lower field resonance is attributable to ^{195}Pt−H coupling.

(13) Using the computational methodology in refs 16−20 (vide infra).

The NMR spectra of the crude reaction product suggest that **2-Pt** is indeed formed. However, efforts to crystallize **2-Pt** by slow addition of ethanol to the THF solution of the crude product[6b] proved unsuccessful. Although a small amount of crystalline material was isolated, it was shown by X-ray crystallography to be **5** (Figure 1), the adduct expected to be formed from addition of ethanol across the strained C−C bond of the three-membered ring in **2-Pt**.[10,14] Since **1-Pt**, $n = 1-3$ can be recrystallized from ethanol/THF, formation of **5** by addition of ethanol to **2-Pt** was surprising, but not unprecedented. In 1974, Wiberg et al. reported that **8** is formed by addition of ethanol to **7-Pt**, the $(Ph_3P)_2$Pt complex of bicyclo[2.2.0]hex-1(4)-ene (**7**) (Scheme 2).[5d,14,15]

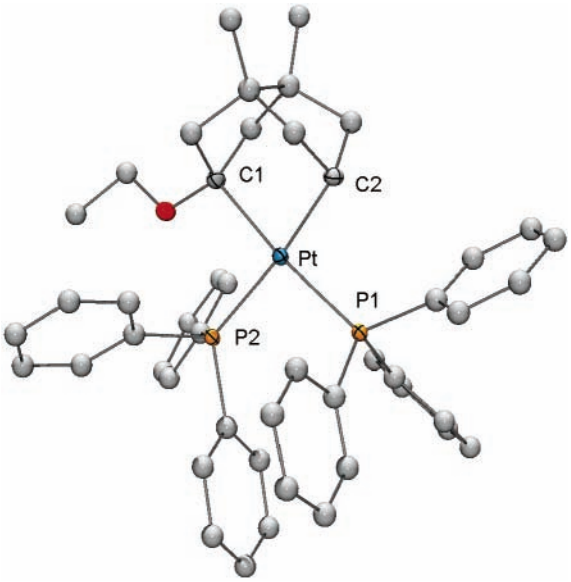
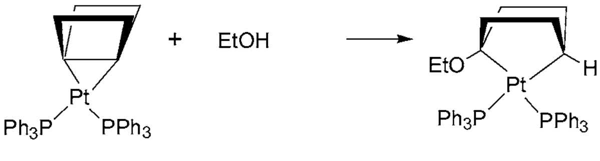


Figure 1. X-ray crystal structure of **5**.

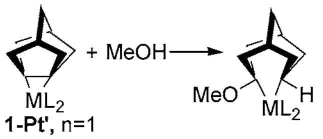
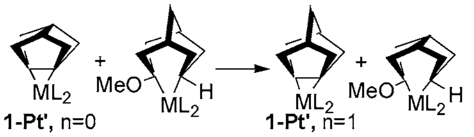
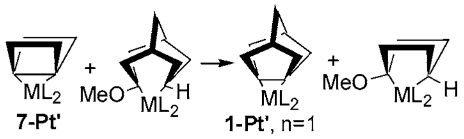
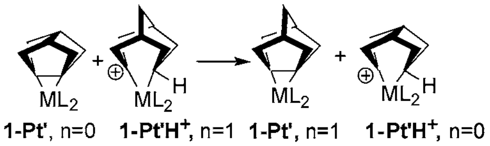
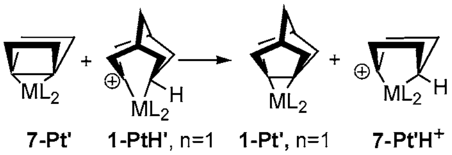
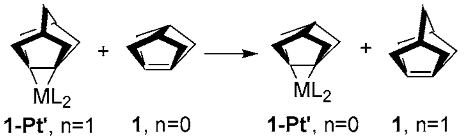
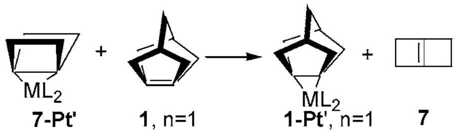
Scheme 2. Ethanolysis of **7-Pt**



7-Pt **8**

A reasonable hypothesis to explain the addition of ethanol to both **2-Pt** and **7-Pt**, but not to **1-Pt**, $n = 1$, is that considerably more strain is released by breaking the C−C bonds in the three-membered rings of the first two complexes than by breaking the analogous C−C bond in the third. To test this explanation, we have performed B3LYP calculations[10,16,17] using the platinum pseudopotential and basis set of Stevens et al.[18] and the Dunning−Huzinaga polarized, double-ζ, D95** basis set for all other atoms.[19,20]

Table 1. Computed Enthalpies (kcal/mol) for Reactions 1−7

	Reaction	Δ*H*
1	 + MeOH → MeO ML2 H **1-Pt′**, n=1	-18.3
2	 **1-Pt′**, n=0 + MeO ML2 H → **1-Pt′**, n=1 + MeO ML2 H	-30.3
3	 **7-Pt′** + MeO ML2 H → **1-Pt′**, n=1 + MeO ML2 H	-34.4
4	 **1-Pt′**, n=0 + **1-Pt′H⁺**, n=1 → **1-Pt′**, n=1 + **1-Pt′H⁺**, n=0	-20.5
5	 **7-Pt′** + **1-PtH′**, n=1 → **1-Pt′**, n=1 + **7-Pt′H⁺**	-15.2
6	 **1-Pt′**, n=1 + **1**, n=0 → **1-Pt′**, n=0 + **1**, n=1	-14.2
7	 **7-Pt′** + **1**, n=1 → **1-Pt′**, n=1 + **7**	-17.5

[a] M = Pt, L = PH_3. **1-Pt′**, $n = 0$, is the computational model for **2-Pt′** and by extension of **2-Pt**.

For the sake of computational simplicity, the triphenylphosphine groups in these three complexes were replaced

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[14] The X-ray structure of **5** shows that the longer C−Pt bond (by 0.032 Å) in **5** is between Pt and the carbon which carries the ethoxy group. This is the opposite ordering of Pt−C bond lengths from that reported for **8**.[5d,15] A surprisingly large difference is also found between the C−O bond lengths in **5** (1.461 Å) and in **8** (1.57 Å).

[15] Jason, M. E.; McGinnety, J. A. *Inorg. Chem.* **1981**, *20*, 4000−4003.

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[17] Lee, CT.; Yang, W.; Parr, R. G. *Phys Rev. B* **1988**, *37*, 785−789.

[18] Stevens, W. J.; Krauss, M.; Bausch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630.

[19] Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1−28.

[20] Calculations were performed with Gaussian 03, Revision C.02: Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2004.

by phosphines (PH_3) with unpolarized basis functions on the hydrogens. In addition, methanol was substituted for ethanol; and calculations were performed on **1-Pt′**, $n = 0$, rather than on **2-Pt′**.[21] The computational results are summarized in Table 1.

The addition of methanol to **1-Pt′**, $n = 1$, was computed to be exothermic by 18.3 kcal/mol, but the addition of methanol to **1-Pt′**, $n = 0$, and to **7-Pt′** was computed to be even more exothermic, by 30.3 and 34.4 kcal/mol, respectively (Table 1, reactions 1−3). Presumably, much larger amounts of strain are released upon cleavage of the C−C bond in the three-membered rings of **1-Pt′**, $n = 0$, and of **7-Pt′** than upon cleavage of the C−C bond in the three-membered ring of **1-Pt′**, $n = 1$. To the extent that these larger exothermicities translate into faster reaction rates, the computational results in Table 1 provide a rationalization for why **2-Pt** and **7-Pt** undergo the alcoholysis reaction; but **1-Pt**, $n = 1$, and its higher homologues (**1-Pt**, $n = 2$ and 3) do not.

The addition reaction is probably initiated by protonation of one of the carbons of the platinacyclopropane ring. Protonation of **1-Pt′**, $n = 0$, and of **7-Pt′** is calculated to be more exothermic than protonation of **1-Pt′**, $n = 1$, by 20.5 and 15.2 kcal/mol, respectively (Table 1, reactions 4 and 5).

Combined with the results for the methanol addition reactions, the protonation enthalpies can be interpreted as showing that bridgehead ions **1-Pt′H**$^+$, $n = 0$, and **7-Pt′H**$^+$ are more strained than **1-Pt′H**$^+$, $n = 1$, by, respectively, 9.8 and 19.2 kcal/mol. The optimized geometries of the three carbocations reveal that the origin of the differences between their strain energies resides in the deviations from planarity at the bridgehead carbocationic centers. Based on the calculated angles between the C^+−Pt bond and the $C-C^+-C$ plane, the carbocationic carbons in **1-Pt′H**$^+$, $n = 1$, **1-Pt′H**$^+$, $n = 0$, and **7-Pt′H**$^+$ are computed to be nonplanar by, respectively, 19.8°, 26.7°, and 37.4°. The carbocation strain energies obviously increase with the degree to which the carbocationic centers are forced to be nonplanar.

We also computed the enthalpies of $(H_3P)_2Pt$ binding to alkenes **1**, $n = 0$, and **7**, relative to alkene **1**, $n = 1$. The $(H_3P)_2Pt$ binding enthalpy of **1**, $n = 1$, is calculated to be 14.2 kcal/mol less than that of the more highly pyramidalized **1**, $n = 0$, alkene but 17.5 kcal/mol more than that of planar **7** (Table 1, reactions 6 and 7).[7b]

Clearly, the calculated strengths of the Pt−C bonds in the $(H_3P)_2Pt$ complexes of alkenes **1**, $n = 0$, **1**, $n = 1$, and **7** are unrelated to the calculated enthalpy changes for methanol addition to the C−C bonds of the platinacyclopropane rings of the complexes. Thus, these computational results provide a rationalization for our experimental finding that **1-Pt**, $n = 0$, which should have considerably stronger Pt−C bonds than **1-Pt**, $n = 1$, nevertheless adds ethanol across the C−C bond of the platinacyclopropane ring, whereas **1-Pt**, $n = 1$, does not. Our calculations on models for these three complexes show that the relative strengths of the Pt−C bonds in these platinacyclopropanes are poor predictors of the relative strengths of the C−C bonds in the three-membered rings.

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Supporting Information Available: Complete list of authors for ref 20, spectroscopic data for new compounds, coordinates and energies of molecules on which calculations were performed, and experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] The substitution of PH_3 for PPh_3 is indicated in the text by using a prime in the symbol for each complex. For example, **2-Pt** stands for the $(Ph_3P)_2Pt$ complex of olefin **2**, whereas **2-Pt′** indicates the $(H_3P)_2Pt$ complex.