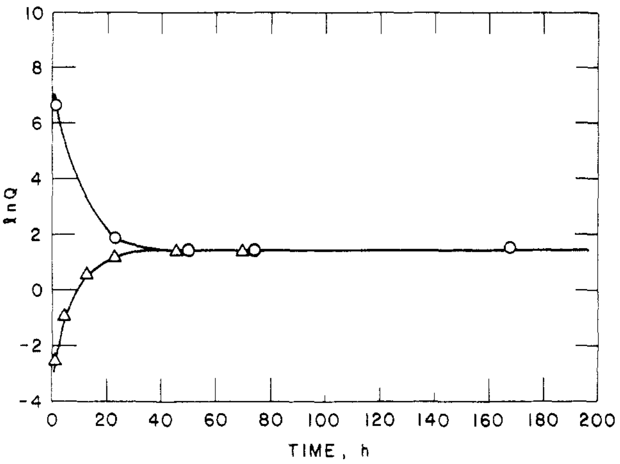

Figure 1. The natural logarithm of the experimental reaction quotients, $Q = [Bu_3SnO_2CH]/[Bu_3SnH]\cdot P_{CO_2}$, vs. time in tetrahydrofuran solution at 150 °C: △, $[Bu_3SnH]_i = 0.29$ M, $[CO_2]_i = 4.5$ atm; ○, $[Bu_3SnO_2CH]_i = 0.29$ M.

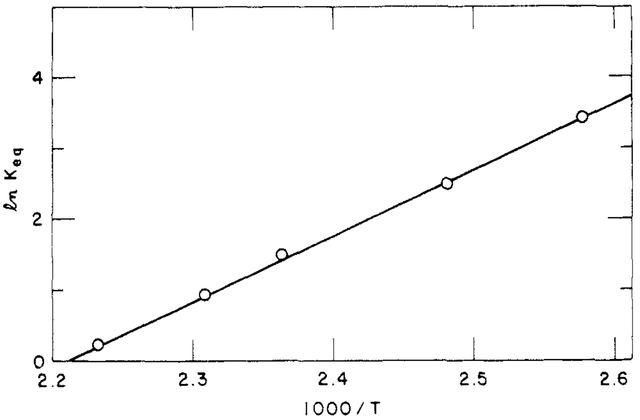

Figure 2. The natural logarithm of the equilibrium constants for tributyltin hydride addition to carbon dioxide in tetrahydrofuran solution vs. the inverse of the temperature over the range 115–175 °C.

Our recent involvement in formate ion disproportionation reactions[6] and a literature report on the synthesis of tin hydride[7] suggested that the tributyltin system (eq 5)

$$Bu_3SnH + CO_2 \rightleftharpoons Bu_3SnO_2CH \qquad (5)$$

might be sufficiently well behaved[8] to obtain accurate equilibrium data. Indeed, the results obtained in tetrahydrofuran solution at 150 °C in Figure 1 (where the experimental reaction quotients[10] defined in eq 6 are plotted

$$Q = [Bu_3SnO_2CH]/[Bu_3SnH]\cdot P_{CO_2} \qquad (6)$$

vs. time) demonstrate that the same equilibrium mixture is obtained by starting with either carbon dioxide plus hydride, triangles, or the corresponding formate ion, circles. Analysis of the temperature dependence of the equilibrium constants thus obtained over the interval 115–175 °C according to the van't Hoff equation in Figure 2 yields $\Delta H = -18.3 \pm 0.2$ kcal mol^{-1} and $\Delta S = -20.2 \pm 0.2$ cal mol^{-1} deg^{-1} from the slope and intercept, respectively. The entropy change is consistent with a condensation reaction which consumed 1 equiv of gas.[12] Interestingly, the enthalpy change for the hydride addition to carbon dioxide (eq 5) is remarkably close to the analogous addition to an olefin[13] (eq 7) for which $\Delta H = -21$ kcal. More important

$$(i\text{-Bu})_2Al\text{-}H + CH_2 = C(CH_3)_2 \rightleftharpoons Al(i\text{-Bu})_3 \qquad (7)$$

however, the enthalpy change for the partial reduction of carbon dioxide according to eq 5 is indeed quite favorable *despite the fact that carbon dioxide is the thermodynamic* end product of many facile reactions. Therefore, carbon dioxide may be a highly reactive component serving to control a steady-state formate ion[14] concentration even in processes which do not result in a net consumption of carbon dioxide. For example, at 200 °C a carbon dioxide partial pressure of only 2 atm is sufficient to maintain roughly equal concentrations of tributyltin formate and tributyltin hydride.[15] It is hoped that by studying homogeneous systems such as that in eq 5 a better understanding of the process in eq 2 may be obtained.[16]

Acknowledgment. Support for this work was provided by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. We thank Professor J. Halpern for helpful discussions and John J. Heiberger for invaluable assistance in the experimental work.

Registry No. Bu_3SnH, 688-73-3; CO_2, 124-38-9; Bu_3SnO_2CH, 5847-51-8.

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[6] (a) Klingler, R. J.; Rathke, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 7650. (b) Klingler, R. J.; Rathke, J. W. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1984**, *29*, 596.

[7] Ohara, M.; Okawara, R. *J. Organomet. Chem.* **1965**, *3*, 484.

[8] A 300-mL Autoclave Engineers vessel was modified such that all components which contact the solution are made of glass. Tributyltin hydride is decomposed to dihydrogen and hexabutylditin on the surface of metals.[9]

[9] Birham, E. R.; Javora, P. H. *Inorg. Synth.* **1970**, *12*, 53.

[10] Tributyltin hydride and tributyltin formate were analyzed by measuring the Sn— and C=O stretching frequencies[11] at 1804 and 1653 cm^{-1}, respectively, with a Perkin-Elmer Model 1500 FTIR. Carbon dioxide was determined by gas chromatography on a 3.5-ft spherocarb column at 100 °C.

[11] Hester, R. *J. Organomet. Chem.* **1970**, *23*, 123.

[12] Hughes, E. A. M. "Chemical Statics and Kinetics of Solutions"; Academic Press: New York, 1971; p 45, 69.

[13] Egger, K. W. *J. Am. Chem. Soc.* **1969**, *91*, 2867.

[14] Recently it has been shown that formate ion is catalytically disproportionated to methanol, carbon monoxide, and carbonate ion with a variety of metal oxide catalysis.[6]

[15] While this is the same carbon dioxide partial pressure which was reported to result in a maximum methanol synthesis rate,[2a] the only clear agreement is that carbon dioxide increases the rate of methanol production over CuO/ZnO catalysts[2b] with syngas in eq 2.

[16] The mechanism for the addition of tributyltin hydride to activated olefins and quinones has been reported[17] and will be compared to that for the reaction in eq 5.

[17] Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

A Novel Reactivity in the Reaction of Cycloheptatetraene with $Pt(PPh_3)_3$

William R. Winchester, Marian Gawron, Gus J. Palenik,* and W. M. Jones*

University of Florida, Department of Chemistry
Gainesville, Florida 32611

Received March 12, 1985

Summary: A number of allene complexes of $(PPh_3)_2Pt$ have been reported, but in no case has further reaction to form a metallocyclopentane been reported. Two equivalents of cycloheptatetraene react with $(PPh_3)_3Pt$ to form a metallocyclopentane which has been characterized by spectra and X-ray structure analysis. Benzocycloheptatetraene reacts in a like manner. The regiochemistry of this reaction is novel and is not consistent with predictions based on EHMO calculations. It is proposed that the dimerization step has much radical character.

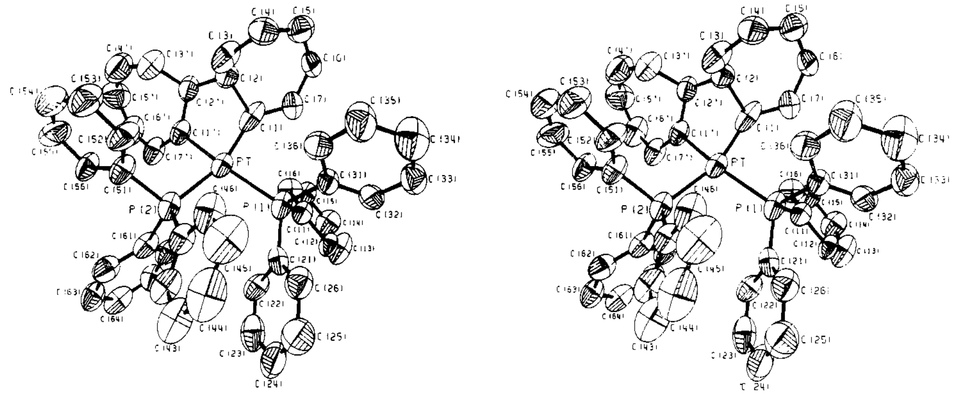
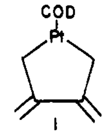


Figure 1. A stereoview of $[(C_6H_5)_3P]_2Pt(C_{14}H_{12})$ showing the atomic numbering and thermal ellipsoids.

Although a number of (allene)$(Ph_3P)_2Pt$ complexes have been reported,[1] to date no case has appeared in which a second allene added to give a metallocyclopentane. In fact, the only Pt(0) induced dimerization of allene is that of Stone and co-workers,[2] who found that treatment of $(COD)_2Pt$ (COD = 1,5-cyclooctadiene) with allene gave 1. It



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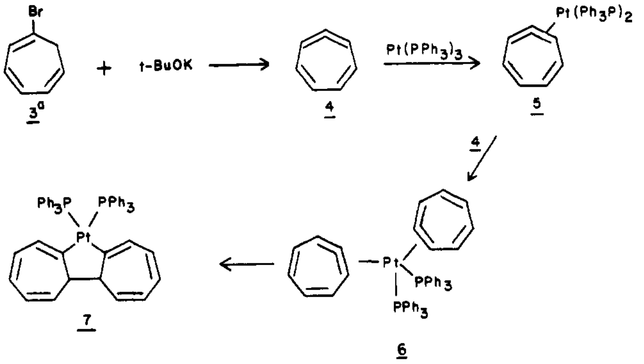
was therefore a surprise when we found that treatment of $(Ph_3P)_3Pt$ (2) with 2 equiv of 3 or 8 in the presence of an excess of *t*-BuOK gave the metallocyclopentanes 7 and 9, respectively. The structures of these complexes are based on analyses (in one case) and ^1H, ^{13}C, and ^{31}P NMR spectra.[3]

In addition, a single crystal X-ray structure (Figure 1) was determined for 7. Crystals of 7 were grown from benzene/EtOH in a refrigerator. The majority of the crystals were imperfect and appeared to contain internal cracks. A small fragment (0.09 × 0.10 × 0.12 mm) which appeared to be clear and fault-free was coated with Apiezon T and placed on a glass fiber. The crystal was triclinic with a = 13.176 (4) Å, b = 11.709 (4) Å, c = 15.757 (5) Å, α = 71.55 (3)°, β = 67.53 (3)°, and γ = 74.03 (3)°. The cell volume is 2098 Å^3, and, with two molecules of $C_{50}H_{42}P_2Pt$, the density is 1.425 g cm^{-3}. Intensity data were measured at a scan rate of 12°/min because of the large cell and air sensitivity of the crystal. A total of 5979 reflections were measured of which 3945 had $I \geq 2\sigma(I)$ and were used in the subsequent analysis. During the data collection, the intensities of the four standard reflections decreased with time, requiring scale factors ranging from 1.000 to 1.288 to place the data on the same relative scale.

Scheme I



a. Mixture of isomers

The structure was solved by the heavy-atom method. The Pt–P peaks in the Patterson were consistent with the space group $P\bar{1}$. Successive Fourier syntheses revealed the entire molecule. Refinement by full-matrix least-squares methods, with anisotropic thermal parameters for the Pt and P atoms, reduced R (the usual residual) to 0.116. Further refinement with anisotropic thermal parameters for all the non-hydrogen atoms reduced R to 0.107. Although the basic structure is certainly correct, the high R value is unsettling. Undoubtably, the poor quality of the small crystals, the fast scan rate, and the deterioration of the standard reflections have combined to yield a less than ideal data set.

The molecule is illustrated in the figure and consists of a Pt atom σ-bonded to two carbon atoms of the bicycloheptatriene ligand and two triphenylphosphine groups. The Pt atom is in the center of a distorted nonplanar arrangement of the P1, P2, C1, and C1′ atoms. The platinole ring is twisted with a mirror plane through C1. The torsion angle C3–C2–C2′–C3′ indicates a cis arrangement of the two sp^3 carbon atoms (C2 and C2′). The average C–C distance for bonds not involving C2 and C2′ is 1.40 (3) Å. A more accurate data set is required to determine whether the double bonds in the cycloheptatriene rings are

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(1) Jacobs, T. L. "The Chemistry of Allenes"; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. II, Chapter 4.

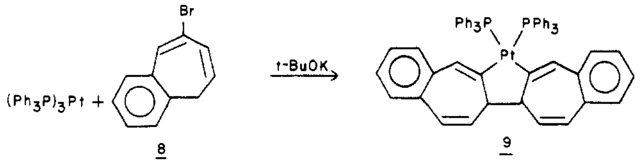
(2) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; *J. Chem. Soc., Dalton Trans.* **1978**, 1839.

(3) In a typical experiment, in a drybox, tris(triphenylphosphine)platinum (1.75 g, 1.78 mmol) and potassium *tert*-butoxide (0.60 g, 5.33 mmol) were weighed into a dry Schlenk tube equipped with a magnetic stirrer. This mixture was dissolved in 15 mL of dry THF and the Schlenk tube sealed with a septum and removed from the drybox. The reaction vessel was connected to a nitrogen line and cooled to 0 °C. Bromocycloheptatriene (0.91 g, 5.33 mmol) in 0.5 mL of dry THF was added dropwise over 10 min. The mixture was stirred and allowed to slowly come to room temperature overnight. The resulting brown solution was filtered through Celite and evaporated to dryness. Trituration of the solid residue with hexane overnight gave 7: 1.48 g, 93%; mp 154–155 °C dec; IR (KBr) 3050 w, 3010 w, 1480 m, 1440 s, 1390 m, 1100 m, 740 m, 700 s, 520 s cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68 (t, $^3J_{PtH}$ = 43.5 Hz, 2 H), 5.65 (t, J_{PtH} = 58.5 Hz, 2 H), 5.75 (m, 2 H), 6.15 (m, 6 H), 6.66–7.4 (m, 30 H, Ph_3P); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.76 (t, $^2J_{PtC}$ = 118.95, C_7), 118.54, 123.64, 125.06 (C_3–C_5), 127.44 (vt, $^3J_{PC}$ = 4.4 Hz, Ph_3P, meta), 129.23 (s, Ph_3P, para), 132.39 (t, $^2J_{PtC}$ = 75 Hz, C_2), 133.58 (vd, $^1J_{PC}$ = 45 Hz, Ph_3P, ipso), 133.62 (C_6), 134.79 (vt, $^2J_{PC}$ = 5.7 Hz, Ph_3P, ortho), 157.62 (dd, $^2J_{P(cis)C}$ = 8.5 Hz, $^2J_{P(trans)C}$ = 105.12 Hz, C_1); ^{31}P NMR (41 MHz, $CDCl_3$) δ 25.7 (t, $^1J_{PtP}$ = 1960.5 Hz). Anal. Calcd for $C_{50}H_{42}P_2Pt$: C, 66.73; H, 4.71. Found: C, 67.25; H, 4.69. **9**: mp 140–146 °C dec; IR (KBr) 3050 w, 3000 w, 1585 m, 1475 s, 1435 s, 1383 w, 1310 w, 1180 w, 1090 m, 1000 m, 840 w, 740 s, 690 s cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 3.38 (t, $^3J_{PtH}$ = 28 Hz, H7), 5.4–6.4 (m, 6 H), 7.2–7.7 (m, Ph_3P, 30 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 57.3 (t, $^2J_{PtC}$ = 98.6 Hz), 123.15, 123.6, 124.6, 125.1, 125.9, 127.6 (d, $^3J_{PC}$ = 5.2 Hz, Ph_3P, meta), 129.4 (s, Ph_3P, para), 129.8, 130.0, 131.9, 132.6 (Ph_3P, ipso), 134.9 (m, Ph_3P, ortho), 137.6, 140.0, 168.6 (dd, $^2J_{P(cis)C}$ = 9.8 Hz, $^2J_{P(trans)C}$ = 103.8 Hz); ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 25.9 ($^1J_{PtP}$ = 1950.8 Hz). The $^1J_{PtC}$ coupling constant was not observed for 7 or for 9. However, it was observed (904.7 Hz) for the DIPHOS derivative of 7 prepared by refluxing 7 with DIPHOS in benzene.

localized between C1–C7, C3–C4, and C5–C6.

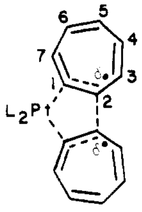
A reasonable pathway for formation of **7** is given in Scheme I. In this we propose dehydrobromination of **3** to give cycloheptatetraene which is trapped by **2** to give a π-complex which then reacts with a second equivalent of the allene to give the dimer.[4a,b]

The anomalous behavior of **4** and the allene from **8** is probably due in part to relief of ring strain which should accelerate both formation of the bis adduct **6** and closure to the metallocyclopentane **7**. However, it would appear that relief of strain alone is not sufficient to cause dimerization since reaction of 1,2-cycloheptadiene with either $(Ph_3P)_2Pt(ethylene)$[7] or $(Ph_3P)_3Pt$ gave only the allene complex; the latter even in the presence of a large excess of the allene.



Conjugation in cycloheptatetraene should also favor the dimerization by stabilizing **6**. MO calculations show that, relative to unstrained allenes, the HOMO of cycloheptatetraene is raised and its LUMO is lowered. Both should favor π-bond formation to Pt(0).

The regiochemistry of dimerization of **4** and the allene from **8** is also anomalous in that it is opposite to that normally found in allene dimerizations induced by group 8 metals.[8] Hoffmann has addressed the regiochemistry question for metal-induced dimerizations of alkenes and has suggested that it is usually dominated by the magnitude of the LUMO coefficients of the uncomplexes olefin (which, in turn, influences the HOMO coefficients in the complex).[9] Application of this theory to cycloheptatetraene dimerization predicts exactly the opposite regiochemistry from that observed. For cycloheptatetraene we therefore suggest that the dimerization step may have significant diradical character as in **10** and that stabilization of the incipient radical by conjugation with the double bonds dictates the regiochemistry and also accelerates the ring closure.[10]



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Acknowledgment. Support by the National Science Foundation is gratefully acknowledged. W.R.W. also acknowledges a fellowship from the Proctor and Gamble Co.; we thank the Center for Instructional Research Computing Activities, University of Florida, for a grant of computer time; and M.G. thanks the Graduate School of the University of Florida for a fellowship under the Polish Exchange Program with Adam Mickiewicz University, Poznân, Poland.

Registry No. 7, 97719-83-0; 8, 97719-86-3; 9, 97719-84-1; i, 97719-85-2; $(Ph_3P)_3Pt$, 13517-35-6; bromocycloheptatriene, 32743-67-2.

Supplementary Material Available: Tables of distances and bond angles, final positional parameters, and structure factors (31 pages). Ordering information is given on any current masthead page.

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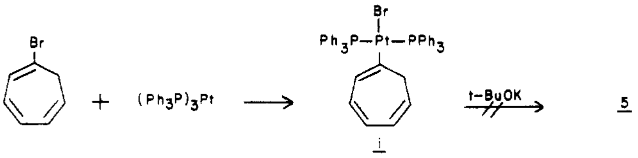
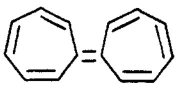
(4) (a) In principle, insertion to form **i** could occur which could then undergo elimination to give **5**.



However, **i**,[5] synthesized in a separate reaction, was found to be inert to *t*-BuOK under the above conditions. Also, implicit in this scheme is the assumption that dimerization occurs after complexation. Consistent with this is our finding the heptafulvalene **ii** is inert to **2**.[6] (b) **Note Added**



ii

in Proof: The π-complex **5** has now been isolated, characterized, and found to react with a second mole of **4** to give **7**.

(5) **i**: mp 216.0–216.5 dec; IR (KBr) 3050 w, 3010 w, 1571 w, 1505 m, 1480 m, 1430 s, 1385 m, 1180 m, 1100 s, 1030 m, 1000 m, 750 m, 700 s, 500 s, cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.23 (td, $^3J_{PtH}$ = 39 Hz, J_{HH} = 7.1 Hz, H7), 4.30 (dt, J = 6.84 Hz, J = 6.0 Hz, 1 H), 5.6 (t, J_{PtH} = 32 Hz, 1 H), 5.64 (s, 2 H), 6.0 (s, 3 H), 7.2 (Ph_3P, 18 H), 7.7 (Ph_3P, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.5 (C7), 115.4, 122.9, 124.58, 127.70 (t, $^3J_{PC}$ = 5.27 Hz, Ph_3P, meta), 130.1 (s, Ph_sP, para), 131.0 (t, $^2J_{PtC}$ = 46 Hz, Ph_3P, ipso), 14.3, 134.45, 135.2 (m, Ph_3P, ortho), 139.4 (C1); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.34 (t, $^1J_{HP}$ = 3215 Hz). Anal. Calcd for $C_{43}H_{37}Br_1P_2Pt_1$: C, 57.94; H, 4.15. Found: C, 57.76, H, 4.23.

(6) Cycloheptatetraene is known to dimerize to heptafulvalene. Waali, E. E.; Jones, W. M. *J. Org. Chem.* **1973**, *38*, 2573 and references cited therein.

(7) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

(8) (a) Ingrosso, G.; Immirizi, A.; Parri, L. *J. Organomet. Chem.* **1973**, *60*, c35. (b) Jolly, P. W.; Kruger, C.; Salz, R.; Skeutowski, J. C. *J. Organomet. Chem.* **1979**, *165*, c39.

(9) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.

(10) If simple allene dimerization is also diradicaloid in nature, the observed regiochemistry (which is opposite to **7** and **9**) would be expected since radicals typically add to the allene terminal carbon to give carbon vinyl radicals that are more stable than the perpendicular allyl radicals that would be formed from attack at the central carbon.

Intramolecular Coupling of η^2-Iminoacyl Functions at Group 4 Metal Centers

Stanley L. Latesky, Anne K. McMullen,
Gerald P. Niccolai, and Ian P. Rothwell*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

John C. Huffman

Molecular Structure Center, Indiana University
Bloomington, Indiana 47405

Received May 8, 1985

Summary: The intramolecular cis coupling of η^2-iminoacyl groups at Ti(IV) and Zr(IV) metal centers to produce chelating enediamide ligands has been shown to be facile. Evidence that coupled products can also be formed containing a trans arrangement of nitrogen atoms has also been obtained.