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Platinum Complexes of Cycloheptatrienylidene and Cycloheptatetraene

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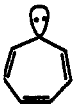
Hydride abstraction from *trans*-bromo[(1-η^1)-cyclohepta-1,3,5-trienyl]bis(triphenylphosphine)platinum, 8, with triphenylcarbenium fluroroborate gives a Pt(II) complex of C_7H_6 that exists exclusively in the carbene (tropylium ion) form 7. In contrast, the Pt(0) complex of C_7H_6 prefers the allene ground-state structure 6. Furthermore, the activation enthalpy for the conversion of 6 to its corresponding valence isomeric carbene form 10 must be at least 26.8 ± 1.3 kcal/mol. The latter was determined by ^1H NMR techniques which showed that, although exchange of H2 and H7 in 6 could be detected using spin saturation transfer, the mechanism of the interconversion is intermolecular.

Introduction

Monocyclic C_7H_6 (seven-membered ring) is a reactive intermediate that has elicited considerable interest among organic chemists.[1] In theory, it can exist in two valence isomeric forms: the carbene **1** and the allene **2**. Experimentally, the latter appears to be the ground state[1a,b,2] while the status of the former remains uncertain; it may be either a transition state or an energy minimum on the path connecting enantiomeric allenes.[1a,3]



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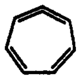

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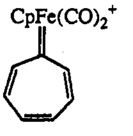
In recent years, we have become interested in the structure of transition metal complexes of monocyclic C_7H_6 and have found that the ground state varies with the metal; complexes of dicarbonylcyclopentadienyliron,[4] dicarbonylcyclopentadienylruthenium,[5] and pentacarbonyltungsten[4] all favor the carbene forms **3–5** while the bis(triphenylphosphine)platinum complex prefers the allene form **6**.[6] One straightforward explanation for this phenomenon is found in EHMO calculations[7] which predict that the structural preference of **3** rests primarily on the availability of a low-lying vacant atomic orbital on the metal that can be used to form the all important σ bond to the carbene carbon and that the bis(triphenylphosphine)platinum complex, **6**, prefers the allene structure, not because the metal is platinum but because it is d^{10} with no low-energy LUMO with a_1 symmetry. This suggests that the simple expedient of converting Pt(0) to Pt(II) may tip the balance in favor of the carbene structure. At this time we report the preparation of an example of a Pt(II) complex of C_7H_6 which does, indeed, prefer the carbene structure with no detectable trace of the allene form. We also report temperature-dependent fluxional studies on the Pt(0) allene complex **6** which indicate that the carbene form corresponding to **3–5** is not only thermally inaccessible but that the activation enthalpy for its isomerization to the carbene form must be greater than 26.8 kcal/mol. Theoretical reasons for these preferences are developed more fully than has previously appeared.



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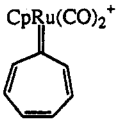

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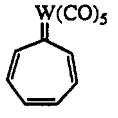

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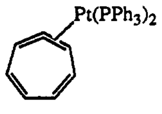

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Results

The Pt(II) carbene complex **7** was prepared by hydride abstraction from **8**. ^1H and ^{13}C NMR spectral data for the C_7H_6 ring of **7** are listed in Tables I and II along with comparison data for complexes **3–5**. For hydrogen assignments, the doublet at δ 8.89 ppm shows typical ^{195}Pt satellites and is therefore assigned to H_α. From a 2D COSY spectrum, H_β (which is buried under the aromatic peaks) and H_γ can be assigned chemical shifts of δ 7.42 and 8.09 ppm, respectively. Assignments of ^{13}C carbon resonances for C_α, C_β, and C_γ are based on a carbon–hydrogen

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[1] (a) For an excellent review, see: Johnson, R. P. *Chem. Rev.* 1989, *89,* 1111. (b) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* 1967, *89,* 3069. (c) Jones, W. M. *Acc. Chem. Res.* 1977, *10,* 353. (d) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chim.* 1980, *4,* 411. (e) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* 1984, *106,* 7973. (f) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* 1986, *108,* 1713. (g) Kuzaj, M.; Luerssen, H.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* 1986, *25,* 480. (h) Janssen, C. L.; Schaefer, H. F. *J. Am. Chem. Soc.* 1987, *109,* 5030. (i) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* 1987, *109,* 2456. (j) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* 1988, *110,* 501.

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[5] Lisko, J. R.; Jones, W. M. *Organometallics* 1986, *5,* 1890.

[6] Winchester, W. R.; Jones, W. M. *Organometallics* 1985, *4,* 2228.

[7] Winchester, W. R. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1985.

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Table I. ^1H NMR Data for Complexes 7, 3, 4, and 5[a]

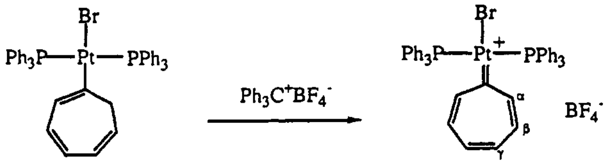
complex	H_α[b]	H_β	H_γ	ref
7	8.89 (11.7)	7.42	8.09	
3	10.01 (10.0)	8.1	8.48	4a
4	9.50 (10.0)	8.13	8.55	5
5	9.96 (10.0)	7.7[c]	8.1[c]	4a

[a] Phenyl resonances are omitted. [b] The numbers in parentheses are the $^3J_{H-H}$ coupling constants. [c] Assignments of these two resonances are tentative.

Table II. ^{13}C NMR Data for Complexes 7, 3, and 4[a]

complex	C_{carb}[b]	C_α	C_β	C_γ	ref
7	210.5	162.5	143.5	146.5	
3	242.3	170.0	138.2[c]	148.3[c]	4a
4	223.6	170.1	140.9	149.2	5

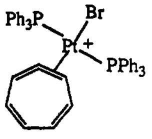
[a] Phenyl resonances are omitted. [b] C_{carb} represents the carbene carbon. [c] Assignments of these two resonances are tentative.



8 7 (1)

heteronuclear correlation 2D NMR spectrum. The carbene carbon at δ 210.5 ppm is distinguished by its large $^1J_{Pt-C}$ coupling constant (969 Hz). The ^{31}P NMR spectrum shows a singlet with platinum satellites ($^1J_{Pt-P}$ = 2777 Hz) as expected for a complex with C_2 symmetry (carbene structure with phosphines trans). The ^{195}Pt NMR spectrum shows a triplet at δ −4095 ppm (from Na_2PtCl_6).

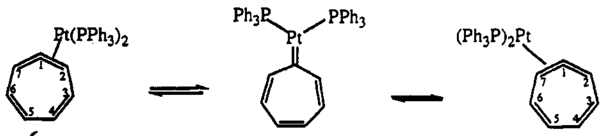
The ^1H NMR spectra of 7 at low temperature shows small upfield shifts of H_α and H_γ as the temperature decreases. For example, at −90 °C, the chemical shifts of H_α and H_γ are δ 8.73 and 8.03 ppm, respectively. Similar upfield shifts are also found in the ^{31}P NMR. However, there is no evidence that suggests that 7 may, in reality, be rapidly equilibrating allene complex 9.[8] This is discussed in more detail in the Discussion.



9

The allene structure of 6 has been rigorously proven in both solution[6] and the crystal.[9] In an attempt to determine the barrier to carbene formation in 6, its temperature-dependent NMR was studied. Evidence for migration of platinum between the allene double bonds (eq 2) was initially sought by coalescence studies. However, even when heated to the limit of its thermal stability (115 °C for a short time in toluene), no significant change in the ^1H NMR was observed.[10]

For thermally unstable compounds, spin saturation transfer (SST), in which one resonance is selectively irradiated (saturated or 180° inverted) and the effects of such irradiation on other resonances are monitored,[11] has an advantage over coalescence for studying fluxional processes because it can detect them at temperatures well below the coalescence temperature. This technique was therefore applied to 6, and indeed, at temperatures above 60 °C, transfer was observed from H2 (δ 3.41 ppm) to the ring hydrogen at δ 6.16 ppm (without loss of Pt–H coupling) but not the hydrogen at δ 4.97 ppm that had originally been assigned to H7.[6] As an example, the SST spectra at 80 °C are shown in Figure 1.



6 10 6 (2)

In an effort to ensure that the earlier reported hydrogen chemical shift assignments were correct, 2D COSY and NOE were applied. In the COSY spectrum (Figure 2), there is a crosspeak between H2 and the resonance at δ 6.16 ppm.[12] This suggests that H3 is at δ 6.16 ppm because three-bond coupling between H3 and H2 should be quite obvious. If this is correct, the original assignment of H7 at δ 4.97 ppm must also be correct. However, in apparent contradiction, a 6% NOE enhancement was found between H2 and the resonance at δ 4.97 ppm. No NOE effect could be detected between H2 and the resonance at δ 6.16 ppm. This result suggests that H3, which is closest in space to H2, should be at δ 4.97 ppm and H7 should be at δ 6.16 ppm. As a result of the contradictory results from 2D COSY and NOE, it became incumbent upon us to unequivocally assign all of the ring hydrogen resonances in 6. This was accomplished by deuterium labeling and 2D COSY NMR. Preparation of 6 deuterated uniquely at C2 and C7 is given in Scheme I. This complex shows no resonances at δ 6.16 and 3.41 ppm in its ^1H NMR spectrum and concomitant resonances in its ^2H NMR spectrum. This unequivocally confirms the chemical shift assignments indicated by the NOE result, i.e., H7 at δ 6.16 ppm and H2 at δ 3.41 ppm.[13] And the 2D COSY spectrum permits unequivocal assignments to the remaining hydrogens. Thus, at temperatures above 60 °C, H2 must transfer magnetization to H7 fast enough to be detected. Further studies showed that H3 transfers magnetization to H6 and H4 to H5.[14] All of the assigned magnetization transfers were confirmed by a NOESY spectrum at 80 °C.

Comprehensive data treatment for SST is quite complicated.[11] However, a reasonable estimate of the activation barrier for the fluxional process can be obtained by applying the approximation of Dahlquist et al.[15] From approximate rate constants at various temperatures, an

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[8] An interesting phenomenon is that the ^{195}Pt satellites of both H_α in the ^1H NMR and phosphorus in the ^{31}P NMR are broadened much more than the central peaks. As a result, at −90 °C these satellites are almost lost in the base line.

[9] Abboud, K. A.; Lu, Z.; Jones, W. M. *Acta. Crystallogr.* **1992**, *C48*, 909.

[10] Due to extensive coupling, proton resonances are too broad for meaningful line-broadening studies.

[11] Freeman, R. A. *Handbook of Nuclear Magnetic Resonance*; Longman Scientific & Technical: New York, 1988; p 198.

[12] This peak overlaps a peak at δ 6.19 ppm which was ultimately determined to be H5.

[13] The absence of a crosspeak between H2 and H3 in the COSY spectrum is due to almost perfect orthogonality between these two hydrogens.[9]

[14] In principle, the SST technique can also be applied to ^{13}C NMR spectra. However, this was not possible for 6 due to limited solubility and thermal instability.

[15] Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.

[16] The pulse sequence used here is completely different from the one used to detect fluxionality in 6, even though both experiments involve spin saturation transfer. This is discussed in detail in the Experimental Section.

[17] If the process were intramolecular, only the central peak of H7 (the ^{194}Pt and ^{196}Pt isotopomers) should appear.

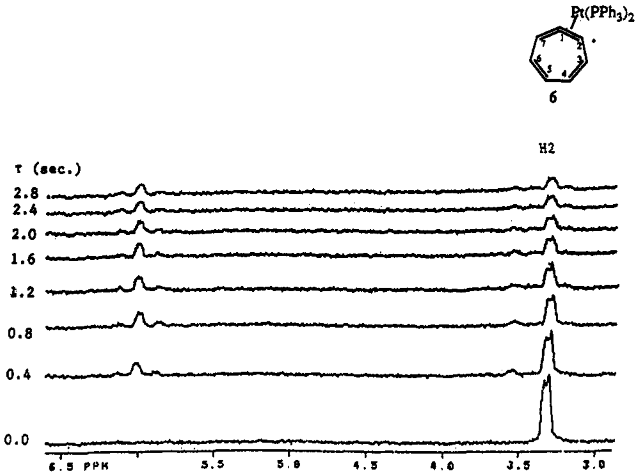


Figure 1. Difference spectra for spin saturation transfer in **6** at 80 °C with varying delay times. H2 is irradiated; saturation is transferred to the resonance at δ 6.16 ppm (H7).

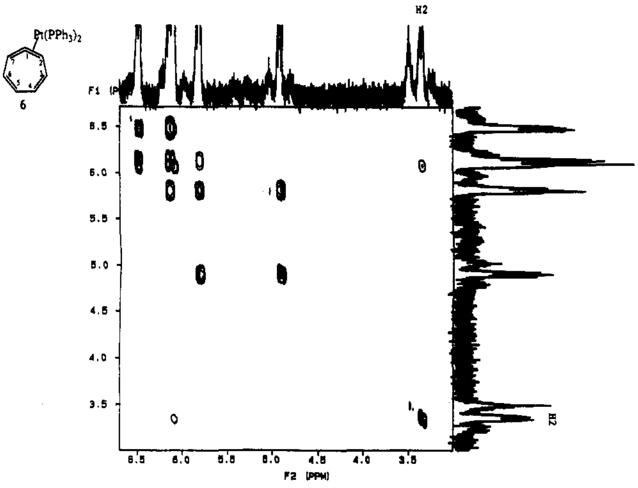
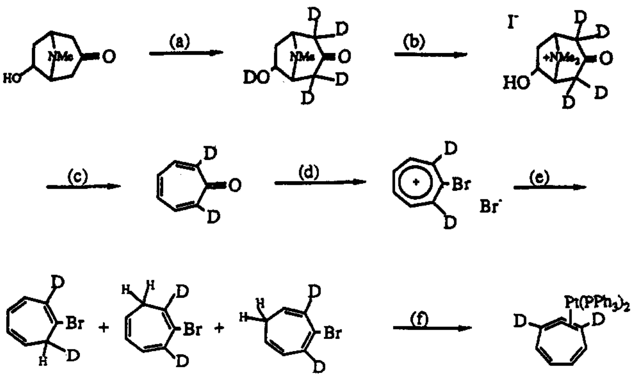


Figure 2. 2D COSY spectrum of complex **6** showing a crosspeak between H2 and the resonance at δ 6.16 ppm (H7).

Scheme I[a]



[a] (a) K_2CO_3, room temperature, D_2O, 24 h; (b) MeI, EtOH, 5 °C, 15 h; (c) $NaCO_3$, D_2O, 60 °C, 10 h; (d) BrOCCOBr, Et_2O, 0 °C; (e) $LiAlH_4$, Et_2O, room temperature, 2 h; (f) $Pt(PPh_3)_3$, *t*-BuOK, THF, room temperature, 8 h.

Arrhenius plot gave $\Delta H^{\ddagger} = 26.8 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger} = 15.1 \pm 1.3$ eu.

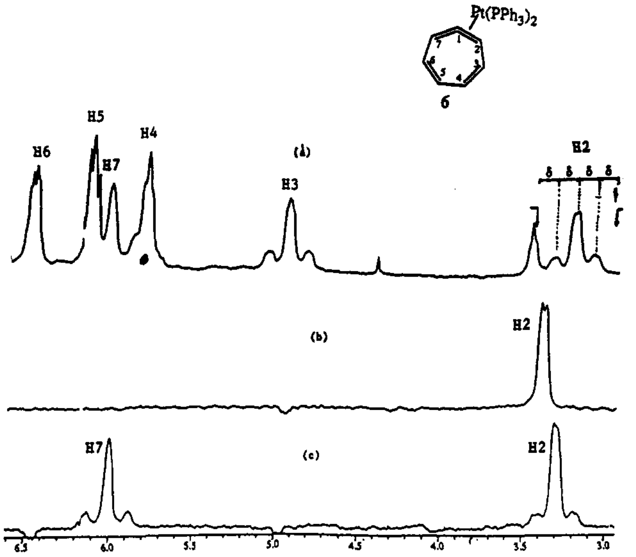
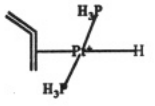


Figure 3. (a) C_7H_6 region of the ^1H NMR spectrum of **6** at 80 °C. (b) Difference spectrum when only the central peak of H2 is irradiated at room temperature. Note the NOE at δ 4.97 ppm (H3) and slight down-field shift of H2 at room temperature. (c) Difference spectrum when only the central peak of H2 is irradiated at 80 °C.

Fluxionality in **6** can occur by either an intramolecular or intermolecular process. To distinguish between these possibilities, advantage was taken of the origin of the apparent triplet for H2 (and H7) in the proton spectrum of **6** (see spectrum a in Figure 3). This triplet results from a mixture of isotopomers; a doublet from the ^{195}Pt isotopomer superimposed on a singlet from the ^{194}Pt and ^{196}Pt isotopomers. Since only the dissociation–recombination mechanism would lead to scrambling of isotopes between allene molecules, the ^1H resonance of H2 in the ^{194}Pt and ^{196}Pt isotopomers of **6** (the central peak) was selectively irradiated and the resonances for H7 were examined for saturation transfer. In such an experiment, intramolecular rearrangement should show transfer to only the central peak of H7 while dissociation–recombination would lead to saturation transfer to both the central peak and its satellites. The results of this experiment are shown in Figure 3. Spectrum a shows a portion of the proton spectrum (H2–H7) of **6** at 80 °C, a temperature at which magnetization transfer occurs. In this spectrum, the H2 singlet and its satellites are clearly visible. In spectrum b, the central peak of H2 is irradiated at room temperature and a difference spectrum is recorded. The purpose of this experiment was to determine a power level low enough to ensure no "spill-over" to the satellites. The temperature was then raised to 80 °C where saturation transfer is known to occur, and using the same power level, a spectrum was recorded (not shown) in which the sample was irradiated 0.116 ppm (which is equal to the chemical shift difference between the satellite peak and the central peak of H2) downfield from the low field satellite of H2 and upfield from the high field satellite. No detectable saturation of the satellite peaks of H2 was observed which confirmed the power setting as appropriate to avoid spill-over at the higher temperature where fluxionality occurs. Finally, spectrum c of Figure 3 shows a difference spectrum in which the central peak of H2 was irradiated at 80 °C using the same power level as in the previous experiments. Appearance of both central and satellite peaks for H7 requires isotope scrambling which, in turn, is only consistent with a dissociation–recombination mechanism. This conclusion was reenforced with a 2D NOESY experiment at 80 °C in which correlation between the satellites of H3 and its central peak were observed. This requires scrambling of isotopes at this temperature although it does not address fluxionality.[18] Finally, the more elegant ^{31}P 2D EXSY experiment which can be used to not only distinguish between inter- and intramolecular fluxional processes[19] but also provide rate constants[20] was attempted but were not successful because **6** could not tolerate the elevated temperature for the very long acquisition time required for data collection.

To explore reasons for differences in structural preferences for the Pt(0) and Pt(II) complexes of C_7H_6, the structures for **6**, **7**, **9**, and **10** were calculated by substituting PH_3 for PPh_3 and optimizing using the MM2 force field[21a] as extended by CAChe.[22b] It is possible to represent olefin–metal complexes three different ways within the CaChe MM2 implementation: (1) as a metallocyclopropane, (2) as a metal–olefin complex with weak but equivalent interactions to the two carbons, or (3) as a metal–olefin complex with a unique metal bond to the center of the olefin. These do not lead to equivalent structures, but for Pt(0) the metallocyclopropane representation appears to be the best and for Pt(II) the metal–olefin complex was best, based upon the comparison of the resulting structures with experiment.[22]

To compare the energies of the isomers, the extended Hückel method[23] was chosen, as implemented in the CAChe system. This method is not reliable for absolute energy differences of valence isomers, but trends should be followed. For Pt(II) the carbene complex is found to be 38 kcal/mol lower in energy than the allene complex, and for Pt(0) the allene is found to be 12 kcal/mol lower in energy (Figure 5). These correspond to the ground states that are found experimentally. To understand these preferences, the orbitals of the metal and organic fragments were examined. However, meaningful conclusions could not be reached due to the complexity of the resulting MO diagrams. Model compounds **11**–**14** were therefore studied. In these, C_3H_4 has been substituted for C_7H_6 and H for Br, which will have a slight destabilizing effect on the Pt(II) fragment LUMO. Interestingly, the lack of aromaticity in **12** and the lack of ring strain in **11** is sufficient to reverse the ordering of allene to carbene in the $Pt^{II}C_3H_4$ system relative to that of the $Pt^{II}C_7H_6$ system. However, the trends on going from Pt(0) to Pt(II) are the same. The interaction diagrams resulting from these calculations are given in Figures 6 and 7 and will be discussed in the following section.



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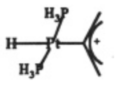

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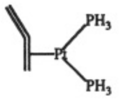

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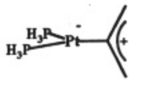

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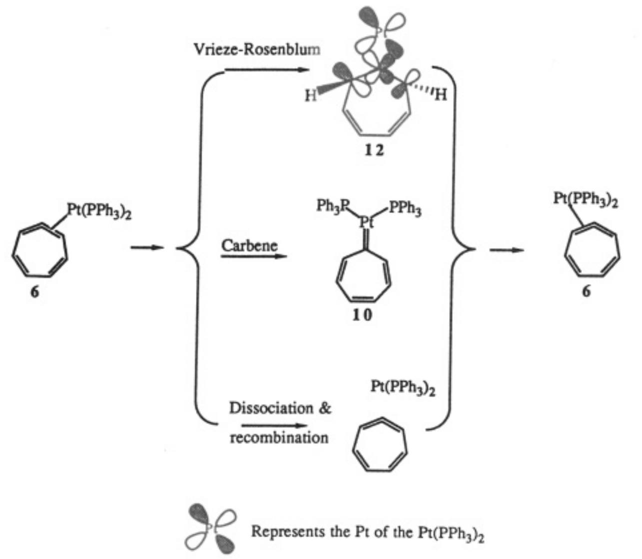

Figure 4. Diagram showing the three possible mechanisms for the fluxionality.

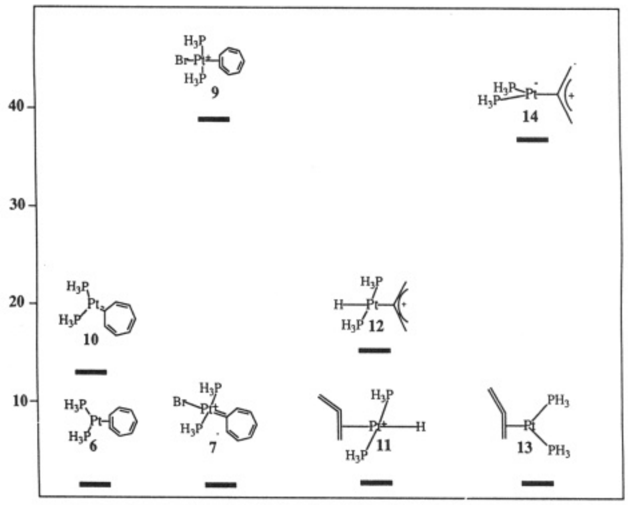

Figure 5. Relative energies in kilocalories per mole of valence isomers as calculated by the extended Hückel method.

Discussion

From the number of resonances in the NMR spectra of **7**, the Pt(II) complex of C_7H_6 could be either a carbene complex or a mixture of rapidly equilibrating allene isomers (eq 3).[24] However, although a single crystal suitable for X-ray analysis could not be grown and, therefore, the structure in the solid remains unknown, there is little question but that the preferred structure in solution is the carbene form. Arguments for this conclusion include the absence of evidence for fluxionality at low temperature (−90 °C) in the ^{1}H and ^{31}P NMR (which requires that if the structure is actually rapidly equilibrating allene

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(18) The NOESY spectrum did not clearly show correlation between the satellites of H2 and its central peak, possibly because the mixing time of the NOESY experiment was not optimized and **6** showed significant decomposition during the long acquisition time required for this spectrum.

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(20) (a) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34. (b) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P. *Organometallics* **1991**, *10*, 394. (c) Farrugia, L. J.; Rae, S. E. *Organometallics* **1991**, *10*, 3919.

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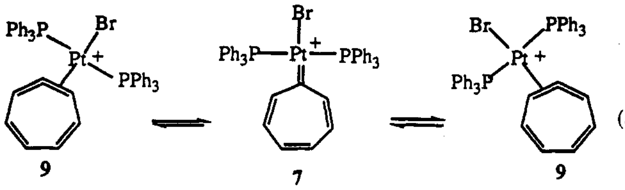
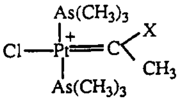


(3)

structures, the barrier for their interconversion must be quite low) and the similarity of the proton and carbon NMR spectra of 7 to those of complexes 3–5 (see Tables I and II) to which carbene structures have been assigned, in one case based on an X-ray analysis.[4] Also notable is the chemical shift of the carbene carbon (δ 210.5 ppm) which is significantly downfield from that expected of the central carbon of an allene complex (e.g. δ 150.1 ppm for the Fp^+ complex of 1,2-cycloheptadiene),[25] and the coupling constant, $^1J_{Pt-C}$, of the carbene carbon compares favorably with those of other Pt(II) carbene complexes (15).[26] [$^1J_{Pt-C}$ = 1125 and 1070 Hz for X = OCH_3 and X = $N(CH_3)_2$ respectively].



$$Cl-\overset{As(CH_3)_3}{\underset{As(CH_3)_3}{Pt^+}}=C(X)CH_3$$

X = OCH_3 or $N(CH_3)_2$

15

The ^{195}Pt chemical shift of 7 (−4095 ppm) is interesting in that it is nearly 350 ppm downfield from 8 (−4439 ppm) although both are Pt(II) complexes. This suggests significant electron delocalization into the ring in 7. Consistent with this are the chemical shifts in all of the carbene complexes in Tables I and II. In both the ^1H and ^{13}C spectra, all the average chemical shifts for H_α, H_β, and H_γ (e.g. 8.13 ppm for 7), and C_α, C_β, and C_γ (e.g. 150.8 ppm for 7) are at higher field than the tropylium ion (^1H = 9.55 ppm,[27a] ^{13}C = 160.6 ppm[27b]). Furthermore, in all of the carbene complexes the chemical shifts follow the same order, $C_\alpha > C_\gamma > C_\beta$, which, interestingly, corresponds to the reverse order of the coefficients of the Hückel LUMO (of symmetry that would permit interacting with the metal) for the tropylium ion (0.12, 0.33, and 0.48 for C_α, C_γ, and C_β, respectively).[28] As unreliable as these calculations may be, this correlation is rather striking, especially for C_α.

The allene structure 6 is unquestionably the ground state of the $Pt(PPh_3)_2$ complex of C_7H_6 in both solution and in the crystal. Furthermore from the spin saturation transfer experiments, a minimum activation enthalpy of about 27 kcal/mol is required for the platinum to move between the double bonds. In principle, the mechanism of this fluxionality could be intramolecular by a Vrieze–Rosenblum mechanism (transition state 12)[29] or a carbene mechanism (transition state or intermediate 10)[29] or intermolecular by dissociation–recombination.[27] All three mechanisms (Figure 4) have been detected.[29,30] From spectrum c in Figure 3, it is clear that irradiation of H2 in the ^{194}Pt and ^{196}Pt isotopomers leads to magnetization transfer to H7 in all three isotopomers, which requires an intermolecular process.[31] Further confirmation of dissociation–recombination is found in the appearance of satellite peaks for H2 in Figure 3c.[32]

The difference in structural preference of C_7H_6 when complexed to Pt(II) and Pt(0) can be understood from an examination of the orbital interaction diagrams for complexes 11–14 shown in Figures 6 and 7.[23d] Beginning with Figure 6, for the allene complex 11, the allene is bent with a CCC angle of 168.6°—consistent with the bending observed in crystal structures and perpendicular to the P–Pt–P plane. The bending removes the degeneracy expected for the allene fragment π-orbitals, raising and lowering the HOMO and LUMO, which will interact with the metal. The dominant interaction here is between the a_1 LUMO of the Pt(II) fragment and the π_2 HOMO of the allene. These orbitals differ in energy by 2 eV and, consistent with the energy criterion of frontier orbital theory, do not interact strongly. Back-bonding between π_3 and Pt(II) b_2 orbitals is observed but does not lead to significant stabilization.

In the carbene complex 12 a strong interaction between the $2a_1$ LUMO of Pt(II) and the a_1 HOMO of the carbene is observed. Here the overlap is good and the two orbitals are close in energy. This leads to a strong interaction. Back-bonding is predicted to be minimal, the LUMO of the carbene fragment has a node at the carbon bonded to Pt, and the next orbital is too high in energy for effective interaction with the Pt. The net result for Pt(II) is that the carbene is favored relative to the allene because of a strong interaction in the carbene between the metal LUMO and the carbene HOMO.

The Pt(0) complexes 13 and 14 show very different interactions between the metal and the C_3H_4 ligand. For the $Pt^0(PH_3)_2$ fragment the LUMO, $3a_1$, is much higher in energy than in the Pt(II) case and this leads to a reversal in the metal's interaction with the two ligands. In the allene complex 15 once again the allene is bent, more so than before; the CCC angle is not 144°, and the allene is in the P–Pt–P plane. The dominant interaction here is between the b_2 HOMO of the Pt(0) fragment and the π_3 LUMO of the allene which, because the two orbitals are close in energy, leads to a significant stabilization. For the carbene 14 there are no strongly bonding interactions. The a_1 HOMO of the carbene interacts with the $1a_1$ and $3a_1$ of the Pt(0) fragment, but the energy difference here is too great for a strong bonding interaction. As in the Pt(II) case, the node in the LUMO of the carbene at carbon prevents any back-bonding. Thus we see that the preference for the allene geometry is the result of the high energy of the Pt(0) LUMO fragment orbital and back-bonding from the Pt(0) b_2 orbital of the allene LUMO.

Experimental Section

NMR spectra were recorded on a VXR-300, a QE-300, or an XL-200 with TMS as reference for ^1H and ^{13}C NMR, 80% H_3PO_4

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[25] Manganiello, F. J.; Jones, Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* 1985, *4*, 1069.

[26] Chisholm, M. H.; Clark, H. C.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* 1975, *14*, 893.

[27] (a) Volz, H.; Volz-de Lecea, M. *Liebigs Ann. Chem.* 1971, *750*, 136. (b) Sabastian, J. F.; Grunwell, J. R. *Can. J. Chem.* 1971, *49*, 1779.

[28] Coulson, C. A.; Streitwieser, A., Jr. *Dictionary of π-Electron Calculations*; Pergamon Press Ltd.: New York, 1965.

[29] For examples of these two intramolecular mechanisms, see: Oon, S. M.; Jones, W. M. *Organometallics* 1988, *7*, 2172 and references cited therein.

[30] Cf.: Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* 1976, *14*, 245.

[31] Unlike temperature-dependent coalescence experiments, retention of coupling in a spin saturation transfer experiment does not distinguish between inter- and intramolecular processes.

[32] It is also interesting that the relative areas of the satellites to that of the central peak for H7 are somewhat less than the theoretical value of 1:4:1 because it may signal some "apparent" intramolecular process—possibly a cage effect. However, the peaks are broad enough that the measured 1:4.7:1 may not be outside of experimental error.

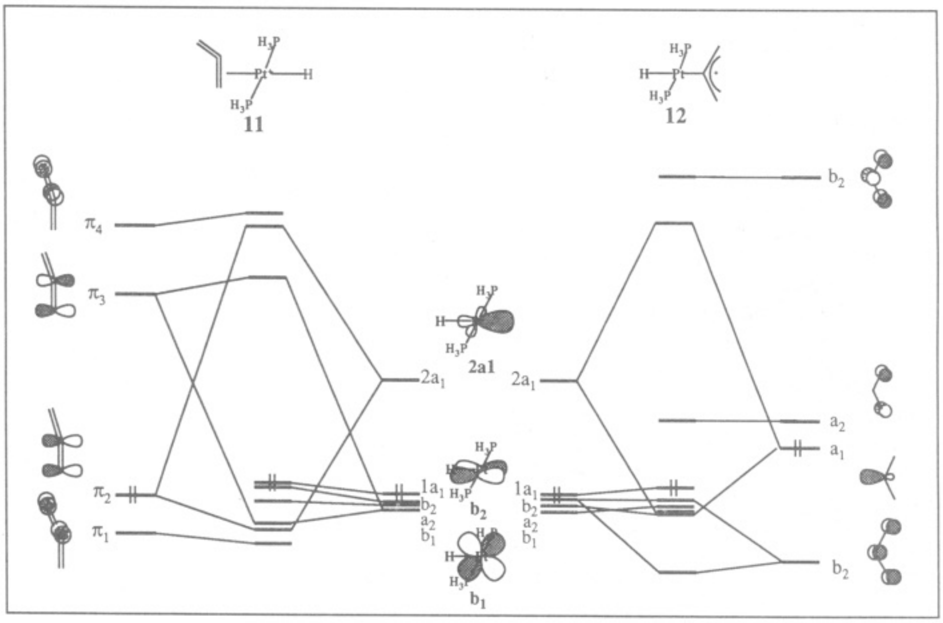

Figure 6. Orbital interaction diagram for $Pt(H)(PH_3)_2(C_3H_4)^+$ compounds **11** and **12**.

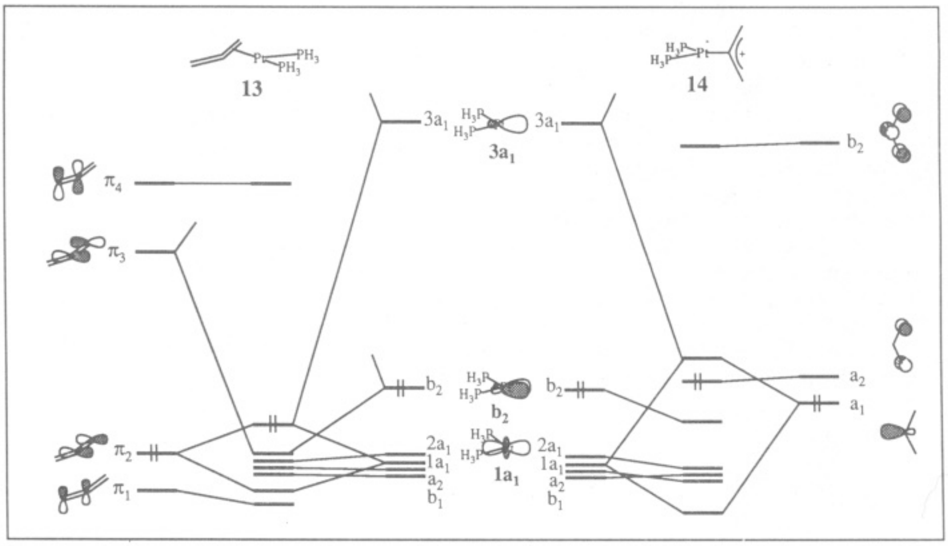

Figure 7. Orbital interaction diagram for $Pt(PH_3)_2(C_3H_4)$ compounds **13** and **14**.

for ^{31}P NMR, Na_2PtCl_6 in D_2O for ^{195}Pt NMR, and the $-CD_3$ resonance of toluene-d_8 (2.09 ppm) for ^2H NMR. IR spectra were obtained in KBr pellets using a Perkin-Elmer 1600 FTIR. Mass spectra were carried out on a Finnigan Mat 95Q. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. All solvents were dried and degassed according to standard procedures. NMR solvents, *t*-BuOK, $Ph_3C^+BF_4^-$, and most other reagents were used as received from Aldrich. 6-Hydroxytropinone was purchased from Aldrich and sublimed before use. Platinum complexes **6** and **8** were prepared as previously reported.[7]

Preparation of *trans*-Bromo[(1-η^1)-cycloheptatrienylidene]bis(triphenylphosphine)platinum (7). To complex **8** (180 mg, 0.2 mmol) dissolved in 15 mL of methylene chloride in a Schlenk tube was added a solution of $Ph_3C^+BF_4^-$ (100 mg, 0.3 mmol) in 5 mL of methylene chloride at room temperature. After the reaction mixture had been stirred for 1 h, 30 mL of hexane was added to give **7** (170 mg, 87% yield) as greenish-yellow crystals which were purified by recrystallization from CH_2Cl_2/hexane. Mp: 263 °C dec. IR: 1586 (w), 1481 (m), 1456 (s), 1435 (s), 1310 (w), 1187 (w), 1056 (s), 998 (m), 745 (m), 693 (s), 618 (w), 593 (w), 499 (m). Anal. Calcd for $C_{43}H_{36}PtBrP_2BF_4$: C, 52.87; H, 3.69. Found: C, 52.84; H, 3.81. FAB MS: *m/e* 889 (M^+), 890 (MH^+). ^1H NMR (300 MHz, CD_2Cl_2, δ): 8.89 (d, $^3J_{Pt-H} = 64.0$ Hz, $^3J_{H-H} = 11.7$ Hz, H_α), 8.09 (m, H_γ), 7.42 (m, H_β), 7.53 (m, Ph), 7.25–7.45 (m, Ph). ^{13}C NMR (75 MHz, CD_2Cl_2, δ): 210.5 (d, $^1J_{Pt-C} = 969.0$ Hz, $^2J_{P-C} = 6.5$ Hz, C_{carb}), 162.5 (s, $^2J_{Pt-C} = 21.2$ Hz, C_α), 146.5 (s, C_γ), 143.5 (s, $^3J_{Pt-C} = 90.0$ Hz, C_β), 135.0 (t, $^2J_{P-C} = 5.9$ Hz, C_{ortho} of Ph), 131.8 (s, C_{para} of Ph), 129.0 (t, $^3J_{P-C} = 5.1$ Hz, C_{meta} of Ph), 128.4 (t, $^2J_{Pt-C} = 30.0$ Hz, $^1J_{P-C} = 30.0$ Hz, C_{ipso} of Ph). ^{31}P NMR (121 MHz, CD_2Cl_2, δ): 20.7 ($^1J_{Pt-P} = 2777.4$ Hz). ^{195}Pt NMR (64 MHz, CD_2Cl_2, δ): −4095.

Preparation of 2,4,6-Cycloheptatrienone-*2,7-d*$_2$.[33] 6-Hydroxytropinone (1 g, 6.44 mmol) and potassium carbonate (anhydrous) (0.5 g) were dissolved in 15 mL of D_2O at room temperature. After 24 h, the D_2O solvent was removed in vacuo and deuterated hydroxytropinone was extracted with 20 mL of ethanol. The solution was concentrated to 5 mL in vacuo and then cooled with ice. To this solution was added cold methyl iodide (3 g). After 15 h of refrigeration (5 °C), colorless crystals precipitated. The crystals were dissolved in 10 mL of D_2O together with sodium carbonate (0.4 g). The solution was kept at 60 °C overnight. The reaction mixture was then extracted five times with 10-mL portions of methylene chloride. The

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[33] This compound has been previously prepared. However, experimental details were not included: Machiguchi, T.; Mizuno, H.; Hasegawa, T.; Ishii, Y.; Otani, H. *Chem. Lett.* **1987**, 1893.

methylene chloride solution was dried over magnesium sulfate overnight. After methylene chloride was removed in vacuo, the residue was distilled to give 0.38 g (54.5%) of product. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.18–6.26 (m, 2H), 6.33–6.42 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 127.5 (t, $^1J_{D-C}$ = 25 Hz), 133 (s), 135 (s).

Preparation of a Mixture of 1-Bromocyclohepta-1,3,5-triene-*2,7-d_2*, 2-Bromocyclohepta-1,3,5-triene-*1,3-d_2*, and 3-Bromocyclohepta-1,3,5-triene-*2,4-d_2*. For preparation, see ref 7. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.21 (dd, $^3J_{H-H}$ = 7.0 Hz, $^3J_{H-D}$ = 0.8 Hz, allyl proton of 2-bromo *1,3-d_2* derivative), 2.28 (t, $^3J_{H-H}$ = 7.0 Hz, allyl proton of 3-bromo *2,4-d_2* derivative), 2.78 (dt, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-D}$ = 2 Hz, allyl proton of 1-bromo *2,7-d_2* derivative), 5.21–5.46 (m), 5.97–6.29 (m), 6.41–6.54 (m).

Preparation of [(1,2-η^2)-Cycloheptatetraene-*2,7-d_2*]bis(triphenylphosphine)platinum. For preparation, see ref 7. ^{1}H NMR (200 MHz, toluene-d_8, δ): 4.97 (m, H3), 5.87 (m, H4), 6.19 (m, H5), 6.54 (m, H6), 7.00–7.45 (Ph). ^{2}H NMR (46 MHz, toluene-d_8, δ): 3.41 (br, D2), 6.16 (br, D7).

Spin Saturation Transfer Experiments. NMR samples were prepared in toluene-d_8 solution in 5-mm NMR tubes, degassed by freeze/pump/thaw procedures, and sealed on a vacuum line. Variable-temperature ^{1}H NMR spectra were collected on a VXR-300 NMR spectrometer. Saturation transfer experiments for detecting fluxionality were performed by inverting (180° selective pulse) the resonance peaks of H2 (3.41 ppm), H3 (4.97 ppm), and H4 (5.87 ppm), respectively, followed by a variable length of delay time τ, a 90° observation pulse, a free induction decay (FID) of 1.872 s, and a prepulse relaxation delay (D1) of 10 s (3–5T_1). After scanning 32 times with this pulse sequence, each spectrum was then subtracted from a normal proton NMR spectrum, also with 32 scans. By this procedure, unrelated resonances were canceled (see Figure 1). Data for calculating rate constants were obtained from the integral values of resonances H2 and H7 at 60, 80, and 90 °C. The fluxional rate constants were obtained from a plot of $\ln[(x + y)/(x - y)]$ versus τ which is based on the equation $\ln[(x + y)/(x - y)] = 2k(\tau)$ (where x is the intensity of H2 and y is that of H7) derived from Dahlquist et al.'s approximation.[15] In the study of the mechanism of fluxionality, a typical NOE pulse sequence was used except that the DLP (decoupler low power in the VXR-300) was adjusted (DLP = 35 corresponding to an irradiation power of about 0.5 W) so that only the central peak of H2 was partially saturated; the satellite peaks of H2 were not affected by this weak irradiation.

Table III. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	$c_1{}^a$	$c_2{}^a$
Pt 5d	−12.59	6.0130	2.6960	0.6334	0.5513
Pt 6p	−5.475	2.5540			
Pt 6s	−9.077	2.5540			
P 3p	−14.0	1.3			
P 3s	−18.6	1.75			
Br 4p	−13.1	2.131			
Br 4s	−22.07	2.588			
C 2s	−21.40	1.625			
C 2p	−11.40	1.625			
H 1s	−13.60	1.30			

[a] Contraction coefficients used in the double ζ expansion.

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Appendix

The calculations were performed using the extended Hückel method[34] with parameters taken from the Alvarez collected parameters.[35] H_{ii}'s and orbital exponents are listed in Table III. Geometries used were those obtained using the MM2 force field[36] as augmented by the CAChe group.

OM9204999

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(34) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179, 3489; **1962**, *37*, 2872.

(35) Tables of Parameters for extended Hückel calculations. Collected by Santiago Alvarez, Universitat de Barcelona, June 1989.

(36) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.