

Preparation and Fluxionality of a Bimetallic Platinum–Molybdenum Complex of 1,2,4,6-Cycloheptatetraene

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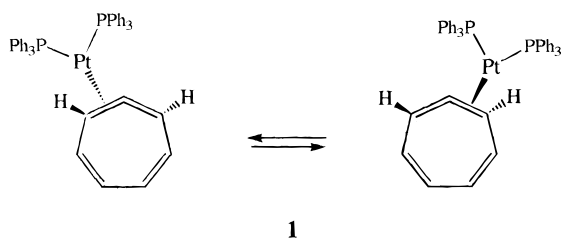
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Summary: Fluxionality in the $(\text{Ph}_3\text{P})_2\text{Pt}/\text{Mo}(\text{CO})_3$ complex of 1,2,4,6-cycloheptatetraene, **2**, is rapid at 20 °C. The process is intramolecular (determined by selective isotopomer irradiation) and requires simultaneous movement of both metals concomitant with inversion of the allene moiety. Fluxionality in the mononuclear complex **1** is intramolecular at 60 °C but has a superimposed intermolecular component at 80 °C.

It is well-established that some transition-metal complexes of allenes exhibit fluxional behavior by a 1,2-metal shift between the double bonds of the allene.¹ Three different mechanisms have been demonstrated for this process: an intermolecular mechanism that occurs by simple dissociation–recombination,² an intramolecular mechanism (the most common of the three and sometimes referred to as the Vrieze–Rosenblum mechanism) that occurs with retention of allene configuration³ and a second intramolecular mechanism (only one example)^{3e} in which allene chirality is lost and which has been suggested to proceed via a planar allyl cation transition state.

Some time ago we investigated the properties of **1** a Pt(0) complex of cycloheptatetraene, and found that it undergoes a fluxional process with an activation barrier of 26.8 kcal/mol.⁴ This barrier was determined by spin saturation transfer techniques, which also demonstrated an intermolecular process as at least one component of the fluxional mechanism.



At this time, we report the preparation of **2**, a bimetallic complex of cycloheptatetraene, which under-

goes a similar fluxional process, but one that both is faster than for the mononuclear complex and also requires an achiral intermediate (or transition state). We also report our discovery that the previously reported intermolecular process for the fluxionality of **1** is in reality superimposed on a lower energy intramolecular process.

The bimetallic complex **2** was prepared by addition of THF to an equimolar mixture of **1** and $(\eta^6\text{-}p\text{-xylene})\text{-Mo}(\text{CO})_3$. The dark brown-red complex was too unstable for isolation but was stable in solution for few hours at 20 °C (complete decomposition occurred within 2 days), which permitted complete characterization by multinuclear NMR spectroscopy. As expected for a complex with C_1 symmetry, the $^{195}\text{Pt}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** exhibit a doublet of doublets at δ –4476 ppm ($^1J_{\text{Pt-P}} = 3180$ Hz, $^1J_{\text{Pt-P}'} = 3209$ Hz) and two doublets flanked with ^{195}Pt satellites at δ 22.83 and δ 24.99 ppm ($^2J_{\text{P-P}'} = 17.5$ Hz), respectively. In addition to PPh₃ signals the ^1H NMR of **2** shows six different resonances. The highest field multiplet at δ 2.46 ppm ($^2J_{\text{H1-Pt}} = 52.2$ Hz) was assigned to H1.⁵ Since H1 and H2 are not coupled (no cross-peak in the 2D COSY spectrum),⁶ the chemical shift of H2 was assigned to the peak at δ 3.13 ppm ($^3J_{\text{H2-Pt}} = 56.1$ Hz) on the basis of an NOE experiment (2% enhancement of H2 was observed upon irradiation of H1). The remaining proton assignments are based on a 2D COSY experiment. The NOE difference spectrum (Figure 1) also showed a strong negative peak at δ 4.57 ppm ($^3J_{\text{H6-Pt}} = 61.2$ Hz) which included satellites and a positive NOE at δ 5.85. These peaks correspond to H6 and H5, respectively, and were particularly interesting because they indicated that saturated spin had been transferred from H1 to H6 (which led to the NOE enhancement at H5); i.e., **3** must be fluxional at 20 °C. Magnetization transfer experiments were carried out which, upon application of the approximation of Dahlquist et al.,⁷ yielded a fluxional rate of 0.18 ± 0.02 s^{–1} at 20 °C. Thermal instability precluded determination of activation parameters for this process (no transfer at 10 °C; rapid decomposition above 20 °C).

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(6) See the Supporting Information.

(7) Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.

(8) In principle, this fluxionality could occur by a process which involves dissociation of the $\text{Mo}(\text{CO})_3$ moiety from the front face of **2** and a 1,2-platinum shift in the resulting cycloheptatetraene complex **1** by either an intermolecular or intramolecular process, followed by reattachment of the $\text{Mo}(\text{CO})_3$ to the open face (front or back) of the seven-membered ring. This possibility is not viable because fluxionality in **2** is faster than in **1**.

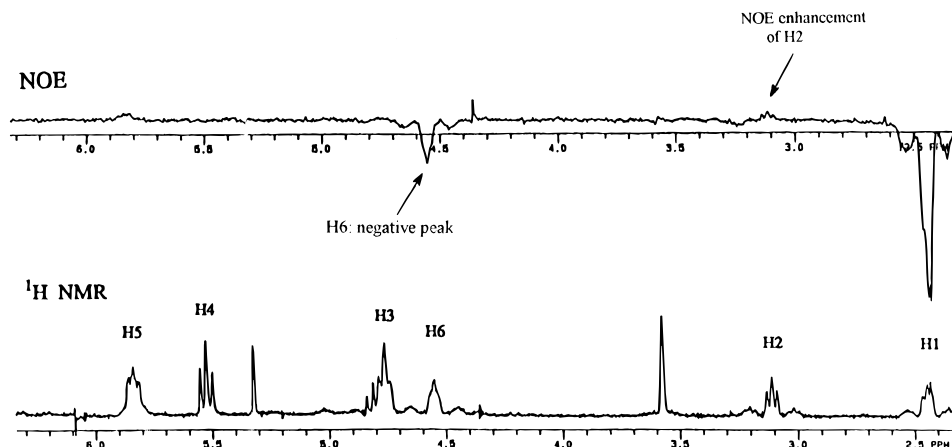
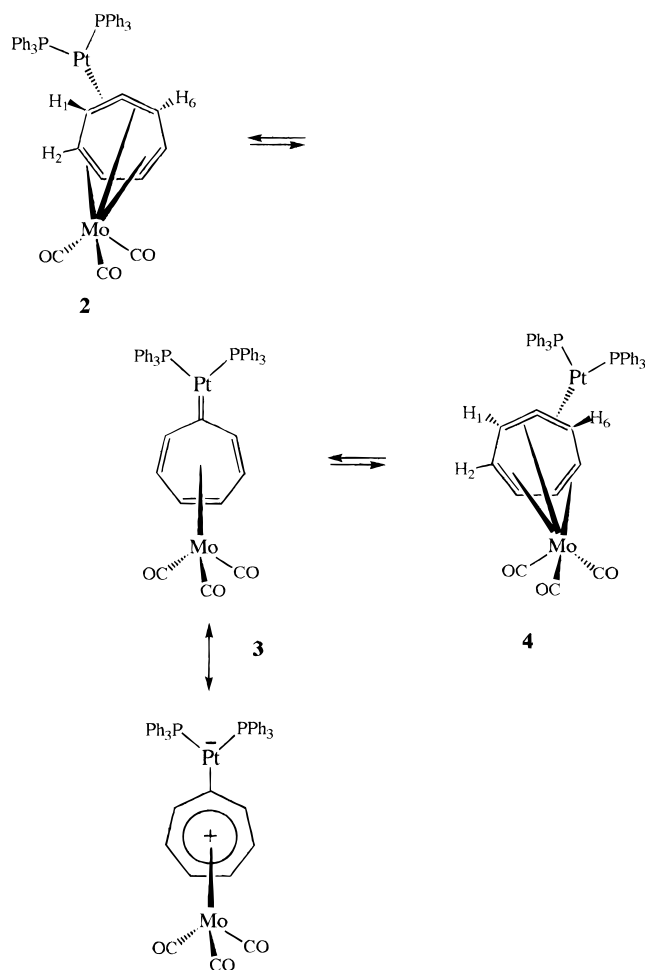


Figure 1. NOE difference spectrum and part of ^1H NMR spectrum of complex **2**.

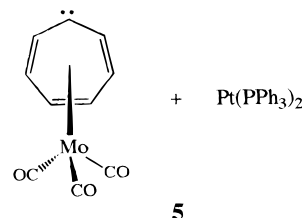
Scheme 1



Even more interesting than the fluxionality rate of **2** (about the same at 20 °C as that of the intramolecular process (*vide infra*) for **1** at 60 °C) are requisite characteristics of the mechanism of this fluxionality process in comparison with other allene complexes. First, both metals must move. As pictured in Scheme 1, the interconversion between enantiomeric pairs **2** and **4** must involve movement of platinum from one allene double bond to the other coupled with simultaneous movement of molybdenum from one heptatriene array to the other. Second, in both **2** and **4**, the platinum is on the "back face" of the cycloheptatriene ring and the molybdenum is on the "front face". In order for the

platinum to move from one double bond of the allene to the other without requiring the molybdenum to move from the front face of the ring to the back, the configuration of the allene must be inverted. This would probably occur by the allene adopting an achiral carbene-tropylium structure as represented by **3** (which could be either an intermediate or a transition state) or a dissociated molybdenum complex as represented by **5**.

To distinguish between the intramolecular process represented by **2** and **4** and the intermolecular process as depicted in **5**, a magnetization transfer experiment was carried out in which H1 was irradiated in only the isotopomers of **2** and **4** with magnetically inactive platinum nuclei (the central peak).⁹ The observation



that magnetization was transferred to H6 in only those isotopomers containing inactive platinum nuclei (no satellite peaks were observed, indicating no scrambling) is strong evidence for an intramolecular process (Figure 2). We therefore suggest that fluxionality occurs through the transition state or intermediate as depicted in **3**, a species that probably has significant tropylium ion character. We further suggest that $\text{Mo}(\text{CO})_3$ accelerates this process relative to **1** by bonding more strongly to the tropylium π -system in the transition state (based on displacement rates¹⁰ and X-ray studies¹¹) than to the highly distorted cycloheptatriene in the ground state.¹²

(9) Crucial to this technique is ensuring selective irradiation of the central peak, leaving the satellite peaks unaffected. For a discussion of control experiments designed for this purpose, see ref 4. In addition, it may be noted that in this case with identical power settings, no satellites were observed at 60 °C but were noted at 80 °C.

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(12) Distortion of the cycloheptatriene moiety in **1** can be clearly seen in its X-ray crystal structure.¹³ For two stable complexes $(\text{PPh}_3)_2\text{-Pt}(\text{CO})_3\text{Mo}$ complexes of 1,2,3,5-cycloheptatetraene and cyclohepta-3,5-dien-1-yne that are isomeric with **2** but do not have distorted triene units, see: Klosin, J.; Abboud, K. A.; Jones, W. M. *Organometallics* **1996**, 15, 596.

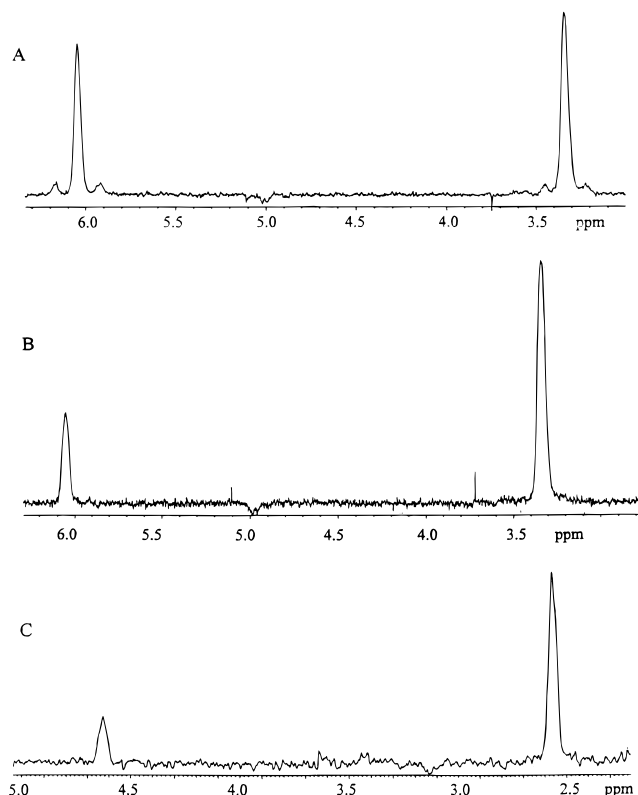
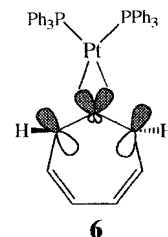


Figure 2. Magnetization transfer difference spectra: (A) complex **1** at 80 °C: selective irradiation at δ 3.33 ppm; (B) complex **1** at 60 °C: selective irradiation at δ 3.33 ppm; (C) complex **2** at 20 °C: selective irradiation at δ 2.66 ppm.

Finally, re-examination of magnetization transfer in **1** reproduced our previously reported results at 80 °C (the only temperature studied); unique irradiation of the central peak of H1 led to transfer to H6 in all isotopomers, but less to the satellites than to the central peak (area ratio of satellites to central peak \sim 7:1). As suggested at that time,⁴ transfer to the satellites requires some intermolecular reaction but incomplete transfer also requires a process that is equivalent to an intramolecular reaction. In our current work, unique irradiation of the magnetically inactive peak was also

studied at 60 °C and, in this case, *only* transfer to the central peak was observed. In other words, at the lower temperature the intermolecular process is no longer observable, which suggests that the latter is superimposed on an intramolecular mechanism. At this time we do not have definitive evidence for the detailed mechanism of this process, although circumstantial evidence points to an achiral transition state similar to **3** rather than chiral **6**.¹⁴



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Supporting Information Available: Text giving experimental details for the preparation of **2** and details of magnetization transfer experiments and figures showing multinuclear and 2D COSY spectra of **2** (10 pages). Ordering information is given on any current masthead page.

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(14) The intramolecular process could go by either a chiral Vrieze-Rosenblum mechanism (**6**) or an achiral carbene mechanism (analogous to **3**). At this time, it is not possible to distinguish between these. However, we have made two observations that are consistent with the carbene mechanism although neither demands it. First, intramolecular fluxionality in **1** is significantly faster (observable as low as 40 °C) than any process (intramolecular or intermolecular) in the corresponding complex of 1,2-cycloheptadiene (barely detectable at 100 °C). This is consistent with a carbene-like transition state analogous to **3** which would be significantly stabilized by the two additional double bonds (this stabilization exceeds 13.9 kcal/mol in the corresponding Fp^+ complexes).^{3d,15} However, this argument is weakened by Pt–P coupling constants^{5a,b} that indicate a stronger ground-state metal–allene bond in the 1,2-cycloheptadiene complex than in **1**. Second, when **1** was prepared from enantiomerically enriched allene (enantiomeric excess confirmed by trapping with diphenylisobenzofuran),¹⁶ within the limit of experimental error the product was racemic. Unfortunately, this simply means that **1** is probably optically unstable; it says nothing about whether the optical instability is associated with the fluxional process.

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