

K_{bo} and K_{wo} are established as a function of temperature and the extent to which the factor $(1 + K_{\text{wo}})/(1 + K_{\text{al}})$, in any particular instance, departs from unity. A more detailed account of these and other considerations will appear elsewhere. However, we consider the present treatment of the temperature dependence of these ionogenic reactions to be more informative than that based on empirical equations which are virtually devoid of theoretical content.

Registry No. Benzoic acid, 65-85-0; water, 7732-18-5.

Preparation and Properties of Sterically Unhindered Cis and Trans Dihydrides of Platinum(II)

Ralph S. Paonessa and William C. Trogler*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

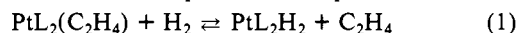
Received November 9, 1981

Dihydrobis(tertiary phosphine) complexes of platinum(II), PtL_2H_2 , undergo a broad spectrum of reactions.¹⁻¹⁷ Examples include insertion,⁵⁻⁷ dimer formation,^{11,12} metallation,⁸ formation of platinum(0) compounds,^{11,15} oxidative addition,^{9,13} and catalysis of the water-gas shift reaction¹⁰ and of alkene hydrogenation.¹¹ Almost all such dihydrides previously prepared contain bulky tertiary phosphine ligands and assume a trans geometry when L is monodentate. The only known cis dihydrides of this class contain bulky chelating diphosphine ligands.^{4,11} In the absence of steric effects, the cis geometry should be electronically favored, since the trans influence of hydride is greater than that of phosphines.¹⁸ The results of a recent ab initio calculation on $\text{Pt}(\text{PH}_3)_2\text{H}_2$ also indicate the cis geometry will be electronically favored.¹⁶

Previous attempts to prepare platinum(II) dihydrides containing small phosphines have met with limited success, and decomposition often occurs.^{1,3,7,11,17} It is generally believed that bulky formation phosphines stabilize* PtL_2H_2 by hindering approach to the PtH_2 moiety.^{1,3,11,17} Conversely, analogues which contain small phosphine ligands should be more reactive. We report the synthesis

and chemistry of stable but highly reactive unhindered *cis*- and *trans*- PtL_2H_2 complexes and the first examples of *cis*-*trans* isomerization of platinum(II) dihydrides. These *cis* dihydrides are to our knowledge the first examples of four-coordinate d^8 ML_2H_2 in which the *cis* geometry is not constrained by chelating ligands.

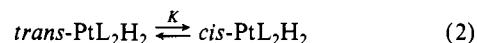
The dihydrides *cis*- and *trans*- PtL_2H_2 (*cis*- and *trans*-**1**, L = PEt_3 ; *cis*- and *trans*-**2**, L = PMe_3) are readily prepared by bubbling hydrogen (1 atm, 25 °C) through solutions of $\text{PtL}_2(\text{C}_2\text{H}_4)$ ¹⁹ (reaction 1). These reactions proceed to completion in about 15



min as ethylene is swept from the system. Ethane was not detected during the reaction by ¹H NMR spectroscopy in solution nor by gas chromatographic analysis of the gas phase. The ratio of *cis* and *trans* isomers formed depends on the solvent (vide infra). All the reactions described here can be conveniently monitored by ³¹P{¹H} NMR spectroscopy, which shows quantitative conversions to products.

The dihydride products are readily identified by examination of their ¹H and ³¹P NMR spectral parameters (Table I). The ¹H NMR spectrum of each *trans*-dihydride complex exhibits a hydride resonance which is a 1:2:1 triplet arising from coupling to the two phosphines *cis* to hydride. The hydride resonance of each *cis* dihydride complex is a second-order doublet of doublets, arising from coupling of each hydride ligand to a *cis* phosphorus nucleus and to a *trans* phosphorus nucleus. The spectral parameters in Table I accord well with those of previously reported *cis* and *trans* dihydrides of platinum(II).^{1-4,8,11,17,20}

Complexes **1** and **2** isomerize in solution to produce an equilibrium mixture of *cis*- and *trans*- PtL_2H_2 (reaction 2). The



equilibrium constant K depends upon both the solvent and the ligand, L (Table II).²¹ Note that, for a given L, the relative concentration of *cis* isomer increases in going from the nonpolar hydrocarbon solvent to the polar solvent acetone. Since the *cis* isomer has a dipole moment, it should be better solvated in polar media. Second, in a given solvent, the *cis* geometry is more favored when L is PMe_3 than when it is PEt_3 . Only 3% *cis*- $\text{Pt}(\text{PEt}_3)_2\text{H}_2$ can be detected in toluene, whereas ca. 20% of the PMe_3 dihydride is present in the *cis* form in this solvent. In acetone *cis*- $\text{Pt}(\text{PEt}_3)_2\text{H}_2$ is still the minor isomer (10%), but upon changing to PMe_3 the *cis* isomer predominates (70%). Similar results are obtained in other hydrocarbon (benzene) and polar (acetonitrile, methanol, tetrahydrofuran) solvents. These results suggest there is a delicate balance among the steric, electronic, and solvation effects that control the equilibrium between *cis* and *trans* isomers.

Analytically pure²² *trans*-**1** can be isolated as off-white crystals by cooling a concentrated *n*-hexane solution of *trans*-**1** under hydrogen. This hygroscopic solid can be handled briefly in air and is indefinitely stable under 0.5 atm of H_2 at room temperature but decomposes slowly under vacuum. Solutions of **1** under hydrogen in hydrocarbon solvents or in acetone are quite stable. (A

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(19) We have prepared $\text{PtL}_2(\text{C}_2\text{H}_4)$ (L = PEt_3 , PMe_3) by the photochemical reaction $\text{PtL}_2(\text{C}_2\text{O}_4) + \text{C}_2\text{H}_4 \xrightarrow{h\nu} \text{PtL}_2(\text{C}_2\text{H}_4) + 2\text{CO}_2$. Paonessa, R. S.; Trogler, W. C., to be submitted. An alternative route has been described: Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* **1981**, *20*, 1312-1314.

(20) The dihydride *trans*-**1** has been observed previously in solution.¹⁷

(21) We are confident that we are observing true equilibrium concentrations in solution since (a) the value of K under a given set of conditions is reproducible among several independently prepared samples, (b) the same value of K is obtained either by dissolving a previously prepared sample of PtL_2H_2 in a given solvent or by generating PtL_2H_2 in that solvent [e.g., by reaction of $\text{PtL}_2(\text{C}_2\text{H}_4)$ and H_2], and (c) after reactions which disturb the equilibrium by partially consuming *cis*- and/or *trans*- PtL_2H_2 (e.g., after adding less than a stoichiometric amount of C_2H_4), the *cis*-*trans* ratio returns to its equilibrium value. We have not studied the rates of isomerization of **1** and **2** in detail; however, solutions of **1** reach equilibrium within ca. 15 min at 25 °C, and solutions of **2** equilibrate much faster. We do not yet know the mechanism of isomerization of **1** and **2**, and, for example, whether isomerization could be catalyzed by traces of impurities.

(22) Anal. Calc. Pt, 45.01; P, 14.29; C, 33.25; H, 7.44. Found: Pt, 44.98; P, 14.55; C, 32.74; H, 7.21.

Table I. NMR Parameters of *cis*- and *trans*-PtL₂H₂^a

compd	L	³¹ P{ ¹ H} NMR		¹ H NMR, hydride			
		chem shift, ppm ^b	¹ J _{Pt-H} , Hz	chem shift, ppm	¹ J _{Pt-H} , Hz	² J _{P-H} ^{cis} , Hz	² J _{P-H} ^{trans} , Hz
<i>trans</i> -1	PEt ₃	27.7 s	2764	-2.96 t	790	18	
<i>cis</i> -1	PEt ₃	18.9 s	1984	-3.56 dd	1030	24	172
<i>trans</i> -2	PMe ₃	-21.1 s	2594	-2.67 t	807	20	
<i>cis</i> -2	PMe ₃	-21.7 s	1875	-3.81 dd	1028	24	179

^a NMR spectra were recorded in acetone-*d*₆ at -30 °C; s = singlet, t = triplet, dd = doublet of doublets. Couplings to platinum indicate 1:3.9:1 satellites arising from ¹⁹⁵Pt (33.8%, *I* = 1/2). ^b Downfield chemical shifts are positive relative to 85% H₃PO₄ at 0 ppm.

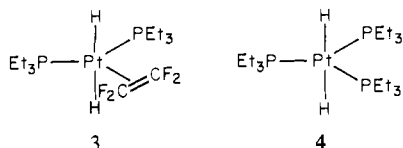
Table II. Equilibrium Constants for *trans*-PtL₂H₂ ⇌ *cis*-PtL₂H₂^K

L	solvent	K	cone angle of L, deg ^a
PEt ₃	toluene	0.03	132
	acetone	0.12	
PMe ₃	toluene	0.3	118
	acetone	2.2	

^a Reference 32a.

solution of **1** in C₆D₆ under 0.5 atm of H₂ showed no signs of decomposition after 1 year at room temperature.) Under vacuum, these solutions slowly decompose to yield Pt(PEt₃)₃ and platinum metal. A detailed investigation of the chemistry of **1** reveals much greater reactivity than that of more sterically hindered analogues. The reactions described below proceed cleanly under mild conditions (25 °C, 1 atm of gases).

Ligands which are π acceptors such as CO, C₂H₄, and C₂F₄ readily displace H₂ from **1** to produce zero-valent compounds Pt(PEt₃)₂L_n (L = CO, *n* = 2; L = C₂H₄, C₂F₄, *n* = 1).²³ The reaction of *trans*-**1** with C₂F₄ rapidly produces an intermediate adduct **3**, which loses H₂ over 0.5 h to produce Pt(PEt₃)₂(C₂F₄).²⁴ Addition of 1 equiv of PEt₃ to a solution of *trans*-**1** in toluene produces the known five-coordinate adduct **4**.²⁵ The formation of **3** and **4** illustrates the ability of unhindered 16-electron PtL₂H₂ complexes to expand their coordination sphere and form 18-electron species. Similar intermediates may be involved in the reactions of **1** with C₂H₄ and CO.



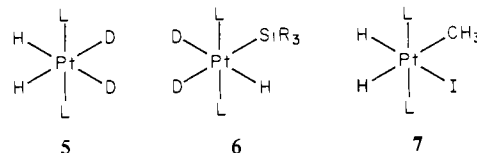
When solutions of **1** in toluene are placed under an atmosphere of D₂, both *trans*-Pt(PEt₃)₂HD and *trans*-Pt(PEt₃)₂D₂ form, along with H₂ and HD. If an excess of H₂ and D₂ are present, they are catalytically scrambled to produce an equilibrium mixture of

(23) The reactions of **1** with carbon monoxide or ethylene are complete within minutes, and no hydrogenation products were observed by ¹H NMR spectroscopy. Gas chromatographic analysis of the gas-phase (Molecular Sieve 5X, 6-ft × 1/8-in. o.d., 210 °C) in the reaction with ethylene showed little or no ethane was produced. At much longer times (1 day), ethane was detected above solutions of **1** under 0.5 atm of H₂ + 0.5 atm of C₂H₄; this apparent catalytic hydrogenation is under study.

(24) (a) The geometry of **3** has been inferred from ³¹P{¹H}, ¹H, ¹⁹F NMR, and IR spectroscopic data. The phosphines, hydrides, and fluorines are, respectively, chemically equivalent. ³¹P{¹H} NMR δ -6.1 (m, ¹J_{Pt-P} = 1734 Hz); ¹H NMR (hydride) δ -9.89 (m, ¹J_{Pt-H} = 749 Hz); ¹⁹F NMR δ 20.8 (m, relative to C₂F₄ at 0 ppm). The low value of ¹J_{Pt-P} is expected for a pseudo platinum(IV) complex. The complex multiplet patterns in the ³¹P{¹H} and ¹⁹F NMR spectra very closely resemble those seen in the respective spectra of Pt(PEt₃)₂(C₂F₄); such a result is reasonable if the phosphines and C₂F₄ are also in the same plane in **3**. Finally, the low value of the platinum hydride IR signal (νPtH₂ = 1812 cm⁻¹) is assignable to the antisymmetric *trans*-H-Pt-H stretch. (b) A number of related platinum(II) adducts have been reported. See, for example: (a) Uguagliati, P.; Baddley, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 5446-5452. (b) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1970**, *9*, 2670-2675. (c) *Ibid.* **1971**, *10*, 18-25. (d) Davies, B. W.; Puddephatt, R. J.; Payne, N. C. *Can. J. Chem.* **1972**, *50*, 2276-2284.

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H₂, HD, and D₂.²⁶ Similarly, Et₃SiH reacts reversibly with **1** to yield *cis*-Pt(PEt₃)₂H(SiEt₃) and H₂. If the reaction is carried out with an excess of Et₃SiH under a D₂ atmosphere, Et₃SiD forms catalytically. The reaction of **1** with methyl iodide immediately produces *trans*-Pt(PEt₃)₂HI and CH₄. It is possible these reactions proceed by oxidative addition to form platinum(IV) intermediates such as **5**, **6**, and **7**; reductive elimination would then lead to the



observed products. There is considerable evidence in favor of platinum(IV) intermediates in a host of reactions of platinum(II) compounds containing phosphine ligands.^{9,13,27} Alternatively, a bimolecular exchange between platinum centers could account for the H/D exchange reactions. This possibility is also reasonable, in light of the ability of hydride to bridge transition-metal centers,²⁸ the growing number of dimers of platinum and phosphines bridged by hydrides,^{12,29} and the formation of dimers via the dehydrogenation of *cis*-Pt(diphos)₂H₂.¹¹ Finally, the possibility of mechanisms involving phosphine dissociation should be considered.³⁰ Whitesides and co-workers have observed such processes in the decomposition of dialkylbis(phosphine)platinum(II) complexes, albeit under much more extreme conditions than those described here;³¹ however, the high trans effect of hydride¹⁸ could promote dissociation of L from *cis*-PtL₂H₂. Careful kinetic and spectroscopic studies will be necessary to identify mechanisms in these very labile systems.

(26) The percentage of HD in the gas phase (determined by gas chromatography) over a stirred benzene solution at 25 °C that contained 1 mol % *trans*-**1** ([*trans*-**1**] = 0.009 M) was monitored as a function of time. Excellent first-order kinetic behavior was observed over three half-lives as the isotopic distribution approached equilibrium. A statistical analysis of the exchange kinetics reveals the turnover number for the degenerate exchange PtL₂H₂ + H₂ → PtL₂H₂ + H₂ (i.e., the gross exchange rate, regardless of isotope) is 1.6 ± 0.4 min⁻¹ at 25 °C. The solutions remain homogeneous, and no induction period is observed; partial decomposition of **1** by introduction of oxygen results in a decrease in the rate of exchange. These observations, along with the well-defined kinetic behavior observed and the demonstrated stability of **1** under the mild catalytic conditions, argue against the possibility that the observed catalysis arises from unseen decomposition products.

(27) See, for example: (a) Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: New York, 1974; pp 95-108, 181-183. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 207-208. (c) Halpern, J.; Falk, C. D. *J. Am. Chem. Soc.* **1965**, *87*, 3523-3524. (d) Belluco, U.; Giustiniani, M.; Graziani, M. *Ibid.* **1967**, *89*, 6494-6500. (e) Bentham, J. E.; Craddock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587-593. (f) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1975**, 809-813. (g) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808-5815. (h) Blacklaws, J. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877-884.

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(29) See, for example: (a) Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671-672. (b) Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155-156. (c) Reference 12.

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The greatly enhanced reactivity of **1**, when compared to bulkier analogues, is no doubt steric in origin, since the electronic properties of PEt_3 and bulkier trialkylphosphines are quite similar.³² The small PEt_3 ligand allows easier access to the metal center, expansion of the coordination sphere, and facile interconversion between cis and trans isomers. Preliminary results indicate **2** is even more reactive than **1** and that the cis isomers react more readily than the corresponding trans isomers.

In addition to the reactions described above, **1** and **2** undergo a series of facile, reversible reactions in protic solvents to produce dimeric complexes. These reactions will be described separately.³³

Acknowledgment. We thank the National Science Foundation (Grants CHE78-01615 and 81-050698) for support of this work and Johnson Matthey, Inc. for a generous loan of platinum.

Registry No. *cis*-**1**, 80581-70-0; *trans*-**1**, 62945-61-3; *cis*-**2**, 80540-35-8; *trans*-**2**, 80581-71-1; **3**, 80540-36-9; **4**, 33937-25-6; $\text{Pt}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$, 76136-93-1; $\text{Pt}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)$, 69547-16-6; $\text{Pt}(\text{PEt}_3)_2(\text{CO})_2$, 76125-09-2; $\text{Pt}(\text{PEt}_3)_2(\text{C}_2\text{F}_4)$, 53987-15-8; *cis*- $\text{Pt}(\text{PEt}_3)_2\text{H}(\text{SiEt}_3)$, 80540-37-0; *trans*- $\text{Pt}(\text{PEt}_3)_2\text{HI}$, 16971-06-5.

(32) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348. (b) Henderson, W. A., Jr.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791-5794.
(33) Paonessa, R. S.; Trogler, W. C., to be submitted.

Indole-2,3-quinodimethan Route to *Aspidosperma* Alkaloids: Synthesis of *dl*-*Aspidospermidine*

Timothy Gallagher and Philip Magnus*

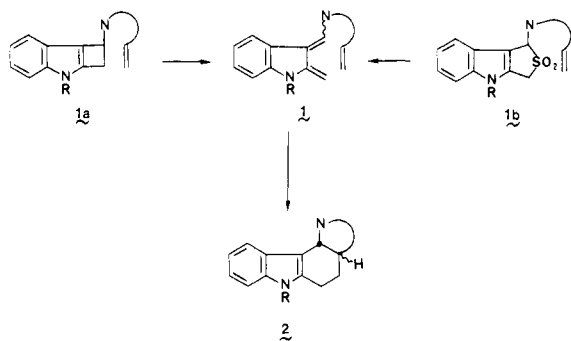
Department of Chemistry, Indiana University
Bloomington, Indiana 47405

John C. Huffman

Molecular Structure Center, Department of Chemistry
Indiana University, Bloomington, Indiana 47405

Received November 30, 1981

The extension of benzocyclobutene or sulfone precursors of *ortho*-quinodimethanes¹ for the generation of an indole-2,3-quinodimethane, **1**, would be difficult. If classical methodology

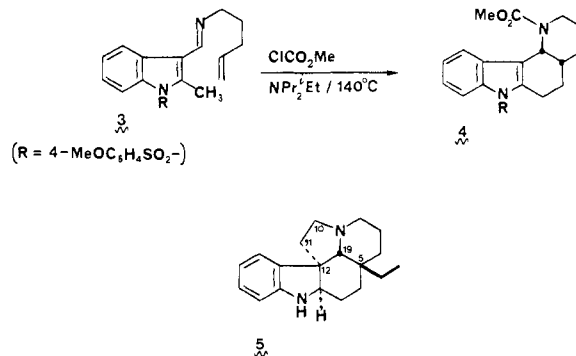


were used it would necessitate the construction of either **1a** or **1b** as substrates for regiospecific intramolecular trapping, leading to **2**. A solution to this problem was forthcoming when we discovered that the imine **3**, on treatment with methylchloroformate in chlorobenzene at 140 °C, in the presence of diisopropylethylamine, gave the tetracycle **4** in 88% yield.²

If this strategy is to be of general use for the synthesis of indole alkaloids, particularly the *Aspidosperma* type **5**, the two-carbon bridge C(10)-C(11) has to be included, and the newly formed ring junction at C(5) must be substituted by an ethyl group. In

(1) For a review of *ortho*-quinodimethans in synthesis see: Oppolzer, W. *Synthesis* **1978**, 793.

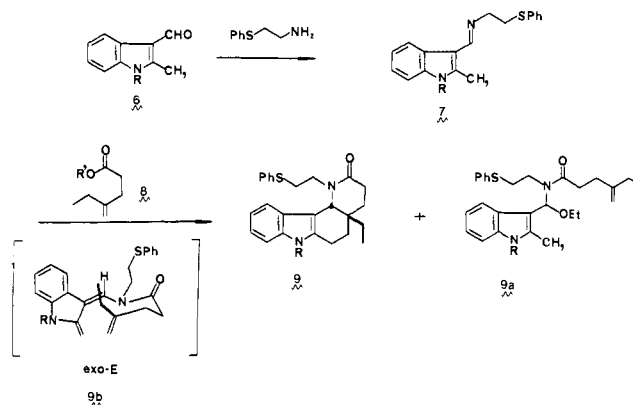
(2) Gallagher, T.; Magnus, P. *Tetrahedron* **1981**, *37*, 3889.



general the previous strategies employed in *Aspidosperma* alkaloid synthesis have C(10) and C(17) present in a tryptamine system and form the bond C(12)-C(19) to complete the carbon skeleton.³

Here we report a straightforward solution to these problems and illustrate this new strategy for indole alkaloid synthesis with the synthesis of *dl*-*aspidospermidine* **5**.

The 3-formyl-2-methylindole **6**² was condensed with 2-(phe-



nylthio)ethylamine⁴ to give the imine **7** in quantitative yield. Treatment of **7** with the mixed anhydride **8** ($\text{R}^1 = \text{EtO}_2\text{C}$) derived from 4-ethylpent-4-enoic acid,⁵ in chlorobenzene at 140 °C for

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