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Mechanism and Energetics of the Ligand-Induced Reductive Elimination of Hydrogen from a Binuclear Platinum Hydride

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Abstract: The mechanism of reaction of tertiary phosphine ligands, L, with $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (I) to give $[Pt_2HL(\mu\text{-dppm})_2]^+$ (II) and H_2 has been studied. It is shown that an intermediate, $[Pt_2H_2(\mu\text{-H})L(\mu\text{-dppm})_2]^+$ (III), is formed and the equilibrium constants associated with formation of III at low temperature have been determined. Hydrogen loss from intermediate III is intramolecular, and there is a primary isotope effect k_H/k_D of 3.5 for the reductive elimination step. Kinetic studies of the reductive elimination have demonstrated a correlation between the equilibrium constants for formation of III and the overall rate of reaction to give II and H_2 and have yielded activation parameters needed to construct a reaction coordinate energy level diagram for the reductive elimination reaction. The probability of the reductive elimination occurring at a single platinum center or across the two platinum centers is discussed.

There has been considerable interest in the mechanisms of activation of small molecules by transition-metal clusters, with the long-term aims of developing and understanding cluster catalysis and of modeling the chemisorption of small molecules on metal surfaces.[1] Oxidative addition or reductive elimination of hydrogen is relevant to many catalytic reactions, and there have been several studies of such reactions with binuclear or polynuclear complexes.[1-9] Although no unequivocal proof of mechanism has been obtained, arguments have been put forward both for true binuclear oxidative addition and for more complex mechanisms in which the actual oxidative addition or reductive elimination may occur at a single metal center. It will therefore be useful to review briefly what is known about reductive elimination of hydrogen from mononuclear complexes.

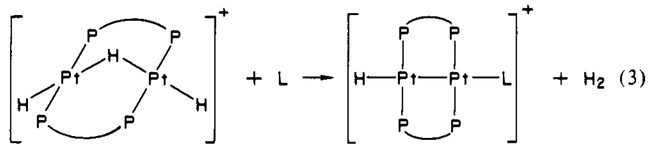
From 18-electron complexes, an intramolecular concerted cis reductive elimination of H_2 has been established in several cases (eq 1 and 2, L = tertiary phosphine or phosphite).[10,11]

$$[IrH_2(CO)_2L_2]^+ \xrightarrow{-H_2} [Ir(CO)_2L_2]^+ \xrightarrow[\text{fast}]{L} [Ir(CO)_2L_3]^+ \quad (1)$$

$$[CoH_2L_4]^+ \xrightarrow{-H_2} [CoL_4]^+ \xrightarrow[\text{fast}]{L} [CoL_5]^+ \quad (2)$$

A similar mechanism was initially proposed for reductive elimination of H_2 from the 16-electron complexes $[PtH_2L_2]$,[12,13] but more recent studies suggest that an associative mechanism may operate. Thus, the reductive elimination occurs readily in the presence of π-acceptor ligands like CO, but the complexes are otherwise thermally stable.[14,15] Theoretical studies indicate that reductive elimination from $[PtH_2L_2]$ must occur from the cis isomer but that the activation energy should be 100–150 kJ mol^{-1}.[16,17] Perhaps coordination of CO lowers this activation energy. In other reductive eliminations from square-planar platinum(II) complexes, involving C–C or C–H bond formation, added ligands may retard, accelerate, or have no effect on the rates of reaction.[18-20] The situation is complex and is not completely understood, and the above mechanistic conclusions for $[PtH_2L_2]$ must be regarded as tentative until more complete studies are reported.

The reductive elimination of H_2 from the cationic binuclear platinum hydride $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (Ia), dppm = $Ph_2PCH_2PPh_2$, has been shown to be induced by addition of soft donor ligands, L, according to eq 3.[7,21] Reactive ligands include



(3)

Ia IIa

tertiary phosphines, isocyanides, and carbon monoxide, and the reactions are probably significant in the catalysis of the water gas shift reaction by Ia.[22] In addition, reactions of alkynes, thiols, and diphenylphosphine with Ia appear to occur according to eq 3 but with subsequent rearrangements,[23,24] and photolysis of Ia

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[1] For recent reviews, see: Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Deeming, A. J. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 391. Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 31. Poilblanc, R. *Ibid.* **1982**, *62*, 75. Chisholm, M. H., Ed. "Reactivity of Metal-Metal Bonds"; American Chemical Society: Washington, DC, 1981; *ACS Symp. Ser. No. 155*, p 327 ff.

[2] Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942. Doi, Y.; Koshizuka, K.; Keii, T. *Inorg. Chem.* **1982**, *21*, 2732.

[3] Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7113.

[4] Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.

[5] Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

[6] Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516.

[7] Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239. Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[8] Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

[9] Davies, S. G.; Hibberd, J.; Simpson, S. J.; Watts, O. *J. Organomet. Chem.* **1982**, *238*, C7.

[10] Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2909. Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *Ibid.* 1970, 3000.

[11] Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 4665.

[12] Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

[13] Clark, H. C.; Goel, A. B.; Wong, C. S. *Inorg. Chim. Acta* **1979**, *34*, 159.

[14] Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 550.

[15] Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138.

[16] Kitaura, K.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1981**, *103*, 2891.

[17] Noell, J. O.; Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4578.

[18] DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.

[19] Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 352.

[20] Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306.

[21] Brown, M. P.; Fisher, J. R.; Mills, A. J.; Puddephatt, R. J.; Thomson, M. *Inorg. Chim. Acta* **1980**, *44*, L271.

[22] Frew, A. A.; Hill, R. H.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 198.

[23] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A. In "Catalytic Aspects of Metal Phosphine Complexes"; Alyea, E. C., Meek, D. W., Eds. American Chemical Society: Washington, DC, 1982; *Adv. Chem. Ser. No. 196*, p 231.

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Table II. ^{1}H NMR Data for Complexes III[a]

L	T, °C	$\delta(H^a)$	$^1J(PtH^a)$, Hz	$\delta(H^b)$	$^1J(PtH^b)$, Hz	$\delta(H^c)$	$^1J(PtH^c)$, Hz
PPh_3	−90	-4.93^b	1140	−9.65	535	-12.38^c	765
	−30	$-8.66^{d,e}$	960	−9.54	535	$-8.66^{d,e}$	960
η^1-dppm	−90	−5.05	1140	−9.50	540	−12.95	750
	−20	-8.95^d	945	−9.40	545	-8.95^d	945
$PPh_2(4\text{-}MeC_6H_4)$	−90	−6.75	*f*	−9.7	*f*	−12.45	770
	−20	$-9.6^{d,g}$	1050	−9.6	530	$-9.6^{d,g}$	1050
$PPh_2(2\text{-}MeC_6H_4)$	−90	*h*		−9.6	520	*h*	
	−20	$-8.49^{d,i}$	*j*	-9.34^i	*j*	$-8.49^{d,i}$	*j*

[a] See Scheme 1 for labeling. [b] $^2J(PtH^a) = 105$ Hz. [c] $^2J(PtH^c) = 95$ Hz. [d] Average value for exchanging H^a and H^c. [e] $^2J(PtH) = 100$ Hz. [f] Not resolved. [g] $^2J(PtH) = 110$ Hz. [h] Very broad. [i] Calculated value from δ vs. [phosphine], in exchanging system. [j] Not calculated.

Table III. Equilibrium Constants for Formation of Complexes III

L	T, °C	method[a]	K, L mol^{-1}
PPh_3	−11	A	380 ± 8
	4	B	136 ± 4
$P(4\text{-}ClC_6H_4)_3$	−14	A	220 ± 5
	−6	A	100 ± 2
	4	B	41 ± 2
$PPh_2(4\text{-}MeC_6H_4)$	−11	A	340 ± 7
$PPh_2(2\text{-}MeC_6H_4)$	−20	C	3.2 ± 0.1
	0	C	1.9 ± 0.1

[a] A, from UV-visible absorption data; B, from kinetic data; C, from NMR data. Solvent was CD_2Cl_2.

also gives reductive elimination of hydrogen.[7,25,26] These binuclear reductive elimination reactions are clearly central to the chemistry of Ia, and the overall binuclear reactions could model the reductive elimination from clusters or platinum surfaces more closely than other available systems. Since the reactions occurred very cleanly, a study of the mechanism was carried out. A preliminary account of some of this work has been published.[27]

Results and Discussion

Characterization of Products. Reaction 3 has been studied earlier with L = PPh_3, $PMePh_2$, PMe_2Ph, and η^1-dppm, and the products IIa–d have been characterized.[7] New derivatives IIe–g were prepared in the same way with L = $PPh_2(2\text{-}MeC_6H_4)$, $PPh_2(4\text{-}MeC_6H_4)$, and $P(4\text{-}ClC_6H_4)_3$ and were characterized by their ^{1}H NMR spectra and IR spectra (Table I, supplementary material). It has been shown already that the reactions are essentially quantitative.[7] In addition, it has been shown that reaction of a mixture of Ia and $[Pt_2D_2(\mu\text{-}D)(\mu\text{-}dppm)_2][PF_6]$ (Ib) with PPh_3 gives largely H_2 and D_2, with very little HD, thus proving that reductive elimination is intramolecular.[26,27] Reaction 3 is irreversible when L is a tertiary phosphine, though the reverse reaction is observed with the ligands L = CO or MeCN.[21,25]

The Detection and Characterization of Intermediates. Kinetic studies (vide infra) showed that reaction 3 occurs by an associative mechanism involving an intermediate or transition state of stoichiometry [Ia·L], III, and attempts were made to identify this. In early experiments using NMR spectroscopy the intermediates were not detected,[27,28] but it is now shown that such intermediates are formed and some aspects of the thermodynamics and kinetics of complex formation have been studied.

The $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR spectra (Tables II and III) of the adduct IIIa, L = PPh_3, at −90 °C gave useful structural data. For these studies a weighed amount of triphenylphosphine was added to a solution of Ia of known concentration in CD_2Cl_2 at −78 °C, to ensure that no reaction to give IIa occurred, and the solution was then inserted into the precooled probe of the NMR spectrometer. Under these conditions, the spectra showed the presence of an equilibrium mixture of Ia and IIIa as the only platinum-containing species, with the equilibrium favoring IIIa as discussed below. In the hydride region of the ^{1}H NMR spectrum, three resonances of equal intensity due to IIIa were observed (Figure 1). One of these (δ −9.65) had satellites due to the coupling $^1J(PtH)$ = 535 Hz of intensity one half of the center peak, proving the presence of a bridging hydride.[29] For comparison, Ia gives $\delta(\mu\text{-}H)$ −5.86 ($^1J(PtH)$ = 540 Hz).[28] In IIIa the two platinum centers must be nonequivalent and it is necessary to assume approximately equal $^1J(PtH)$ values. In addition, there were two PtH resonances each with the approximately 1:1:4:1:1 intensity ratio due to coupling to ^{195}Pt characteristic of terminal hydride signals in binuclear platinum complexes.[28] For one of these resonances, the parameters [δ −4.93 ($^1J(PtH)$ = 1140, $^2J(PtH)$ = 105 Hz)] resemble those for the terminal hydrides of Ia [δ −6.86 ($^1J(PtH)$ = 1138, $^2J(PtH)$ = 103 Hz)], but for the other resonance the couplings were considerably lower [δ −12.38 ($^1J(PtH)$ = 765, $^2J(PtH)$ = 95 Hz)].

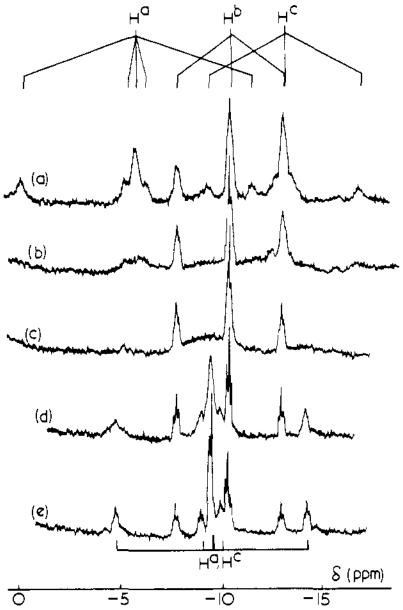

Figure 1. Low-temperature $^1H\{^{31}P\}$ NMR spectra at 100 MHz of IIIa in the PtH region. Spectra were recorded at (a) −90 °C, (b) −80 °C, (c) −60 °C, (d) −40 °C, and (e) −20 °C. For labeling see Scheme I.

The $^{31}P\{^1H\}$ NMR spectrum (40.5 MHz) of IIIa at −90 °C contained three resonances with intensity ratios of 2:2:1. The first two appeared as complex multiplets with unresolved fine structure and are assigned to the dppm phosphorus atoms [δ 12.24 ($^1J(PtP)$ = 2720 Hz) and −5.00 ($^1J(PtP)$ = 3125 Hz)], while the peak of intensity 1 is assigned to coordinated PPh_3 [δ 6.0 ($^1J(PtP)$ = 2350 Hz)]. A peak due to free PPh_3 was also observed (δ −9.8). $^{31}P\{^1H\}$ NMR spectra at 81 MHz were also recorded to confirm these assignments (Figure 2).

As the sample was warmed, the two separate peaks due to dppm phosphorus atoms broadened and then coalesced, giving an average

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[24] Puddephatt, R. J.; Thomson, M. A. *Inorg. Chem.* **1982**, *21*, 725.

[25] Foley, H. C.; Morris, R. H.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7337.

[26] Hill, R. H.; de Mayo, P.; Puddephatt, R. J. *Inorg. Chem.* **1982**, *21*, 3642.

[27] Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277.

[28] The temperature used earlier[27] was such that only the fast-exchange spectrum, which resembles that for Ia, was observed. Careful reexamination of the spectra confirms that III was formed.

[29] Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516.

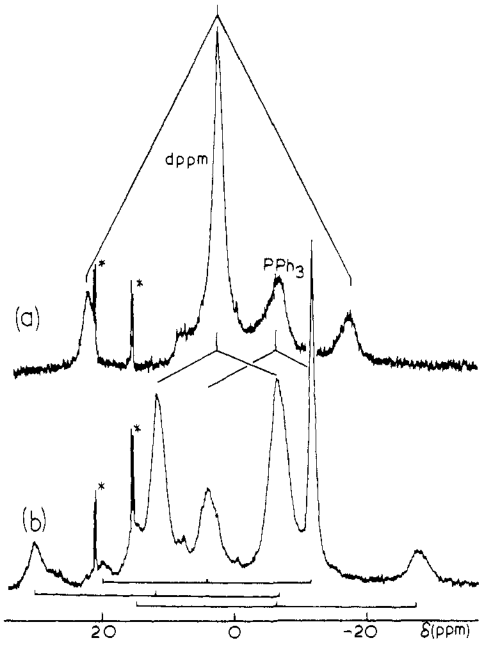
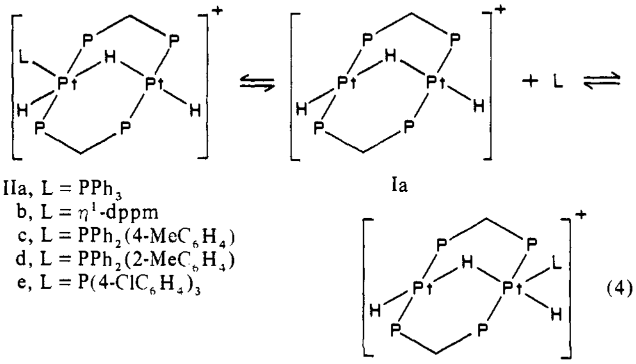


Figure 2. $^{31}P\{^1H\}$ NMR spectra (81 MHz) of IIIa with excess PPh_3. Spectra were recorded at (a) −45 °C (the ^{195}Pt satallites of the dppm phosphorus atom signal are indicated above) and (b) −81 °C (in the slow exchange region, corresponding resonances in a are indicated above and ^{195}Pt satellites are indicated below). The peaks labeled with an asterisk are due to an impurity, $[PtH(PPh_3)(dppm)]^+$.

chemical shift and $^1J(PtP)$ coupling constant [δ 4.04 ($^1J(PtP) = 2965$, $^3J(P^AP^{A''}) + {}^3J(P^AP^{A'''}) = 75$, $^3J(P^AP^{A''}) - {}^3J(P^AP^{A'''}) = 50$ Hz)], while the $^1J(PtP)$ coupling to the PPh_3 resonance was lost and an average signal due to free and coordinated PPh_3 was seen (Figure 2). Similarly in the ^1H NMR spectra, the two terminal Pt–H resonances broadened and coalesced as the temperature was raised from −90 °C (Table II, Figure 1) but the bridging hydride resonance was not significantly changed. These data indicate a fluxional process as shown in eq 4.



IIIa, L = PPh_3
b, L = η^1-dppm
c, L = $PPh_2(4\text{-}MeC_6H_4)$
d, L = $PPh_2(2\text{-}MeC_6H_4)$
e, L = $P(4\text{-}ClC_6H_4)_3$

Ia

(4)

The rapid reversible addition of PPh_3 to one of the platinum atoms without disruption of the $Pt_2(\mu\text{-}H)$ group is the only mechanism that is consistent with all the data. However, the structure of IIIa shown in eq 4 is only one of four possible structures varying in the stereochemistry at the five-coordinate platinum atom. The NMR data do not distinguish between structures in which this platinum has square-pyramidal or trigonal-bipyramidal structures and in which attack by PPh_3 occurs exo or endo with respect to the A-frame but do indicate that the dppm phosphorus atoms remain mutually trans. Structure IIIa is considered probable because its formation from Ia involves little distortion and because steric effects are expected to favor the exo addition shown in eq 4.[30] It was expected, a priori, that phosphine addition would lead to cleavage of the $Pt_2(\mu\text{-}H)$ group giving a complex, IV or V (Scheme I) with two 16-electron square-planar platinum(II) centers but the NMR data are not consistent with either of these structures.

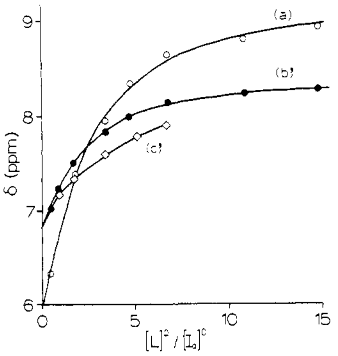
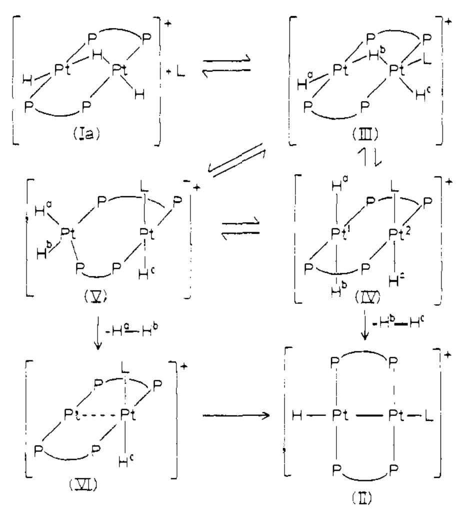


Figure 4. Observed points and best fit lines in graph of $\delta(PtH)$ vs. $[L]^0/[Ia]^0$, where $L = PPh_2(2\text{-}MeC_6H_4)$, in CD_2Cl_2: (a) data for $Pt_2(\mu\text{-}H)$ resonance at −20 °C, (b) data for terminal PtH resonance at −20 °C, and (c) data for terminal PtH resonance at 0 °C. Computed shifts for IIId are given in Table II, and computed equilibrium constants are in Table III.

Scheme I



Low-temperature $^1H\{^{31}P\}$ NMR spectra for complexes IIIb–f were also recorded and indicate that the same structure is present in all cases at −90 °C (Table II). However, for $L = PPh_2(2\text{-}MeC_6H_4)$ the slow-exchange limit was not reached at −90 °C and only the $Pt_2(\mu\text{-}H)$ resonance was observed for IIId, with the terminal hydride resonance being too broad to observe.

For the case with $L = PPh_3$, a more complete NMR study was carried out to study the kinetics of dissociation of IIA according to eq 4. The lifetimes of IIIa at different temperatures were determined from the line broadening in the slow-exchange region, from the coalescence point, and then from the line narrowing in the fast-exchange limit as the sample was warmed slowly from −90 °C. Independent lifetimes were obtained by study of both the exchanging terminal hydride signals in the $^1H\{^{31}P\}$ NMR spectra and the exchanging dppm phosphorus signals of IIIa in the $^{31}P\{^1H\}$ NMR spectra. From these data the activation parameters at 273 K for dissociation of PPh_3 from complex IIIa were found to be $\Delta H^\ddagger = 49 \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger = 70 \pm 13$ J K^{-1} mol^{-1}, and $\Delta G^\ddagger = 29 \pm 7$ kJ mol^{-1}. The Arrhenius plot is shown in Figure 3 (supplementary material).

Equilibrium Constants for Intermediate Formation. Equilibrium constants for formation of complexes III according to eq 4 have

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(30) Theoretical studies indicate that either exo or endo (often termed attack at the pocket position of the A frame) attack is possible, and examples of both are known: Hoffman, D. M.; Hofmann, R. *Inorg. Chem.* **1981**, *20*, 3543 and references therein.

(31) This would also be predicted by analogy with studies of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with ligands, L, to give $[Os_3H(\mu\text{-}H)(CO)_{10}L]$ with cleavage of one of the $Os_2(\mu\text{-}H)$ bonds: Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304 and references therein.

Table IV. Observed Second-Order Rate Constants ($k_{obsd} = kK$ L mol^{-1} s^{-1}) for the Reaction of Eq 3 in 1,2-Dichloroethane

L	T, °C	kK,[a] L mol^{-1} s^{-1}
PPh_3	25	1.6
	35	2.9
	44	5.9
	53	9.9
	60	12.7
PPh_3	25	0.46[b]
$P(4\text{-}ClC_6H_4)_3$	25	0.16
	35	0.26
	44	0.34
	53	0.51
$PPh_2(4\text{-}MeC_6H_4)$	25	0.89
$PPh_2(2\text{-}MeC_6H_4)$	25	3.9×10^{-2}
dppm	25	10.9
dppm	25	3.15[b]

[a] Generally obtained from first-order rate constants vs. [L]. [b] Value for reaction with $[Pt_2D_2(\mu\text{-}D)(\mu\text{-}dppm)_2][PF_6]$.

been determined at low temperatures by a number of methods. The direct methods will be described here, and a kinetic method will be described later.

For the complex with $PPh_2(2\text{-}MeC_6H_4)$ the equilibrium was studied by ^1H NMR spectroscopy at −20 and 0 °C, under conditions where reaction to give II did not occur. A fixed concentration of Ia was treated with increasing amounts of ligand, and the chemical shift of the $Pt_2(\mu\text{-}H)$ signal was measured in each case. In these fast-exchange spectra, $\delta((\mu\text{-}H)_{obsd}) = \rho(Ia)\delta(Ia) + \rho(IIId)\delta(IIId)$, where ρ represents the fraction of the complex present and δ(Ia) and δ(IIId) are the chemical shifts of the $Pt_2(\mu\text{-}H)$ resonances for the respective complexes. Figure 4 shows a graph of $\delta((\mu\text{-}H)_{obsd})$ vs. $[PPh_2(2\text{-}MeC_6H_4)]^0/[Ia]^0$. The equilibrium constant K and the unknown shift δ(IIId) were determined by an iterative procedure[52] to give the best fit shown in Figure 4. This gave $K = 3.2$ L mol^{-1} at 253 K and $K = 1.9$ L mol^{-1} at 273 K for formation of IIId. From these data approximate thermodynamic parameters for formation of IIId were calculated to be $\Delta H° = -15 \pm 1.5$ kJ mol^{-1}, $\Delta S° = -50 \pm 5$ J K^{-1} mol^{-1}, and $\Delta G° = -1.4 \pm 0.3$ kJ mol^{-1} at 273 K. In other cases, this NMR method was not satisfactory because the equilibrium constants were too large to give accurate values of K at the high concentrations needed in this method.

Equilibrium constants for formation of IIIa, IIIc, and IIIf were determined at 262 K by using UV–visible spectrophotometry. At 420 nm the absorbances due to complex Ia and free tertiary phosphine ligand are small, so that the absorbance is largely due to complex III. The absorbance for unit path length is given by $A = \epsilon(Ia)[Ia] + \epsilon(L)[L] + \epsilon(III)[III]$. The only unknown constant is ϵ(III), the molar extinction coefficient of complex III, and the concentration terms are related to the initial concentrations $[Ia]^0$ and $[L]^0$ by the unknown equilibrium constant K. With use of a fixed concentration of Ia and varying concentrations of added ligand L, a graph of absorbance (420 nm) vs. $[L]^0/[Ia]^0$ was drawn in each case (Figure 5). An iterative method[52] was used to give the best fit between observed and calculated absorbance values (Figure 5, supplementary material), and the unknown constants K and ϵ(III) were thus determined. The values obtained are given in Table IV.

For L = $P(4\text{-}ClC_6H_4)_3$, the equilibrium constant was determined at 267 and 259 K by this method, while for L = PPh_3 and $P(4\text{-}ClC_6H_4)_3$ the equilibrium constants were determined at 277 K by a kinetic method to be described later. From these limited data, approximate thermodynamic constants for formation of IIIa were calculated as $\Delta H° = -41$ kJ mol^{-1} and $\Delta S° = -108 \pm 4$ J K^{-1} mol^{-1} at 273 K, and for formation of IIIf the corresponding values were $\Delta H° = -55 \pm 2$ kJ mol^{-1} and $\Delta S° = -167 \pm 4$ J K^{-1} mol^{-1} at 273 K. These parameters, though approximate, are entirely consistent with the associative nature of the reaction, with the enthalpy term favoring complex formation and the entropy term favoring dissociation of complex III.

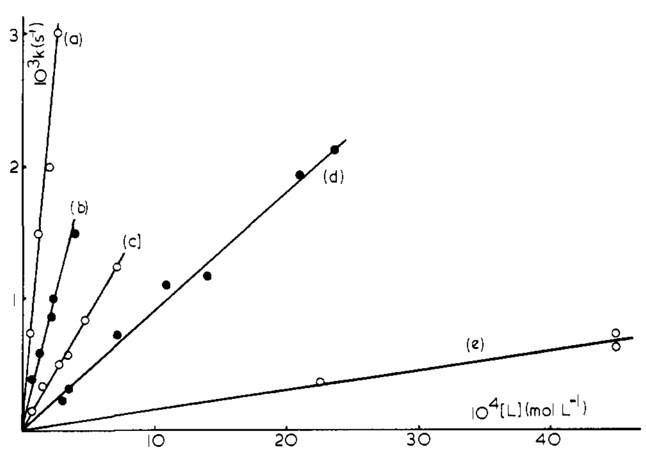

Figure 7. Graphs of pseudo-first-order rate constants for the reaction of eq 3 vs. concentration of ligand L at 25 °C: (a) Ia with dppm, (b) Ib with dppm, (c) Ia with PPh_3, (d) Ia with $PPh_2(4\text{-}MeC_6H_4)$, and (e) Ia with $P(4\text{-}ClC_6H_4)_3$.

It is clear that the steric effects due to the ortho methyl substituents in $PPh_2(2\text{-}MeC_6H_4)$ cause the equilibrium constant for formation of IIId to be much lower than for IIIc. We also note that the equilibrium constant for formation of IIIf is lower than for IIIa or IIIc, which might be taken to indicate that the weaker donor $P(4\text{-}ClC_6H_4)_3$ gives a weaker PtP bond than PPh_3. However, we note that the entropy term appears to be dominant in determining this order, and a more detailed study involving a wider range of ligands is needed to determine if there is a significant electronic effect on the equilibrium constants for formation of III.

Kinetic Studies of the Reactions. Kinetic studies of reaction 3 were carried out by using UV–visible spectrophotometry to monitor the reactions. Samples of complex Ia in 1,2-dichloroethane solution were allowed to react with a large excess of the tertiary phosphine ligand, L, in a quartz cuvette held in the thermostated cell compartment of the spectrophotometer. Complexes II are yellow while Ia is colorless, and so an increase in absorbance in the region 300–360 nm was observed as the reaction occurred (Figure 6, supplementary material). For reactions conducted at 298 K or higher the equilibrium concentration of intermediate III could be calculated to be 5% or less of the concentration of complex Ia, and the spectral changes observed are those expected for conversion of Ia to III. Under these conditions, the reactions followed good first-order kinetics and graphs of the observed first-order rate constants vs. ligand concentration were found to give good straight line plots passing through the origin (Figure 7). Thus, the reactions follow overall second-order kinetics, first order in both platinum complex Ia and phosphine ligand, L. Data at 298 K were obtained for L = PPh_3, dppm, $PPh_2(4\text{-}MeC_6H_4)$, $PPh_2(2\text{-}MeC_6H_4)$, and $P(4\text{-}ClC_6H_4)_3$. Reliable kinetic data could not be obtained for L = PMe_2Ph or $PMePh_2$. These ligands, when used in excess, appeared to displace dppm from platinum. Qualitative studies, using NMR to monitor reactions, showed that they reacted much faster than PPh_3 with Ia. The derived second-order rate constants for reaction 3 are given in Table IV. It can be seen that steric effects of the ligand are of prime importance, with the observed second-order rate constants falling in the sequence L = PMe_2Ph, $PMePh_2$ > dppm > PPh_3, $PPh_2(4\text{-}MeC_6H_4) \gg PPh_2(2\text{-}MeC_6H_4)$. Electronic effects are also significant since the poorer donor $P(4\text{-}ClC_6H_4)_3$ gives a lower rate than PPh_3.

The primary isotope effect on the rate of reaction of PPh_3 or dppm with Ia or Ib was determined from kinetic studies (Table IV). In both cases a significant isotope effect, $k_H/k_D = 3.5 \pm 0.1$, was found. For comparison, the related isotope effect for loss of H_2 from $[IrH_2(CO)_2L_2]^+$ is 2.1,[10] for addition of H_2 to $[IrCl(CO)L_2]$ it is 1.22,[32] and for loss of CH_4 (or CH_3D) from *cis*-[PtH(or D)Me$(PPh_3)_2$] it is 3.3.[33] The result clearly indicates

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(32) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

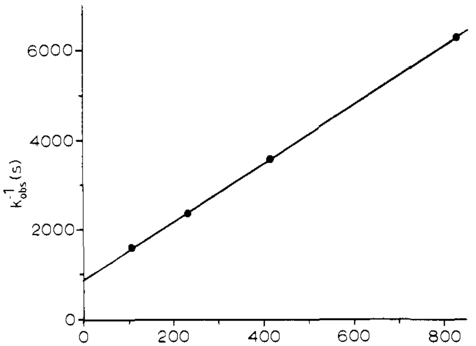


Figure 10. Graph of $1/k_{obsd}$ vs. $1/[L]$ for reaction of PPh_3 with Ia at 4 °C.

that Pt–H bond cleavage is involved in the transition state and, if the slow step involves reductive elimination, that the transition state is less "productlike" than in reductive elimination from $[IrH_2(CO)_2L_2]^+$.

The data described above support the mechanism shown in eq 5. There is a rapid preequilibrium giving III, followed by

$$\text{Ia} + \text{L} \overset{K}{\rightleftharpoons} \text{III} \xrightarrow{k} \text{II} + H_2 \qquad (5)$$

rate-determining loss of hydrogen. The kinetics should therefore be described by the expression

$$d(\text{II})/dt = \{kK/(1 + K[\text{L}])\}\{[\text{II}]_\infty - [\text{II}]\}[\text{L}] \qquad (6)$$

Under conditions where $K[\text{L}]$ is much less than unity, that is when the equilibrium concentration of III is small, this will lead to observed second-order rate constants given by $k_{obsd} = kK$, and most of our kinetic results were obtained in this regime. For the case with L = PPh_3, a variable-temperature study was carried out and, from the observed second-order rate constants at temperatures from 298 to 333 K (Table IV), the overall activation parameters from the Arrhenius plot (Figure 8, supplementary material) were calculated. This gave $\Delta H^{\ddagger}_{obsd} = 51 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger}_{obsd} = -63 \pm 7$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{obsd} = 68 \pm 5$ kJ mol^{-1}, calculated at 273 K. Now since the thermodynamic parameters associated with the preequilibrium were known, the true activation parameters for the rate-determining step, associated with the rate constant k, could be calculated. This gave $\Delta H^{\ddagger} = 92 \pm 5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 45 \pm 10$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 80 \pm 8$ kJ mol^{-1}, calculated at 273 K.

At low temperatures, the rate constant k decreases but the equilibrium constant K increases. Hence conditions can be found where the more general rate expression of eq 6 must be used to describe the kinetics. For L = PPh_3, this was the case at 277 K and so a kinetic study was made at this temperature. Again good first-order plots were obtained under conditions where a large excess of phosphine was used. The presence of significant concentrations of complex III is immediately obvious from the UV–visible spectra (Figure 9, supplementary material, compare Figure 6). Since IIIa absorbs more strongly than IIa in the region of <420 nm, an isosbestic point is seen for runs at high phosphine concentrations. The first-order rate constants in this regime are given by the expression

$$k_{obsd} = kK[\text{L}]/\{1 + K[\text{L}]\} \qquad (7)$$

and the observed rate constants are no longer proportional to [L] but rise to a plateau level as [L] is increased. The expression 7 can be rearranged to give

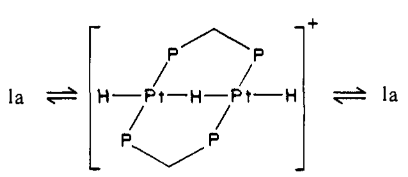
$$1/k_{obsd} = 1/kK[\text{L}] + 1/k \qquad (8)$$

Hence a plot of $1/k_{obsd}$ vs. $1/[\text{L}]$ gives a straight line of slope $1/kK$ and intercept $1/k$, from which both k and K can be determined. The plot is shown in Figure 10, and analysis gave $K = 135$ L mol^{-1} and $k = 1.1 \times 10^{-3}$ s^{-1}. This value of K at 277 K, together with that measured directly at 262 K, was used to calculate the thermodynamic parameters associated with the preequilibrium step when L = PPh_3.

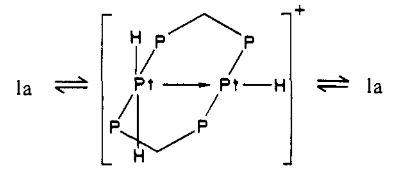
A similar variable temperature study of the reaction kinetics of Ia with $P(4\text{-}ClC_6H_4)_3$ was carried out over the range 277–326 K, to obtain the activation parameters from the Arrhenius plot (Figure 8). In this case the parameters were $\Delta H^{\ddagger}_{obsd} = 30 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger}_{obsd} = -150 \pm 7$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{obsd} = 68 \pm 5$ kJ mol^{-1} calculated at 273 K. From the reaction at 277 K, K was also calculated as 41 L mol^{-1}. Again the true activation parameters (at 273 K) associated with the rate constant k (eq 5) could be calculated and gave $\Delta H^{\ddagger} = 85 \pm 5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 17 \pm 13$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 80 \pm 9$ kJ mol^{-1}.

Discussion

Because this appears to be the first detailed mechanistic study of a reaction involving oxidative addition or reductive elimination of dihydrogen to a binuclear transition-metal complex, an attempt has been made to determine the reaction mechanism and also to understand the energetics of the reaction. The energetics of some relevant fluxional processes of complex Ia have been studied previously and the free energies of activation of the processes shown in eq 9 (at 253 K) and 10 (at 338 K) have been determined to be 45 and 68 kJ mol^{-1}, respectively.[34]



(9)



(10)

The first reaction involves inversion of the "A frame" through an intermediate with a linear Pt(μ-H)Pt group, while the second involves overall bridging for terminal hydride exchange. The reaction of eq 10 occurs more rapidly in pyridine solution than in dichloromethane solution, but, in the slow-exchange limit, the chemical shifts and coupling constants of the hydride ligands of Ia are almost identical in the two solvents. Thus hard ligands like pyridine do not appear to form complexes with Ia of structure III in detectable quantities. The UV–visible and IR spectra of Ia in pyridine and dichloromethane are also almost identical, confirming the lack of complex formation in pyridine. Complex Ia has good thermal stability in pyridine and solutions can be heated to 90 °C without change.

In contrast, tertiary phosphines form complexes with Ia of probable structure III and also induce reductive elimination of hydrogen from Ia. The observation of the rate expression of eq 6 for the overall reductive elimination reaction is fully consistent with complex III being an intermediate in the reductive elimination reaction, as indicated in eq 5, and this conclusion is supported by the observation of a good correlation between the equilibrium constants K for formation of III and the observed second-order rate constants ($k_{obsd} = kK$) for reaction 3, for the ligands PPh_3, $PPh_2(4\text{-}MeC_6H_4)$, and $PPh_2(2\text{-}MeC_6H_4)$. This correlation also suggests that reductive elimination occurs from the platinum center remote from the coordinated phosphine ligand, L, since the bulky o-tolylphosphine would be expected to accelerate reductive elimination relative to the less bulky ligands if hydrogen were lost from the near platinum center.[36]

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(33) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

(34) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642.

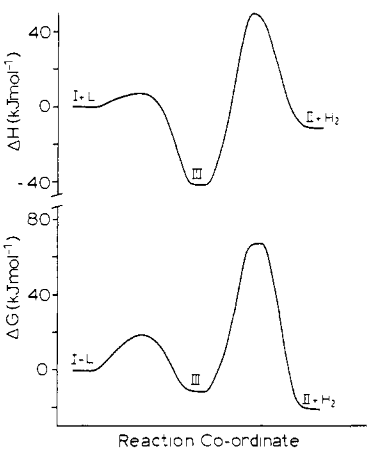
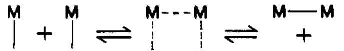


Figure 11. Reaction coordinate diagram for the reaction of eq 5 (L = PPh_3).

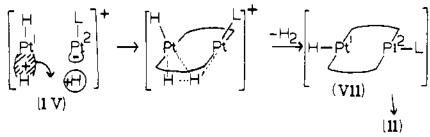
The problem now is to understand the detailed mechanism of the reductive elimination of H_2 from intermediate III of eq 5. Two reasonable mechanisms are shown in Scheme I. Of the complexes shown in Scheme I, IV, V, and VI have not been detected directly and so a brief justification of their possible roles as intermediates is necessary. It is difficult to envisage reductive elimination of hydrogen from III directly since the hydrogen atoms are too far apart for a concerted mechanism to be feasible and so a rearrangement to complex IV or V is proposed. There are good models for complex IV in the "face-to-face" complexes such as $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$ and similar complexes.[37,38] but we know of no good models for complex V.[39] However, if reductive elimination occurs at a single metal center as has been thought probable in some related systems,[1] complex V is the most probable intermediate since the mutually cis hydrogen atoms H^a and H^b can be eliminated in a concerted mechanism. Complex V could be formed directly from III or by isomerization of IV.[40] Reductive elimination from V would give VI, a platinum(0)-platinum(II) species, which would rearrange to product II, probably by hydrogen migration.[41]

An attractive alternative to this mechanism would involve a true binuclear reductive elimination of hydrogen atoms H^b and H^c from complex IV to give II directly. Such a mechanism has not been favored in the past, perhaps because the simplest mechanism involving a four-center transition state (eq 11) is orbitally forbidden.



$$\begin{array}{c}M\\|\\H\end{array} + \begin{array}{c}M\\|\\H\end{array} \rightleftharpoons \begin{array}{c}M\text{---}M\\\vdots\quad\;\vdots\\H\text{---}H\end{array} \rightleftharpoons \begin{array}{c}M\text{—}M\\+\\H\text{—}H\end{array} \tag{11}$$

However, there is evidence for a binuclear mechanism in some cases,[9,42] and a more detailed examination of the specific case of complex IV indicates that a binuclear reductive elimination may be feasible. In complex IV (Scheme I), the hydrogen atom H^c is expected to be protonic[43] whereas H^b, being trans to a strong σ donor, is expected to be much more hydridic. Thus transfer of electron density from the σ(Pt-H^b) orbital (HOMO)[44] to the σ^*(Pt-H^c) orbital (LUMO) should occur readily as illustrated in eq 12, and H-H bond formation and Pt-H bond cleavage result naturally.[45]



(12)

It is clear that this process does not lead to Pt-Pt bond formation, since the PtPt interaction resulting from eq 12 is weakly antibonding in nature, and a $Pt^2(0)$-$Pt^1(II)$ species (VII) might be expected. However, as the positive charge on Pt^1 develops, it would presumably lead to a $Pt^2{\rightarrow}Pt^1$ donor-acceptor bond,[46] using nonbonding d-electron density on Pt^2, and effectively lead to direct formation of product II. This mechanism is most attractive when a "hydridic" and "protonic" hydride are eliminated, as in the present case, but is possible in other cases also.[9,48]

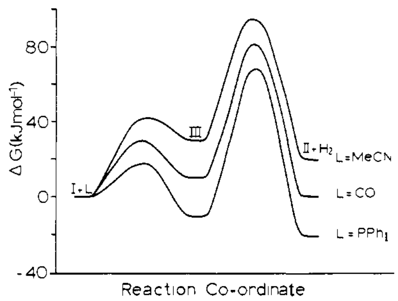


Figure 12. Proposed reaction coordinate diagrams for the reaction of eq 5 for L = PPh_3, CO, and MeCN.

The reaction coordinate diagram for the reaction of eq 5 with L = PPh_3 is shown in Figure 11, and a brief discussion of its derivation is given next. The thermodynamic parameters for the preequilibrium involving formation of IIIa (eq 4) were determined experimentally, and the activation parameters for dissociation of PPh_3 from IIIa were also determined directly. Hence the activation parameters for reaction of PPh_3 with Ia to give IIIa could be calculated, and this procedure yielded $\Delta G^{\ddagger} = 8 \pm 5$ kJ mol^{-1}, $\Delta G^{\ddagger} = 18 \pm 10$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -38 \pm 17$ J K^{-1} mol^{-1} at 273 K. The enthalpy of activation is very small, consistent with the formation of IIIa from Ia with very little distortion of the bonding framework.

The activation parameters for decomposition of IIIa to give IIa and H_2 were determined experimentally, but the thermodynamic parameters ΔG° and ΔH° could not be obtained. We have used the values $\Delta H^\circ = +30$ kJ mol^{-1}, $T\Delta S^\circ = +40$ kJ mol^{-1}, and hence $\Delta G^\circ = -10$ kJ mol^{-1}.[49] These values are reasonable,[49] but the

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(35) The kinetic expression (eq 6) does not constitute a proof of the proposed mechanism, since a similar expression would be obtained if the mechanism were described by the equation

$$III \overset{K}{\rightleftharpoons} Ia + L \xrightarrow{k} II + H_2$$

(36) The accelerating effect of bulky ligands on reductive elimination in mononuclear complexes is well-established. See for example: Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205.

(37) Balch, A. L. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L., Ed.; Plenum Press: New York, in press.

(38) Puddephatt, R. J.; Thomson, M. A. *J. Organomet. Chem.* **1982**, *238*, 231. Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 581.

(39) The closest model is $[Pt_2Me_3(\mu\text{-dppm})]^+$, which contains the cis-trans stereochemistry shown in V, but has a donor-acceptor metal-metal bond in place of the Pt-L bond of V. Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500.

(40) It has been shown that cis-trans isomerization occurs readily in mononuclear complexes $[PtH_2L_2]$,[15] and reductive elimination of the mutually trans H^a and H^b in complex IV (Scheme I) is unlikely.[15-17]

(41) Hydride migration in binuclear platinum complexes by terminal ⇌ bridging hydride transformations is well-known.[7,29,34]

(42) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676. Bitterwolf, T. *J. Organomet. Chem.*, in press.

(43) Complexes such as $[HPt(PPh_3)_3]^+$ are deprotonated readily to give $[Pt(PPh_3)_3]$. Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: New York, 1974; pp 2-4.

(44) We recognize that the HOMO may actually be a nonbonding d orbital on Pt, but this will be the highest σ-MO.

(45) Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley: New York, 1976.

(46) Metal-metal donor-acceptor bonds are now common in this area of chemistry.[39,47]

(47) McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 859.

(48) Note that a mechanism involving loss of H^+ from IV followed by formal recombination with H^- is ruled out by the proof that the reductive elimination is intramolecular.

absolute values are of less significance than the expected result that the reductive elimination of H_2 from IIIa is an entropy-driven reaction.

Little entropy change is expected for the overall reaction of eq 3, and the reactivity of Ia with added ligands can be understood in terms of the strength of the Pt–L bond formed. When L = PPh_3, a strong Pt–L bond is formed and hence both intermediate III and product II are stable with respect to Ia. The ligand L = CO gives a weaker Pt–L bond, and now the forward and back reactions of eq 3 occur at very similar rates, suggesting that $\Delta G° \approx 0$, and intermediate III cannot be detected.[21] When L = MeCN, only the back reaction of eq 3 occurs (except with photochemical activation) and again intermediate III cannot be detected.[25,26] Thus as the Pt–L bond strength decreases in the sequence Pt–P > Pt–CO > Pt–NCMe, reaction 3 changes from being thermodynamically favorable to unfavorable (Figure 12), and the remarkable differences between the reactivity of Ia with soft ligands like PPh_3 and CO and hard ligands like pyridine and acetonitrile are rationalized.

It is important to determine which is the rate-determining step in the reductive elimination reactions. The most compelling evidence comes from the entropy of activation when L = PPh_3. Although the overall apparent entropy of activation for reaction 3 is -63 ± 7 J K^{-1} mol^{-1}, when the value of $\Delta S°$ of -108 ± 4 J K^{-1} mol^{-1} for the preequilibrium step is subtracted, the true value of $\Delta S^{\ddagger}$ for loss of H_2 from IIIa is $+45 \pm 11$ J K^{-1} mol^{-1}. This suggests that the reductive elimination step, which is of course dissociative, is rate determining and the large isotope effect, $k_H/k_D = 3.5$, on the rate is fully consistent with this conclusion.[50]

The enthalpy of activation for the reductive elimination of H_2 from IIIa is 92 ± 5 kJ mol^{-1}, very close to the value of 100 kJ mol^{-1} calculated by Noell and Hay for reductive elimination from *cis*-$[PtH_2(PMe_3)_2]$. However, the apparent agreement is illusory since a significant component of the observed $\Delta H^{\ddagger}$ must arise from the preliminary rearrangement of III to IV or V[51] (Scheme I) and the true $\Delta H^{\ddagger}$ for the reductive elimination step must be considerably less than 92 ± 5 kJ mol^{-1}. It is probable that a Pt–Pt interaction, indicated by the dotted line in intermediate VI (Scheme I) or VII (eq 12) in the binuclear system allows a lower activation energy than in the mononuclear system where the high-energy species PtL_2 must be formed. It is likely that cooperative effects of this kind, leading to lower activation energies, may explain differences between mononuclear and polynuclear complexes in their ability to activate small molecules.

Conclusions

We have shown that reductive elimination of H_2 from $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ induced by tertiary phosphine ligands is an intramolecular process and that an intermediate $[Pt_2H_2(\mu\text{-}H)L(\mu\text{-dppm})_2]^+$ is involved. The intermediates have been characterized by a number of methods, and the energetics associated with their formation have been studied. The rate-determining step involves reductive elimination of hydrogen, but it is thought that prior rearrangement to a second intermediate having no $Pt_2(\mu\text{-}H)$ group is necessary before the reductive elimination can occur. It has not been possible to determine whether the slow step involves reductive elimination at a single platinum center or a true binuclear reductive elimination, but it is shown that the activation energy for reductive elimination is less than that expected for reductive elimination from a mononuclear $[PtH_2L_2]$ complex and hence that cooperative effects in binuclear complexes can lead to enhanced reactivity.

Experimental Section

The synthesis of $[Pt_2(\mu\text{-}H)H_2(dppm)_2][PF_6]$ and the deuterated analogue have been described previously.[26,29]

NMR spectra were recorded by using a Varian XL-100 spectrometer. Unless otherwise noted the ^1H spectra were obtained at 33 °C. Chemical shifts are quoted from Me_4Si (^1H NMR) or external $PO(OMe)_3$ (^{31}P NMR). Infrared spectra were obtained as Nujol mulls by using a Beckmann 4250 spectrophotometer. UV–visible spectra were recorded by using a Cary 118 spectrophotometer. Mass spectra were obtained on a Varian MAT 311A spectrometer. C and H analyses were carried out by Guelph Chemical Laboratories Ltd.

Preparation of New Complexes II. Complex Ia (0.10 g, 7.65×10^{-5} mol) was dissolved in CH_2Cl_2 (3 mL). The ligand (7.65×10^{-5} mol) was dissolved in CH_2Cl_2 (2 mL) and added dropwise to the platinum-containing solution. Solutions turned yellow and gas was produced. After reaction was complete [20 min, L = $PPh_2(4\text{-}MeC_6H_4)$; 1 h, L = $P(4\text{-}ClC_6H_4)_3$; 72 h, L = $PPh_2(2\text{-}MeC_6H_4)$], the product was precipitated by addition of *n*-pentane. The solid samples were then dried under high vacuum. Anal. Calcd for $[Pt_2H\{PPh_2(4\text{-}MeC_6H_4)\}(dppm)_2][PF_6]$: C, 52.4; H, 3.9. Found: C, 52.3; H, 4.0. Calcd for $[Pt_2H\{PPh_2(2\text{-}MeC_6H_4)\}(dppm)_2][PF_6]$: C, 52.4; H, 3.9. Found: C, 52.3; H, 4.0. Calcd for $[Pt_2H\{P(4\text{-}ClC_6H_4)_3\}(dppm)_2][PF_6]$: C, 48.9; H, 3.6. Found: C, 48.9; H, 3.6.

Studies of Reaction Rates. The solvent in these studies CH_2ClCH_2Cl was purified by distillation from K_2CO_3. It is essential that the solvent by dry and acid free.

In a typical reaction $[Pt_2H_3(dppm)_2][PF_6]$ (0.0097 g) was dissolved in CH_2ClCH_2Cl (100 mL) and $PPh_2(4\text{-}MeC_6H_4)$ (0.0500 g) was dissolved in CH_2ClCH_2Cl (25 mL). A 2.0-mL sample of the platinum-containing solution was added to a clean dry 5.0-mL volumetric flask. A 0.25-mL phosphine solution was added to this, and then CH_2ClCH_2Cl was added to a final volume of 5.0 mL. This was taken as time zero. The flask was shaken vigorously for ~40 s, and then 2.5 mL of the solution was transferred to a quartz optical cell and put in the thermostated (25 °C) compartment of a Cary 119 spectrophotometer.

The optical density of the region from 320 → 400 nm was recorded as a function of time. A plot of $\ln (A_\infty - A_t)$ vs. t was made and found to be linear, giving a first-order rate constant of 2.39×10^{-4} s^{-1}.

The volume of ligand solution added was varied to allow determination of first-order rate constants as a function of [L]. For the series [L] = 3.623×10^{-4}, 7.246×10^{-4}, 10.87×10^{-4}, 14.49×10^{-4}, 21.24×10^{-4}, and 23.7×10^{-4}, the following first order rate constants were observed: $k = 3.2 \times 10^{-4}$, 7.5×10^{-4}, 11.4×10^{-4}, 11.6×10^{-4}, 19.4×10^{-4}, and 21.2×10^{-4} s^{-1}, respectively. A plot of k vs. [L] was found to be linear, giving rise to the second-order rate constant 0.89 L mol^{-1} s^{-1}.

The above procedure was repeated at 25 °C for L = PPh_3. Again the reaction was first order in both complex Ia and L, giving a second-order rate constant of 1.6 L mol^{-1} s^{-1}. This was repeated with $Pt_2(\mu\text{-}D)D_2(dppm)_2^+$, and a rate constant of 0.455 L mol^{-1} s^{-1} was found.

Single experiments were conducted at T = 35, 44, 53, and 60 °C and the rate law assumed to be second order, giving k = 2.9, 5.89, 9.86, and 12.73 L mol^{-1} s^{-1}, respectively.

Equilibrium Constant Determinations by UV–Visible Spectroscopy. In a typical experiment complex Ia (0.0774 g) was dissolved in CH_2ClCH_2Cl (50 mL). A 2.5-mL sample of this solution was transferred to a UV cell and cooled to ~−70 °C. A solid sample of $PPh_2(4\text{-}MeC_6H_4)$ (0.0158 g) was then added to this, and the spectrum between 400 and 600 nm was recorded on the warmed (−11 °C) sample. This procedure was repeated by using different weights of ligand. Cooling was achieved by circulating a cooled ethylene glycol–water mixture through the cell compartment. The absorbance at 420 nm was then used in order to calculate the equilibrium constant.

This procedure was repeated at −11 °C for two different concentrations of Ia with L = PPh_3 and was also performed at −6 and −14 °C for L = $P(4\text{-}ClC_6H_4)_3$. An attempt was made to determine the equilibrium constant for L = dppm at −11 °C by this method, but this was unsuccessful due to reaction to give II.

The extinction coefficients of III and the K_{eq} values were then solved from the following relationship: $A = \epsilon_I[I] + \epsilon_{III}[III] + \epsilon_L[L]$, where $K = [III]/[I]^0[L]^0$ and $[I]^0$ and $[L]^0$ are known.

A best fit to the observed graph of absorbance vs. $[L]^0/[I]^0$ was found by using a standard computer program.[52]

Equilibrium Constant Determination by NMR Spectroscopy. In an NMR tube, complex Ia (0.1189 g) was dissolved in CD_2Cl_2 (0.5 mL) and a small amount of Me_4Si was added. The spectrum was obtained at −20

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(49) Noell and Hay calculated $\Delta H° = +30$ kJ mol^{-1} for reductive elimination of H_2 from *cis*-$[PtH_2(PMe_3)_2]$.[17] If we assume that $\Delta H°$ for reaction III → V balances that for the rearrangement of VI → II, then the reaction III → II + H_2 will also have $\Delta H° = \sim +30$ kJ mol^{-1}. Note that $T\Delta S = +40$ kJ mol^{-1} is a typical value for a dissociative reaction and that IIIa → Ia + PPh_3 gives $T\Delta S = +42$ kJ mol^{-1}.

(50) If the bridge splitting reaction III → V were rate determining, a significant isotope effect might also be observed but a smaller value for $\Delta S^{\ddagger}$ would be expected.

(51) Note for example that H^a and H^b in complex V are equivalent, yet no exchange between terminal and bridging hydride in IIIa is seen up to 253 K. Hence $\Delta G^{\ddagger}$ for III → V must be greater than 50 kJ mol^{-1}, and it is probable that V is significantly higher in energy than III.

(52) Shapiro, B. L.; Johnston, M. D., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8185.

°C for the region δ +1 to −10. The sample was then removed from the probe and cooled to −78 °C. Solid $PPh_2(2\text{-}MeC_6H_4)$ (0.0119 g) was added to this sample. The sample was then shaken for 30 s, returned to the probe at −20 °C, and allowed to equilibrate, and the NMR spectrum was recorded. The sample was removed and cooled to −78 °C, an additional amount of ligand (0.0108 g) was added, and the NMR spectrum was recorded. This was repeated several more times. The shift of the $Pt_2(\mu\text{-}H)$ proton was then used to calculate K from a nonlinear regressive fit of the observed shift vs. $[L]^0/[Ia]^0$ curve.[52] The value thus obtained was 3.2 L mol^{-1}. This procedure was repeated at 0 °C to give K = 1.9 L mol^{-1}.

Kinetics of Dissociation of PPh_3 from Complex IIIa. A sample of complex Ia in CD_2Cl_2 (0.18 M) in an NMR tube was cooled to −90 °C in the probe of the NMR spectrometer, and the spectrum was recorded. PPh_3 was added as a solid to give a 0.20 M solution. The cold tube was shaken to give a homogeneous solution, being careful to keep it cold, and was returned to the NMR probe at −90 °C. The spectrum was recorded, and further spectra were obtained at 10 °C intervals as the probe was slowly warmed. Lifetimes were calculated from the spectra at each temperature. A similar experiment was carried out by using ^{31}P NMR spectroscopy.

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Registry No. Ia, 65911-00-2; IIa, 77275-76-4; IIe, 86528-20-3; IIe$^+$PF$_6^-$, 86528-26-9; IIf, 86528-21-4; IIf$^+$PF$_6^-$, 86528-27-0; IIg, 86528-28-1; IIg$^+$PF$_6^-$, 86528-29-2; IIIa, 86528-22-5; IIIc, 86528-23-6; IIId, 86528-24-7; IIIf, 86528-25-8; H_2, 1333-74-0; deuterium, 7782-39-0.

Supplementary Material Available: Table I, spectroscopic data for complexes II and Figures 3, Arrhenius plot for dissociation of IIIa, 5, observed points and best fit lines in graphs of absorbance vs. $[L]^0/[Ia]^0$, 6, changes in absorption spectrum for reaction of Ia with PPh_3 at 25 °C, 8, Arrhenius plots for reactions of eq 3, and 9, changes in absorption spectrum for reaction of Ia with PPh_3 at 4 °C (8 pages). Ordering information is given on any current masthead page.

Syntheses, Properties, and X-ray Crystal Structures of Stable Methylidene Complexes of the Formula $[(\eta\text{-}C_5Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$

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Abstract: Reaction of $Re_2(CO)_{10}$ with pentamethylcyclopentadiene at 150–210 °C yields $(\eta\text{-}C_5Me_5)Re(CO)_3$ (**6**). Treatment of **6** with $NO^+BF_4^-$ gives $[(\eta\text{-}C_5Me_5)Re(NO)(CO)_2]^+BF_4^-$ (**7**). Reaction of **7** with $C_6H_5I^+\text{–}O^-/CH_3CN$ yields $[(\eta\text{-}C_5Me_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ (**8**), which is subsequently treated with L (**a**, L = PPh_3; **b**, L = $P(OPh)_3$) to give $[(\eta\text{-}C_5Me_5)Re(NO)(L)(CO)]^+BF_4^-$ (**9a**, **9b**). Reduction of **9a** and **9b** with $Li(C_2H_5)_3BH/BH_3$ and $NaBH_4$, respectively, yields $(\eta\text{-}C_5Me_5)Re(NO)(L)(CH_3)$ (**10a**, **10b**). When **10a** and **10b** are treated with $Ph_3C^+PF_6^-$, the stable (>100 °C as solids) methylidene complexes $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**4**) and $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+PF_6^-$ (**5**) form. Properties of the $=CH_2$ ligands in **4** and **5** are studied in detail: $\Delta G^\ddagger_{rot}$ (~114 °C) $\gtrsim$ 19 kcal/mol; IR $\nu_{=CH_2}$: **4**, 2987/2972 and 2922 cm^{-1}; **5**, 2987/2976 and 2920 cm^{-1}; $\nu_{=CD_2}$: **4**-d_2, 2246/2239 and 2181 cm^{-1}; **5**-d_2, 2245/2238 and 2187 cm^{-1}; NMR $^1J_{^{13}C\text{-}^1H}$(**5**) = 154 and 143 Hz. The −160 °C X-ray crystal structure of **4** shows $=CH_2/NO$ disorder. The room-temperature X-ray crystal structure of **5** indicates space group $P2_1/c$, a = 8.666 (3) Å, b = 12.387 (5) Å, c = 34.90 (1) Å, β = 102.34 (3)°, V = 3360 (2) Å^3, Z = 4, ρ_{calcd} = 1.82 g cm^{-3}. For 3038 reflections ($I_o \geq 3.0\sigma(I_o^2)$), R = 0.057 and R_w = 0.064. The $Re{=}CH_2$ bond length is 1.898 (18) Å, and the $=CH_2$ plane is essentially parallel to the Re–NO bond. This provides optimal overlap with the d orbital HOMO on rhenium.

The synthesis, isolation, and characterization of transition-metal methylidene complexes, $L_nM{=}CH_2$, have been highly sought objectives of organometallic chemists over the past two decades. In addition to the intrinsic interest in stabilizing the normally reactive CH_2 moiety,[3] $L_nM{=}CH_2$ species play key roles in metal-catalyzed olefin metathesis[4] and olefin cyclopropanation.[5]

Some of the earliest attempts to prepare transition-metal methylidene complexes came from the laboratories of Pettit[6] and Green.[7] These investigators found that the addition of acid to $(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2OCH_3)$ gave a species that could convert cyclohexene to norcarane. The intermediacy of $[(\eta\text{-}C_5H_5)Fe(CO)_2(=CH_2)]^+$ (**1**) was proposed. However, workup of the reaction mixture afforded mainly ethylene complex $[(\eta\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CH_2)]^+$. Brookhart subsequently found that **1** was too unstable to be observed by ^1H NMR at −80 °C.[8]

Herrmann has studied the reaction of $(\eta\text{-}C_5H_4R)Mn(CO)_2(THF)$ with CH_2N_2.[9] No $(\eta\text{-}C_5H_4R)Mn(CO)_2(=CH_2)$ was detected, but the plausible methylidene decomposition products $(\eta\text{-}C_5H_4R)Mn(CO)_2(H_2C{=}CH_2)$ and $(\eta\text{-}C_5H_4R)(CO)_2Mn\text{-}CH_2\text{-}Mn(CO)_2(\eta\text{-}C_5H_4R)$ were isolated. The latter was the first example of a bridging CH_2 complex. Such species are now relatively common.[10]

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(3) See references cited by: March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 178–181.

(4) (a) Caldernon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449 and earlier reviews cited therein. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

(5) (a) Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108. (b) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *Ibid.* **1978**, *100*, 3443. (c) Doyle, M. P.; Davidson, J. G. *J. Org. Chem.* **1980**, *45*, 1538. (d) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *Ibid.* **1980**, *45*, 695.

(6) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044.

(7) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508.

(8) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(9) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

0002-7863/83/1505-5804$01.50/0