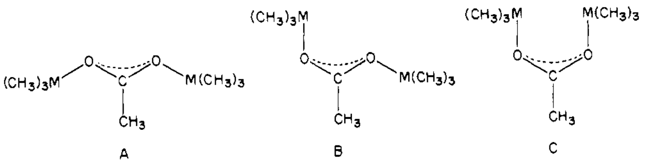

Figure 5. Possible conformations for the $[M_2(CH_3)_6CH_3COO]^-$ anions.

Table VIII. Comparison of Distances (Å) within the $(CH_3)_3M-O$ Unit

	M		
	Al	Ga	increase
M-O(av)	1.871 (4)	2.069 (1)	0.20
M-C(av)	1.94 (2)	2.00 (1)	0.06
covalent radius[a] M^{3+}	0.50	0.62	0.12

[a] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; 4th ed.; Interscience: New York, 1980; p 14.

Rb–O nonbonded interactions in the gallium analogue. Evidence of a small degree of strain in the anions is manifested by the wide C–O–M angles of 135.1 (7) and 136.3 (7)° for the aluminum and 132.9 (8) and 136.6 (8)° for the gallium derivatives. The corresponding angle in $[Al_2(CH_3)_6NO_3]^-$ is 129 (5)°. The possibility that the driving force could be the greater delocalization in A over that in B cannot be ruled out.

Another feature of interest in the anions is the relative M–O and M–C distances. As can be seen from Table VIII a bond lengthening on the order of 0.12 Å as one progresses from Al to Ga might be expected on the basis of ionic radii. In fact, however, it is seen that the M–O distances show a larger than expected increase of 0.20 Å and that the M–C distances give a considerably smaller increase of 0.06 Å. A similar effect is seen in the M–N distances in the $[M(CH_3)_3NCS]^-$ anions.[3] Clearly the group 3 congeners exhibit different bonding patterns which cannot easily be predicted. Further comparative studies are therefore in order.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$, 81432-62-4; $Rb[Ga_2(CH_3)_6CH_3COO]$, 82456-38-0.

Supplementary Material Available: Thermal parameters and observed and calculated structure factors for both compounds (22 pages). Ordering information is given on any current masthead page.

A β-Elimination Reaction Involving a Binuclear Ethylplatinum(II) Complex

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The new ethylplatinum complexes $[PtEt_2(dppm)]$, $[PtClEt(dppm)]$, $[Pt_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2][SbF_6]$ (IIb), and $[Pt_2Et_3(\mu\text{-}dppm)_2][SbF_6]$ (Ib) have been prepared and characterized (dppm = $Ph_2PCH_2PPh_2$). Of particular interest is the facile reaction of Ib to give IIb and ethylene in solution, which is formally a binuclear β-elimination process. Reaction of $[Pt(CH_2CD_3)_2(dppm)]$ with $H[SbF_6]$ gave the analogue of Ib in which scrambling of H and D within the ethyl groups had occurred, while thermolysis of a mixture of Ib and $[Pt_2(CD_2CD_3)_3(\mu\text{-}dppm)_2][SbF_6]$ (Ic) gave C_2H_4 and C_2D_4 as volatile products. Thermolysis of Ib in 1,2-dichloroethane, acetone, or acetonitrile followed first-order kinetics, and the reaction was not retarded by added dppm. From consideration of the Arrhenius parameters for thermolysis of Ib and from the low isotope effect on the rate of thermolysis of Ic, it is argued that neither the β elimination nor the ethylene dissociation step is rate-determining in the thermolysis of Ib.

Introduction

Platinum metal is an important catalyst, for example, in alkene hydrogenation, and efforts have been made to model reactions proposed to occur in such catalysis by study of discrete platinum complexes. The insertion of ethylene into a Pt–H bond or the reverse β elimination of ethylene from an ethylplatinum group have been studied in great detail in mononuclear platinum complexes.[2-4] Binuclear platinum complexes should be better models (although still highly imperfect) for a platinum surface, since it is then at least possible that cooperative effects involving both platinum atoms may be involved in the organometallic reactions, as is often proposed to occur in surface catalysis.[5] However, no reactions of alkenes with binuclear platinum hydrides or β-elimination reactions from binuclear alkylplatinum complexes have been reported.[6,7] In this article a new triethyldiplatinum(II) complex cation, $[Pt_2Et_3(\mu\text{-}dppm)_2]^+$ (dppm =

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(1) (a) University of Western Ontario. (b) University of Liverpool.

(2) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981,** *103,* 1676, 3396.

(3) Thorn, D. L., Hoffman, R. *J. Am. Chem. Soc.* **1978,** *100,* 2079.

(4) Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977,** *55,* 189.

(5) Muetterties, E. L. *Catal. Rev.—Sci. Eng.* **1981,** *23,* 69.

(6) Reactions of alkynes with binuclear platinum hydrides have been studied. Puddephatt, R. J.; Thomson, M. A. *Inorg. Chim. Acta* **1980,** *45,* L281; *Inorg. Chem.*, in press. Also, reactions of alkenes and alkynes with cluster hydrides such as $[OS_3H_2(CO)_{10}]$ have been known for some time. Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974,** 1415. Muetterties, E. L.; Rhodin, T. N.; Band, E.; Bruker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979,** *79,* 91.

(7) β Elimination has been noted in binuclear ethylmolybdenum complexes. Chisholm, M. H.; Haitko, D. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1978,** *100,* 6262. Chisholm, M. H.; Haitko, D. A. *Ibid.* **1979,** *101,* 6784. Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *Ibid.* **1982,** *104,* 2138.

0276-7333/82/2301-1183$01.25/0

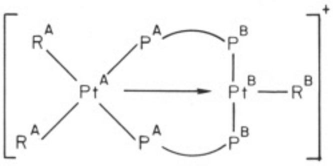
$Ph_2PCH_2PPh_2$) is reported together with a study of its thermal decomposition to the cation $[Pt_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ and ethylene.

Results and Discussion

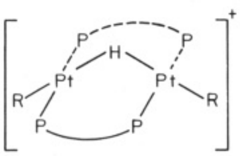
Synthesis and Characterization of $[Pt_2Et_3(\mu\text{-}dppm)_2]^+$. In previous articles, the complex cations $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$ (Ia) and $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (IIa) were reported.[8,9] Cation IIa was formed, for example, by reaction of Ia with sodium borohydride, while Ia could be prepared by reaction of $[PtMe_2(dppm)]$ with an acid having a poorly coordinating anion (eq 1, R = Me).

$$2[PtR_2(dppm)] + HX \xrightarrow{-RH} [Pt_2R_3(\mu\text{-}dppm)_2]^+X^- \qquad (1)$$
$$\text{Ia, R = Me, X = } PF_6,\ SbF_6,\ ClO_4$$
$$\text{Ib, R = Et, X = } SbF_6$$

It was suggested that the structure and spectroscopic properties of Ia were best interpreted in terms of the presence of a $Pt^{II} \rightarrow Pt^{II}$ donor–acceptor bond[8,10] whereas IIa, like other binuclear platinum hydrides,[11] has a bridging hydride ligand.



Ia, R = Me
Ib, R = Et



IIa, R = Me
IIb, R = Et

The complexes $[PtEt_2(dppm)]$ (III) and $[PtClEt(dppm)]$ (IV) were prepared by standard methods and were characterized as monomers by the ^1H and $^{31}P\{^1H\}$ NMR spectra (Experimental Section). For example, the $^{31}P\{^1H\}$ NMR spectrum of complex IV consisted of an [AB] quartet with satellites of one-fourth intensity due to coupling with ^{195}Pt and with coupling constants similar to those for the known $[PtClMe(dppm)]$.[12,13] Complex IV rearranged in solution to $[Pt_2(\mu\text{-}Cl)Et_2(\mu\text{-}dppm)_2]Cl$, characterized in solution by the ^1H and $^{31}P\{^1H\}$ NMR spectra, in a reaction exactly analogous with that of $[PtClMe(dppm)]$.[12]

Reaction of III with $H[SbF_6]$ gave the desired complex Ib, according to eq 1. Isolation of Ib in pure form is not easy, since it decomposes in solution, and rapid, careful workup of the reaction mixture is essential. The complex is a yellow solid, which is stable for several months when stored as a solid in the dark but which decomposes in solution in a few days at room temperature.

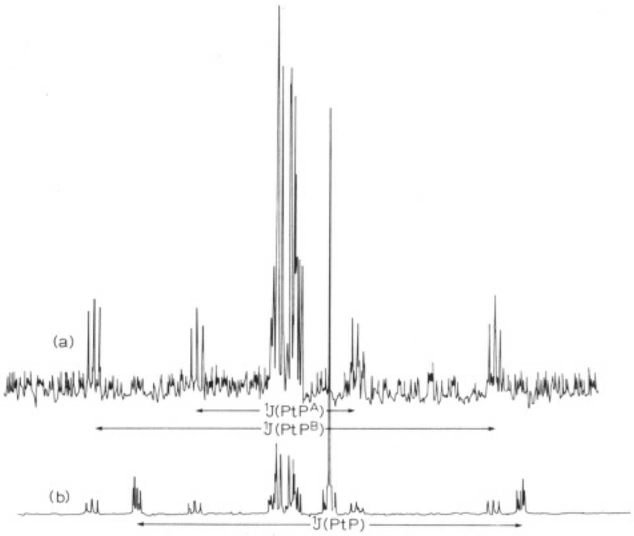


Figure 1. $^{31}P\{^1H\}$ NMR spectra at 36.2 MHz. (a) Freshly prepared solution of Ib in CH_2Cl_2. The satellites due to $^1J(PtP)$ coupling are indicated below, and the spectrum was accumulated from $t = 0$ to t 0.22 h. (b) Spectrum accumulated from the same solution between 4.54 and 5.56 h after preparation. The new singlet is due to IIb, and the $^1J(PtP)$ coupling is indicated below.

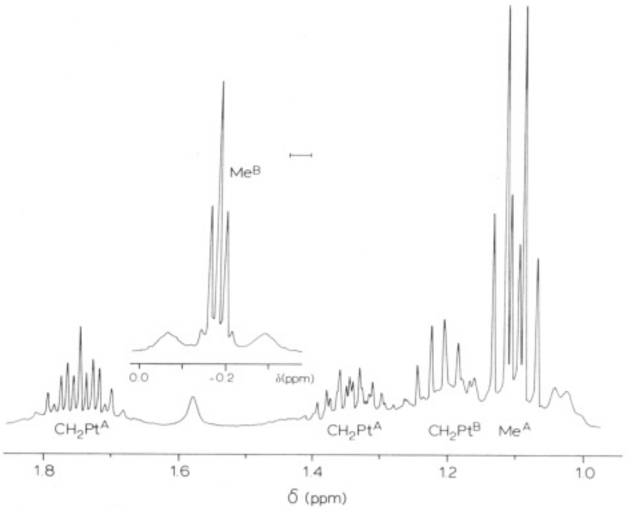


Figure 2. ^1H NMR spectrum (400 MHz) of complex Ib in the EtPt region. Inset shows the $MeCH_2Pt^B$ resonance on a different scale from the remainder of the spectrum.

The $^{31}P\{^1H\}$ NMR spectrum of Ib (Figure 1) closely resembles that of Ia, which has been analyzed in detail and is very characteristic of the unusual structure.[8] The ^1H NMR spectrum (Figure 2) is fully consistent with structure Ib. The ethyl group bound to Pt^B (structure I) gives the expected features, but the resonances due to the $EtPt^A$ groups are more complex. The complexity arises as a result of the absence of a plane of symmetry containing an $EtPt^A$ bond, and the methylene protons of a given ethylplatinum group are therefore nonequivalent. The two complex resonances, for which individual lines have not been assigned, at δ 1.35 and 1.75 are due to these methylene protons. The observed nonequivalence of the CH_2P_2 protons of the dppm ligands arises for a similar reason.[12] These results show that the molecule is not fluxional. Thus neither exchange of ethyl groups between platinum centers (which would render all ethyl groups equivalent) nor reversible cleavage of the Pt^APt^B bond (which would render equivalent the $MeCH_2Pt^A$ and CH_2P_2 protons) occurs rapidly on the NMR time scale.

Decomposition of $[Pt_2Et_3(\mu\text{-}dppm)_2]^+$. Preliminary experiments showed that, when complex Ib was exposed to light either as a solid or in dichloromethane solution, the gaseous products were ethylene and ethane in approximately equal amounts. However, the slower thermal decomposition in dichloromethane solution in the dark gave only ethylene as gaseous product, and the complex

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(8) 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.

(9) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Organomet. Chem.* **1980**, *198*, C33.

(10) Bancroft, G. M.; Chan, T.; Puddephatt, R. J.; Brown, M. P. *Inorg. Chim. Acta* **1981**, *53*, L119.

(11) Bonding in these electron-deficient "A-frame" complexes has been discussed by: Hoffman, D. M.; Hofmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

(12) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374.

(13) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

$[Pt_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2][SbF_6]$ (IIb) could be isolated from the solution.

Complex IIb is thermally stable, but it was decomposed on exposure to light, giving ethylene and ethane in approximately 1:2 molar ratio when the solid was irradiated and ethane only when a solution in dichloromethane was irradiated. The structure of IIb was determined from the ^1H and $^{31}P\{^1H\}$ NMR spectra, by comparison with the spectra of IIa which has also been characterized by X-ray crystallography.[9] The ^1H NMR signals due to the $Pt_2(\mu\text{-}H)$ and the CH_2P_2 groups each appeared as 1:8:18:8:1 quintets due to coupling with ^{195}Pt, confirming the bridging nature of these groups.[9,12] The expected resonances due to the ethylplatinum groups were observed, and the $^{31}P\{^1H\}$ NMR spectrum was very similar to that of IIa (Figure 1).

Further experiments were carried out to determine the stoichiometry of the reaction. First, solutions of Ib in CH_2Cl_2 or CD_2Cl_2 in sealed NMR tubes were allowed to stand in the dark for 2 weeks. At the end of this period, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed only peaks due to IIb (and ethylene), indicating that reaction occurred cleanly within the limits of detection of other products by NMR. In another experiment, analysis of ethylene by gas chromatography was made. A sample of Ib, shown to contain ~10% impurity of IIb, gave an 83% yield of ethylene in 4 days at room temperature in dichloromethane solution. The true yield of ethylene is thus over 90%, but experimental inaccuracy in ethylene determination and the uncertainty in the extent of impurity of IIb present in the initial sample have frustrated attempts to show unequivocally that ethylene formation is quantitative. The reaction is thus described by eq 2 and is probably quantitative.

$$\text{Ib} \rightarrow \text{IIb} + C_2H_4 \qquad (2)$$

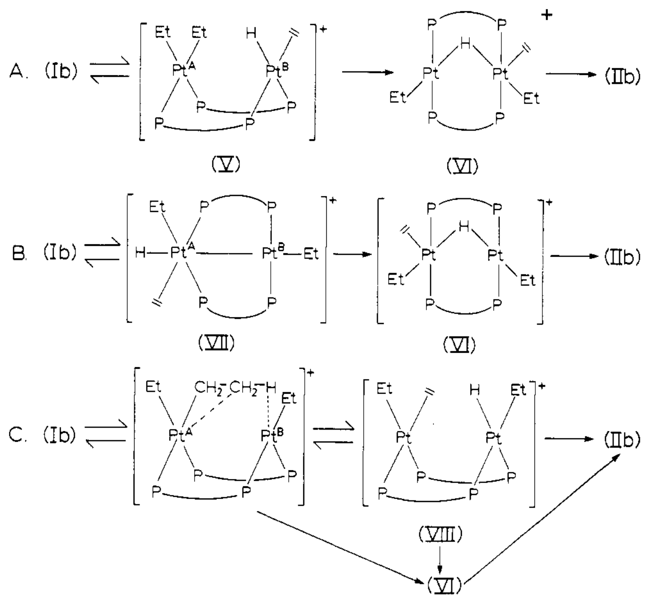
Complex IIb is remarkably stable to further β elimination; the solid can be heated to 100 °C and solutions heated under reflux in benzene without decomposition, provided light is excluded. Reaction 2 is not reversible under normal conditions. Thus, no reaction occurred on treating IIb with ethylene at pressures from 1 to 10 atm at room temperature or at 60 °C.

Mechanistic Studies

The reaction of eq 2 is unique in platinum chemistry, since dialkylplatinum(II) complexes usually give platinum(0) species, alkene, and alkane on decomposition.[2] The thermal stability of IIb is probably due to the fact that the ethyl and hydrido groups are mutually trans so that reductive elimination of ethane cannot occur. Although the complex is formally electron deficient, the $Pt_2(\mu\text{-}H)$ grouping is robust and the complex does not show properties expected for a coordinatively unsaturated complex (vide infra). Hence further β elimination does not occur easily, and complex IIb is stable to both reductive elimination and β elimination. Reaction 2 is therefore clearly suitable for mechanistic studies.

Three possible mechanims of reaction are shown in Scheme I. In mechanism A the β elimination involves the $EtPt^B$ group to give an intermediate (V)[14] and an ethyl group transfer[15] and dissociation of ethylene are then needed to give IIb. In mechanism B the β elimination occurs at Pt^A, but the Pt–H group would be formed trans to the Pt–Pt bond and an intramolecular rearrangement would be needed as shown to give IIb. Mechanism C is the only truly binuclear β-elimination process. In this mechanism dissociation of the PtPt bond allows the electron-deficient Pt^B to act as an acceptor for the β-hydride of an $EtPt^A$ group, and then ethylene dissociation from an intermediate (VIII or VI) gives the product.

Scheme I



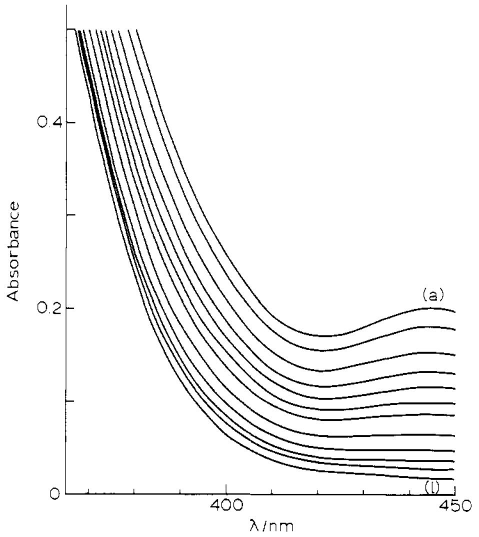


Figure 3. UV–visible spectra recorded during the decomposition of Ib (10^{-4} M solution) to IIb in acetone at 45 °C. Absorbance decreases with time and spectra (a→l) were recorded after 3, 10, 21, 31, 40, 50, 60, 80, 100, 120, 140, and 180 min.

Our studies were aimed at determining whether the reaction was an intra- or intermolecular process, whether or not the rate-determining step was the β-elimination reaction, and whether or not the β elimination was a true binuclear process. It will be seen that the first two questions were answered but the third was not.

Kinetic studies of the decomposition of Ib in solution were carried out by using both $^{31}P\{^1H\}$ NMR spectroscopy and UV–visible spectroscopy to monitor the reactions. The NMR study was carried out in CH_2Cl_2 solution at 30 °C, estimating the concentrations of Ib or IIb by comparing the peak height of a major peak of Ib or the central peak of IIb with that of the reference compound. Graphs of either ln [Ib] or ln $\{[IIb]^{\infty}-[IIb]\}$ vs. time gave good straight line plots over at least 3 half-lives (r = 0.999 and 0.991,

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[14] A trans to cis rearrangement of the Pt^BP_2 unit is probably necessary to create a vacant site cis to the ethyl group.[2-4]

[15] Intermolecular transfer of alkyl groups between platinum centers in mononuclear complexes occurs readily if the acceptor platinum center has a vacant site or loosely bound ligand. Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219.

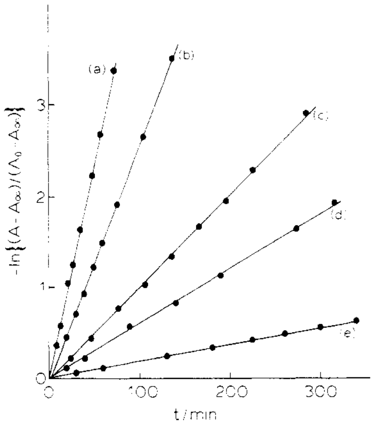

Figure 4. First-order plots for decomposition of complex Ib: (a) 1,2-dichloroethane at 60 °C; (b) acetone at 50 °C; (c) acetone at 40 °C; (d) 1,2-dichloroethane at 40 °C; (e) 1,2-dichloroethane at 30 °C.

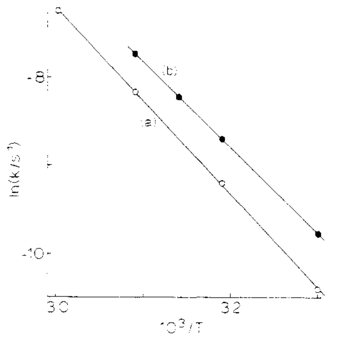

Figure 5. Arrhenius plots for decomposition of complex Ib: (a) 1,2,-dichloroethane solution; (b) acetone solution.

respectively) and yielded the first-order rate constants 2.8 × 10^{-5} and 2.9 × 10^{-5} s^{-1}, respectively.

More complete kinetic data were obtained by using UV–visible spectroscopy to monitor the reaction. A set of spectra obtained during a typical kinetic run is shown in Figure 3 and shows the decrease in absorbance over the region 360–450 nm as the yellow Ib decomposes to the almost colorless IIb. There are no crossover points in the series of spectra, but, as a routine procedure, first-order kinetic plots were drawn for absorbances at several wavelengths in the 370–450-nm region. Good first-order plots of ln $(A - A_\infty)$ vs. time were obtained for all wavelengths, and the slopes showed good agreement. Thus, although there were no isosbestic points, the reaction appears to occur cleanly without side reactions under the UV–visible conditions. The spectrum at infinity agrees well with that measured independently for pure IIb. As further confirmation, the first-order rate constant obtained at 30 °C in 1,2-dichloroethane was 3.0 × 10^{-5} s^{-1}, a result very similar to that obtained by the NMR technique in the similar solvent dichloromethane at 30 °C of (2.8–2.9) × 10^{-5} s^{-1}.

Typical first-order plots are shown in Figure 4 and Arrhenius plots in Figure 5. The complete kinetic data are given in Table I, and the following points may be noted.

(a) The first-order rate constants at 50 °C follow the sequence for solvent MeCN (0.51 × 10^{-3} s^{-1}) > acetone (0.44 × 10^{-3} s^{-1}) > CH_2ClCH_2Cl (0.28 × 10^{-3} s^{-1}). This is the order of solvent polarity and of coordinating power for platinum, but the range is small. There may be a slightly greater degree of polarity in the transition state than in the ground state, but the range is too small for it to be likely that direct solvent coordination is involved in the transition state. The Arrhenius plot (Figure 5) shows that the rate in CH_2ClCH_2Cl would exceed that in acetone at high temperature.

Table I. Kinetic Data for Decomposition of Ib and Ic

complex	solvent	T/°C	$10^4k/s^{-1}$
Ib	CH_2ClCH_2Cl [a]	30	0.301
		40	1.00
		50	2.81
		60	7.23
Ib	$(CH_3)_2CO$ [b]	30	0.563
		40	1.66[3]
		45	2.67
		50	4.36
Ib	CH_3CN	50	5.13
Ib	CH_2ClCH_2Cl	48	2.20
Ic	CH_2ClCH_2Cl	48	2.11
Ib	$(CH_3)_2CO$	48	3.63
Ic	$(CH_3)_2CO$	48	3.14
Ib	$(CH_3)_2CO$	50	4.58 [c]
Ib	$(CH_3)_2CO$	50	5.06 [d]

[a] E_a = 88 kJ mol^{-1}; log A = 10.7; $\Delta S^{\ddagger}$(300 K) = −41 J K^{-1} mol^{-1}. [b] E_a = 81 kJ mol^{-1}; log A = 9.7; $\Delta S^{\ddagger}$(300 K) = −59 J K^{-1} mol^{-1}. [c] [dppm] = 6.0 × 10^{-4} M. [d] [dppm] = 1.5 × 10^{-3} M.

(b) Addition of free dppm causes a slight *acceleration* in the rate of reaction. However, the effect is again small, and it has not been studied in detail. It is possible that an additional mechanism involving phosphine attack on Ib is possible in the presence of free phosphine. The experiment indicates strongly that phosphine dissociation as a preliminary step to the β elimination is not operative. This situation may be compared with the thermolysis of $[PtEt_2(PEt_3)_2]$ for which, in the absence of free phosphine, the rate-determining step involves dissociation of a phosphine ligand and for which the rate of thermolysis is strongly *retarded* in the presence of free phosphine.[2] The binuclear and mononuclear systems are quite different in this respect.

(c) The isotope effects, k_H/k_D, obtained by comparison of the rates of thermolysis of Ib and $[Pt_2(C_2D_5)_3(\mu\text{-dppm})_2][SbF_6]$ (Ic), were 1.1 in acetone and 1.0 ± 0.1 in 1,2-dichloroethane solution. These are very low values, and it thus appears most unlikely that the β-elimination step is rate determining.

(d) The Arrhenius parameters (small log A or substantial negative $\Delta S^{\ddagger}$) are surprising for a reaction which is dissociative overall. Such values would not be expected, for example, if ethylene dissociation were rate determining. The result could be explained if the platinum complex was more ordered in the transition state than in the ground state or if increased polarity in the transition state [see a above] led to stronger and hence more ordered solvation.[16]

The above observation of simple first-order kinetics is an indication but not proof that the β elimination is an intramolecular reaction. However, taken together with the observation that thermolysis of a mixture of Ib and Ic gave C_2H_4 and C_2D_4 as the only volatile products, it is considered almost certain that the β elimination is intramolecular.[17]

Having shown that the β-elimination step is not rate-determining, we wished to determine whether the slow step occurred before or after the β elimination. This can, in

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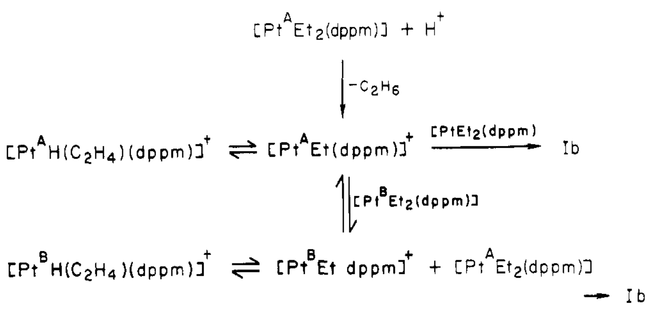
[16] However, there is one known case in which rate-determining dissociation of alkyne from a five-coordinate platinum complex is associated with a similar value for $\Delta S^{\ddagger}$. Chaudhury, N.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 467.

[17] The only other possiblity involves the sequence

$$\text{Ib} \xrightarrow{\text{slow}} \text{Ib*} \xrightarrow[\text{irreversible}]{\text{Ib, fast}} \text{IIb}$$

This is considered most improbable.

Scheme II



principle,[2] be determined by study of the complex $[Pt_2(CH_2CD_3)_3(\mu\text{-dppm})_2]^+$, but our attempted synthesis of this from $[Pt(CH_2CD_3)_2(dppm)]$ and $H[SbF_6]$ was unsuccessful. Complete scrambling of the deuterium label had occurred in the product, and this could occur prior to formation of the labeled Ib as shown in Scheme II.[15] Similarly, our attempts to prepare unsymmetrical derivatives needed to determine whether β elimination involved an $EtPt^A$ or $EtPt^B$ group were unsuccessful. For example, reaction of $[PtMe_2(dppm)]$ with $[PtClEt(dppm)]$ gave complex IIa rather than the desired $[Pt_2Me_2Et(\mu\text{-dppm})_2]^+$; other attempted reactions of this kind are mentioned in Experimental Section.

Because the labeling experiments were unsuccessful, we have not been able to distinguish between the mechanisms A, B, and C of Scheme I. However, the results are useful when compared to the mechanistic results of Whitesides and co-workers for the thermolysis of mononuclear ethylplatinum(II) complexes.[2] For all cases, it seems that the β-elimination step itself is not rate determining. However, while the rate-determining step for thermolysis of *cis*-$[PtEt_2(PEt_3)_2]$ may involve either phosphine dissociation (prior to β elimination) or reductive elimination of ethane (after β elimination), neither of these steps is involved in the thermolysis of the binuclear complex Ib. Instead, the kinetic results for thermolysis of Ib and Ic are most easily interpreted if an intramolecular isomerization is rate determining. This could, for example, involve either Pt–Pt bond cleavage (prior to β elimination) or an alkyl-transfer reaction (after β elimination).

Further, this work illustrates the general problems which may be expected in attempting to determine detailed organometallic reaction mechanisms in binuclear and polynuclear complexes. In the only comparable work known to us, Chisholm and co-workers have also been unable to distinguish between a true binuclear β-elimination mechanism and mechanisms in which the result leads to an overall binuclear reaction but in which the actual β-elimination occurs at a single metal center, in studies of $[Mo_2Et_2(NMe_2)_4]$.[7]

Experimental Section

General techniques have been described previously.[8,12] NMR spectra were recorded by using Varian XL-100 or Bruker WP-400 spectrometers. Kinetic studies were carried out by using a Carey 118 spectrophotometer, and temperature was controlled by circulating water of the required temperature through the cell compartment.

CD_3CD_2Li. A solution of CD_3CD_2Br (2.5 g) in dry diethyl ether (25 mL) was added dropwise to a suspension of Li powder (0.5 g) in diethyl ether (25 mL) over a period of 2 h. Gentle refluxing was maintained by a warm water bath, and the mixture was vigorously stirred. Stirring under reflux was continued for 2 h after the addition of CD_3CD_2Br ceased. After the reaction, the contents of the flask were allowed to cool down to room temperature. The clear ethereal solution of CD_3CD_2Li was obtained by filtration under N_2. Yield was determined by the removal of a 1-mL portion of clear solution, treatment with water, and titration with standard acid.

Solutions of CD_3CH_2Li were prepared in the same way from CD_3CH_2Br.

$[PtEt_2(dppm)]$. A solution of ethyllithium in ether (8 mL, 1.5 M) was added dropwise to a suspension of $[PtCl_2(dppm)]$ (1.0 g, 1.54 mmol) in dry ether (15 mL) under an atmosphere of nitrogen. After 1 h of stirring, the brown solution was hydrolyzed with saturated aqueous NH_4Cl solution (10 mL), the ether layer was separated, the aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to a low volume in a stream of N_2. Addition of several drops of MeOH followed by hexane gave a precipitate of pure $[PtEt_2(dppm)]$, which was recrystallised from CH_2Cl_2/MeOH/hexane as an off-white solid: 0.62 g, 63%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta(^{31}P)$ −35.88 ($^1J(PtP)$ = 1281 Hz); ^1H NMR (CD_2Cl_2) $\delta(CH_3)$ 1.35 (m, $^3J(PtH)$ = 80 Hz), $\delta(CH_2Pt)$ 1.62 (m, $^2J(PtH)$ = 80 Hz), $\delta(CH_2P_2)$ 4.17 (t, $^2J(PH)$ = 9.0 Hz, $^3J(PtH)$ = 21.8 Hz).

$[Pt(CD_2CD_3)_2(dppm)]$. An ethereal solution (40 mL) of CD_3CD_2Li (7.3 mmol) was added slowly (0.5 h) to a suspension of $PtCl_2(dppm)$ (0.59 g, 0.9 mmol) in diethyl ether (20 mL) at 0 °C. The yellow suspension was stirred for 2 h at 0 °C. Dry THF (10 mL) was added to the yellow suspension which was then stirred at room temperature for 1 h. Any excess CD_3CD_2Li was hydrolyzed at 0 °C by adding ice-cold saturated solution of NH_4Cl. A small amount of off-white solid residue was obtained. This was filtered out, and the aqueous and etheral layers were separated. The solid was then treated with CH_2Cl_2 (~10 mL) to give a yellow solution. This was conbined with the brown/red ether solution and dried over $MgSO_4$ (1 h). The solution was then filtered and reduced in volume. Addition of *n*-hexane yielded a white precipitate which was washed with methanol and dried under vacuum; yield 0.19 g, 33%; ^1H NMR (CD_2Cl_2) $\delta(CH_2P_2)$ 4.12 ($^2J(PH$ = 9.5 Hz, $^3J(PtH)$ = 21.8 Hz).

$[Pt(CH_2CD_3)_2(dppm)]$. This was prepared by the above method by using CD_3CH_2Li: ^1H NMR (CD_2Cl_2) $\delta(CH_2Pt)$ 1.55 (br s, $^2J(PtH)$ = 78 Hz), $\delta(CH_2P_2)$ 4.13 ($^2J(PH)$ = 9.1 Hz, $^3J(PtH)$ = 21.5 Hz, CH_3 peak absent), $\delta(^{31}P)$ −35.86 ($^1J(PtP)$ = 1280 Hz).

$[PtClEt(dppm)]$. A solution of CH_3COCl (0.12 g, 1.55 mmol) in CH_2Cl_2 (4.2 mL) was added over ~10 min at 20 °C with stirring to $[PtEt_2(dppm)]$ (1.0 g, 1.55 mmol) in CH_2Cl_2 (7 mL) and MeOH (7 mL). The solution was stirred for an additional 10 min, the solvent was evaporated in a stream of N_2, and the product was washed with benzene (3 mL) and recrystallized from CH_2Cl_2/hexane as white crystals: 0.55 g, 54%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta(^{31}P)$ −32.8 (trans to Et, $^1J(PtP)$ = 1076 Hz), −37.1 (trans to Cl, $^1J(PtP)$ = 4138 Hz, $^2J(PP)$ = 37 Hz); ^1H NMR (CD_2Cl_2) $\delta(CH_3)$ 0.99 (m, $^3J(HH)$ = 7.6 Hz, $^4J(PH)$ = 12.2, 2.8 Hz, $^3J(PtH)$ = 50 Hz), $\delta(CH_2Pt)$ 1.56 (m, $^3J(HH)$ = 7.6 Hz, $^3J(PH)$ = 7.6, 3.6 Hz, $^2J(PtH)$ = 68 Hz), $\delta(CH_2P_2)$ 4.21 ($^2J(PH)$ = 10.8, 8.4 Hz, $^3J(PtH)$ = 45 Hz). Anal. Calcd for $[PtClEt(dppm)]$: C, 50.4; H, 4.2; Cl, 5.5; P, 9.6. Found: C, 50.1; H, 4.1; Cl, 5.7; P, 9.4.

$[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$. A solution of $[PtEt_2(dppm)]$ (0.71 g, 1.1 mmol) in CH_2Cl_2 (8 mL) was added, with stirring, to $HSbF_6\cdot 6H_2O$ (0.285 g, 0.83 mmol) in a dry flask. The solution immediately became deep orange in color. After 10 min, the volume of solvent was reduced under a stream of nitrogen and the product was precipitated as a yellow solid by addition of MeOH (1 mL) and hexane (1 mL). Recrystallization from CH_2Cl_2/MeOH/hexane gave pure $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$-$CH_2Cl_2$: 0.55 g, 67%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta(P^A)$ 25.43 ($^1J(Pt^AP^A)$ = 1310 Hz, P^A trans to Et), $\delta(P^B)$ 22.72 ($^1J(Pt^BP^B)$ = 3180 Hz, P^B trans to P, $^2J(Pt^AP^B)$ = ~30 Hz, $^2J(Pt^BP^A)$ = ~30 Hz, $J(P^AP^B)$ = 50 Hz, $J(P^AP^{B'})$ = 45 Hz); ^1H NMR (CD_2Cl_2) $\delta(Me^A)$ 1.11 (m, $^3J(HH)$ = 7.5 Hz, $^4J(PH)_{cis} + {}^4J(PH)_{trans}$ = 10 Hz, $^3J(Pt^AMe^A)$ = 53 Hz), $\delta(MeCH_2{}^A)$ 1.35 (m), 1.75 (m), $\delta(Me^B)$ −0.18 (m, $^3J(HH)$ = 7.5 Hz, $^3J(Pt^BMe^B)$ = 91 Hz, $^4J(Pt^AMe^B)$ = 13 Hz), $\delta(MeCH_2{}^B)$ 1.22 (m, $^3J(P^BH^B)$ = 7.5 Hz), $\delta(CH_2P_2)$ 3.81, 3.96 (complex multiplets). Anal. Calcd for $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]CH_2Cl_2$: C, 43.6; H, 3.9; Cl, 4.5; F, 7.3; P, 7.9. Found: C, 43.4; H, 3.9; Cl, 4.4; F, 7.5; P, 7.9.

In some preparations the product was contaminated with 5–10% of $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2][SbF_6]$, and, when this occurred, we were unable to separate the product and impurity.

Complex Ic was prepared similarly by using $[Pt(CD_2CD_3]_2(dppm)]$. Attempts to prepare $[Pt_2(CH_2CD_3)_3(\mu\text{-dppm})_2][SbF_6]$

were also carried out in a similar way. The ^1H NMR spectrum showed that scrambling of deuterium between the methyl and methylene groups of both the $EtPt^A$ and $EtPt^B$ groups was essentially complete. Decomposition of this product gave complex II with significant ^1H content in the bridging hydride position [$\delta(Pt_2H)$ −7.6 ($^1J(PtH)$ = 485 Hz)].

Attempts To Prepare $[Pt_2R_2R^1(\mu\text{-dppm})_2]^+$. Reaction of $[PtPh_2(dppm)]$ with $[PtClMe(dppm)]$ failed to occur, but only slow dimerization of the latter to $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ was observed. Reaction of $[PtEt_2(dppm)]$ with $[PtClMe(dppm)]$ gave intractable mixtures, and $[PtMe_2(dppm)]$ with $[PtClEt(dppm)]$ gave $[Pt_2(\mu\text{-H})Me_2(\mu\text{-dppm})_2]Cl$ as the only isolated product. These reactions are evidently complicated by alkyl transfer leading to scrambling effects.

$[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2][SbF_6]$. A solution of $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$ (0.70 g, 0.47 mmol) in CH_2Cl_2 (12 mL) was stored in a closed flask for 70 h in the dark. The color changed from deep orange to dull yellow. The volume of solvent was reduced, and hexane was added to precipitate the product, which was recrystallised from CH_2Cl_2/hexane as an off-white solid: 0.47 g, 69%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) $\delta(^{31}P)$ 14.27 ($^1J(PtP)$ = 3086, $^2J(PtP)$ = 34, $^2J(PP)$ = 51, $^3J(PP)$ = 11 Hz); ^1H NMR (CD_2Cl_2) $\delta(CH_3)$ −0.14 (t, $^3J(HH)$ = 7.8 Hz, $^3J(PtH)$ = 59 Hz), $\delta(CH_2Pt)$ 0.83 (m), $^3J(HH)$ = 7.8 Hz, $^3J(PH)$ = 7.8 Hz), $\delta(CH_2P_2)$ 4.53 (q, $^3J(PtH)$ = 38.5 Hz, $^2J(PH)$ = 3.7 Hz, $^4J(HH)$ = 1.5 Hz), $\delta(PtH)$ −7.65 (m, $^1J(PtH)$ = 488 Hz, $^2J(PH)$ = 9 Hz). Anal. Calcd for $[Pt_2Et_2H(dppm)_2][SbF_6]\cdot 0.1CH_2Cl_2$: C, 44.4; H, 3.8; Cl, 0.5; F, 7.8; P, 8.5. Found: C, 44.4; H, 3.8; Cl, 0.6; F, 7.8; P, 8.5.

Ethylene Analysis. A sample of $[Pt_2Et_3(\mu\text{-dppm})_2][SbF_6]$ (0.050 g, 0.034 mmol) was placed in a small sealable vessel and dissolved in CH_2Cl_2 (1 mL). The vessel was sealed and kept in the dark to prevent photolysis. After 48 h samples of vapor were withdrawn and analyzed by GC. Only ethylene (with no ethane) was detected (82% yield). The solvent was evaporated and the sample redissolved in CH_2Cl_2 (1 mL) as before. After another 48 h a further 1.3% yield of ethylene was obtained, and a third treatment yielded only traces of ethylene and ethane. The GC calibration was made by injecting known volumes of pure ethylene into the above reaction flask containing only CH_2Cl_2 (1 mL) and then, after allowing time for equilibration, sampling as described above. The residue was identified as pure $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2][SbF_6]$ by the ^{31}P NMR spectrum, and the starting material was also shown to contain some of this material by the ^{31}P NMR spectrum. Integration of the complex spectra is inaccurate, but ~10% impurity of IIb in the sample of Ib was detected in this way.

The isotopic analysis was carried out by allowing a solution of Ib and Ic (0.02 g each) in $CHCl_2CHCl_2$ (2 mL) contained in a small vessel fitted with a Teflon tap and quickfit connector to decompose over 48 h at room temperature in the dark. The vessel was cooled in liquid nitrogen, and the volatiles were admitted directly to the mass spectrometer through the gas inlet system. Similar experiments with Ib and Ic separately were carried out, and analysis at 20 and 70 eV was made.

Kinetic Studies. The solution of Ib (0.0029 g in 10 mL of solvent, 2×10^{-4} M solution) was made up in a volumetric flask (10 mL) immediately prior to use and then transferred to a 1-cm cuvette in the thermostated cell compartment of the spectrophotometer. Spectra (370–450 nm) were recorded at suitable intervals. When an additive was required, this was weighed out and mixed with Ib before dissolution. The spectra obtained were identical with those in the absence of added dppm (absorbance by dppm in the range 370–450 nm is very low), indicating that dppm does not interact with either Ib or IIb under the conditions used.

Registry No. Ib, 82311-98-6; Ic, 82312-00-3; IIb, 82312-02-5; III, 52621-09-7; $H[SbF_6]$, 16950-06-4; CD_3CD_2Li, 1629-55-6; CD_3CD_2Br, 3675-63-6; CD_3CH_2Br, 7439-86-3; CH_3CH_2Li, 811-49-4; $PtCl_2(dppm)$, 52595-94-5; $Pt(CD_2CD_3)_2(dppm)$, 82312-03-6; $Pt(CH_2CD_3)_2(dppm)$, 82312-04-7; IV, 82312-05-8; CH_3COCl, 75-36-5; D_2, 7782-39-0.

Reactions of Transition-Metal Nucleophiles with Transition-Metal Electrophiles. Reactions of Acyliron, Acylnickel, and Cobalt Carbonyl Anions with (π-Allyl)palladium Complexes

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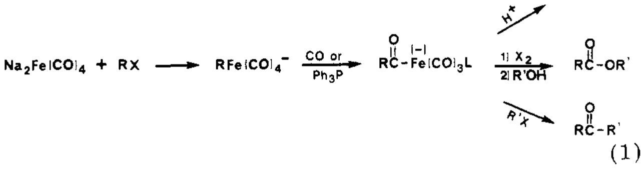
(π-Allyl)palladium chloride complexes react with anionic acyliron tetracarbonyl complexes and anionic acylnickel carbonyl complexes to produce α,β- and β,γ-unsaturated ketones, resulting from acylation of the π-allyl ligand. A variety of π-allyl complexes and acylmetal complexes were studied. Palladium(II) complexes, including (π-allyl)palladium halides, catalyzed the carbomethoxylation of allyl acetates by $NaCo(CO)_4$. The key step in all of these reactions was thought to be nucleophilic attack of the anionic metal carbonyl complex on a (π-allyl)palladium species.

Introduction

Anionic transition-metal carbonyl complexes have found significant application in organic synthesis because they are at least modest nucleophiles and are quite reactive toward organic electrophiles. A particularly well-studied complex is disodium tetracarbonylferrate, $Na_2Fe(CO)_4$.[1] This strong base (pK_a = 14) and nucleophile reacts in S_N2 fashion with organic halides to produce alkyliron species, which insert carbon monoxide to produce acyl iron species. These can be converted to acylated organic derivatives by further reaction with electrophiles (eq 1).[2,3] A related



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