

Synthesis and Dynamic Behaviour of Bis(ethylene)(tertiary phosphine)-platinum Complexes

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Reactions of ethylene-saturated solutions of bis(cyclo-octa-1,5-diene)platinum in light petroleum with tertiary phosphines or triphenylarsine afford white crystalline bis(ethylene)platinum complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ [$\text{L} = \text{PMe}_3$, PMe_2Ph , PMePh_2 , PPh_3 , $\text{P}(\text{C}_6\text{H}_{11})_3$, or AsPh_3]. Bis(ethylene)(tricyclohexylphosphine)platinum reacts with tetrafluoroethylene to give the mixed-olefin complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$. These 16-electron platinum(0) complexes show dynamic behaviour in solution with rotation of the ethylene ligands. N.m.r. studies (^1H and ^{13}C) at various temperatures establish an apparent equivalence of methylene-group sites at ambient temperatures, but at low temperatures there are two CH_2 group signals in agreement with a molecular structure in which the ligand atom L, the platinum atom, and the carbon atoms of the ethylene molecules are coplanar. Activation energies for ethylene rotation in the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ fall in the range $(10.2\text{--}13.0) \pm 0.4 \text{ kcal mol}^{-1}$. Substitution in $[\text{Pt}(\text{C}_2\text{H}_4)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ of C_2H_4 by C_2F_4 results in a 3 kcal mol^{-1} lowering of the barrier to rotation of the remaining ethylene molecule.

PLATINUM(0) derivatives of the type $[\text{Pt}(\text{PR}_3)_n]$ ($\text{R} = \text{aryl}$, $n = 3$ or 4) were first reported in 1957–1958 by Malatesta and his co-workers.¹ These and related complexes undergo oxidative-elimination reactions with great ease, so that during the last 20 years they have been used extensively for the synthesis of organo-platinum complexes, and for the activation of small molecules (*e.g.* O_2 , SO_2 , CS_2 , *etc.*) by adduct formation.² The reactivity of $[\text{Pt}(\text{PR}_3)_n]$ is related to their ability to dissociate phosphine ligands in solution, thereby creating vacant sites on platinum, and also to their nucleophilicity which is enhanced by replacement of the aryl groups in PR_3 by electron-donating alkyl groups. It was for the latter reason that complexes such as $[\text{Pt}(\text{PEt}_3)_3]$ were prepared.^{3–5} The relatively new family

of 14-electron bis(tertiary alkylphosphine)platinum complexes, typified by bis(tricyclohexylphosphine)-platinum,^{6–8} combines the prerequisites for high reactivity, namely strong σ -donor groups on the platinum and vacant sites, but suffers from the disadvantage that the phosphine ligands are bulky and, therefore, sterically inhibiting. Moreover, since the ligands are tenaciously retained in reactions, the complexes $[\text{Pt}(\text{PR}_3)_2]$ have limitations in those syntheses which are directed towards catalysis or metal-cluster formation. In this context a class of compound of great potential in synthesis is the bis(ethylene)(tertiary phosphine)-platinum complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ ⁹ because such

⁵ R. G. Pearson, W. Louw, and J. Rajaram, *Inorg. Chim. Acta*, 1974, **9**, 251.

⁶ A. Immirzi, A. Musco, P. Zambelli, and G. Carturan, *Inorg. Chim. Acta*, 1975, **13**, L13.

⁷ S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Amer. Chem. Soc.*, 1976, **98**, 5850.

⁸ J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1007.

⁹ M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 449.

¹ L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323; L. Malatesta and M. Angoletta, *ibid.*, 1957, 1186.

² L. Malatesta and S. Cenini, 'Zerovalent Compounds of Metals,' Academic Press, London, 1974.

³ D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

⁴ J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178; *J.C.S. Dalton*, 1975, 179.

species by loss of ethylene can act as sources of the fragment 'Pt(PR₃)'. Indeed, we have recently reported¹⁰ their use in the preparation of novel *trans*-di-μ-hydrido-diplatinum complexes [$\{\text{Pt}(\mu\text{-H})(\text{SiR}_3)(\text{PR}'_3)\}_2$] which were subsequently employed as catalysts in hydrosilylation studies.¹¹

In this paper we describe the synthesis of the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ [L = PMe₃, PMe₂Ph, PMePh₂, PPh₃, P(C₆H₁₁)₃, or AsPh₃], as well as their n.m.r. properties which reveal dynamic behaviour in solution.

RESULTS AND DISCUSSION

Following the discovery¹² of tris(ethylene)platinum it became apparent that this 'pure-olefin' metal complex

complexes are very soluble in light petroleum. The other three complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ [L = PPh₃, P(C₆H₁₁)₃, or AsPh₃] may be safely handled in air but are best stored for long periods in an inert atmosphere. They are only slightly soluble in light petroleum, but dissolve readily in aromatic solvents to give reasonably stable solutions.

The molecular structures of tris(olefin) complexes $[\text{Pt}(\text{olefin})_3]$ in the solid state have been established¹² as trigonal 'planar' (1), in accord with a theoretical analysis.¹³ It is likely that the ground-state molecular structure of the bis(olefin) derivatives $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ would be similar, with the ethylenic carbon atoms and the phosphorus atom coplanar with the metal atom as in

TABLE 1
Analytical^a and i.r. data for the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$

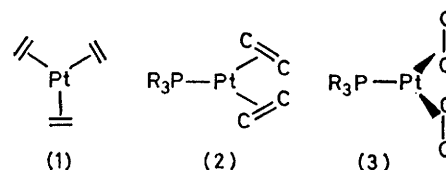
L	M.p. ^b (°C)	Analysis (%)		I.r. bands (cm ⁻¹) ^c
		C	H	
PMe ₃	30—35	25.3 (25.7)	5.8 (5.2)	3 025w, 1 470w, 1 412s, 1 295w, 1 278m, 1 255w, 1 180m, 1 170s, 955s, 932s, 845s, 800br, 728m, 675m, 400br, 355br
PMe ₂ Ph ^d	29—33	39.6 (37.0)	5.6 (4.4)	3 055m, 1 490m, 1 468s, 1 380w, 1 328w, 1 315w, 1 300m, 1 290s, 1 195m, 1 185s, 1 110s, 1 080w, 1 040w, 1 010w, 950br,s, 920br,s, 875w, 855w, 850m, 750s, 740m, 730w, 720m, 705s, 695m, 500m, 450br, 410br
PMePh ₂	25—30	44.8 (45.2)	5.0 (4.7)	3 030w, 1 478m, 1 430s, 1 410w, 1 370w, 1 303w, 1 280w, 1 190m, 1 175s, 1 155s, 1 100s, 1 070w, 1 030w, 1 000w, 950w, 910w, 885s, 745m, 740s, 722s, 690s, 510s, 490m, 450m, 435br, 400br
PPh ₃	82—85	51.0 (51.5)	4.4 (4.5)	3 025w, 1 470s, 1 425s, 1 300w, 1 255w, 1 230w, 1 190m, 1 180s, 1 175m, 1 150w, 1 110w, 1 090m, 1 065w, 1 023w, 995m, 950w, 800m, 750m, 745m, 695s, 530m, 500m, 445w, 390br
P(C ₆ H ₁₁) ₃	135—140	49.5 (49.7)	8.2 (7.8)	3 050m, 1 411w, 1 342w, 1 322w, 1 298w, 1 291w, 1 260w, 1 223w, 1 194w, 1 188m, 1 178s, 1 163w, 1 129w, 1 111w, 1 048w, 1 008m, 946w, 935w, 917w, 898w, 887w, 848m, 818w, 741m, 738 (sh), 529m, 518m, 495w
AsPh ₃	82—86	47.7 (47.6)	4.2 (4.1)	3 050m, 1 580m, 1 475s, 1 435s, 1 420m, 1 380m, 1 310m, 1 220m, 1 200s, 1 190s, 1 180m, 1 160m, 1 090s, 1 035m, 1 010m, 970m, 932w, 920w, 865w, 760s, 750s, 705s, 680w, 490s, 478s, 415br, 395br

^a Calculated values are given in parentheses. ^b With decomposition. ^c Nujol mulls except for L = PMe₃ and PMe₂Ph, measured as liquid films. ^d Complex retains solvent.

could be used as a route to $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ by treating $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ in a 1 : 1 molar ratio with a suitable phosphine or arsine donor L. Subsequently it was found that it was unnecessary to isolate $[\text{Pt}(\text{C}_2\text{H}_4)_3]$, instead when bis(cyclo-octa-1,5-diene)platinum was dissolved in light petroleum and saturated with ethylene after addition of a tertiary phosphine or triphenylarsine the desired complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ (Table 1) were obtained as white crystals in good yield.

The complex $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ is the least robust of the series, decomposing at room temperature in a few hours in the solid state even when stored under nitrogen. However, decomposition is inhibited by storage under ethylene. The two complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ (L = PMe₂Ph or PMePh₂) are somewhat more stable than the trimethylphosphine derivative, but nevertheless slowly decompose even in an inert atmosphere. All three

(2). Indeed, an X-ray crystallographic study¹⁴ reveals coplanarity of the phosphorus, platinum, and olefinic carbon atoms in the mixed-olefin complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$. The alternative ground-state structure (3) differs from (2) in that the methylene groups



have similar environments whereas in (2) these groups occupy two non-equivalent molecular sites. N.m.r. studies (¹³C and ¹H), therefore, allow a distinction to be made between (2) and (3) in solution, assuming the

¹⁰ M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Chem. Comm.*, 1976, 671; M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, 1978, 801.

¹¹ M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, 1977, 1519, 1525.

¹² M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

¹³ N. Rösch and R. Hoffmann, *Inorg. Chem.*, 1974, **13**, 2656.

¹⁴ J. A. K. Howard and P. Mitprachachon, unpublished work.

absence of rotation about the platinum–ethylene bonds. It was anticipated, however, that these molecules would

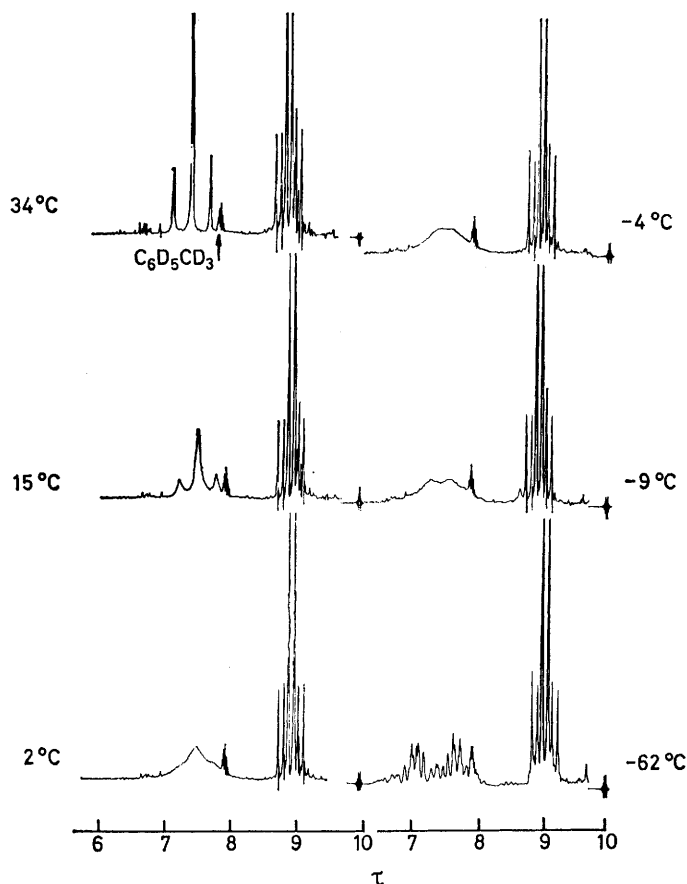


FIGURE 1 Hydrogen-1 n.m.r. spectra of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ from 35 to -60°C

show dynamic behaviour in solution, but that by decreasing the temperature of the measurements a slow-exchange limit on the n.m.r. time scale would be reached. From such studies it would be possible to estimate the activation energies for olefin rotation in these d^{10} platinum(0) complexes, and compare these with earlier results for d^8 platinum(II) complexes $[\text{PtX}(\text{pd})\text{-(olefin)}]$ and $[\text{PtX}(\text{Y})(\text{C}_2\text{H}_4)\text{L}]$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}$, or O_2CCF_3 ; $\text{pd} = \text{pentane-2,4-dionate}$),¹⁵ and for the d^8 rhodium(I) species $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2]$.¹⁶

Examination of the ^1H and ^{13}C n.m.r. spectra of the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ revealed the anticipated variation of line shape with temperature, with the upper limit indicating an apparent equivalence of methylene-group sites and the lower limit establishing the presence of two non-equivalent molecular sites as in structure (2).^{*} Measurements spanned the temperature range -80 to

^{*} The nature of the exchange process observed establishes that the dynamic behaviour taking place is a rotation about the platinum–ethylene bonds rather than about the C–C axes of the olefins (see B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1312).

¹⁵ J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776 and refs. therein.

$+35^\circ\text{C}$. Figures 1 and 2 show the variable-temperature ^1H and ^{13}C n.m.r. spectra, respectively, of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$.

At low temperatures the four protons of each ethylene ligand in the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ form an $(\text{AB})_2\text{X}$ spin system ($\text{X} = ^{31}\text{P}$) giving rise to a many-line pattern in the ^1H n.m.r. spectra which is further complicated by the platinum satellites. For $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ the spectrum was sufficiently well resolved for a computer analysis to be made, using the program LACX,¹⁷ and a good fit of experimental and theoretical spectra was obtained by iterative procedures (Figure 3). This treatment gave the following values: τ_A 7.1, τ_B 7.7; $J(\text{PH}_A)$ -7.8 , $J(\text{PH}_B)$ 7.9, $J(\text{PtH}_A)$ 60, $J(\text{PtH}_B)$ 53, $J(\text{H}_A\text{H}_B)$ 11.7 and 9.2, and $J(\text{H}_A\text{H}_A) = J(\text{H}_B\text{H}_B)$ ca. 5 Hz. For the other complexes only approximate values of the two proton chemical shifts could be extracted from the low-temperature spectra and these are given in Table 2, which lists ^1H and ^{13}C n.m.r. data for the ethylene ligands for all the complexes studied. N.m.r. data for the phosphine and arsine ligands are given in Table 3.

The n.m.r. data obtained for $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ at low temperatures may usefully be compared with similar parameters for free olefins and cyclopropanes. In particular, the vicinal H–H coupling constants are much nearer to values observed in cyclopropanes (typically 9

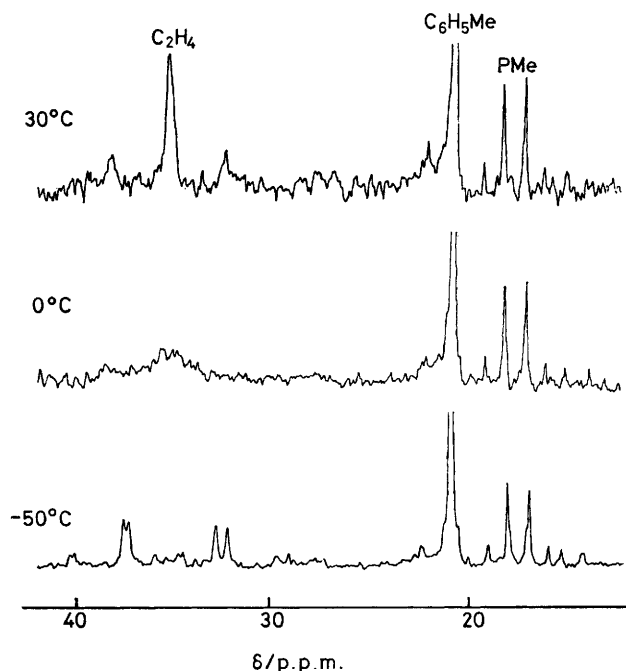


FIGURE 2 Carbon-13 n.m.r. spectra of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ at 30, 0, and -50°C

and 7 Hz) than in free ethylene (19.1 and 11.7 Hz) supporting the metallacyclopropane model^{18,19} for the

¹⁶ R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

¹⁷ C. W. Haigh, *Ann. Rep. N.M.R. Spectroscopy*, 1971, **4**, 311.

¹⁸ S. D. Ittel and J. A. Ibers, *Adv. Organometallic Chem.*, 1976, **14**, 33.

¹⁹ D. M. P. Mingos, *Adv. Organometallic Chem.*, 1977, **15**, 1.

bonding of ethylene to platinum. On the other hand, the values of the ^{195}Pt - ^{13}C coupling constants are considerably lower than would be expected for a normal σ bond between platinum and carbon.²⁰

The observation of platinum satellites associated with the resonances due to the ethylene (^1H and ^{13}C) and phosphine (^1H and ^{31}P) ligands at all the temperatures eliminates any dissociative mechanism for the site

usually negative while *trans* are positive. This assignment is also supported by the ^{13}C chemical shifts and coupling constants, which show a large variation with the ligand L for C_B , the carbon (*trans* to L) having the larger ^{31}P - ^{13}C coupling constant (Table 2).

In view of the complicated nature of the ^1H n.m.r. data it was not possible to carry out a full line-shape analysis of the temperature-dependent spectra, and the long

TABLE 2

N.m.r. data ^a for the C_2H_4 groups in the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$ and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$

Complex	Hydrogen-1 ^b				Carbon-13 ^c								
	Fast exchange		Slow exchange		Fast exchange			Slow exchange ^d					
	τ	$J(\text{PtH})$ ^e	τ_{A}	τ_{B}	δ	$J(\text{PtC})$	$J(\text{PC})$	δ_{A}	δ_{B}	$J(\text{PtC}_{\text{A}})$	$J(\text{PtC}_{\text{B}})$	$J(\text{PC}_{\text{A}})$	$J(\text{PC}_{\text{B}})$
[Pt(C ₂ H ₄) ₂ (PMe ₃)]	7.5	-57	7.1	7.7	35.7 ^f	146		37.9	33.0	139	158	-7	16
[Pt(C ₂ H ₄) ₂ (PMe ₂ Ph)]	7.4	-57	7.0	7.7	37.6 ^f	146		39.5	34.4	139	159	-6	15
[Pt(C ₂ H ₄) ₂ (PMePh ₂)]	7.4	-57	6.9	7.6	39.6	146	4	42.0	36.3	137	156	-6	15
[Pt(C ₂ H ₄) ₂ (PPh ₃)]	7.3	-57	6.8	7.5	42.3	146	2	45.6	38.4	137	154	-5	12
[Pt(C ₂ H ₄) ₂ {P(C ₆ H ₁₁) ₃ }] ^g	7.4	-57	7.0	7.6	36.9	146	2						
[Pt(AsPh ₃)(C ₂ H ₄) ₂]	7.2	-63	6.8	7.4	39.6	164		41.6	37.1	136	193		
[Pt(C ₂ H ₄)(C ₂ F ₄){P(C ₆ H ₁₁) ₃ }]	7.0	-45	6.4	7.5									

^a Spectra measured in toluene- $[\text{D}_6]$ toluene over the range -80 to $+35$ °C for all the complexes. Coalescence temperatures in Table 4. Coupling constants in Hz. ^b Chemical shifts in τ . ^c Hydrogen-1 decoupled; chemical shifts (δ) relative to SiMe_4 , positive values to high frequency. ^d C_A and C_B are *cis* and *trans* carbon atoms with respect to ligand L in structure (2) (see text). ^e Sign established by double-resonance experiments for $\text{L} = \text{PMe}_3$, signs assumed for the other complexes. ^f No ^{31}P - ^{13}C splitting resolved, linewidths *ca.* 5 Hz. ^g At slow exchange rates the ^{13}C resonances due to the C_2H_4 ligands could not be observed owing to low complex solubility and interference from carbon atoms of the cyclohexyl group.

TABLE 3

N.m.r. data ^a for ligand L in the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$

Complex	Hydrogen-1 for PMe_3 ^b			Phosphorus-31 ^c		Carbon-13 ^d					
	τ	$J(\text{PH})$ ^e	$J(\text{PtH})$ ^e	δ	$J(\text{PtP})$	δ	$J(\text{PC})$	$J(\text{PtC})$	δ	$J(\text{PC})$	$J(\text{PtC})$
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$	8.9	-8	+31	27.8	3 204	17.8	28	50			
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})]$ ^f	8.6	-8	+31			17.3	28	46			
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMePh}_2)]$ ^f	8.2	-8	+31	-4.6	3 320	16.7	29	48	132.0 (C^2)	11	22
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$				-25	3 425				135.8 (C^1)	44	18
									133.8 (C^2)	12	20
									128.0 (C^3)	11	
									37.8 (C^1)	20	31
									30.4 (C^2)		21
									28.0 (C^3)	10	
									27.0 (C^4)		
									136.9 (C^1)		
									133.5 (C^2)		
$[\text{Pt}(\text{C}_2\text{H}_4)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$				-29.4	3 295						
$[\text{Pt}(\text{AsPh}_3)(\text{C}_2\text{H}_4)_2]$ ^f											

^a Measured in toluene- $[\text{D}_6]$ toluene, coupling constants in Hz. ^b Chemical shifts in τ . ^c Hydrogen-1 decoupled, chemical shifts in p.p.m. to low frequency of 85% H_3PO_4 (external). ^d Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of SiMe_4 . ^e Sign determined by double-resonance experiment for $\text{L} = \text{PMe}_3$, signs assumed for the other complexes. ^f Carbon-13 resonances of Ph partially or entirely obscured by solvent signals.

exchange of the CH_2 groups in (2). The lack of phosphorus coupling in the fast-exchange ^1H spectra is due to the fact that the two ^{31}P - ^1H coupling constants are fortuitously equal in magnitude but of opposite sign. A similar effect is observed in the ^{13}C spectra where the low-temperature couplings (6 and 15 Hz) average *ca.* 5 Hz in the high-temperature spectra, showing that they are also of opposite signs. We tentatively attribute the smaller of these coupling constants to the carbon in a *cis* relation to the phosphine in the static structure (2), since *cis* couplings are generally smaller in magnitude than *trans* couplings. Moreover, *cis* couplings are

* Throughout this paper: 1 cal = 4.184 J.

²⁰ B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

acquisition times needed for the ^{13}C spectra, due to limited solubility, prevented accurate determination of coalescence temperatures from these spectra. Activation parameters were obtained, therefore, from the ^1H spectra by application of the relation (1) ²¹ which only

$$\Delta G_{T_c}^\ddagger = -RT_c \ln (\pi \Delta \nu h / 2^{\frac{1}{2}} k T_c) \quad (1)$$

strictly applies to a simple two-site exchange with no coupling. However, the errors involved in applying this equation to AB systems are relatively small so that the values (Table 4) we obtain for $\Delta G_{T_c}^\ddagger$ are accurate to ± 0.4 kcal.*

²¹ H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.

With the exception of the triphenylphosphine complex, the activation energies for olefin rotation are remarkably similar for the $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ complexes (Table 4). Steric factors do not appear to be involved because the energies for rotation when $\text{L} = \text{PMe}_3$ or

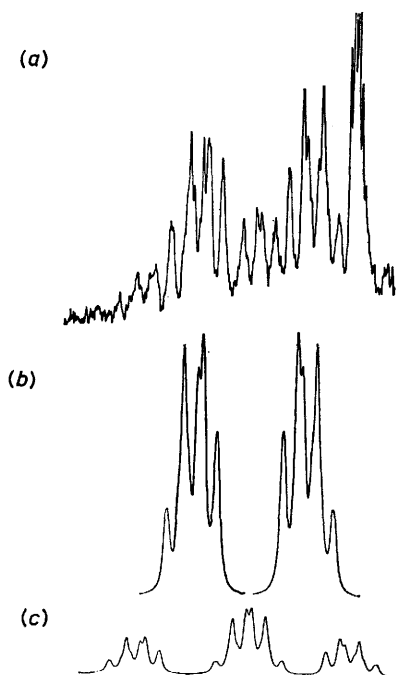


FIGURE 3 Hydrogen-1 n.m.r. spectra of $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ at -60°C , shown as expanded-scale display of the ethylenic region: (a) experimental spectrum; (b) theoretical spectrum, calculated using the parameters quoted in the text, for non-active platinum nuclei; and (c) as for (b) but including the effect of ^{195}Pt nuclei (platinum-satellite spectrum)

$\text{P}(\text{C}_6\text{H}_{11})_3$ are the same, yet these ligands are generally considered to be comparable σ donors but to differ widely

TABLE 4
Activation energies for olefin rotation

Complex	$\Delta G_{T_c}^{\ddagger a}$		T_c^b
	kcal mol $^{-1}$	kJ mol $^{-1}$	
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$	13.0	54.4	269
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})]$	12.4	51.9	257
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMePh}_2)]$	12.2	51.0	254
$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$	10.2	42.7	225
$[\text{Pt}(\text{C}_2\text{H}_4)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$	12.8	53.6	264
$[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$	9.8	41.0	211
$[\text{Pt}(\text{AsPh}_3)(\text{C}_2\text{H}_4)_2]$	11.3	47.3	235

^a Calculated from the ^1H n.m.r. spectra. ^b The coalescence temperatures are believed to be accurate to within $\pm 4^\circ\text{K}$. This uncertainty, together with the errors arising from the application of a simple rate equation to our system, leads to an error of *ca.* ± 0.4 kcal mol $^{-1}$ in the values for $\Delta G_{T_c}^{\ddagger}$.

in their steric requirements. The relatively lower barrier for ethylene rotation in the PPh_3 and AsPh_3 complexes is as expected. These ligands are poorer σ donors to the metal so that there will be relatively less electron density synergistically transferred to the π^* orbitals of the ethylene ligands. The less the back bonding from platinum to the antibonding orbitals of the ethylenes the lower will be the barrier to rotation. This effect shows

up strongly when an ethylene group in $[\text{Pt}(\text{C}_2\text{H}_4)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ is replaced by tetrafluoroethylene, the barrier to rotation of the remaining ethylene being lowered by *ca.* 3 kcal mol $^{-1}$ with the coalescence temperature decreasing to -62°C . Moreover, in contrast to the ^1H spectra of the ethylene ligand, the ^{19}F n.m.r. spectrum of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ in CFCl_3 at ambient temperatures shows that the $\text{Pt}(\text{C}_2\text{F}_4)$ group is rigid with two environmentally distinct CF_2 groups, the ^{19}F chemical shifts of the two types of fluorine being at 126.4 and 128.5 p.p.m. (relative to CCl_3F at 0.0 p.p.m.). Tetrafluoroethylene is a strong π acceptor removing charge from the platinum²² so that back bonding to the π^* orbitals of the remaining ethylene is reduced thereby making its rotation easier. Similar behaviour has been observed previously¹⁶ between the two complexes $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2]$ and $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$, but for d^8 rhodium the barrier is lowered less (*ca.* 1.4 kcal mol $^{-1}$) in replacing C_2H_4 by C_2F_4 than in the d^{10} platinum complex.

There is remarkable similarity between the activation energies listed in Table 4 and those reported previously by Lewis and his co-workers¹⁵ for platinum(II) complexes, even though different metal co-ordinations and oxidation states are involved in the two classes of compound. Thus the values found¹⁵ for $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{PET}_2\text{Ph})]$ and $[\text{PtCl}_2(\text{AsPh}_3)(\text{C}_2\text{H}_4)]$ are 12.8 and 11.8 kcal mol $^{-1}$, respectively, to be compared with 12.4 kcal mol $^{-1}$ for $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})]$ and 11.3 kcal mol $^{-1}$ for $[\text{Pt}(\text{AsPh}_3)(\text{C}_2\text{H}_4)_2]$. Back bonding from platinum to ethylene would be stronger in the platinum(0) than in the platinum(II) species, leading to higher barriers to olefin rotation in the former. However, this is apparently offset by the presence of two C_2H_4 groups in the platinum(0) complexes so that the electron density available for $d_{\pi}\text{-}\pi^*$ bonding has to be divided between two olefin ligands rather than one in the platinum(II) complexes. Moreover, with the latter, steric effects are more likely to inhibit olefin rotation, since the metal is bonded to four ligands rather than three.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz with SiMe_4 (τ 10.00) as internal reference. Fluorine-19, ^{31}P , and ^{13}C n.m.r. spectra were obtained on a JEOL PFT-100 spectrometer at 94.1, 40.48, and 25.15 MHz respectively; chemical shifts are relative to CCl_3F , H_3PO_4 , and SiMe_4 , respectively, as external references. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. $30\text{--}40^\circ\text{C}$.

Synthesis of the Complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{L}]$.—Bis(ethylene)-(tricyclohexylphosphine)platinum. A two-necked round-bottomed flask (250 cm 3) was fitted with a magnetic stirring bar, charged with light petroleum (90 cm 3), and cooled to 0°C . The apparatus was flushed with ethylene

²² F. G. A. Stone, *Rev. Pure Appl. Chem.*, 1972, **30**, 551 and refs. therein.

to saturate the solvent, and small portions (*ca.* 0.2 g) of bis(cyclo-octa-1,5-diene)platinum (3.7 g, 9 mmol) were added, each portion being allowed to dissolve before the next was inserted. A light petroleum solution of tricyclohexylphosphine (2.5 g, 9.0 mmol in 15 cm³) was added, leading to gas evolution and formation of product. The ethylene source was removed, and the flask flushed with a slow stream of nitrogen for 1 h. The supernatant liquid was decanted and the white *crystals* washed with light petroleum (4 × 10 cm³), the washings being added to the mother liquor. Additional product could be obtained by evaporating the solutions to dryness *in vacuo*, dissolving the residue in light petroleum (50 cm³) under ethylene, and filtering through a short alumina column (2 × 10 cm³) under ethylene pressure. Evaporation of solvent gave a second crop of crystals, the total amount formed in the synthesis being 4.0 g (80%).

Bis(ethylene)(trimethylphosphine)platinum. A Schlenk tube (50 cm³) containing a magnetic stirring bar was charged with light petroleum (15 cm³) and flushed with ethylene. The solvent was degassed and ethylene again admitted to the tube which was cooled to 0 °C. Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was added in small portions. The ethylene supply was disconnected and the Schlenk tube attached to a high-vacuum line and cooled to −196 °C. Trimethylphosphine (0.076 g, 1 mmol) was distilled into the tube which was removed from the vacuum line and warmed to 0 °C, with stirring and re-admission of ethylene gas. After 0.5 h the mixture was filtered through a 1-cm alumina pad into a clean Schlenk tube under ethylene pressure. The ethylene source was

replaced by nitrogen and the solution cooled to −78 °C affording *crystals* of [Pt(C₂H₄)₂(PMe₃)]. A second crop of crystals was obtained from the recovered mother liquors by evaporation to *ca.* 5 cm³ *in vacuo* and cooling to −78 °C (total yield 0.13 g, 40%).

The other complexes [Pt(C₂H₄)₂L] were also prepared using Schlenk techniques, the ligands L being added as solids (PPh₃ or AsPh₃) or as light petroleum solutions to ethylene-saturated light petroleum solutions of [Pt(cod)₂] (cod = cyclo-octa-1,5-diene) (1 mmol) to give the products in the yields indicated: L = PMe₂Ph (40), PMePh₂ (50), PPh₃ (90), and AsPh₃ (90%). Analytical and other data are given in Table 1.

Synthesis of Ethylene(tetrafluoroethylene)(tricyclohexylphosphine)platinum.—A suspension of [Pt(C₂H₄)₂{P(C₆H₁₁)₃}] (0.65 g, 1.2 mmol) in light petroleum (40 cm³) contained in a Schlenk tube was cooled to −196 °C, the tube was evacuated, and C₂F₄ (3 mmol) was condensed in. The mixture was warmed to 20 °C, stirred for 8 h, and then cooled to −10 °C to allow the product to crystallize. The supernatant liquid was removed with a syringe and the white crystalline residue (crude yield 0.6 g) washed with light petroleum (3 × 2 cm³). Recrystallization from a large volume of light petroleum gave small white *prisms* of [Pt(C₂H₄)(C₂F₄){P(C₆H₁₁)₃}] (0.45 g, 62%), m.p. 140–145 °C (decomp.) (Found: C, 44.4; H, 6.2. C₂₂H₃₇F₄PPt requires C, 43.7; H, 6.2%).

We thank the S.R.C. for support, and Dr. R. Goodfellow for double-resonance experiments.

[8/022 Received, 6th January, 1978]