Olefin Rotation in Platinum(II) Olefin Complexes. Part III [1]

By **J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The barriers to rotation of ethylene in complexes $PtXYL(C_2H_4)$ (X = Cl, Br, or CF_3CO_2 *trans* to the olefin; Y = Cl, Br *cis* to the olefin, L = tertiary phosphines, phosphites, arsines, or a primary amine *cis* to the olefin) have been measured by n.m.r. spectroscopic techniques. The measured $\Delta G^{\ddagger}_{T_c}$ values span the range 10·5—13·9 kcal mol^{-1} and depend on the nature of the ligands. Comparison of the barriers with the i.r. stretching frequency of the terminal CO group in the analogous complexes PtXYL(CO) demonstrates a significant steric contribution to the energy of rotation. There is n.m.r. spectroscopic evidence for twisting of the olefin about the carbon–carbon axis and of a barrier to rotation of the phosphine ligand of 13 kcal mol^{-1} in $PtCl_2[(2\text{-}MeOC_6H_4)_3P](C_2H_4)$.

ALTHOUGH a number of studies have been made on olefin-rotation in metal complexes, the factors which govern the barriers to rotation have not been elucidated. Two main factors may be considered, namely the electronic distribution within the molecule, which will depend upon both the π- and σ-bonding properties of the other ligand groups, and the steric effects of the other ligand molecules, which will be primarily associated with groups *cis* to the olefin. This study was designed to determine the relative importance of these two effects. We have synthesised a range of olefin complexes of general type $[PtXYL(C_2H_4)]$, where X and Y are halogen or carboxylic acid groups and L is a nitrogen, phosphorus, or arsenic base. The steric restraint of the ligand *cis* to the olefin has been varied by changing the substituents in the phosphorus and arsenic bases, but it must be recognized that variation in the nature of the substituent normally also has an effect on both the π-acidity and σ-basicity of the ligand. In an attempt to compare the variation in the barriers to rotation with the variation in π-donor capacity of the metal ion we have correlated the data with the changes in the CO stretching frequency in the related complexes [PtXYL(CO)]. If a Dewar–Chatt model is assumed for the metal–olefin bond then the π-interaction within the olefin–metal orbital manifold will be restricted to the d_{xy} orbital (in-plane π-bond) and the d_{xz} orbital, or a d_{xz}–p_z hybrid (out-of-plane π bond), the metal–olefin bond being defined as on the *x* axis and the metal–ligand plane as the *xy* plane. Whilst the d_{xy} orbital may be utilized in the π-bonding pattern of the group *cis* to the olefin, the d_{xz}–p_z orbital set will be explicitly employed in π-bonding to the ligand *trans* to the olefin. In the rotation process for the olefin, both sets of π-orbitals will be employed and the barrier to rotation will be related to the energy separation of the bonding molecular orbitals formed for the in-plane and out-of-plane bonding situations. Substitution in the *cis*-ligand may lead to a radical variation in the π-acceptor properties and this would be indicated directly in the energy of rotation of the olefin. The π-interaction with the carbonyl group in the related carbonyl complexes will also employ the same metal π-orbitals but the variation in the CO stretching frequency may not reflect to the same degree variation in the π-capacity of the *cis*-group, as the major interaction may occur *via* the alternative π-orbital (d_{xz}–p_z) or the interaction of this hybrid orbital enhanced by competitive interaction with the d_{xy} orbital. Thus although the variation in the carbonyl frequency will be a measure of the *overall* change in π-electron density, the barrier to rotation in the olefin complexes is more related to the *differences* in π-density in the two alternative environments.

The Barrier to Olefin Rotation.—The n.m.r. spectra of the complexes $PtXYL(C_2H_4)$ at ambient temperatures showed a single resonance, with ^{195}Pt satellites, for the ethylene protons. At lower temperatures (−20 to −80 °C), second-order AA′BB′ spectra with ^{195}Pt–^1H coupling were observed, this being the predicted pattern for an olefin perpendicular to the square plane defined by the complex, having non-equivalent *cis*-ligands. This temperature-dependent behaviour was first observed by Cramer in rhodium–ethylene complexes,[2] and was attributed to a rotation of the olefin about either the metal–olefin axis or about the olefinic carbon–carbon axis. It has since been shown that for platinum(II) complexes [3] the ground-state structure of the molecule is that with the olefin perpendicular to the plane and that rotation about the metal–olefin axis is the most probable operative mechanism.

The values of $\Delta G^{\ddagger}_{T_c}$ measured in the complexes (1)—(18) for the averaging of the two proton environments observed in the frozen-out spectra are listed in Table 1.† The values of ν_{CO} for the analogous CO complexes are shown for comparison.

Comparing the $\Delta G^{\ddagger}_{T_c}$ value for the triethylarsine derivative (2) with that of the related triphenylarsine complex (4) and that of the triethylphosphine adduct (6) with the triphenylphosphine complex (16), we see that the energy differences between the trialkyl- and the better π-acceptor triaryl-ligand complexes are 0·9 and 0·6 kcal mol^{-1} respectively. The analogous differences in ν_{CO} are 5 and 9 cm^{-1}. The differences in $\Delta G^{\ddagger}$ between triethyl-arsine (2) and -phosphine (6) and between triphenyl-arsine (4) and -phosphine (16) are 1·9 and 1·7 kcal mol^{-1}. However the differences in ν_{CO} are only 2

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† The $\Delta G^{\ddagger}_{T_c}$ values are measured at different temperatures and thus entropy factors are neglected. Although ΔS values for ethylene reorientation in Pt^{II} complexes are not known, the difference in ΔG for a temperature rise of 30 °C is probably +0·4 kcal mol^{-1} by comparison with values for other olefins.[3]

[1] Part II, C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1653.

[2] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[3] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 53.

and 6 cm^{-1}. The increase in energy barrier on passing from arsenic to phosphorus may therefore be steric in nature, reflecting the decreased distance between the olefin and the substituents on the smaller Group V element. The electron-withdrawing groups attached to the phosphorus in the triethyl phosphite and trichlorophosphine complexes (12) and (15) markedly affect the value of ν_{CO} but the values of $\Delta G^{\ddagger}_{T_c}$ are similar to those for ligands of approximately equal bulk [*e.g.* (6) or (14)], implying a greater sensitivity of the changes in carbonyl frequency to electronic factors than the rotational energy changes of the olefin.

TABLE 1

Thermodynamic data for $PtXYL(C_2H_4)$

	L	X	Y	$\Delta G^{\ddagger}_{T_c}$ ± 0·2/kcal mol^{-1}		Coalescence temperature T_c ± 2 °C	I.r. spectroscopic data for PtXYL(CO) CO stretching frequency/cm^{-1} ($CHCl_3$)
(1)	Et_3As	CF_3CO_2	Cl	10·5	$CDCl_3$	−65	2122
(2)	Et_3As	Cl	Cl	10·9	$CDCl_3$	−52	2101
(3)	Et_2PhAs	Cl	Cl	11·0	$CDCl_3$	−45	2100
				10·9	CD_3CN	−45	2106
(4)	Ph_3As	Cl	Cl	11·8	$CDCl_3$	−36	2106
				11·9	CD_3CN	−27	
				12·1	$(CD_3)_2CO$	−35	
(5)	Et_3P	CF_3CO_2	Cl	12·2	$CDCl_3$	−30	2120
(6)	Et_3P	Cl	Cl	12·8	$CDCl_3$	−13	2103
(7)	Et_3P	Br	Br	12·4	$CDCl_3$	−20	2098
(8)	Et_2PhP	CF_3CO_2	Cl	12·2	$CDCl_3$	−25	2124
(9)	Et_2PhP	Cl	Cl	12·8	$CDCl_3$	−8	2105
(10)	Et_2PhP	Br	Br	12·4	$CDCl_3$	−17	2102
(11)	Me_2PhP	Cl	Cl	12·3	$CDCl_3$	−20	2103
				12·5	SO_2	−23	
(12)	$(EtO)_3P$	Cl	Cl	12·4	$CDCl_3$	−25	2119
				12·6	SO_2	−35	
				12·5	$(CD_3)_2CO$	−26	
(13)	amph *	Cl	Cl	12·6	SO_2	−28	
(14)	Bu^n_3P	Cl	Cl	12·8	$CDCl_3$	−12	2103
(15)	Cl_3P	Cl	Cl	12·8	$CDCl_3$	−15	2120
(16)	Ph_3P	Cl	Cl	13·4	$CDCl_3$	+4	2112
				13·2	CD_3CN	0	
				13·5	SO_2	+10	
(17)	$(4\text{-}FC_6H_4)_3P$	Cl	Cl	13·2	$CDCl_3$	+4	2110
(18)	$(2\text{-}MeO{\cdot}C_6H_4)_3P$	Cl	Cl	13·9	$CDCl_3$	−10	2103
(19)	Pr^i_3As	As	Cl				2096
(20)	Pr^i_3Sb	Cl	Cl				2090

* amph = $PhCH_2CH(CH_3)NH_2$.

The negative inductive effect of the fluorine substituent in the aromatic ring in the tri-(*p*-fluorophenyl)-phosphine derivative has little effect on either ν_{CO} or $\Delta G^{\ddagger}$, but the electron-releasing methoxy-group in the 2-methoxy-substituted phenylphosphine complex (18) lowers the i.r. stretching frequency to that of the triethylphosphine derivative (6) but raises $\Delta G^{\ddagger}_{T_c}$ to a value greater than that for either the triphenylphosphine or *p*-fluorophenylphosphine complexes (16) or (17). This is most probably correlated with a strong steric interference with the rotation process by the *o*-methoxy-group.

Attempts to measure the barrier to ethylene rotation in arsine (19) and antimony adducts (20), in which electron-releasing characteristics are combined with bulky groups, were not successful, since the equilibrium with free ethylene was rapidly set up and spectra due to intermolecular exchange of ethylene were observed at temperatures down to −95 °C.

In the amine complex (13) the lack of π-bonding with the amine ligand shows no major effect on the value of $\Delta G^{\ddagger}$; however the inavailability of tertiary amine complexes and CO analogues prevented any correlation of steric and electronic effects.

In the triethylphosphine complex (7) and the ethyldiphenylphosphine adduct (10) the chloride had been replaced by bromide ion. The changes in $\Delta G^{\ddagger}_{T_c}$ compared with the related chlorides (6) and (9) are probably not significant, and a similar lack of any major effect on replacing chloride by bromide was observed for the complexes $PtX(acac)(C_2H_4)$ (X = Cl or Br).[1] Any increase due to the greater size of the bromide ion may have been outweighed by the greater electron density in the d_{xy} and d_{xz} orbitals suggested by the increase in ν_{CO}.[4]

A more marked effect is observed in the trifluoroacetate complexes (1), (5), and (8) where the trifluoroacetate group is *trans* to the olefin. The lowering of the energy barrier for olefin rotation relative to the chloride appears to be significant for this series of complexes. A marked variation also occurs in the ν_{CO} for these derivatives implying a lower π-bonding capacity in the trifluoroacetate complexes. The resultant lower energy barrier to rotation implies a more equal energy distribution for the π-orbitals of the olefin in the complex. This variation therefore appears to be primarily electronic in nature but secondary steric effects may arise by a weakening of the olefinic π-bond with concomitant lengthening

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[4] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

of the metal–olefin bond which would decrease non-bonded interactions with adjacent ligands.

Although the complexes are not very soluble and the selection of suitable solvents for variable-temperature ^1H n.m.r. is limited, no significant solvent effect was noted within the small range of solvents used.

Chemical Shifts and Coupling Constants.—The values of the relative chemical shifts of the two proton environments, and the platinum–proton coupling constants associated with each, in the ground state spectra are shown in Table 2.

TABLE 2

N.m.r. data for $PtXYL(C_2H_4)$

	C_2H_4 chemical shift averaged spectrum/τ	C_2H_4 chemical shift separation ground-state spectrum/Hz		J_{PtH} Low field	J_{PtH} High field
(1)	5·77	22	$CDCl_3$	68	59
(2)	5·72	40	$CDCl_3$	68	58
(3)	5·97	63	$CDCl_3$	68	60
	5·95	75	CD_3CN		
(4)	5·94	55	$CDCl_3$	66	56
	5·96	35	CD_3CN		
	5·94	30	$(CD_3)_2CO$		
(5)	5·80	25	$CDCl_3$	69	56
(6)	5·83	43	$CDCl_3$	69	56
(7)	5·70	40	$CDCl_3$	66	56
(8)	6·12	38	$CDCl_3$	69	55
(9)	5·94	75	$CDCl_3$	69	55
(10)	5·80	65	$CDCl_3$	68	54
(11)	5·90	50	$CDCl_3$	69	57
	5·90	39	SO_2		
(12)	5·49	25	$CDCl_3$	58	70
	5·60	10	SO_2		
	5·50	16	$(CD_3)_2CO$		
(13)	5·62	26	SO_2	66	60
(14)	5·73	45	$CDCl_3$	68	54
(15)	5·01	39	$CDCl_3$	63	56
(16)	6·00	85	$CDCl_3$	68	58
	5·98	72	CD_3CN		
	5·99	91	SO_2		
(17)	5·90	96	$CDCl_3$	68	52
(18)	5·62	10	$CDCl_3$	70	50
(19)	5·58	—	$CDCl_3$	64 average	
(20)	5·58	—	$CDCl_3$	64 average	

The protons adjacent to the phosphorus or arsenic atom are shielded more than those close to the halide ion and appear at higher field. The presence of a phenyl group on the *cis*-ligand results in greater shielding and consequently greater peak separation.

The presence of electronegative oxygen atoms in the triethyl phosphite complex (12) and the 2-methoxy-substituted phosphine adduct (18) causes strong deshielding of the protons close to the phosphorus atom resulting in small relative shifts and, in the case of (12), a reversal of the assignments of peaks. The assignment of the low-field section of the spectrum to the protons next to the halide ion in all complexes but the triethyl phosphite complex (12) is confirmed by a study of platinum–hydrogen coupling constant J_{PtH}. The platinum–proton coupling constants for the low-field resonances are 6—20 Hz lower than the high-field counterparts. Twisting of the olefin around the carbon–carbon axis to minimize steric interaction with the bulky phosphine or arsine forces one set of protons closer to the platinum atom and this increases the value of J_{PtH}. The difference between the coupling constants in these complexes is greater than that observed in complexes PtCl(acac)(olefin) [1] which is consistent with the greater bulk of the ligands. In the spectrum of (12) the larger J_{PtH} value is associated with the high-field resonance. Although no rigid trend in the difference of the two coupling constants is apparent, the lower values, 8—10 Hz, correspond to the lower barriers to rotation, 10—12 kcal mol^{-1}; while the higher, 10—20 Hz, are associated with higher barriers, 12—13·9 kcal mol^{-1}. The smallest difference is for the trichlorophosphine complex (15).

The spectra of all complexes except (15) and (18) are of the AA′BB′ type, and while the spectra were usually too poorly resolved for analysis, spectra were synthesised by use of internal coupling constants J_{cis} *ca.* 8 Hz, J_{gem} *ca.* −1 Hz, J_{trans} *ca.* 13 Hz which were superimposable on the observed spectra [Figures 1(a) and (b)]. This is another example of the decrease in olefinic coupling constants on co-ordination to a metal, suggestive of a tendency toward sp^3 character of the carbon atoms.

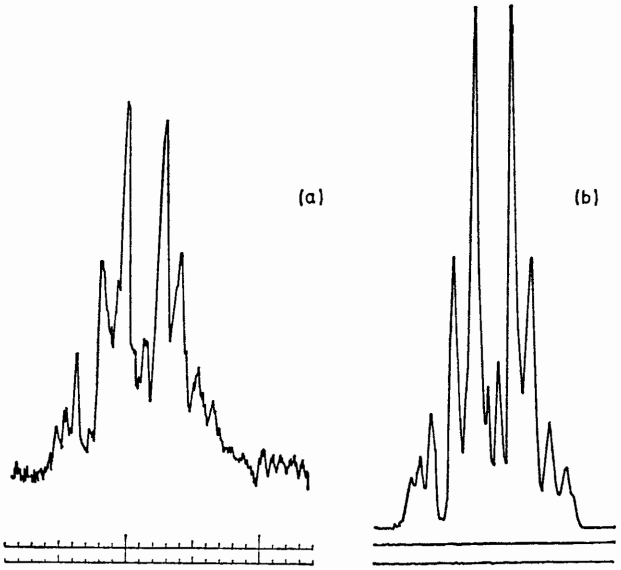

FIGURE 1 (a) ^1H N.m.r. spectrum of $PtCl_2(Et_3P)(C_2H_4)$ at −60 °C; ethylene protons; (b) synthesised spectrum

The Barrier to Rotation of the Phosphine.—The ground-state spectrum of the trichlorophosphine (15) is not symmetrical and is probably due to an AA′BC spin system. The high-field portion of the spectrum with the largest J_{PtH} value consists of two resonances separated by 10 Hz [Figures 2(a) and (b)]. Either the olefin is not in the perpendicular orientation or this must arise from differing environments owing to the phosphine substituents which can only occur if the phosphine has stopped rotating.

In the spectrum of 2-methoxyphenylphosphine adduct (18) the resonance due to the methoxyl group at τ 6·5 splits, on cooling, into three equally intense resonances at τ 5·93, 6·76, and 6·86. This is consistent with a slowing of the rotation of the phosphine about the metal–phosphorus bond, or of the rotation of the phenyl groups about the carbon–phosphorus bonds. The energy barrier of this process is 13 kcal mol^{-1}.

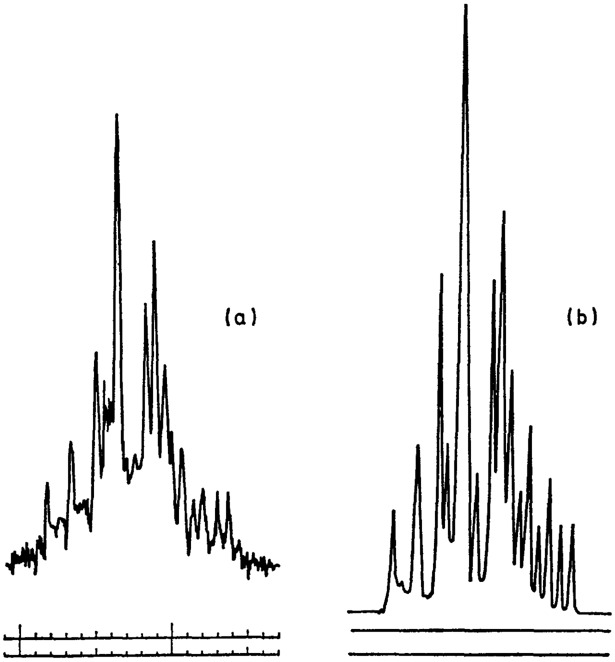

FIGURE 2 (a) ^{1}H N.m.r. spectrum of $PtCl_2(PCl_3)(C_2H_4)$ at −50 °C; ethylene protons; (b) synthesised spectrum

A similar phenomenon is observed on cooling $PtCl_2[(2\text{-}MeO\cdot C_6H_4)_3P](CO)$. The methoxyl resonance at τ 6·42 splits into three equal resonances at τ 6·16, 6·30, and 6·66. The energy barrier is 12·5 kcal mol^{-1}. Changes are also observed in the phenyl resonances; in both cases a signal of one proton intensity (a doublet of doublets separated by 7 and 17 Hz) moves to τ 1·3. This low chemical shift is probably due to the proximity of a methoxyl oxygen atom or a chloride ion. A model shows that rotation about the phosphorus–carbon bond is highly hindered in the free phosphine, but the n.m.r. spectrum of the free phosphine is independent of temperature so that the ground state of this molecule must be symmetrical. The observed asymmetry is due to co-ordination and probably arises from loss of free rotation of the phosphine. The formation of conformers by hindered rotation of bulky phosphines has been observed by Shaw and his co-workers [5] in the complexes *trans*-$PtCl_2(Bu^t{}_2PH)_2$ and in similar rhodium and iridium complexes.

Maitlis and his co-workers [6] have observed a large difference in the barrier to rotation of ethylene in the complexes $(C_5Me_5)Rh(C_2H_4)_2$ and $(C_5Me_5)Ir(C_2H_4)_2$. They concluded that this difference in the energy of rotation on changing the metal was electronic in nature. It appears from our studies that for a given metal ion (*viz.* Pt^{II}), the *differences* in the energy barrier to rotation on changing the ligands adjacent to the olefin are largely dependent on non-bonded interactions.

EXPERIMENTAL

Solutions (*ca.* 0·1M) of the olefin complexes were prepared in the solvents stated in Table 1 with tetramethylsilane as internal reference. Variable-temperature n.m.r. studies were carried out on Varian HA-100 spectrometers. Probe temperatures were measured from the precalibrated internal chemical shift of a methanol sample.

It is appropriate to summarize the basic assumptions in the method used to determine the barrier to rotation in these olefin-metal complexes. As yet, no simple accurate method for the determination of energy barriers of processes leading to the collapse of an AA′BB′ spin system (and AA′BB′X on ^{195}Pt) to an A_4 system (A_4X on ^{195}Pt) has been devised, and even in computer line-shape analyses for such spin systems, approximate methods have been employed.[7] Since variable-temperature n.m.r. is the only convenient technique available to measure the rate of rotation of ethylene on metal complexes of high molecular weight and fairly low thermal stability, it is important to emphasize the approximations made in this approach.

Cramer and Mrowca [8] used the approximate equation (1),

$$\Delta G^{\ddagger}_{T_c} = -RT \ln \frac{\pi \Delta\nu h}{2kT} \qquad (1)$$

where $\Delta\nu$ = relative chemical shift of the peaks at slow exchange, h is Planck's constant, k is Boltzmann's constant, and T_c is the coalescence temperature, for proton-site averaging in the bisethylenerhodium complexes and obtained values similar to those obtained by computer line-shape analysis. This equation has been shown to give values in good agreement with those from line-shape analysis [9] for coalescing uncoupled singlets when $\Delta\nu > 3$ Hz or for a coalescing AB system where $\Delta\nu/J > 3$.

The ΔG values tabulated in this work were calculated from coalescence data by use of this equation. A second approach to the problem would be to treat the AA′BB′ system as a simple AB system where $J_{''AB''} = |J_{AB'} + J_{AB}|$ = *ca.* 12 Hz and to use the rate equation $k_c = (\pi/\sqrt{2})\sqrt{(\Delta\nu^2 + 6J^2)}$ which has been shown to give valid ΔG values for $\Delta\nu > J$. Application of this equation to our data systematically lowers the displayed ΔG values by 0·2 kcal mol^{-1} and thus does not affect any conclusions drawn, except in the one case (18) where $\Delta\nu < J$, where the value is 0·5 kcal mol^{-1} lower than shown. However since the second equation approaches a lower limit of $k_c = (\pi/\sqrt{3})\,J$, whereas the line-shape analysis and the first equation approach zero as $\Delta\nu$ approaches zero, a ΔG value obtained by the second equation when $\Delta\nu < J$ would be erroneously low. Thus although the ΔG values obtained may not be absolutely accurate they are relatively precise and we conclude that any conclusions drawn are valid.

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[5] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826; B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.

[6] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

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

[8] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, 528.

[9] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

The complexes $PtXYL(C_2H_4)$ (X = Y = Cl or Br) were prepared after the method of Chatt *et al.*[4] by treating an acetone solution of $Pt_2X_4L_2$ with ethylene., usually at atmospheric pressure. The bridged dimers $Pt_2X_4L_2$ were in general prepared by Chatt's route,[10] by heating $Pt_2X_2L_2$ with PtX_2 in a high-boiling solvent such as xylene or decalin, but $Pt_2Cl_4[(2\text{-}MeO{\cdot}C_6H_4)_3P]_2$ was prepared by treating one mole of $Pt_2Cl_4(C_2H_4)_2$ with two moles of the phosphine. The trichlorophosphine dimer was obtained from the reaction of PCl_5 with Pt metal at 200 °C, and $Pt_2Cl_4(EtO_3P)_2$ by ethanolysis of this product.[10] The amine complex was prepared by the method of Panunzi and Paiaro.[11]

The complexes PtXYL(CO) were obtained by treatment of either $Pt_2X_2Y_2L_2$ or $PtXYL(C_2H_4)$ with carbon monoxide at atmospheric pressure. When the bridged dimer was used a transient species, probably the *trans*-isomer, was observed. In cases where these complexes had previously been prepared, the m.p. and i.r. data were in reasonable agreement with earlier workers' data.[4]

Preparation of Complexes $Pt(CF_3CO_2)Cl(L)(C_2H_4)$.—These compounds were produced by two methods: (*a*) treatment of the bridged dimers with thallium trifluoroacetate and subsequent treatment with ethylene, and (*b*) reaction of the olefin complex with an excess of $CF_3{\cdot}CO_2Tl$. Typically, for method (*a*), to $Pt_2Cl_4(Et_3P)_2$ (150 mg, 0·2 mmol) in methylene dichloride (10 ml) was added thallium trifluoroacetate (65 mg, 0·2 mmol) (prepared by reaction of thallous carbonate with excess of trifluoroacetic acid). The solution was stirred for 10 min and pale yellow crystals were formed. The solution was decanted, the crystals were dissolved in acetone, and the solution was filtered and then evaporated *in vacuo* to yield $Pt_2(CF_3CO_2)_2Cl_2(Et_3P)_2$ (105 mg, 0·11 mmol, 55%), m.p. 140 °C (ν_{CO} 1645 cm^{-1}). The product (100 mg, 0·1 mmol) in acetone (20 ml) was treated with ethylene at atmospheric pressure for 16 h. The solution was filtered and evaporated *in vacuo* to yield a white solid that was recrystallized from methylene dichloride–hexane (70 mg, 0·15 mmol, 75%), m.p. 122 °C (decomp.) (ν_{CO} 1696 cm^{-1}).

(*b*) $PtCl_2Et_3P(C_2H_4)$ (105 mg, 0·25 mmol) in methylene dichloride (10 ml) was treated with excess of thallium trifluoroacetate. The solution was stirred for 10 min, filtered, and then hexane (5 ml) was added. The solvent was removed in a stream of nitrogen yielding white crystals of $Pt(CF_3CO_2)Cl(Et_3P)(C_2H_4)$ (101 mg, 0·22 mmol, 87%).

The trifluoroacetate group in the dimer must have replaced the non-bridging halides, since the i.r. spectrum indicates non-bridging carboxylate. Bridge splitting with ethylene with the minimum of molecular rearrangement would yield the isomer with CF_3CO_2 *trans* to C_2H_4. The same product is isolated from the reaction of the *cis*-ethylene complex with $CF_3{\cdot}CO_2Tl$ which is consistent with the *trans*-labilizing effect of the olefinic ligand. Analyses are in Table 3.

TABLE 3

Analytical data for olefin complexes

Complex (see Table 1)	Found (%)				Required (%)			
	C	H	Br Cl	Pt	C	H	Br Cl	Pt
(1)	22·5	3·6			22·4	3·6		
(2)	21·2	4·2	13·4		21·0	4·2	15·3	
(3)	29·2	3·6	14·2		28·6	3·8	14·1	
(4)	39·8	3·4	11·9		40·0	3·2	11·8	
(5)	24·2	3·9		41·0	24·6	3·9		40·0
(6)	23·3	3·5	17·0		23·3	3·6	17·2	
(7)	21·8	3·4			21·7	3·4		
(8)	31·4	3·5	6·3	42·2	31·2	3·5	6·0	42·0
(9)	31·9	4·4	15·1		31·3	4·2	15·4	
(10)	26·8	3·8	29·2		26·3	3·5	29·1	
(11)	27·5	3·6	16·7		27·8	3·5	16·4	
(12)	21·2	4·4	15·5		20·9	4·2	15·4	
(13)	31·2	3·5	15·9	46·0	31·0	3·5	16·7	45·6
(14)	34·7	5·6	14·3		34·3	5·3	14·5	
(15)	5·5	1·9	39·9		5·6	0·9	41·4	
(16)	43·3	3·8	12·8		43·2	3·4	12·8	
(17)	40·0	2·7	12·3		39·3	2·6	12·5	
(18)	42·8	3·8		31·9	42·7	3·9		30·2
(19)	27·1	3·9		40·1	26·5	5·0		39·2
(20)	24·9	4·5		36·0	24·2	4·6		35·4

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