Metallation of the Isopropenyl Group by Platinum(II): Mechanism of Formation of Isomeric σ-Allylic and σ-Vinylic Six-membered Chelate Rings. *X*-Ray Structure of the σ-Vinylic Complex Di-μ-acetato-bis-{[2-(*o*-diphenylarsinophenyl)propenyl-*C'As*]platinum(II)}

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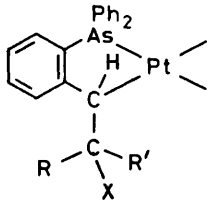
The (*o*-isopropenylphenyl)diphenylarsine (ipa) complex [Pt(ipa)(acac)][BF_4] (acac = acetylacetonate) reacts with nucleophiles including acetate to give [Pt{*o*-$CH_2C(=CH_2)C_6H_4AsPh_2$}(acac)] (1) in which the ligand is bonded as a σ-allylic group. The complex [$PtCl_2$(ipa)] reacts with silver acetate to give the complex [{Pt(*o*-$CH=CMeC_6H_4AsPh_2$)}$_2$(μ-$O_2CMe)_2$] (2) shown from *X*-ray analysis to have the deprotonated olefin bonded as a σ-vinyl group. Crystals are monoclinic, space group *C*2/*c*, *a* = 31.633(5), *b* = 11.345(5), *c* = 18.450(5) Å, β = 141.37(2)°, *U* = 4 133.6 Å^3, *Z* = 4, and *R* = 0.059 for 2 093 reflections. The σ-allylic complex (1) is converted to the σ-vinylic complex (2) by acetic acid. Mechanisms for the formation, protonation, and interconversion of the two isomeric forms of the metallated olefin have been deduced; carbonium ion complexes are strongly indicated as reactive intermediates. The σ-allylic and σ-vinylic forms appear to be the consequence of intermolecular and intramolecular attack respectively of a nucleophile on the co-ordinating olefin.

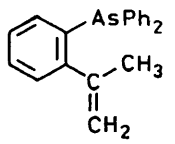
THE reaction of Pt^{II} complexes of diphenyl(*o*-vinylphenyl)arsine (vpa),[1,2] [*o*-(2-methylpropenyl)phenyl]-diphenylarsine (mpa),[3] and diphenyl[*o*-(propenyl)-phenyl]arsine (ppa)[3] with nucleophiles leads to attack at the β-carbon of the co-ordinated olefin and formation of products containing a five-membered chelate ring with Pt σ-bonded to the α-carbon and the nucleophile to the β-carbon.



R = R' = H ('vpa') X = OMe, O_2CMe, OH, or acac

R = H, R' = Me ('ppa')
R = R' = Me ('mpa')
X = OMe

We now report the interesting observation that reactions of similar Pt^{II} complexes of the ligand (*o*-isopropenylphenyl)diphenylarsine (ipa) with nucleophiles do not follow the same pattern.



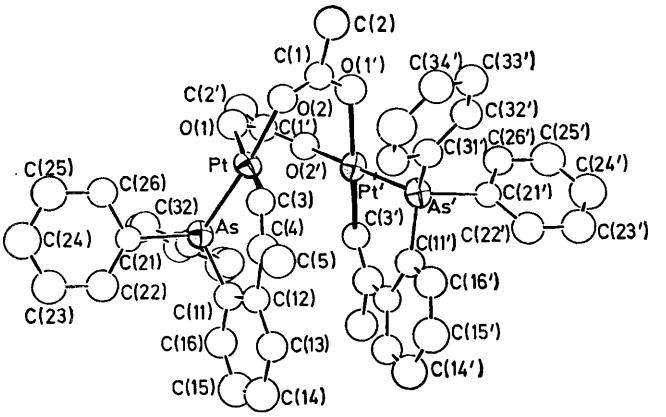
ipa

RESULTS AND DISCUSSION

The reaction of the (*o*-isopropenylphenyl)diphenylarsine complex [Pt(ipa)(acac)][BF_4] (acac = acetylacetonate) with any one of the nucleophiles methoxide, hydroxide, or acetate did not give a product containing the nucleophile. In each case the σ-allylic compound (1) (Scheme 1) was obtained.[4] The ^{1}H n.m.r. spectrum of (1) shows terminal vinylic proton signals (δ 5.29, 5.36) and a singlet due to the σ-bonded methylene group (δ 2.99) strongly coupled to Pt [*J*(Pt–H) 121 Hz]. A medium-intensity i.r. band assigned to the C=C stretch (1 612 cm^{-1}) and a strong absorption due to the out-of-plane hydrogen deformation mode of the RR'=CH_2 group (875 cm^{-1})[5] confirm this structure.

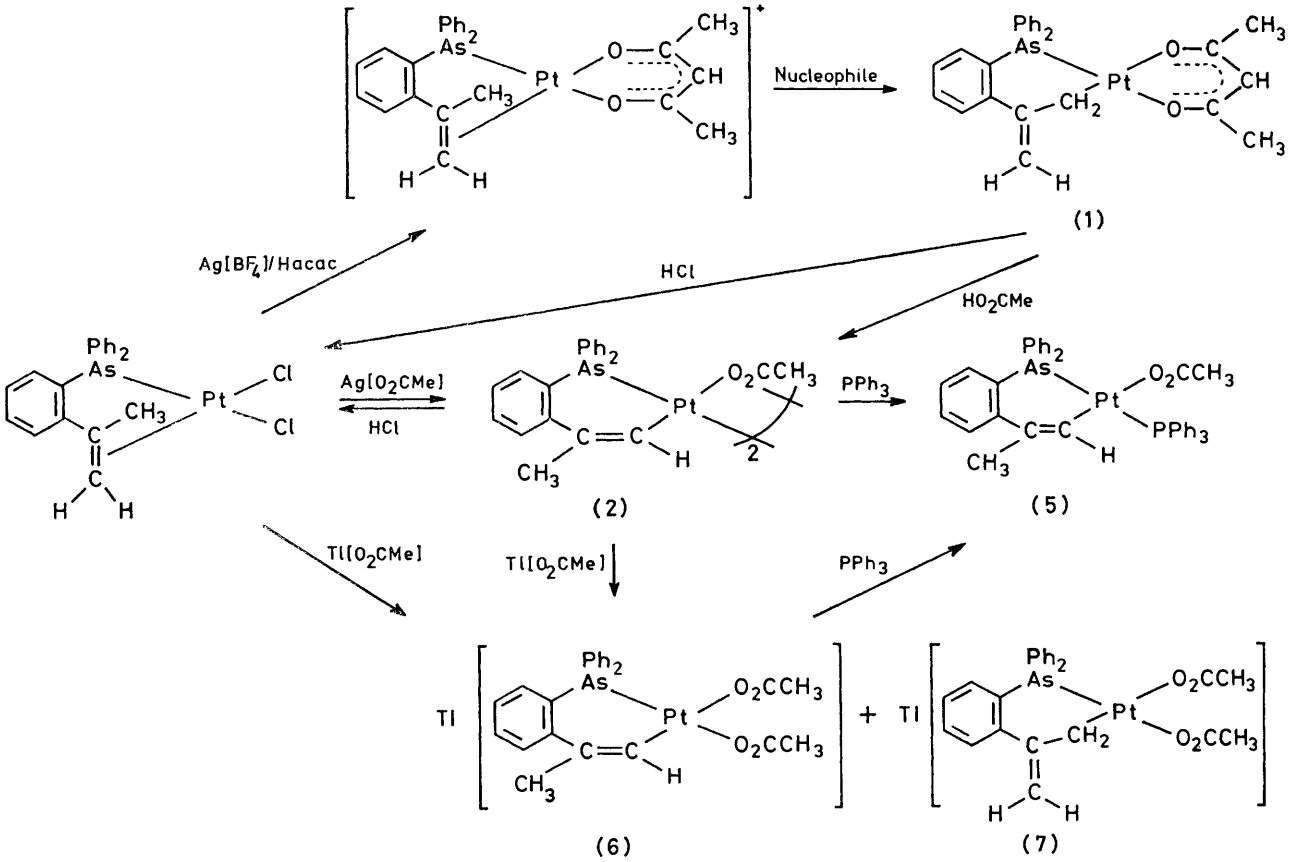
The reaction of silver acetate with [$PtCl_2$(ipa)] is also different from its reactions with the other [$PtCl_2$L] complexes (L = vpa, mpa, or ppa); whereas dark tars were formed with the latter compounds, reaction with a chloroform solution of [$PtCl_2$(ipa)] (Ag : Pt > 3 : 1) yielded on filtration a clear solution which developed an orange colour over several hours. Orange crystals of the σ-vinylic compound (2) were obtained from this solution on dilution with methanol (Scheme 1).

X-Ray analysis of (2) has shown it to have an acetate-bridged dimeric structure (Figure) which has crystallographic C_2 symmetry. The Pt atom and the four donor atoms, C(3), O(1), O(2), As, are planar to within 0.1 Å; the dimer is bridged by two *cis* acetate groups with an angle of 141.6° between the co-ordination planes. Acetate bridges occur in tetrameric platinum(II) acetate in which there is considerable metal–metal bonding;[6] the Pt–Pt distance of 2.989 Å in (2) is much longer than the average value of 2.495 Å observed in the tetramer so it seems probable that any metal–metal bonding in (2) is weak. The Pt–As bond of 2.267 Å is the shortest so far reported. From the limited data available on Pt–As bonds it has been concluded that there is considerable back bonding from Pt^{II} to arsenic, and very short Pt–As bonds have also been observed in other Pt^{II} compounds



The structure of the dimeric molecule of (2). The molecule has C_2 symmetry and the primed atoms are at positions $\frac{1}{4} - x, y, \frac{1}{4} - z$ where x, y, and z are given in Table 1

where there are no competing π-acid ligands.[2] The Pt–C(3) bond of 1.99(2) Å is shorter than the values of 2.026(8) Å for the Pt–C (σ-vinyl) bond in *cis*-1,2-bis(methoxycarbonyl)ethenyl[*o*-(diphenylphosphino)phenyl-*C*^{1}*P*]-(triphenylphosphine)platinum(II) [7] (3) and of 2.022(8) Å for the σ-styryl bond in *trans*-bromo(*trans*-styryl)bis-(triphenylphosphine)platinum(II) [8] (4) but these differences are of little significance. However, the difference between the value for the Pt–C(3)–C(4) angles of 138(2)° and the angle of 120° which would be expected for sp^2 hybridisation at C(3) is highly significant. In (3), the corresponding angle is 126.7(7)° and in (4), 123.8(6)°. The five atoms, Pt, C(3), C(4), C(5), C(12), are coplanar to within 0.02 Å and this plane is twisted 16.8° from the plane of the phenyl ring. It is well established that σ-bonded carbon atoms show a very large *trans* influence



SCHEME 1 A summary of reactions of some Pt^{II} complexes of ipa

in platinum(II) compounds.[9] In (2), the Pt–O(1) bond which is *trans* to the σ-vinyl group is 0.06 Å (4σ) longer than the Pt–O(2) bond *trans* to the arsenic atom. This is consistent with the observation that although the arsine group exerts a comparatively strong *trans* influence in Pt^{II} compounds it is significantly less than that of σ-bonded carbon atoms.[2]

The presence of the dimeric molecule (2) in solution was supported by its ^1H n.m.r. spectrum [δ 1.96 (s, Me), 1.43 (s, O_2CMe), 7.21 (=CH)] and its reaction with triphenylphosphine to yield a pale yellow monomer, (5) (Scheme 1). The latter compound was shown by the magnitude of its ^{31}P–^{195}Pt coupling constant (3 780 Hz)[10] to have the phosphine ligand *trans* to the arsenic donor.

The formation of the dimeric molecule (2) by the reaction between $[PtCl_2(ipa)]$ and excess silver acetate was shown to occur in two successive steps, reactions (i) and (ii). This mechanism was deduced by following the

$$[PtCl_2(ipa)] + 2\ Ag[O_2CMe] \longrightarrow [Pt(O_2CMe)_2(ipa)] + 2\ AgCl \quad (i)$$

$$2[Pt(O_2CMe)_2(ipa)] \longrightarrow (2) + 2\ MeCO_2H \quad (ii)$$

reaction using ^1H n.m.r., i.r., and u.v.–visible spectroscopy. A yellow reaction solution in $CDCl_3$, filtered from excess silver acetate, initially gave ^1H n.m.r. signals characteristic of a co-ordinated isopropenyl group [δ 2.28 (s, Me), J(Pt–H) 38 Hz; 3.52 (s, =CH *trans* to Me), J(Pt–H) 56 Hz; 4.72 (s, =CH *cis* to Me), J(Pt–H) 67 Hz]. In conjunction with two non-equivalent acetate group signals (δ 1.78, 2.08) this spectrum indicated formation of the intermediate species $[Pt(O_2CMe)_2(ipa)]$. Infrared absorptions of the same solution at 1 630, 1 370, and 1 310 cm^{-1} are also characteristic of monodentate acetate groups.[5] The ^1H n.m.r. spectrum of the initial yellow solution additionally showed small peaks due to (2) and these grew in intensity over several hours at the expense of the resonances of $[Pt(O_2CMe)_2(ipa)]$. Conversion to (2) was essentially complete after 3—4 h by which time the solution was deep orange and signals due to the hydroxy and methyl groups of acetic acid had become strong. Over the same period, the i.r. absorptions of the monodentate acetate groups became less intense and peaks appeared at 1 560 and 1 425 cm^{-1} which are within the usual range for the ν(C=O) and ν(C–O) vibrations of bridging acetate groups.[11] The concomitant appearance and growth of a peak at 1 715 cm^{-1} was consistent with the formation of acetic acid. The colour change from yellow to orange was due to the development of a peak in the u.v.–visible spectrum at 362 nm [for a pure sample of (2), $\varepsilon = 1.0 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$]. Compound (2) is stable in $CDCl_3$ solution free from strong acids and can be recrystallised from acetic acid without change.

On warming (1) in acetic acid, the pale yellow solid dissolved to give an orange solution from which crystals of (2) appeared on cooling. A two-step mechanism (below) for this interconversion between the two isomeric forms of deprotonated ipa was determined by monitoring the ^1H n.m.r. spectrum as the reaction took place in $CDCl_3$ solution to which a little acetic acid had been added, see reactions (iii) and (iv). The reaction

$$(1) + 2\ MeCO_2H \longrightarrow [Pt(O_2CMe)_2(ipa)] + Hacac \quad (iii)$$

$$2\ [Pt(O_2CMe)_2(ipa)] \longrightarrow (2) + 2\ MeCO_2H \quad (iv)$$

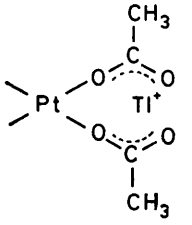
period decreased at higher temperatures and with increased concentrations of acetic acid.

Interesting differences from the previously discussed reactions were observed when thallium(I) acetate was substituted for silver acetate. For example, the filtered solution from the reaction of $[PtCl_2(ipa)]$ with excess thallium(I) acetate did not turn orange as it did when the silver salt was used. Moreover, the ^1H n.m.r. spectrum of the $CDCl_3$ reaction solution showed signals characteristic of *both* the σ-vinyl and σ-allyl forms of the deprotonated ipa ligand. To interpret these observations the orange solution of the dimer (2) in $CDCl_3$ was treated with two molar equivalents of thallium(I) acetate. This gave a clear yellow solution which appears to contain complex (6) (Scheme 1), the thallium(I) salt of the diacetatoplatinum anion containing the σ-vinyl form of deprotonated ipa [^1H n.m.r. of (6): δ 7.02 (s, Pt–C*H*=CMe), 2.35 (s, Pt–CH=C*Me*), 2.13 (s, O_2CMe), 1.77 (s, O_2CMe)]. Treatment of this solution with two equivalents of PPh_3 yielded a solution of (5) and white crystals identified as thallium(I) acetate by their i.r. spectrum. This explains why, unlike the reaction with silver acetate, the reaction of $[PtCl_2(ipa)]$ with excess thallium(I) acetate does not give the orange dimer (2). The stable yellow solution obtained (see above) can be seen by ^1H n.m.r. spectroscopy to contain some compound (6). The remaining signals can be accounted for by the isomeric *cis*-diacetatoplatinum complex (7) (Scheme 1) containing the σ-allyl form of deprotonated ipa [(7): δ 5.52 (m, =C*H trans* to phenyl), 5.20 (m, =C*H cis* to phenyl), 3.07 (m, Pt–CH_2–), 2.16 (s, O_2CMe), 1.79 (s, O_2CMe)].

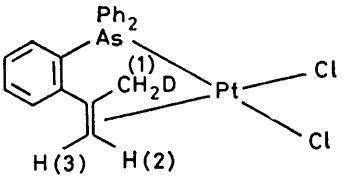
There is evidence that the isomers (6) and (7) do not interconvert in solution. A solution of (6) prepared from (2) and thallium(I) acetate gives no ^1H n.m.r. signals due to (7) even after extended reaction periods. It seems likely that the two isomers are formed simultaneously but independently from the intermediate $[Pt(O_2CMe)_2(ipa)]$. We reserve discussion of the mechanisms until after the evidence presented below.

The i.r. spectra of chloroform solutions of thallium(I) acetate adducts such as (6) and (7) exhibit two very strong absorptions at 1 570 and 1 395 cm^{-1}. Since these frequencies are in the usual range of bridging rather than terminal acetate groups,[11] it is possible that in solution the thallium(I) ion, unlike silver(I), stabilises *cis*-diacetatoplatinum(II) species by some association with the acetate groups, *e.g.* as shown below. All attempts to isolate (6) and (7) failed. Concentration of their chloroform solutions, or the addition of other solvents

likely to induce precipitation, resulted in a mixture of thallium acetate and unidentified products.

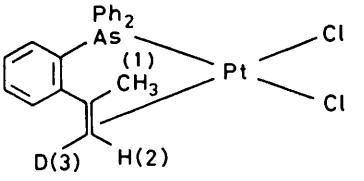


Compounds containing either isomeric form of the deprotonated isopropenyl group react immediately with hydrochloric acid to regenerate the parent compound [$PtCl_2$(ipa)]. As a result of this we were able to determine the fate of the proton incorporated into the ligand in these reactions by the use of deuterium chloride, the deuteriated products being characterised by ^1H n.m.r. In this way it was shown that treatment of (1) and (2) with a solution of DCl gave respectively (8) and (9). The deuteriation patterns of (8) and (9) alone are not sufficient to determine the mechanism(s) of the deuteriation reactions. For instance, (8) may have been formed from (1) by attack of a deuteron at either the sp^3 carbon σ-bonded to platinum, or at the terminal sp^2 carbon of the olefin accompanied by a shift in the positions of the double bond. Using the two forms of deuterium-labelled [$PtCl_2$(ipa)] (8) and (9), two independent experiments were designed to distinguish between the alternative sites of protonation. Similarly, the terminal olefinic carbon that receives the proton with a concomitant shift in the position of the double bond. A similar mechanism for protonation of a σ-allyl group has



(8)

Observed proton ratios H(1) : H(2):H(3) = 2.3:1:1

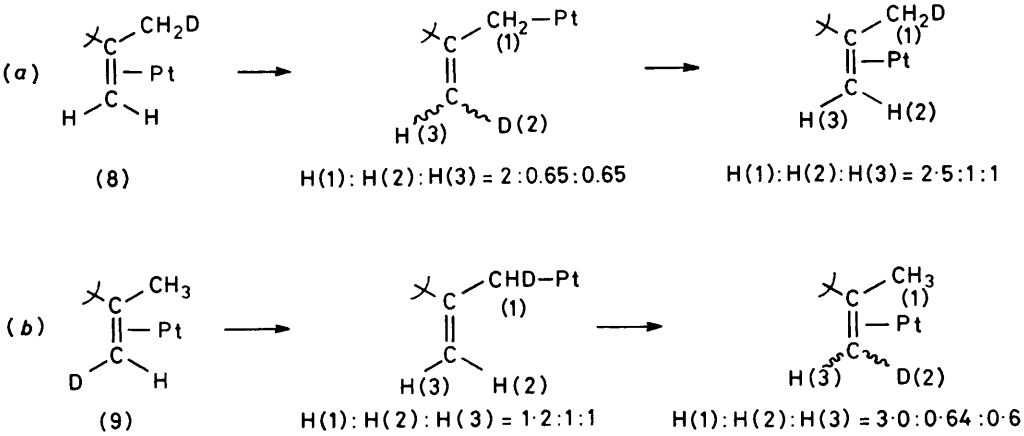


(9)

Observed proton ratios H(1) : H(2): H(3) = 3 : 1 : 0.2

been postulated by Green and Nagy [12] for an iron(II) complex.

The course of these reactions may be rationalised in terms of the tendency of platinum to stabilise carbonium ions in the reactions of σ-bonded unsaturated

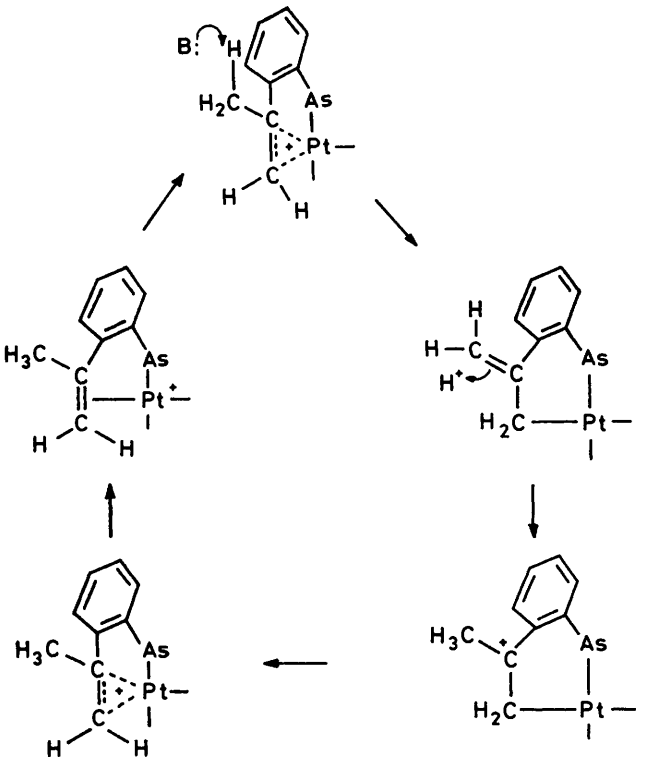


SCHEME 2 Observed patterns of deuteriation and proton integral ratios on deprotonation of the ligand to give the σ-allyl group followed by protonation to regenerate the co-ordinated olefin: (*a*) for complex (8), (*b*) for complex (9)

source of the proton abstracted in the formation of the σ-vinyl and σ-allyl functions from the co-ordinated isopropenyl group was determined.

Scheme 2 displays the patterns of deuteriation observed through the cycle of reactions from both forms of [$PtCl_2$([^2H]ipa)] to the σ-allyl complex and back to [$PtCl_2$([^2H]ipa)]. These results reveal that the co-ordinated isopropenyl group was deprotonated at the methyl carbon to form the σ-allyl complex (1). Further, they show that on treatment of (1) with HCl it is the hydrocarbons.[13] As shown in Scheme 3 (B = base), the transfer of charge to and from the metal may be determined by the intermediate formation of platinum-stabilised carbonium ions.

With the aid of the labelled complexes (8) and (9), we have also investigated the mechanisms of the reaction of [$PtCl_2$(ipa)] with acetate to form the σ-vinylic compound (2) and of the reaction of (2) with acid to regenerate [$PtCl_2$(ipa)]. The deuteriation patterns observed through this cycle of reactions starting with each of (8)



SCHEME 3 The postulated roles of platinum-stabilised carbonium ions in the formation and protonation of the σ-allyl group

and (9) are shown in Scheme 4. These observations imply that the terminal olefinic proton *trans* to the methyl group is lost in the formation of the σ-vinyl complex and regained on treatment with acid without re-arrangement of the olefinic group. To account for this mechanism of formation of the σ-vinyl group, we postulate an interaction between the co-ordinated acetate *cis* to the olefin in $[Pt(O_2CMe)_2(ipa)]$ and the isopropenyl proton *trans* to the ligand methyl group, followed by elimination of acetic acid.

In conclusion, we note that the formation of the σ-allyl and σ-vinyl complexes is an interesting example of the different consequences of *cis* and *trans* attack, in this case by the same nucleophile on the same co-ordinated ligand. The σ-allyl group appears to result from an intermolecular nucleophilic attack (*trans* attack) by acetate on the co-ordinated olefin of $[Pt(ipa)(acac)][BF_4]$ or $[Pt(O_2CMe)_2(ipa)]$. In contrast, we propose that an intramolecular *cis* attack by co-ordinated acetate on the co-ordinated olefin of $[Pt(O_2CMe)_2(ipa)]$ results in formation of the σ-vinyl complex (2).

EXPERIMENTAL

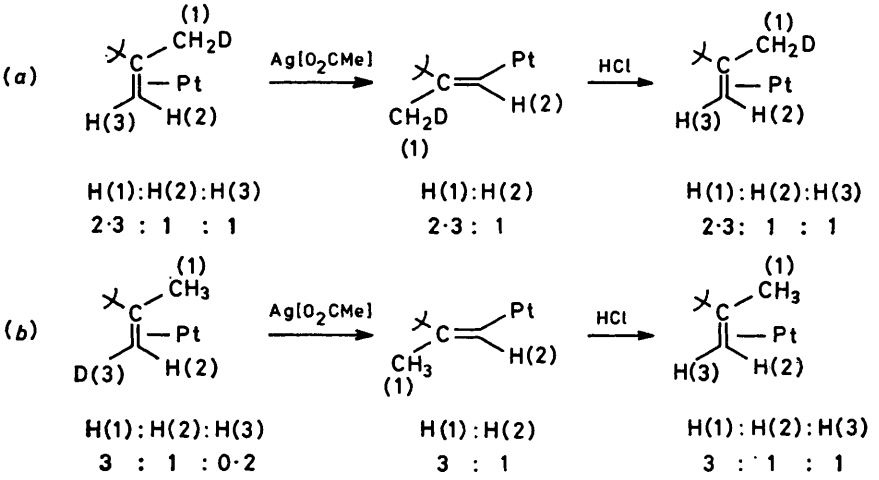
Apparatus and Techniques.—Proton n.m.r. spectra were obtained on Varian XL100 or Perkin-Elmer–Hitachi R-24B spectrometers and chemical shifts (δ) were measured in p.p.m. downfield from the internal standard, $SiMe_4$. Phosphorus-31 n.m.r. spectra were recorded on a Bruker HFX-90 (36.43 MHz) spectrometer operating in the Fourier mode with broad-band proton decoupling.

Infrared spectra were obtained on a Perkin-Elmer PE457 grating i.r. spectrophotometer as either Nujol mulls between CsI plates, or as solutions in 0.1-mm pathlength cells and calibrated against polystyrene.

Microanalyses were performed by the Australian Microanalytical Service (CSIRO, Melbourne) or by Alfred Bernhardt, Elbach, West Germany.

Crystal Data.—Compound (2), $C_{46}H_{42}As_2O_4Pt_2$, M 1 200.9, Monoclinic, space group $C2/c$, a = 31.633(5), b = 11.345(5), c = 18.450(5) Å, β = 141.37(2)°, U = 4 133.6 Å^3, Z = 4, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 80.79 cm^{-1}.

Data Collection.—Intensity measurements in the range $3 \leqslant \theta \leqslant 25°$ on a crystal of dimensions *ca.* 0.10 × 0.10 × 0.12 mm were made on a Philips PW1100 four-circle diffractometer using a θ—2θ scan technique and Mo-K_α radiation from a graphite crystal monochromator. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were omitted; I_t is the intensity at the maximum of the reflection peak and I_b is the mean of two preliminary 5-s background measurements at the extremities of the scan. The background measuring time for each reflection was proportional to I_b/I_i, where I_i is the total count recorded in the first scan. Reflections for which I_i was less than 500 counts were scanned a second time. A constant scan speed of



SCHEME 4 Observed patterns of deuteriation and proton integral ratios of ligands on deprotonation to form the σ-vinyl group followed by protonation to regenerate the co-ordinated olefin: (*a*) for complex (8), (*b*) for complex (9)

0.05° s^{-1} and a scan width of 0.6° were used. Three standard reflections were measured at intervals of 6 h during data collection and showed no significant variation in intensity. The standard deviation of the intensity (I) was taken as $[\sigma_c(I)^2 + (0.04I)^2]^{\frac{1}{2}}$, where $\sigma_c(I)$ is the standard deviation from counting statistics and the term in I^2 was introduced to allow for other sources of error.[14] I and $\sigma(I)$ were corrected for Lorentz and polarisation factors using a program written for the PW1100 diffractometer,[15] and equivalent reflections were averaged giving a total of 2 093 data with $I/\sigma(I) \geqslant 3.0$. Absorption corrections were not applied.

TABLE 1

Fractional atomic co-ordinates * with estimated standard deviations in parentheses

Atom	x	y	z
(*a*) Independent atoms			
Pt	0.121 5(0)	0.104 6(1)	0.060 2(0)
As	0.171 3(1)	−0.014 2(2)	0.028 0(1)
O(1)	0.164 0(5)	0.251 7(14)	0.080 5(7)
O(2)	0.069 9(4)	0.212 2(13)	0.075 1(6)
C(1)	0.065 6(6)	0.264 0(19)	0.118 9(9)
C(2)	0.027 5(8)	0.351 4(23)	0.114 7(11)
C(3)	0.080 8(6)	−0.027 0(19)	0.039 5(9)
C(4)	0.082 1(7)	−0.138 5(20)	0.034 9(10)
C(5)	0.039 3(7)	−0.207 8(22)	0.018 5(10)
C(11)	0.162 1(7)	−0.172 8(19)	0.044 4(9)
C(12)	0.120 4(6)	−0.219 2(19)	0.045 7(8)
C(13)	0.116 3(7)	−0.335 1(20)	0.052 8(9)
C(14)	0.149 5(8)	−0.417 5(24)	0.056 6(10)
C(15)	0.190 9(8)	−0.369 8(24)	0.057 4(11)
C(16)	0.196 5(7)	−0.252 1(21)	0.051 8(10)
(*b*) Rigid group atoms			
C(21)	0.1712	−0.0206	−0.0551
C(22)	0.1863	−0.1185	−0.0827
C(23)	0.1870	−0.1176	−0.1426
C(24)	0.1726	−0.0188	−0.1750
C(25)	0.1575	0.0791	−0.1475
C(26)	0.1568	0.0782	−0.0875
C(31)	0.2301	0.0215	0.0554
C(32)	0.2539	0.0906	0.0213
C(33)	0.2950	0.1259	0.0430
C(34)	0.3123	0.0922	0.0987
C(35)	0.2886	0.0231	0.1327
C(36)	0.2475	−0.0122	0.1110

* For the $F2/d$ cell, $a = 31.633$, $b = 11.345$, $c = 23.208$ Å, $\beta = 96.95°$.

Structure Solution and Refinement.—The platinum and arsenic atoms were located from a Patterson synthesis. The remaining non-hydrogen atom positions were obtained from a difference-Fourier synthesis. The platinum and arsenic atoms were assigned anisotropic temperature factors and the non-chelating phenyl rings were refined as rigid groups (C–C 1.395 Å). Hydrogen atoms of the phenyl rings were included at calculated positions (C–H 1.08 Å). Full-matrix refinement of the positional and thermal parameters with the reflections weighted as $1/\sigma^2(F_o)$ gave a final R of 0.059, $R' = 0.058$ ($R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$).* The final atomic fractional co-ordinates are listed in Table 1 and the bond lengths and angles in Table 2. Intermolecular contact distances of less than 3.5 Å for (2), details of least-squares planes, thermal parameters, and the observed and calculated structure factors are in Supplementary Publication No. SUP 23196 (20 pp.).†

* As the standard unit cell ($C2/c$) had an angle of $\beta = 141.37°$, the solution and refinement was carried out using the non-standard space group $F2/d$ which had an angle of 96.95°.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

The scattering factors used for all atoms were those of Cromer and Mann [16] and corrections for the real and the imaginary part of the anomalous dispersion were included for all atoms. SHELX computer programs [17] were used throughout the solution and refinement.

TABLE 2

Principal bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bond lengths

Pt–As	2.267(2)	O(1)–C(1′)	1.29(2)
Pt–C(3)	1.99(2)	O(2)–C(1)	1.20(2)
Pt–Pt	2.989(2)	C(1)–C(2)	1.55(3)
Pt–O(1)	2.16(2)	C(4)–C(5)	1.57(3)
Pt–O(2)	2.10(1)	C(4)–C(3)	1.27(3)
As–C(11)	1.87(2)	C(4)–C(12)	1.51(3)
As–C(21)	1.93(1) *	C(11)–C(12)	1.42(3)
As–C(31)	1.93(1) *		

(*b*) Angles

As–Pt–O(1)	95.4(4)	As–C(11)–C(12)	122(2)
As–Pt–O(2)	169.9(4)	As–C(11)–C(16)	120(2)
O(1)–Pt–O(2)	89.5(6)	C(11)–As–C(21)	100.7(8) *
As–Pt–C(3)	86.0(6)	C(11)–As–C(31)	107.8(8) *
O(1)–Pt–C(3)	177.8(7)	C(21)–As–C(31)	102.8(6) *
O(2)–Pt–C(3)	89.0(7)	O(1′)–C(1)–O(2)	129(2)
Pt–O(2)–C(1)	126(1)	O(1′)–C(1)–C(2)	115(2)
Pt–O(1)–C(1′)	121(1)	O(2)–C(1)–C(2)	115(2)
Pt–As–C(11)	112.0(6)	C(5)–C(4)–C(3)	119(2)
Pt–As–C(21)	115.7(4) *	C(5)–C(4)–C(12)	113(2)
Pt–As–C(31)	116.5(5) *	C(3)–C(4)–C(12)	128(2)
Pt–C(3)–C(4)	138(2)	C(4)–C(12)–C(13)	122(2)

* E.s.d calculation based solely on contribution from atoms not in rigid group.

(o-*Isopropenylphenyl*)*diphenylarsine* (ipa).—*o*-Bromo(isopropenyl)benzene was prepared from *o*-bromobenzoic acid by treatment of its methyl ester with excess MgMeI, yielding upon hydrolysis 2-(*o*-bromophenyl)propan-2-ol which was dehydrated to the alkene by heating with 85% H_3PO_4 (yield 59%).

o-Bromo(isopropenyl)benzene (10.5 g, 53 mmol) was reacted with magnesium (1.23 g, 51 mmol) in dry tetrahydrofuran (thf) (200 cm^3) for 4 h at room temperature. To the resulting clear solution cooled to 0 °C, a diethyl ether solution of chlorodiphenylarsine (13.4 g, 51 mmol) was added slowly and the mixture allowed to come to room temperature and stirred for 2 h before pouring into a saturated solution of NH_4Cl (100 cm^3). The ether extracts of this mixture were washed with water, dried ($Mg[SO_4]$), and concentrated at reduced pressure to give a yellow oil. The oil was dissolved in hot ethanol and cooled to −70 °C (dry ice–acetone) to yield a white powder (29 g, 47% based on *o*-bromobenzoic acid). A second recrystallisation from hot ethanol gave clear colourless crystals, m.p. 79.5—80.0 °C (Found: C, 72.7; H, 5.45; As, 21.6. Calc. for $C_{21}H_{19}As$: C, 72.8; H, 5.55; As, 21.6%).

$[PtCl_2(ipa)]$.—A stirred suspension of platinum(II) chloride (1 g, 3.8 mmol) in chloroform was treated with a solution of ipa (1.43 g, 4.1 mmol) in chloroform dropwise over 10 min. The mixture was refluxed for 30 min, after which only a small amount of brown material remained in suspension, and then filtered through a pad of Kieselguhr. Concentration of the yellow-orange filtrate to a small volume at reduced pressure followed by dilution with ethanol gave yellow crystals (yield 2.2 g, 95% based on Pt). If an unscratched flask was used, a supersaturated solution could be formed that gave, on storing at −15 °C overnight, a high yield of large yellow

crystals. Analytical samples were recrystallised from dichloromethane–methanol, m.p. >200 °C (decomp.) (Found: C, 40.65; H, 3.25; Cl, 12.1. Calc. for $C_{21}H_{19}AsCl_2Pt$: C, 41.2; H, 3.15; Cl, 11.6%).

[Pt(ipa)(acac)][BF_4].—A dichloromethane solution of [$PtCl_2$(ipa)] (1 g, 1.6 mmol) was added to an excess quantity of Ag[BF_4] (1 g) and stirred vigorously for 5 min. A three molar excess of acetylacetone was then added and stirring was continued for 10 min. The mixture was filtered through a bed of Kieselguhr and the solvent evaporated under reduced pressure. The residual oil was taken up by acetone (1 cm^3) and then diethyl ether was added dropwise while inducing crystallisation. The white microcrystals were filtered and dried under high vacuum (yield 95%). The product [Pt(ipa)(acac)][BF_4] was recrystallised for analysis from acetone–diethyl ether, m.p. 176—178 °C (Found: C, 43.15; H, 3.55; F, 10.4; Pt, 26.6. Calc. for $C_{26}H_{26}AsBF_4O_2Pt$: C, 42.95; H, 3.60; F, 10.45; Pt, 26.8%).

[Pt{*o*-$CH_2C(=CH_2)C_6H_4AsPh_2$}(acac)] (1).—(*A*) A solution of [Pt(ipa)(acac)][BF_4] (95 mg, 0.13 mmol) in chloroform (1 cm^3) was treated with two drops of triethylamine and allowed to stand for 15 min. Light petroleum (15 cm^3, b.p. 60—80 °C) was added and the yellow lower layer that formed was removed. The upper layer was filtered through phase-separating filter paper, diluted with more light petroleum (2 cm^3), and kept at −15 °C for 2 days. Colourless crystals were filtered off, washed with light petroleum, and dried under vacuum (yield 46 mg, 55%).

(*B*) A solution of [Pt(ipa)(acac)][BF_4] (100 mg, 0.14 mmol) in methanol (10 cm^3) containing potassium acetate (0.1 g) was kept just below the reflux point for 30 min. During this time the colour of the solution changed from yellow to orange and a crop of cream crystals formed. The product was filtered off and washed with methanol (yield 69%).

(*C*) A solution of [Pt(ipa)(acac)][BF_4] (100 mg, 0.14 mmol) in $CDCl_3$ (0.5 cm^3) was vigorously stirred with an aqueous solution of sodium hydroxide (0.1 mol dm^{-3}, 1.5 cm^3) for 5 min. The organic layer was separated and dried (Na_2[SO_4]). The ^1H n.m.r. spectrum of this solution was identical to solutions of (1) as obtained above. Complex (1): m.p. 180—183 °C (Found: C, 48.75; H, 3.95; As, 11.8; Pt, 30.6. Calc. for $C_{26}H_{25}AsO_2Pt$: C, 48.85; H, 3.95; As, 11.7; Pt 30.5%).

[{Pt(*o*-$CH{=}CMeC_6H_4AsPh_2$)}$_2$(μ-$O_2CMe)_2$] (2).—A solution of [$PtCl_2$(ipa)] (0.5 g, 0.83 mmol) in chloroform (30 cm^3) was stirred with silver acetate (0.30 g) for 15 min. The filtered solution was allowed to stand overnight then concentrated at reduced pressure to *ca.* 2 cm^3 and diluted with methanol (15 cm^3). On storing at −15 °C overnight orange crystals were formed. These were filtered off, washed with methanol (0.39 g, 80%), and recrystallised from CH_2Cl_2–CH_3OH. Complex (2): m.p. >220 °C (decomp.) (Found: C, 46.05; H, 3.6; Pt, 32.3. Calc. for $C_{46}H_{42}As_2O_4Pt_2$: C, 46.1; H, 3.55; Pt, 32.55%).

[Pt{*o*-(*trans*-$CH{=}CMeC_6H_4AsPh_2$}(O_2CMe)(PPh_3)] (5).—A solution of (2) (0.10 g, 0.083 mmol) in chloroform was treated with a solution of triphenylphosphine (44 mg, 0.17 mmol) in chloroform (2 cm^3). On warming, the orange colour of the solution changed to yellow. The solution was diluted with light petroleum (5 cm^3) and cooled to −15 °C. Scratching of the flask wall initiated the formation of pale yellow crystals which were filtered off and washed with light petroleum (0.110 g, 77%); recrystallisation was from $CHCl_3$–light petroleum. Complex (5): m.p. >200 °C (decomp.) (Found: C, 56.8; H, 4.1; Pt, 22.35. Calc. for $C_{41}H_{36}AsO_2PPt_2$: C, 57.15; H, 4.2; Pt, 22.65%).

Tl[Pt(*o*-$CH{=}CMeC_6H_4AsPh_2$)($O_2CMe)_2$] (6).—A solution of (2) (80 mg, 0.067 mmol) in $CDCl_3$ (0.5 cm^3) was vigorously stirred with thallium acetate (35 mg, 0.14 mmol) for 10 min. The mixture was centrifuged and the yellow supernatant solution removed by syringe and filtered into an n.m.r. tube.

Mixture of (6) *and* Tl[Pt{*o*-CH_2–$C(=CH_2)C_6H_4AsPh_2$}($O_2CMe)_2$] (7).—A solution of [$PtCl_2$(ipa)] (100 mg, 0.16 mmol) in $CDCl_3$ (0.5 cm^3) was vigorously stirred with thallium acetate (0.13 g, 0.48 mmol) for 18 h. The reaction vessel was centrifuged and the yellow supernatant solution removed by syringe and filtered into an n.m.r. tube.

The Deuteriated Ligand Reactions.—Formation of the deuteriated ligand complexes [$PtCl_2$([^{2}H]ipa)]. A solution of (1) or (2) (0.15 g) in chloroform (5 cm^3, which was purified by passage down a column of activated alumina) was shaken with two or three drops of a 20% solution of DCl in D_2O. The mixture was diluted with [$^2H_1$]ethanol causing crystallisation of the complexes [$PtCl_2$([^{2}H]ipa)] (nearly quantitative yields).

Formation of the deuteriated forms of (1). The complexes [$PtCl_2$([^{2}H]ipa)] were converted to [Pt([^{2}H]ipa)(acac)]-[BF_4] and then to (1) by method (*C*) above.

Formation of the deuteriated forms of (2). Solutions of the deuteriated forms of [$PtCl_2$(ipa)] (100 mg, 0.16 mmol) in chloroform (2 cm^3) were stirred with silver acetate (0.13 g, 0.48 mmol) for 10 min. The reaction vessels were centrifuged and the supernatant removed by syringe and diluted with methanol (8 cm^3). Storage at −15 °C overnight gave orange crystals of the products (2) (yields about 65%).

Re-formation of [$PtCl_2$(ipa)] *from the deuteriated forms of* (1) *and* (2). A solution of (1) or (2) (0.15 g) in chloroform (5 cm^3) was shaken with a 36% solution of HCl in water. Addition of ethanol precipitated the complexes [$PtCl_2$([^{2}H]ipa)] (yields *ca.* 95%).

[0/1782 *Received*, 19*th November*, 1980]

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