The *trans* Influence and *trans* Effect of the Arsine Group. The *X*-Ray Structures of Dichloro[diphenyl(*o*-vinylphenyl)arsine]platinum(II) and [1-(*o*-Diphenylarsinophenyl)-2-methoxyethyl-*As*,C^1](hexafluoroacetylacetonato)platinum(II) †

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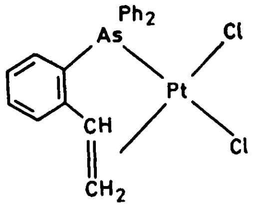
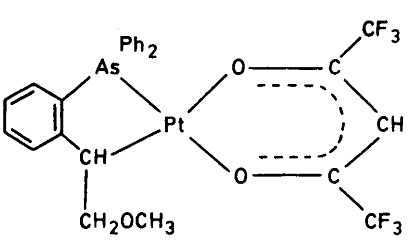
The *X*-ray analyses of dichloro[diphenyl(*o*-vinylphenyl)arsine]platinum(II) (1) and a derivative (2) of nucleophilic attack by methoxide at its co-ordinated olefinic group are reported. Crystals of (1) are monoclinic, space group $P2_1/c$, with a = 9.288(3), b = 18.112(6), c = 12.413(4) Å, β = 118.33(2)°, and Z = 4. Crystals of (2) are orthorhombic, space group *Pbca*, with a = 24.078(7), b = 12.327(4), c = 18.500(6) Å, and Z = 8. Full-matrix least-squares refinement using diffractometer data (Mo-K_α; Pt, As, Cl, and F anisotropic) has given an R of 0.047 for 2 258 reflections for (1) and an R of 0.057 for 2 345 reflections for (2). In (1) the olefin group makes an angle of 83.6° with the co-ordination plane. In (2) there is a five-membered chelate ring containing a Pt–C σ bond and an exocyclic methoxy-group. A relatively high *trans* influence of the arsine group is inferred. The course of bridge-cleavage reactions of a related chloride-bridged dimeric compound shows the *trans* effect of the arsine to be close to that of the alkyl carbon group.

CHELATE ligands containing both an olefin and a Group 5 donor atom were introduced by Nyholm and co-workers [1] to stabilize mono-olefinic derivatives of the transition metals. They have also been useful for isolating intermediates of reactions at the co-ordinated olefin. The ligand diphenyl(*o*-vinylphenyl)arsine is of this type. We report here the *X*-ray structure analyses of its complex with platinum(II) chloride, dichloro[diphenyl(*o*-vinylphenyl)arsine]platinum(II), (1), and also of a compound derived from nucleophilic attack by methoxide at the co-ordinated olefin, [1-(*o*-diphenylarsinophenyl)-2-methoxyethyl-*As*,C^1](hexafluoroacetylacetonato)platinum(II), (2). The *X*-ray analysis of (2) confirms the structure previously deduced from n.m.r. data.[2] Very few crystal structures of platinum(II) arsine-donor complexes have been reported.[3-8] From those that have and the present work we are able to infer that the arsine group exerts a strong *trans* influence. We have also studied the *trans* effect of the arsine group by determining the products of some bridge-cleavage reactions of a related chloro-bridged dimeric compound.



(1)



(2)

EXPERIMENTAL

Preparations.—The ligand diphenyl(*o*-vinylphenyl)arsine was prepared as described by Bennett and Tomkins [9] except that recrystallization was from ethanol (m.p. 80—82 °C, lit.[9] 68—70 °C). The compounds (1) and (2) were prepared as previously reported.[2] It should be noted that in ref. 2 the calculated analytical figures were based erroneously on C_{24} rather than C_{26}. The correct data are as follows. Found: C, 40.95; H, 2.85; As, 10.0; F, 15.1; Pt, 25.75. Calc. for $C_{26}H_{21}AsF_6O_3Pt$: C, 40.8; H, 2.75; As, 9.80; F, 14.9; Pt, 25.5%.

Apparatus and Techniques.—The course of the bridge-cleavage reactions was followed by n.m.r. on Varian HA100 (for ^1H) and Bruker HX-90 (for ^{31}P) instruments. Approximately 20% w/v solutions of di-μ-chloro-bis{[1-(*o*-diphenylarsinophenyl)-2-methoxyethyl-*As*,C^1]platinum(II)} (9) in $CDCl_3$ were mixed with the calculated amount of ligand. Spectra were recorded after 15 min. No changes in the isomer ratios were observed after 3 d. Chemical shifts were measured relative to triphenyl phosphite as an external reference but are quoted relative to 85% H_3PO_4 using the correction factor of 128 p.p.m.

Crystal Data.—(1). $C_{20}H_{17}AsCl_2Pt$, M = 598.3, Monoclinic, a = 9.288(3), b = 18.112(6), c = 12.413(4) Å, β = 118.33(2)°, U = 1 838.1 Å^3, Z = 4, $F(000)$ = 1 128, D_c = 2.162 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 117.0 cm^{-1}. The space group $P2_1/c$ was unambiguously determined from systematic absences in the data: $h0l$, $l = 2n + 1$; and $0k0$, $k = 2n + 1$.

(2). $C_{25}H_{21}AsF_6O_3Pt$, M = 753.4, Orthorhombic, a = 24.078(7), b = 12.327(4), c = 18.500(6) Å, U = 5 491.0 Å^3, Z = 8, $F(000)$ = 2 880, D_c = 1.822 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69Å, μ(Mo-K_α) = 66.2 cm^{-1}. The space group *Pbca* was unambiguously determined from systematic absences in the data: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$.

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† Systematic names are dichloro(1—2-η-*o*-diphenylarsinophenylethylene-*As*)platinum(II), (1), and [1-(*o*-diphenylarsinophenyl)-2-methoxyethyl-*As*,C^1](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)platinum(II), (2).

Intensity Measurements.—For (1) and (2), intensity measurements 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 $I_t - 2\sqrt{I_t} < I_b$ on the first scan were omitted; I_t is the intensity at the maximum of the reflections 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 during the scan. For (1) a crystal of *ca.* 0.12 × 0.08 × 0.10 mm was used with a constant scan speed of 0.025° s^{-1} and a scan width of 0.7°, to examine reflections in the range θ 2—28°. For (2) the scan speed was 0.05° s^{-1} and the scan width 1.4°, with a range of θ 3—30°, using a crystal of *ca.* 0.16 × 0.14 × 0.13 mm. Three standard reflections were measured at intervals of 5 h during data collection for (1) and (2) and showed no significant variation in intensity.

TABLE 1

Fractional atomic co-ordinates for (1) with standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Independent atoms			
Pt	0.417 36(7)	0.131 30(3)	0.224 70(6)
As	0.179 8(2)	0.169 0(1)	0.054 6(1)
Cl(1)	0.666 2(5)	0.100 3(3)	0.390 3(4)
Cl(2)	0.371 8(6)	0.011 9(2)	0.160 8(5)
C(1)	0.484 8(19)	0.248 0(10)	0.247 1(16)
C(2)	0.404 8(19)	0.227 5(9)	0.317 3(15)
C(11)	0.237 9(17)	0.269 3(8)	0.039 2(14)
C(12)	0.388 2(17)	0.291 0(8)	0.131 6(13)
C(13)	0.451 0(19)	0.359 9(9)	0.123 2(15)
C(14)	0.354 8(20)	0.405 1(9)	0.020 2(16)
C(15)	0.203 8(20)	0.383 6(9)	−0.068 9(16)
C(16)	0.140 6(19)	0.314 3(9)	−0.060 9(15)
(*b*) Rigid-group atoms			
C(21)	0.122 8	0.121 7	−0.098 4
C(22)	−0.040 1	0.106 2	−0.180 9
C(23)	−0.080 2	0.074 9	−0.294 4
C(24)	0.042 6	0.059 2	−0.325 4
C(25)	0.205 5	0.074 7	−0.242 8
C(26)	0.245 6	0.105 9	−0.129 3
C(31)	−0.010 4	0.171 8	0.073 0
C(32)	−0.079 1	0.238 7	0.081 0
C(33)	−0.215 7	0.239 2	0.099 8
C(34)	−0.283 6	0.172 7	0.110 7
C(35)	−0.078 3	0.105 4	0.083 9
C(36)	−0.214 9	0.105 8	0.102 7

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[10] The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04\ I)^2$, where the term in I^2 was introduced to allow for other sources of error.[11] I and $\sigma(I)$ were corrected for Lorentz and polarization factors but not absorption, and 2 258 reflections for (1) and 2 345 reflections for (2) having $I > 3\sigma(I)$ were used.

Structure Solution and Refinement.—The platinum, chlorine, and arsenic atoms in (1) were located from a Patterson synthesis. The other non-hydrogen atom positions were obtained from a difference-Fourier synthesis. Full-matrix refinement of the positional and thermal parameters with the reflections weighted as $1/\sigma^2(F_o)$ gave a final R 0.047 and $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o| = 0.055$. The phenyl rings were refined as rigid groups (C–C 1.395 Å) and the platinum, chlorine, and arsenic atoms were assigned anisotropic temperature factors.

For (2) the platinum and arsenic atoms were located from a Patterson synthesis. The non-hydrogen atoms were located from subsequent difference-Fourier synthesis. The electron density of the fluorine atoms of the trifluoromethyl groups indicated considerable rotational disorder, but it was not possible to resolve the atoms into separate orientations. The fluorine atoms presented some difficulty in subsequent refinement. The most satisfactory results were obtained by initially refining all the atoms for two cycles with isotropic thermal parameters. The fluorine atoms were refined in separate cycles to the other atoms, with a damping factor of 0.6 applied to their parameters. This gave an R of 0.081. Further refinement of the non-fluorine atom parameters, with anisotropic thermal parameters assigned to the platinum and arsenic atoms and the non-chelating phenyl rings treated as rigid groups (C–C 1.395 Å), reduced R to 0.065. Two cycles of refinement of anisotropic thermal parameters of the fluorine atoms only, with damping factors of 0.6, reduced R to 0.058. Some of the fluorine thermal parameters were very large and undoubtedly reflected the rotational disorder of the trifluoromethyl groups. The fluorine atoms were not refined further; two cycles of full-matrix refinement of the parameters of the other atoms produced a final R of 0.057, $R' = 0.071$. The scattering factors used for all atoms in (1)

TABLE 2

Fractional atomic co-ordinates for (2) with standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Independent atoms			
Pt	0.102 19(3)	0.056 55(4)	0.015 94(3)
As	0.107 56(7)	−0.127 68(10)	0.013 13(10)
F(1) *	0.052 3	0.042 86	0.017 7
F(2) *	0.131 5	0.434 3	0.063 4
F(3) *	0.124 4	0.481 2	−0.032 5
F(4) *	0.234 2	0.272 5	−0.167 8
F(5) *	0.253 0	0.111 2	−0.140 8
F(6) *	0.191 6	0.140 1	−0.210 1
O(1)	0.091 7(5)	0.221 5(8)	0.028 9(6)
O(2)	0.159 9(5)	0.083 2(9)	−0.067 9(6)
O(3)	0.115 2(5)	0.019 6(8)	0.186 5(6)
C(1)	0.043 5(6)	0.035 1(12)	0.095 3(8)
C(2)	0.067 6(7)	0.081 9(13)	0.165 8(8)
C(3)	0.136 7(8)	0.049 5(15)	0.257 9(11)
C(4)	0.101 3(11)	0.403 8(20)	0.016 0(14)
C(5)	0.119 0(7)	0.291 1(13)	−0.007 8(10)
C(6)	0.158 3(8)	0.281 2(14)	−0.059 8(11)
C(7)	0.173 5(8)	0.321 6(16)	0.414 1(10)
C(8)	0.215 8(12)	0.183 3(21)	−0.148 0(15)
C(11)	0.048 6(6)	−0.169 1(11)	0.074 6(8)
C(12)	0.032 1(8)	−0.276 3(14)	0.091 4(10)
C(13)	−0.015 9(9)	−0.288 5(15)	0.142 6(11)
C(14)	−0.039 9(8)	−0.203 1(15)	0.166 6(11)
C(15)	−0.022 7(8)	−0.094 5(14)	0.152 2(10)
C(16)	0.023 2(7)	−0.080 1(12)	0.106 6(8)
(*b*) Rigid-group atoms			
C(21)	0.095 8	−0.191 4	−0.079 9
C(22)	0.131 3	−0.159 7	−0.135 6
C(23)	0.125 0	−0.203 9	−0.204 5
C(24)	0.083 3	−0.279 9	−0.217 7
C(25)	0.047 8	−0.311 6	−0.162 0
C(26)	0.054 0	−0.267 3	−0.093 1
C(31)	0.172 9	−0.197 9	0.048 9
C(32)	0.205 2	−0.145 4	0.100 8
C(33)	0.252 2	−0.196 4	0.128 9
C(34)	0.266 9	−0.299 9	0.105 1
C(35)	0.234 5	−0.352 4	0.053 3
C(36)	0.187 5	−0.301 4	0.025 2

* The fluorine atoms appeared to be disordered; their parameters were not refined in the final cycles.

and (2) were those of Cromer and Mann [12] and corrections for the real part of the anomalous dispersion were included for platinum, arsenic, and chlorine. Computer programs were those of the '*X*-Ray '74' crystallographic system.[13] The final atomic co-ordinates for (1) and (2) are given in Tables 1 and 2 respectively.

TABLE 3

Bond distances (Å) and angles (°) for (1) with standard deviations in parentheses

(*a*) Distances

Pt–As	2.317(1)	As–C(11)	1.93(1) *
Pt–Cl(1)	2.318(4)	As–C(21)	1.91(1) *
Pt–Cl(2)	2.274(4)	As–C(31)	1.89(1) *
Pt–C(1)	2.19(2)	C(1)–C(2)	1.44(3)
Pt–C(2)	2.12(2)	C(1)–C(12)	1.50(2)

(*b*) Angles

As–Pt–Cl(1)	175.4(2)	C(11)–As–C(31)	108.0(5) *
As–Pt–Cl(2)	91.3(1)	C(21)–As–C(31)	107.4(1) *
As–Pt–C(1)	85.6(4)	Pt–C(1)–C(2)	68.2(10)
As–Pt–C(2)	88.8(4)	Pt–C(1)–C(12)	112.1(10)
Cl(1)–Pt–Cl(2)	91.2(2)	C(2)–C(1)–C(12)	117.9(15)
Cl(1)–Pt–C(1)	91.0(4)	Pt–C(2)–C(1)	72.9(11)
Cl(1)–Pt–C(2)	90.4(4)	As–C(11)–C(12)	114.0(10)
Cl(2)–Pt–C(1)	163.7(6)	As–C(11)–C(16)	122.8(10)
Cl(2)–Pt–C(2)	157.2(6)	C(1)–C(12)–C(11)	123.9(14)
C(1)–Pt–C(2)	38.9(8)	C(1)–C(12)–C(13)	116.9(12)
Pt–As–C(11)	100.2(4)	As–C(21)–C(22)	120.8(1) *
Pt–As–C(21)	117.9(1) *	As–C(21)–C(26)	119.2(1) *
Pt–As–C(31)	116.1(1) *	As–C(31)–C(32)	121.2(1) *
C(11)–As–C(21)	106.3(5) *	As–C(31)–C(36)	148.7(1) *

* Estimated standard deviation calculation based solely on contributions from atoms not in rigid groups.

The intramolecular bond lengths and angles for (1) and (2) are listed in Tables 3 and 4 respectively. Supplementary Publication No. SUP 22688 (27 pp.) * contains isotropic and anisotropic thermal parameters for (1) and (2), intermolecular contacts of less than 3.5 Å for (2), details of least-square planes, and the observed and calculated structure factors for (1) and (2).

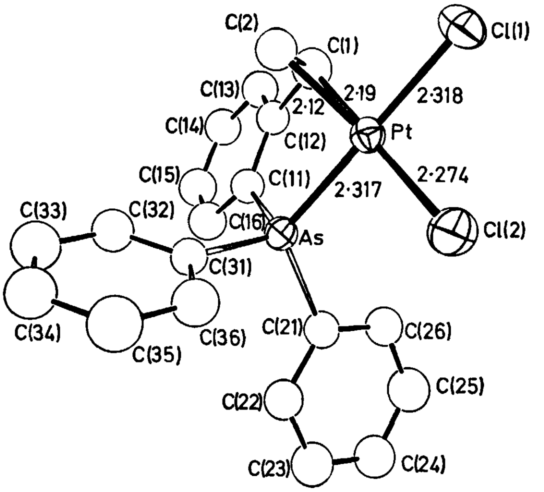

FIGURE 1 The structure of (1) showing the principal bond lengths (Å)

RESULTS AND DISCUSSION

The molecular structures of (1) and (2) are shown in Figures 1 and 2 respectively together with the atom numbering and the principal bond lengths. The intramolecular bond lengths and angles for (1) and (2) are listed in Tables 3 and 4 respectively. In (1) there are no intermolecular contacts of less than 3.5 Å involving non-hydrogen atoms; those for (2) are listed in the Supplementary Publication.

TABLE 4

Bond distances (Å) and angles (°) for (2) with standard deviations in parentheses

(*a*) Distances

Pt–As	2.275(2)	C(4)–F(2)	1.20(3)
Pt–O(1)	2.06(1)	C(4)–F(3)	1.42(3)
Pt–O(2)	2.11(1)	C(8)–F(4)	1.24(3)
Pt–C(1)	2.05(2)	C(8)–F(5)	1.27(3)
As–C(11)	1.89(2)	C(8)–F(6)	1.40(3)
As–C(21)	1.913(2) *	C(1)–C(2)	1.54(2)
As–C(31)	1.913(2) *	C(2)–O(3)	1.43(2)
O(1)–C(5)	1.28(2)	O(3)–C(3)	1.47(2)
C(5)–C(6)	1.36(3)	C(1)–C(16)	1.52(2)
C(6)–C(7)	1.41(3)	C(11)–C(12)	1.41(2)
C(7)–O(2)	1.26(2)	C(12)–C(13)	1.50(3)
C(5)–C(4)	1.52(3)	C(13)–C(14)	1.28(3)
C(7)–C(8)	1.54(3)	C(15)–C(16)	1.40(2)
C(4)–F(1)	1.22(3)	C(16)–C(11)	1.39(2)

(*b*) Angles

As–Pt–O(1)	173.4(3)	F(2)–C(4)–F(3)	91(2)
As–Pt–O(2)	95.8(3)	F(4)–C(8)–F(5)	113(2)
As–Pt–C(1)	85.8(4)	F(4)–C(8)–F(6)	104(2)
O(1)–Pt–O(2)	90.7(4)	F(5)–C(8)–F(6)	96(2)
O(1)–Pt–C(1)	87.7(5)	Pt–C(1)–C(16)	116.2(10)
O(2)–Pt–C(1)	177.4(5)	Pt–C(1)–C(2)	107.3(10)
Pt–As–C(11)	102.3(4)	C(16)–C(1)–C(2)	110.8(12)
Pt–As–C(21)	114.9(1) *	C(1)–C(2)–O(3)	109.1(12)
Pt–As–C(31)	119.4(1) *	C(2)–O(3)–C(3)	112.9(12)
C(11)–As–C(21)	108.6(5) *	As–C(11)–C(12)	126.6(12)
C(11)–As–C(31)	106.7(5) *	As–C(11)–C(16)	111.9(11)
C(21)–As–C(31)	104.3(1) *	C(1)–C(16)–C(11)	122.6(14)
Pt–O(1)–C(5)	122.6(10)	C(1)–C(16)–C(15)	117.1(14)
O(1)–C(5)–C(6)	132.6(16)	C(16)–C(11)–C(12)	121.4(15)
C(5)–C(16)–C(7)	120.4(17)	C(11)–C(12)–C(13)	116.6(15)
C(6)–C(7)–O(2)	132.8(18)	C(12)–C(13)–C(14)	119.0(18)
C(7)–O(2)–Pt	120.7(11)	C(13)–C(14)–C(15)	125.1(19)
O(1)–C(5)–C(4)	108.5(16)	C(14)–C(15)–C(16)	117.4(16)
C(6)–C(5)–C(4)	118.9(17)	C(15)–C(16)–C(11)	120.2(14)
C(6)–C(7)–C(8)	113.2(18)	As–C(21)–C(22)	117.3(1) *
O(2)–C(7)–C(8)	114.0(17)	As–C(21)–C(26)	122.7(1) *
F(1)–C(4)–F(2)	119(2)	As–C(31)–C(32)	119.2(1) *
F(1)–C(4)–F(3)	103(2)	As–C(31)–C(36)	120.8(1) *

* Estimated standard deviation does not include contribution from atoms of rigid groups.

In (1) the midpoint of the olefin is 0.205 Å out of the plane containing the platinum atom and the other donor atoms As, Cl(1), and Cl(2). The olefin makes an angle of 83.6° with this plane. The difference from the values of 90° expected for a symmetrically π-bonded olefin may be attributed to the steric requirement of the chelate ring. The platinum–olefin bond distance [from platinum to the midpoint of C(1)–C(2)] is 2.030 Å and is close to the value found in other π-bonded olefin platinum(II) complexes. The olefinic bond length is 1.44(3) Å which is significantly longer than the 1.34 Å of unco-ordinated ethylene. Similar lengthening of olefinic bonds on co-ordination to platinum(II) has been observed in a number of other complexes.[14] The plane of olefin co-ordination, Pt–C(1)–C(2), is at an angle of 81.5° to the plane of the chelating phenyl ring.

Interpretation of the n.m.r. data for (2) indicated a

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

structure with a five-membered chelate ring.[2] This is now confirmed. The ligand is bidentate with the platinum atom bonded to the α-carbon atom, C(1), and the arsenic atom. The Pt–C(1) bond length of 2.05(2) Å is similar to that observed in other platinum(II) complexes[14] and is consistent with a strong Pt–C σ bond. The co-ordination plane is completed by the two oxygen atoms of the bidentate hexafluoroacetylacetonato-ligand (hfac).

The platinum–arsenic bond length in (1) is 2.317(1) Å and in (2) 2.275(2) Å. The difference in these values is highly significant and the Pt–As length in (2) is the shortest reported for a platinum(II) complex. A list of the limited number of platinum(II)–arsenic bond lengths so far obtained from X-ray studies is given in Table 5 in order of decreasing length. All of these are shorter than the sum of the covalent radii for Pt and As (2.49 Å). This may arise from a π interaction between the atoms. It is possible to rationalize the difference in the Pt–As bond lengths in these compounds, which vary from 2.437 Å in *trans*-chloromethylbis(trimethylarsine)-platinum(II)–hexafluorobut-2-yne (3) to 2.275 Å in (2), by invoking two main factors. First, other π-acid ligands, if present, compete with the arsenic atom for the π-electron density of the platinum atom, thereby reducing the π component of the Pt–As bond, and so a relatively longer bond would be observed. Secondly, the presence of a ligand that has a strong *trans* influence, such as a σ-bonded carbon atom, would also lengthen the Pt–As bond. The two longest Pt–As bonds reported are in the bis(arsine) complex (3); these lengths of 2.437 and 2.431 Å may in part be attributed to the presence of three π-bonded ligands, *i.e.* the two arsines and the hexafluorobut-2-yne group, and partly to the five-co-ordinate structure of the complex. In four-co-ordinate platinum(II) complexes the longest Pt–As bond (2.402 Å) is *trans* to the carbon in the *cis* bis(arsine) complex (4). Much of the lengthening of this bond may be attributed to the high *trans* influence of the σ-bonded carbon atom of the 2,2,3,3-tetracyano-oxacyclopropane ligand, as the second Pt–As bond which is *trans* to an oxygen atom has a length of 2.341 Å. In the bis[*o*-phenylenebis(dimethylarsine)]platinum(II) cation (5), the relatively long Pt–As bond undoubtedly arises from a combination of factors including the presence of four π-acceptor ligands, the positive charge on the complex, and the high mutual *trans* influence of the co-ordinated arsenic atoms (see below). The compound *trans*-bis(dimethyl-*o*-thiolophenylarsine)platinum(II) (6) has four π-acceptor ligands and the Pt–As bond length is 2.354 Å. The complex (1), shown in this study to have Pt–As bond length of 2.317 Å, is shorter than any of those mentioned above, indicating more efficient Pt–As π bonding. In this complex the olefin is the only other π-bonding ligand competing for the π-electron density from the platinum atom. Three of the platinum(II) complexes have no π-acceptor ligands competing with the arsine group and have atoms of low *trans* influence opposite the arsenic atom. The Pt–As bond lengths still show marked differences being 2.346 Å in *trans*-dichloro-[*N*-(*p*-methylbenzylidene)methylamine]triethylarsine-platinum(II) (7), 2.308 Å in di-μ-chloro-*af*-dichlorobis-(trimethylarsine)diplatinum(II) (8), and 2.275 Å in (2). This range of bond lengths may be largely attributed to decreasing π-acceptor ability of the arsine ligands in the order triaryl > trimethyl > triethyl which would be consistent with the relative electron-withdrawing or electron-releasing properties of the organic substituents.

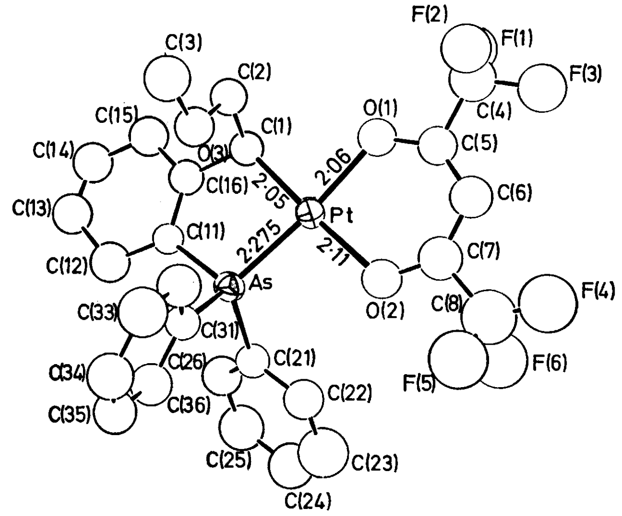


FIGURE 2 The structure of (2) showing the principal bond lengths (Å) (for clarity the fluorine atoms have been assigned isotropic thermal parameters)

TABLE 5

Pt–As Bond lengths in platinum(II) complexes

Complex	Pt–As distance (Å)	Ref.
(3) *trans*-Chloro(hexafluorobut-2-yne)-methylbis(trimethylarsine)platinum(II)	2.437 2.431	3
(4) *cis*-(2,2,3,3-Tetracyano-oxacyclopropyl)-bis(triphenylarsine)platinum(II)	2.402 2.341	4
(5) Dichloro[*o*-phenylenebis(dimethylarsine)]-platinum(II)	2.375	5
(6) Bis(dimethyl-*o*-thiolophenylarsine)-platinum(II) *	2.354	6
(7) *trans*-Dichloro[*N*-(*p*-methylbenzylidene)-methylamine]triethylarsineplatinum(II)	2.346	7
(1) Dichloro[diphenyl(*o*-vinylphenyl)-arsine]platinum(II)	2.317	This work
(8) Di-μ-chloro-*af*-dichlorobis(trimethyl-arsine)diplatinum(II)	2.308	8
(2) [1-(*o*-Diphenylarsinophenyl)-2-methoxy-ethyl-As,C^1](hexafluoroacetylacetonato)-platinum(II)	2.275	This work

* More systematically named as bis(*o*-dimethylarsinobenzene-thiolato)platinum(II).

Both alkyl and phosphine groups have been shown to exhibit significant *trans* influences in platinum(II) complexes.[14] Evidence that arsine ligands may have a comparable *trans* influence was obtained from the structure of (8) where the bridging Pt–Cl bonds *trans* to the arsenic atoms are 0.082 Å longer than the *cis*-bridging Pt–Cl bonds.[8] In the present study, the arsine ligands in both (1) and (2) also appear to show considerable *trans* influence. In (1) the Pt–Cl(1) bond length trans to the Pt–As bond is 2.318(4) Å whereas the Pt–Cl(2) bond length *trans* to the olefin is 2.274(4) Å. The difference (0.044 Å) in these bond lengths (11σ) is highly significant showing that the arsine ligand has a strong *trans* influence relative to that of the olefin. In (2) the two Pt–O bonds from the potentially symmetrical hexafluoroacetylacetonato-ligand are unequal in length, the longer bond is Pt–O(1) [2.11(1) Å], which is *trans* to the σ-bonded C(1), whereas Pt–O(2), *trans* to the arsine, has a length of 2.06(1) Å. The difference in these bonds is clearly due to the very strong *trans* influence which σ-bonded carbon atoms are known to exert in platinum(II) complexes. However, a very much larger difference in the Pt–O bond lengths was observed in the bis(acetylacetonato)chloroplatinate(II) anion (which has one bidentate acetylacetonato-ligand and one unidentate one through a σ bond from the methine carbon)[15] where the Pt–O bond *trans* to the σ-bonded carbon is 0.104 Å longer than that *trans* to the chlorine atom. The observation of a much smaller difference in the Pt–O bond lengths in (2) may be taken as further evidence for the strong *trans* influence of the tertiary arsine group in platinum(II) complexes.

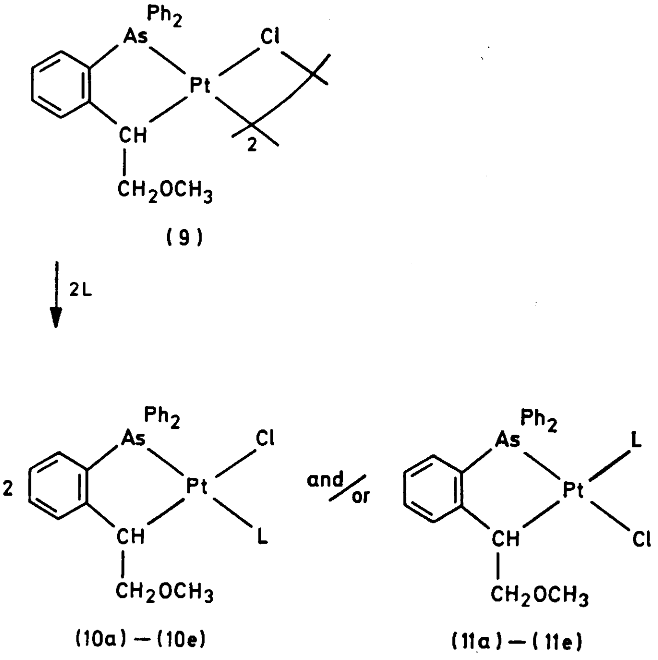
There is evidence that for a good σ-donor ligand there is some parallel between its *trans* influence, a ground-state effect, and its kinetic *trans* effect.[16] In the kinetic effect the group *trans* to the σ-donor ligand would be labilized, not only by the weakening of its bond to the metal (*trans* influence), but also by a lowering of the energy difference between the ground and the transition states of the complex.[16] A chemical study of the course of bridge-cleavage reactions of the dimer (9) (see Scheme), containing the same chelating ligand as (2), has been used to give some indications of the *trans* effect of the tertiary arsine group, shown by the *X*-ray results to have a strong *trans* influence. The proportion of the product (10) or (11) (see Scheme) obtained should be related to the respective *trans* effects of the alkyl and arsine donors of the chelating ligands.[17]

Several neutral bridge-cleavage reagents were used for this purpose including the substantially non-π-acid ligand 4-methylpyridine (4Me-py) and four phosphorus ligands of varying π acidity. Proton and ^{31}P n.m.r. analyses were used to determine the ratio of geometrical isomers [(10) or (11)] formed.

For the 4Me-py monomer, duplication of each of the methyl, methoxy-, and α-pyridine proton resonances showed the presence of two isomers in the ratio of 1 : 1.1. Which of (10a) or (11a) is present in greater abundance is not known because these resonances cannot be assigned to a given isomer. The methine group σ bonded to platinum also gave two signals (δ 4.35 and 3.83) but the integral could not be interpreted because other resonances overlapped them. Nevertheless, the *trans* effect of the tertiary arsine and the alkyl carbon appear about equal for 4-methylpyridine.

The ^{1}H n.m.r. spectrum of a solution containing 2 mol of trimethyl phosphite to 1 mol of (9), 15 min after mixing, shows two signals (δ 3.07 and 3.00) of equal intensity assignable to the methoxy-groups of the chelate ligand, and two pairs of doublets [centres at δ 3.92 and 3.59, ^{3}J(PH) = 12 Hz for both] of equal intensity assignable to the phosphite protons. When the spectrum was run immediately after mixing, these resonances were observed in identical ratios, as measured by peak height, but integration was complicated due to signals from unreacted dimer and trimethyl phosphite.

Similarly, in the ^{31}P n.m.r. spectrum there are two signals of equal intensity [δ 132.6, J(PtP) = 3.29 kHz and δ 107.0, J(PtP) = 6.09 kHz] showing an equal abundance of (10b) and (11b). One of these isomers is considerably more soluble in methanol than the other. The product obtained by precipitation with methanol is responsible for the lower-field phosphite doublet and the higher-field methoxy-signal in the ^{1}H n.m.r.



a ; L = 4Me-py
b ; L = P(OMe)$_3$
c ; L = P(Ph)$_3$
d ; L = P(Bu^n)$_3$
e ; L = P(C$_6$H$_{11}$)$_3$

In the ^{31}P n.m.r. spectrum this is the isomer with the larger coupling constant which we assign to (10b) where the arsenic is *trans* to the phosphorus. In the other isomer (11b) the phosphorus is *trans* to the σ-bonded carbon, a ligand of high inductive *trans* influence, which makes the Pt–P bond less covalent and thus lowers the Pt–P coupling constant. The ratio of compounds (10b) and (11b) in solution does not change over several days nor does pure (10b) isomerize. It may therefore be inferred that the *trans*-labilizing effects of the triarylarsine group and the σ-bonded carbon are equivalent for trimethyl phosphite as the entering ligand.

TABLE 6

Phosphorus-31 n.m.r. data for isomers (10) and (11)

		Isomer (10)		Isomer (11)		Ratio
L	pK_a	δ/p.p.m.*	J(PtP)/kHz	δ/p.p.m.*	J(PtP)/kHz	(10) : (11)
$P(OMe)_3$	−6.5	107.0	6.09	132.6	3.29	1 : 1
PPh_3	2.7	25.9	3.72	21.8	1.91	3 : 1
PBu^n_3	8.4	7.0	3.34	6.4	1.89	3 : 1
$P(C_6H_{11})_3$	9.7	22.1	3.59	26.3	1.93	7 : 1

* Relative to 85% H_3PO_4, positive values downfield.

Similar experiments were performed with the phosphines PR_3 (R = Ph, Bu^n, or cyclohexyl) and ^{31}P n.m.r. spectra showed that two isomers were formed in each case (Table 6). The major product in each case was responsible for the signal with the larger Pt–P coupling constant which was assigned for the reasons given above to isomers (10c, 10d, and 10e). When these phosphines are the entering ligands it appears that the triarylarsine group exerts a stronger *trans*-labilizing effect than does the σ-bonded carbon.

The higher proportion of isomer (10) when a phosphine is the entering ligand is probably better rationalized on the basis of the pK_a values (Table 6). Increasing pK_a indicates not only increasing σ-donor ability of the entering ligand but also in the case of the phosphorus ligands decreasing π acidity; both of these factors should enhance substitution *trans* to the π-acid arsine ligand.

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