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Infrared Spectra of Some Organic Compounds of Group V B Elements

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On the basis of a comparative study of the infrared spectra of compounds of the type Ph_3MY (Ph = phenyl; M = P, As, Sb; Y = O, S, Se) in the range 400–3000 cm^{-1} the following values have been found for the infrared absorption frequencies of the groups M=Y and Ph-M: P=O 1191 cm^{-1}; P=S 637 cm^{-1}; P=Se 561 cm^{-1} As=O 881 cm^{-1}; As=S 495 cm^{-1}; Ph-P_{as} 511–540 cm^{-1}; Ph-As_{as} 474–479 cm^{-1}. No absorption due to the Sb=O group could be identified, in accordance with the pseudoionic character of the Sb-O bond. The Ph-Sb frequency is probably near 450 cm^{-1}, but is hidden by a strong phenyl band. The Ph-Bi vibration of Ph_3Bi is tentatively assigned to a weak band at 435 cm^{-1}. In the infrared spectra of halides of the type Ph_3MX_2 (M = As, Sb, Bi; X = Cl, Br, I) no bands due to M-X vibrations could be localized; it is concluded that they fall below 400 cm^{-1}.* A significant difference was, however, noted in the spectra of the As compounds and the Sb or Bi compounds, respectively, in accordance with a conclusion of an earlier work that the arsine dihalides differ in structure from the stibine or bismuthine dihalides.

The infrared spectra of co-ordination compounds of phosphines, arsines and stibines with $HgCl_2$ or $PtCl_2$ are very similar to the spectra of the parent compounds and a significant influence of the co-ordinative bond on the C-M stretching frequency could be found only in the case of the triphenylarsine complexes. By comparison of the spectra of $PtCl_2$ complexes of triethylphosphine, triethylarsine and triethylstibine the C-P, C-As and C-Sb stretching vibrations of triethylphosphine, triethylarsine and triethylstibine were localized to 766 cm^{-1}, 595 cm^{-1} and 529 cm^{-1}, respectively.

The great similarity between the elements of the third and fourth period of the periodic system, Si, P, S, Cl and Ge, As, Se, Br, respectively, is also reflected in the infrared spectra of organic derivatives of these elements. Because the bond types and bond strengths are not changed essentially when

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* Note added in the proof: According to an investigation by Niels Groving the far infrared spectra of Ph_3SbBr_2 and Ph_3BiBr_2 show strong absorption in the 200–300 cm^{-1} range which may be assigned to Sb-Br and Bi-Br vibrations; see Addendum.

an element of the third period is exchanged with the corresponding element of the fourth period (or even, in some cases, with a corresponding element of the fifth period: Sn, Sb, Te, I) the spectra will be very similar except for bands due to vibrations in which the elements in question are directly involved. A comparison of the infrared spectra of corresponding organic compounds containing elements within the same periodic group may therefore be used to determine specific vibrations within related molecules. We have used this method to localize C-S bands in organic sulfur compounds by comparison of infrared spectra of corresponding sulfur and selenium compounds[1] and in this paper we investigate the possibilities of this method in the study of the spectra of group V B elements. Comparisons of this type are not unknown in the literature, but they have not been used in a systematic way. Of course, the possibilities of such an empirical method are rather limited, but then the results may be considered unambiguous.

The compounds studied are the compounds of the general types R_3MY and R_3MX_2, where R is phenyl or alkyl, M is P, As, Sb or Bi, Y is O, S or Se and X is Cl, Br or I. In addition some co-ordination compounds of phosphines, arsines and stibines have been studied. The infrared absorptions are tabulated in Tables 1—6.

The $M=Y$ group. The most outstanding feature of the results collected in Table 1 is the distinct separation of the bands due to $M=O$, $M=S$ and $M=Se$ asymmetrical stretching modes. Some of these bands have previously been assigned. The $P=O$ absorption in triphenylphosphine oxide was found by Halmann and Pinchas [2] at 1202 cm^{-1} (s) in CCl_4 and 1190 cm^{-1} (s) in nujol mull, the assignment supported by the shift to 1172 cm^{-1} (s) when ^{18}O was substituted for ^{16}O. Corresponding values have been given by other authors [3-6], and further support is found in our results, the 1191 cm^{-1} band (vs) disappearing when S or Se is substituted for O in triphenylphosphine oxide. The $P=S$ group generally absorbs in the range 840—600 cm^{-1} (*cf.* Bellamy [8]), the value for triphenylphosphine sulfide at 637 cm^{-1} (s) falling well within this region. The $P=Se$ stretching frequency at 561 cm^{-1} (vs) does not seem to have been described, either for aromatic or for aliphatic phosphorus compounds.

Phillips and Tyree [7] record a value of 879 cm^{-1} for the $As=O$ frequency in triphenylarsine oxide from a study of the lowering of the frequency produced by co-ordination through the oxygen atom. Their findings are supported by the shift from 881 cm^{-1} (vs) to 495 cm^{-1} (vs) produced by changing the oxygen atom in triphenylarsine oxide with sulfur. The failure in detecting an absorption corresponding to the $As=Se$ group can possibly be attributed to the strong phenyl absorption at 460 cm^{-1} which may well mask it. The complete absence of a $Sb=O$ band may be indicative of the nature of triphenylstibine oxide. This high-melting and insoluble compound probably forms a pseudo-ionic layer lattice and not individual molecules.

The phenyl group. The presence of the phenyl ring is easily recognized by the considerable number of vibrational modes appearing in the spectra recorded in Table 1. As regards the assignment of the various absorption bands for the R_3MY compounds the correlations given in the literature [9-11] for compounds of the type R_3MX of group IV B elements are of particular interest because the symmetry class is the same (C_{3v} for R_3MX and R_3MY

Table 1. Infrared absorptions (cm^{-1}) of compounds Ph_3M and Ph_3MY ($M = P, As, Sb, Bi; Y = O, S, Se$).

Ph_3P	Ph_3PO	Ph_3PS	Ph_3PSe	Ph_3As	Ph_3AsO	Ph_3AsS	Ph_3AsSe	Ph_3Sb	Ph_3SbO	Ph_3SbS	Ph_3Bi *	
420 w	445 w,br	429 w	428 w	—	—	—	—	—	—	—	—	C-P s.
—	—	—	—	—	—	—	—	—	—	—	435 w	C-Bi as.
—	—	—	—	—	—	—	—	—	—	446 s	—	
430 w	456 w	456 w	452 w	—	458vw,br	457 w	460 s	454m,br	458 m,br	454 s	450 s	Phenyl
—	—	478 w	—	—	—	467 m	469 s	—	—	—	—	
—	—	—	—	474 s,br	479 vs	474 m	474 s	—	—	—	—	C-As as.
—	—	—	—	—	—	495 vs	—	—	—	—	—	As-S stretch
493 vs	505 m	510 s	504 s	—	—	—	495 vw	—	—	—	—	
499 vs	540 vs	516 vs	511 s	—	—	—	—	—	—	—	—	C-P as.
540 m	—	—	—	—	—	—	—	—	—	—	—	
—	—	—	561 vs	—	—	—	—	—	—	—	—	P-Se stretch
617 vw	616 vw	612 m	617 w	612 vw	614 vw	614 vw	614 vw	—	613 vw	—	610 vw	Phenyl
—	—	637 s	—	—	—	—	—	—	—	—	—	P-S stretch.
694 vs	695 vs	690 vs	689 vs	694 vs	693 vs	688 vs	690 vs	695 vs	692 vs	692 vs	693 vs	Phenyl
720 w	719 vs	710 vs	709 s	—	—	—	—	—	—	—	—	
740 vs	747 m,sh	745 m	743 s	732 vs	740 vs	736 vs	734 vs	728 vs	732 vs	729 vs	722 vs	Phenyl
745 vs	752 m	750 m	748 s	738 vs	—	741 vs	739 vs,sh	—	—	—	728 vs	Phenyl
752 s	—	—	—	—	—	—	—	—	—	—	—	
—	—	—	—	—	881 vs	—	—	—	—	—	—	As-O stretch
995 w	996 m	1000 w	998 m	999 m	995 w	997 m	998 w	996 m	997 m	996 m	995 m	Phenyl
1026 m	1026 w	1028 w	1026 w	1024 m	1024 w	1023 w	1023 w	1019 w	1020 w	1019 w	1014 m	Phenyl
1070 w	1072 m	1069 w	1067 w	1067 w	1068 w,sh	1065 w	1065 w	probably hidden			1060 m	Phenyl
—	1095 m	—	—	—	—	—	—	—	—	—	—	
1090 m	1121 vs	1105 vs	1098 vs	1074 m	1083 s	1080 s	1075 m	1065 m	1065 m	1065 m	1055 m	'X-sensitive'
1118 vw	—	—	1120 vw	1080 w,sh	—	—	—	—	—	—	—	
1154 vw	1166 vw	1159 vw	1157 vw	1155 vw	1164 vw	1156 vw	1155 vw	1154 vw	1156 vw	1155 vw	1156 vw	Phenyl
1178 w	hidden	1182 w	1180 w	1183 vw	1184 vw	1180 vw	1180 w	1183 w	1183 w	1178 vw	1182 vw	Phenyl
—	1191 vs	—	—	—	—	—	—	—	—	—	—	P-O stretch.
1307 w	1312 w	1308 w	1305 w	1304 w	1324 w	1305 w	1304 w	1301 w	1301 m,br	1302 w	1298 w	Phenyl
1322 vw	1330 vw	1333 vw	1330 vw	1335 w,sh	1344 vw	1333 vw	1331 vw	1329 w	1326 w,sh	1330 w	1325 w	Phenyl
1436 s	1442 s	1438 vs	1436 vs	1436 s	1442 vs	1439 s	1436 s	1432 s	1435 s	1435 s	1428 s	Phenyl
1477 m	1487 m	1483 m	1481 m	1482 m	1482 m	1482 m	1481 m	1479 m	1480 m	1479 m	1474 m	Phenyl
1583 w	1592 w	1574 vw	1570 vw	1580 w	1582 vw	1577 vw	1576 w	1575 w	1575 m	1574 w	1567 m	Phenyl
—	—	1585 vw	1584 vw	—	—	—	—	—	—	—	—	

At the concentrations used (1-2 mg/300 mg KBr) most of the compounds had vw-w absorptions in the 650–80, 840–60, 900–928, 970–80, 1265–80, 1375–90 and 1600–2000 cm^{-1} regions. They all showed an unresolved C-H-stretching band with maximum between 3060–3075 cm^{-1}. * See also Addendum.

when the R-groups are considered to be concentrated in points, or if not, conceivably C_3). These correlations of bands due to the phenyl group are strongly supported by our own findings.

The spectral features of the 1050—1125 cm^{-1} range have aroused considerable interest, and their characteristics have been studied in some detail by Kross and Fassel[12] and by Henry and Noltes[13] for the $(C_6H_5)_4Si$ — $(C_6H_5)_4Pb$ series. These authors were able to show that the strong absorption appearing in this region is very sensitive to changes in the mass and electronegativity of the M-atom. It is referred to as the "X-sensitive vibration". Kross and Fassel[12] have established an approximately linear relationship when this frequency is plotted against the electronegativity of the M-atom.

In agreement with this, we have found a weak absorption at *ca.* 1070 cm^{-1}, probably obscured in the Sb-compounds, which is an "X-sensitive vibration". In the correlations of the "X-sensitive vibration" with the electronegativity of the M-atom we have noted the expected shifts to higher frequencies, when M is bonded to O, S or Se, respectively, the effect being greater with the more electronegative oxygen atom. The considerable shift for triphenylphosphine and its oxide (30 cm^{-1}) has been discussed by Halmann and Pinchas[2] who tentatively ascribe it to a resonance effect. This, too, explains the enhanced intensity of the band. We found this trend much less marked for triphenylarsine and its oxide, the corresponding shift being only 10 cm^{-1}, and it is completely absent in the antimony series. It appears likely, that the progressive lowering of the effect parallels the increasing mass of the M-atom, indicating only negligible transmission through the heavy Sb-atom.

The "X-sensitive vibration" which probably can be attributed to a C-H in-plane deformation mode has been proposed by Henry and Noltes[13] to be characteristic of a phenyl group bound to a heavy metalloid atom, as this frequency is found to be independent of minor changes of other substituents at the M-atom. The absorption is, however, subject to some alteration when highly electronegative substituents are bonded to the M-atom, as seen in Table 1. It should, however, be reliable in studies concerned only with heavy atoms. The proposal[14,3] that the band at 1430—1440 cm^{-1} should be correlated with the phenyl-M link has been critizised by Henry and Noltes[13] and by Rao *et al.*[15]; it is evident too from our results that this band is due to the phenyl groups only.

The existence of mass effects in the phenyl vibrating modes are obvious when the compounds listed in Table 1 are considered, thus supporting the evidence given by Rao *et al.*[15] It has been shown[16] that the frequency of the absorption band in the 725—800 cm^{-1} region diminishes linearly with the reduced mass of the diatomic grouping C-M within compounds of the Ph_nMe ($n = 3$ or 4) type. We cannot confirm this directly, since the frequencies in this range show a splitting, as has also been pointed out by Rao *et al.*[15] and by Steger and Stopperka[10]. The latter attribute this to the effect of the solid phase, as the splitting disappears in solution.

The overtone region. Griffiths and Derwish[11] have confirmed their assignments of the C-H out-of-plane bending modes through a study of the overtone region. We found the peaks very weak, but experiments with triphenylphosphine, triphenylarsine and triphenylstibine in high concentrations using

Table 2.

	Ph_3P		Ph_3As		Ph_3Sb	
	calc.	found	calc.	found	calc.	found
ν_4		744		740		733
ν_7		971		970		968
ν_{11a}		850		849		850
ν_{11b}		696		697		698
ν_{19a}		990		990		987
ν_{19b}		918		914		911
$\nu_4 + \nu_{19b}$	1662	1660	1654	1650	1644	1639
$\nu_{11a} + \nu_{19b}$	1768	1755	1763	1753	1761	1750
$\nu_7 + \nu_{11a}$	1821	1810	1819	1808	1818	1807
$\nu_7 + \nu_{19b}$	1889	1881	1884	1874	1879	1870
$\nu_7 + \nu_{19a}$	1961	1960	1960	1956	1955	1954

carbon disulfide as solvent proved the existence of 5 stronger summation bands. These have been correlated with the fundamental frequencies in Table 2, using the numbering of the fundamental modes given by Griffiths and Derwish [11]. The spectral features in this range are thus those commonly reported for monosubstituted phenyl compounds [8]. We have noted that the bands at *ca.* 1750 cm^{-1}, 1875 cm^{-1} and 1955 cm^{-1} occur as partly resolved doublets which we tentatively attribute to splitting due to the three phenyl groups or the occurrence of further combination bands (*cf.* Griffiths and Derwish [11]). The frequencies presented in Table 2 are those of the strongest band in each doublet. When the spectra are run in concentrated chloroform solutions in a 1.14 mm NaCl-cell there appear in addition a great variety of bands in the 2000—4000 cm^{-1} range; however, no safe assignments could be made.

The phenyl-M vibrations. No systematic study of the absorptions due to phenyl-M (or $C_{\text{arom.}}$—M) stretching modes (M = P, As, Sb, Bi) has been carried out, and reliable data are few. In addition consistent evidence is lacking in the M = Si, Ge, Pb-series, allowing no conclusive arguments of analogy.

Earlier evidence has been summarised by Bellamy [8] for C-P and C-Si vibrations, concluding that indications might be found in the 1000—1100 cm^{-1} and 1400 cm^{-1} region for the groupings. However, it is pointed out by various workers in this field [10,13,15,17] that these bands should be attributed to phenyl group vibrations, which is unambigously supported by our results. The suggestion put forward by Steger and Stopperka [10] that the symmetrical P-C stretching frequency for triphenylphosphine is coincident with the weak 422 cm^{-1} band are consistent with our findings. Nevertheless, other assignments remain. Wittig and Benz [17] have associated the 748 and 753 cm^{-1} absorptions with the P-C link in tetraphenylphosphonium iodide, and Horner and Oediger [18] quote the ranges 1440—1450 cm^{-1} and 995—1000 cm^{-1} for P-phenyl as well as for As-phenyl vibrations. Griffiths and Derwish [11] assign the symm. and asymm. stretching frequencies at 1066 cm^{-1} and 1164 cm^{-1}, respectively, to the Sn-C grouping in Ph_3SnCl, and Kriegsmann and Schowtka [9] regard the 500 cm^{-1}

absorption in Ph_3SiCl as the asymm. Si-C stretching frequency; obviously at least one of these assignments must be incorrect.

Further work on this problem is clearly desirable before definite assignments can be given. However, our results indicate that the only satisfactory correlations are those given in Table 3. These correlations are consistent with the fact that a linear relationship is obtained when the P-C stretching frequencies are plotted against the Pauling electronegativity of the O, S, and Se atoms, in excellent agreement with theory: the more electronegative the substituent on the phosphorus atom, the greater is the corresponding shift towards higher frequencies.

The As-C asymm. stretching frequency is indicated in Table 1 and further supported by the spectra of the other arsenic compounds given in Tables 4 and 5. The Sb-C-frequency is obscured by the strong phenyl absorption at 454—458 cm^{-1}, but probably gives rise to the doubling of this band in the spectrum of triphenylstibine sulfide. In line with these correlations we have tentatively assigned the asymm. Bi-C vibration to a weak peak occurring at 435 cm^{-1} in the spectrum of triphenylbismuthine. There can be little doubt that the Si-C, Ge-C, Sn-C and Pb-C vibrations should also be found in the same range as that proposed for the P-C, As-C, Sb-C and Bi-C vibrations.

The halides Ph_3MX_2. In the spectra of 6 halides of this type (Table 4) we were unable to detect the absorptions due to the M-X stretching mode. Probably they fall below 400 cm^{-1}.* This is in accordance with the reported failure to recognize the corresponding Sn-Cl bands in Ph_3SnCl [11] and the fact that the Si-Cl stretching frequency in Ph_3-Si-Cl is [9] as low as 543 cm^{-1}.

However, we found that the spectra of the arsenic compounds showed some significant differences from the spectra of the antimony and bismuth compounds. The arsenic compounds showed a strong peak at 770—772 cm^{-1}, a weak peak at 1200 cm^{-1} and strong bands in the 2290—3000 cm^{-1} range, all missing in the spectra of the corresponding antimony and bismuth compounds. This difference is attributed to the fact that the arsine dichlorides and dibromides have an ionic character, whereas the stibine and bismuthine dihalides have a covalent structure, as pointed out earlier [19]. The arsine tetraiodide seems, however, to be of the same type as the stibine and bismuthine halides.

Table 3.

	Ph_3P[10]	Ph_3PO	Ph_3PS	Ph_3PSe
ν_{as} C-P	493 vs 499 vs 514 vs	540 vs	516 vs	511 s
ν_s C-P	422 w	445 w, br	429 w	428 w

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* *Cf.* Addendum.

Table 4. Infrared absorptions (cm^{-1}) of arsine, stibine and bismuthine halides.

Ph_3AsCl_2. 455 m, 469 s, 613 vw, 687 s, 744 vs, 772 s, 850 vw, 920 vw, 975 vw, 998 m, 1021 w, 1067 w, sh, 1086 s, 1161 w, 1182 m, 1200 w, 1280 w, 1311 w, 1336 w, 1390—1410 w,br, 1443 s, 1486 m, 1580 w, 1765 vw, 1815 vw, 1898 vw, 1983 vw, 2285 s, 2480 s, 2500—3000 m,sh, 3020—3080 w.

Ph_3AsBr_2. 454 m, 469 s, 685 s, 742 vs, 770 s, 850 vw, 920 vw, 972 vw, 983 vw, 996 m, 1020 w, 1065 w,sh, 1086 m, 1161 w, 1181 m, 1200 w, 1279 vw, 1310 vw, 1335 vw, 1395 w,br, 1442 s, 1483 m, 1577 w, 1765 vw, 1813 vw, 1900 vw, 1977 vw, 2290 s, 2480 s, 2500—3000 m,sh, 3020—3070 w.

Ph_3AsI_4. 452 m,sh, 459 m, 474 m, 612 vw, 668 vw,sh, 681 s, 737 vs, 749 m,sh, 840 vw, 915 vw, 995 m, 1019 w, 1073 m, 1083 w, 1160 w, 1183 w, 1275 vw, 1307 w, 1333 w, 1380 vw, 1438 s, 1479 m, 1573 w, 3070 w.

Ph_3SbCl_2.* 455 s, 667 w,sh, 683 s, 731 vs, 748 m,sh, 840 vw, 910 vw, 985 vw,sh, 996 s, 1019 m, 1059 m, 1090 vw, 1160 w, 1180 w, 1270 vw, 1305 w, 1331 m, 1375—1420 m,sh, 1440 vs, 1480 s, 1575 w, 2960 vw, 3090 w.

Ph_3SbBr_2.* 455 m, 682 s, 729 vs, 835 vw, 903 vw, 994 m, 1017 w, 1056 w, 1087 vw, 1157 vw, 1179 w, 1300 vw, 1328 w, 1375 vw,br, 1437 s, 1475 m, 1570 w, 3060 w.

Ph_3SbI_2. 454 m, 665—70 w,sh, 681 s, 727 vs, 902 vw, 985 vw, 994 s, 1017 w, 1055 w, 1090 vw, 1158 vw, 1186 vw, 1263 vw, 1300 vw, 1327 m, 1372 vw, 1438 s, 1476 m, 1570 w, 3070 w.

Ph_3BiBr_2. 641 m, 673 s, 691 vw, 721 vs, 730 s,sh, 822 vw, 835 vw, 900 vw, 960 w, 982 vs, 1008 m, 1041 w, 1054 w, 1085 w, 1159 w, 1181 m, 1255 w, 1299 w, 1320 m, 1345 vw, 1368 vw, 1435 s, 1466 s, 1554 m, 1570 w,sh, 3040 m.

* See also Addendum.

Co-ordination compounds. The infrared spectra of the co-ordination compounds of phosphines, arsines and stibines with mercury(II)-chloride and platinum(II)-chloride (Table 5) are very similar to those of the parent compounds. A small difference could be found in the 450—475 cm^{-1} region for triphenylarsine complexes, possibly correlated with an influence of the coordinative bond on the C-As stretching frequency. In the spectra of the phosphine complexes no significant influence of the metal atom was evident. This is in agreement with our more extensive studies of infrared spectra of phosphine complexes of nickel and cobalt in which an influence of the metal atom on the

Table 5. Infrared absorptions (cm^{-1}) of complex compounds of triphenylphosphine and triphenylarsine.

$(Ph_3P)_2HgCl_2$. 435 w,br, 490—500 m,sh, 504 s, 520 s, 614 vw, 689 vs, 710 m, 744 s, 845 vw, 920 vw, 998 m, 1026 w, 1070 w, 1100 s, 1160 w, 1185 w, 1286 vw, 1310 w, 1330 w, 1390 vw, 1438 vs, 1483 m, 1571 w, 1584 w, 1810 vw, 1890 vw, 1975—85 vw, 3070 w.

$(Ph_3As)_2HgCl_2$. 460 m,br, 665 vw,sh, 687 s, 733 vs, 840 vw, 996 m, 1021 w, 1075 m, 1155 vw, 1181 vw, 1270 vw, 1303 w, 1331 vw, 1380 vw, 1436 s, 1481 m, 1574 w, 2850 vw, 2935 vw, 3060 w.

$(Ph_3As)_2PtCl_2$. 469 s, 475 m,sh, 665—75 w,sh, 690 vs, 736 vs, 842 vw, 914 vw, 1000 m, 1025 w, 1079 m, 1159 vw, 1186 w, 1272 vw, 1306 w, 1335 vw, 1388 vw, 1438 s, 1485 m, 1580 w, 1815 vw, 1885 vw, 1975 vw, 3010 w,sh, 3060 w.

Table 6. Infrared absorptions (cm^{-1}) of Pt-complexes of triethylphosphine, triethylarsine and triethylstibine.

cis- or *trans-* $[PtCl_2(Et_3P)_2]$*	*cis-* or *trans-* $[PtI_2(Et_3P)_2]$*	*trans-* $[PtBr_2(Et_3As)_2]$	*trans-* $[PtI_2(Et_3As)_2]$	*cis-* $[PtCl_2(Et_3Sb)_2]$	*cis-* $[PtBr_2(Et_3Sb)_2]$	*Assignments*
—	—	—	—	521 m,sh; 529 m	521 m,sh; 528 m	C-Sb stretch.
—	—	557 w; 577 w,sh	563 w; 580 w,sh	—	—	
—	—	595 m	595 m	—	—	C-As stretch.
631 w; 710 m;	631 w; 713 m;	695 vw; 705 vw;	693 vw; 733 s	675 w,sh; 700 s;	675 w,sh; 700 s;	Skeletal and
733 s	723 m,sh	735 s		722 m	723 m	CH_2-rock
765 s	766 s	—	—	—	—	C-P stretch.
1005 w	1005 w	975 w; 993 m	993 m	975 m	975 m	C-C stretch.
1033 s	1033 s	1035 s	1033 s	1018 s	1017 s	C-CH_3 rock.
1255 w	1240 w	1238 m	1235 m	1213 m	1212 m	CH_2 wag.
1375 w	1378 w	1381 w	1381 w	1382 m	1382 m	CH_3 s. deform.
1418 m	1414 m	1417 m	1415 m	1431 w	1430 w	CH_2 scissor
1452 m	1456 m	1456 m	1456 m	1461 w	1460 m	CH_3 as. deform.

* No significant difference has been found in the infrared spectra of *cis-trans*-isomeric Pt-complexes.

C-P stretching frequency could only be ascertained for the trimethylphosphine complexes [20].

The infrared spectra of the platinum complexes of triethylphosphine, triethylarsine and triethylstibine (Table 6) are very similar, except, for a strong band at 766 cm^{-1}, found only in the spectra of the triethylphosphine complexes (and in the spectrum of liquid triethylphosphine [21]), a strong band at 595 cm^{-1}, found only in the triethylarsine complexes, and a medium-strong band at 529 cm^{-1}, present only in the spectra of the triethylstibine complexes. None of the complexes with trialkylphosphines [20] (trimethyl-, triethyl-, tripropyl-, and tributylphosphine) show any absorption between 450 cm^{-1} and 600 cm^{-1}, whereas the tripropylarsine complex *trans*-$[PtCl_2(Pr_3As)_2]$ has an absorption band at nearly the same frequency as the triethylarsine complexes (570 cm^{-1}). Accordingly it seems reasonable to assign the three above mentioned absorption bands to asymmetric P-C, As-C and Sb-C stretching, respectively.

EXPERIMENTAL *

The infrared spectra were recorded on a Perkin Elmer model 21 double beam Infrared Spectrophotometer with NaCl and CsBr optics using the KBr-technique. The 400—800 cm^{-1} range was investigated with the use of a scale expander, giving a somewhat higher accuracy of these values.

Most of the compounds were prepared according to directions given in the literature [22,23,19].

Triphenylarsine sulfide was prepared by dissolving triphenylarsine dibromide in ethanolic ammonia and passing hydrogen sulfide through the solution while cooling simultaneously in ice-salt bath, until slight excess as indicated by a persisting yellow colour. Colourless crystals separated slowly. M.p. 163.5°C, after recrystallisation from ethanol (lit.[23]: 162°C). The compound could not be prepared directly from triphenylarsine and sulfur in carbon disulfide, even after prolonged refluxing.

Triphenylarsine selenide has only been described once [24] and the m.p. was not given. We prepared it in the following way: 2 N aqueous ammonia was saturated with hydrogen selenide at 0° under nitrogen. The yellow solution was added to freshly prepared triphenylarsine dichloride and reacted quickly with separation of metallic selenium. Hydrochloric acid was added in small excess, the reaction mixture was filtered and the precipitate dried over calcium chloride *in vacuo*. The residue was extracted with cold ethanol, filtered, and evaporated without heating, as the selenide is very sensitive to heat. The white crystals, which slowly separated, were dried *in vacuo* over concentrated H_2SO_4. Analyses showed considerable admixture of triphenylarsine oxide, most of which could be separated by recrystallisation from water-ethanol. After further crystallisations from abs. ethanol a reasonably pure sample was obtained. (Found: C 57.7; H 3.7. Calc. for $C_{18}H_{15}AsSe$: C 56.1;H 3.9). This sample was used for the infrared spectra. White crystals; m.p. 125—130°C (quick heating).

Attempts to prepare the corresponding antimony compound in the same way were unsuccessful; triphenylstibine dichloride did not react with the ammonia-hydrogenselenide solution, even on prolonged refluxing.

Mercury chloride complexes. These were prepared directly by mixing the components in ethanolic solutions [23,25].

Platinum complexes. Samples prepared in an older work [26] were used. According to their melting points they were still unchanged.

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* Microanalyses by Mr. Preben Hansen, the microanalysis department of this laboratory.

ADDENDUM, ADDED IN THE PROOF

Mr. Niels Groving has made some results available to us obtained in an investigation on far infrared spectra, carried out in collaboration with Grubb Parsons Ltd., Newcastle upon Tyne, England.

The spectra were obtained using an NPL Interferometric Spectrometer[27] manufactured by Grubb Parsons. This instrument has an optical range from 20 to 500 cm^{-1}, the limit of resolution being 0.1 cm^{-1}. As the interferometer curves did not suggest very detailed spectra the limit of resolution was for simplicity chosen to 2 cm^{-1} and calculation of the spectra was carried out only in the range 100 – 400 cm^{-1}.

Among other compounds $(C_6H_5)_3SbBr_2$, $(C_6H_5)_3BiBr_2$ and $(C_6H_5)_3Bi$ were investigated. The samples were powdered and pressed to discs together with polyethylene powder. All compounds showed a broad complex absorption of considerable intensity in the low-frequency end of the spectra, and at somewhat higher frequencies the two bromine compounds each showed two strong, sharp absorption bands. A number of weak absorptions were also observed.

$(C_6H_5)_3SbBr_2$ 238 cm^{-1} and 294 cm^{-1}, both strong and sharp; from 162 cm^{-1} to 196 cm^{-1} a broad, strong, partly resolved band having peaks at 162, 170, 186, and 196 cm^{-1}.

$(C_6H_5)_3BiBr_2$ 219 cm^{-1} and 242 cm^{-1}, both strong and sharp; from 148 cm^{-1} to 170 cm^{-1} a strong, broad, partly resolved band with peaks at 148, 155, and 163 cm^{-1} and a shoulder at 168 cm^{-1}; besides there is a weaker absorption at 192 – 197 cm^{-1}.

$(C_6H_5)_3Bi$ strong complex absorption with sharp peaks at 216, 224, and 236 cm^{-1}.

It seems reasonable to assume that the only strong absorptions found in the spectrum of $(C_6H_5)_3Bi$ are phenyl-Bi vibrations, showing a triplet since the phenyl groups vibrate in the crystal field which may remove the expected degeneracy. This explanation is in accordance with the shift to *ca.* 155 cm^{-1} in the spectrum of $(C_6H_5)_3BiBr_2$, the bonding of the phenyl groups being weakened when bromine enters into the compound.

This explanation is also in accordance with the assumption that absorption near 190 cm^{-1} in the spectrum of $(C_6H_5)_3SbBr_2$ are due to phenyl-Sb vibrations since the lighter antimony atom should give rise to somewhat higher frequencies than the bismuth atom.

The explanation of the absorption at 294 and 238 cm^{-1} as Sb – Br vibrations is similarly in accordance with the assignment of the absorption at 242 and 219 cm^{-1} as Bi – Br vibrations. This explanation is further supported by the absence of this absorption in the spectrum of $(C_6H_5)_3Bi$.

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