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# Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. VI.[1] Complexes of Copper(I) and Silver(I)

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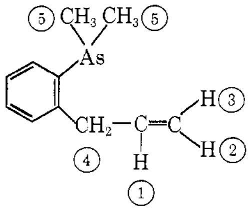
Complexes of the potentially chelate ligands *o*-allylphenyldimethylarsine, $C_{11}H_{15}As$ (AA), *o*-allylphenyldiphenylphosphine, $C_{21}H_{19}P$ (AP), and *o*-(2-methallyl)phenyldiphenylphosphine, $C_{22}H_{21}P$ (MP) with copper(I) halides and silver nitrate have been prepared and studied by infrared and nmr spectroscopy, in order to establish whether the olefinic double bond is coordinated. The infrared spectra of the complexes $[CuX\cdot AP]_2$ (X = Cl, Br, or I), $[CuI\cdot MP]_2$, and $AgNO_3\cdot AA$ suggest that the ligands behave as bidentate chelate groups, whereas in the complexes $CuI(AA)_2$, $AgX(AP)_2$ (X = Cl, Br, or I), AgI(AP), and $AgNO_3$(AP), the group V atom only is attached to the metal. Possible structures for the complexes are discussed. The preparative and spectroscopic results support the idea that olefins coordinate more strongly to copper(I) than to silver(I).

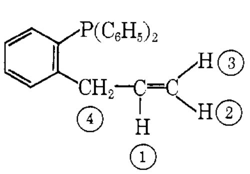
## Introduction

Owing to their instability at room temperature, complexes of straight-chain monoolefins with copper(I) halides and silver nitrate have been characterized mainly by distribution studies in solution and, in the case of gaseous olefins, by measurements of the pressure of olefin in equilibrium with the solid complex.[2] Only recently have solid complexes of silver nitrate with ethylene[3] and butadiene[4] been isolated; in the latter case, the double bonds are probably bound to different silver ions. Both compounds decompose above about −30°. The ligand 2-allylpyridine is reported to form chelate complexes with copper(I) chloride, silver nitrate, and platinum(II) chloride,[5] although the insolubility of the copper and silver compounds precluded extensive measurements. Diphenylvinylphosphine also forms stable 1:1 and 2:1 adducts with silver nitrate in which both the phosphorus and the double bond are thought to be coordinated to silver.[6]

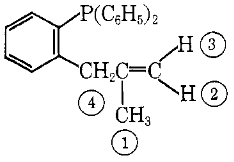
In other papers of this series, we have shown that certain olefinic tertiary phosphines and arsines form stable, chelate, monoolefin complexes with platinum(II),[7-10] palladium(II),[9] and the zerovalent group VI metal carbonyls,[1,10] and we have now extended this work to include copper(I) and silver(I). The ligands used in this investigation are *o*-allylphenyldimethylarsine, *o*-$CH_2{=}CHCH_2C_6H_4As(CH_3)_2$ (AA), *o*-allylphenyldiphenylphosphine, *o*-$CH_2{=}CHCH_2C_6H_4P(C_6H_5)_2$ (AP), and *o*-(2-methallyl)phenyldiphenylphosphine (MP).



AA



AP



MP

## Experimental Section

**Measurements.**—Infrared spectra in the range 4000–400 cm$^{-1}$ were recorded on a Grubb–Parsons double-beam grating spectrophotometer, Type G.S. 2A, and on a Perkin-Elmer 337 double-beam grating spectrophotometer. The samples were examined either as thin films (liquids) or as mulls in Nujol and hexachlorobutadiene (solids), using potassium bromide plates coated with polystyrene if necessary to prevent exchange reactions with the complexes. The spectra were calibrated with polystyrene and are accurate to within ±3 cm$^{-1}$ in the range 1500–1700 cm$^{-1}$.

Proton magnetic resonance spectra were recorded on a Varian HA 100-Mc instrument using deuteriochloroform solutions containing *ca.* 1% tetramethylsilane as the internal standard.

Melting points (uncorrected) were determined on a Gallenkamp electrically heated hot-stage apparatus. Molecular weights were determined at 25° using a Mechrolab vapor pressure osmometer, Model 301A. Conductance measurements were carried out at 25° on *ca.* $10^{-3}$ *M* solutions in Analar acetone or nitrobenzene using a Wayne–Kerr universal bridge, Type B 221, and conventional dip-type bright platinum electrodes. The cell was calibrated using 1 *N* aqueous potassium chloride.

X-Ray powder photographs were recorded on a Nonius–Guinier camera using nickel-filtered copper K$\alpha$ radiation.

Microanalyses were carried out by the microanalytical laboratory of this department, by Messrs. Weiler and Strauss, Oxford, and by Alfred Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany.

Analytical, molecular weight, and melting point data are summarized in Table I.

**Preparation of Compounds.**—*o*-Allylphenyldimethylarsine and *o*-allylphenyldiphenylphosphine were prepared as previously described.[8,10] Copper(I) chloride and copper(I) bromide were

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[1] Part V: M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometal. Chem.* (Amsterdam), in press.

[2] For a summary of references through early 1962, see M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[3] K. Tarama, M. Sano, and K. Tatsuoka, *Bull. Chem. Soc. Japan*, **36**, 1366 (1963).

[4] J. W. Kraus and E. W. Stern, *J. Am. Chem. Soc.*, **84**, 2893 (1962).

[5] R. E. Yingst and R. E. Douglas, *Inorg. Chem.*, **3**, 1177 (1964).

[6] C. Wu and F. J. Welch, *J. Org. Chem.*, **30**, 1229 (1965).

[7] M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

[8] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *ibid.*, *Sect. A*, 501 (1967).

[9] M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *Inorg. Chem.*, **7**, 556 (1968).

[10] L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *ibid.*, **5**, 2212 (1966).

TABLE I

ANALYTICAL DATA, MOLECULAR WEIGHTS, AND MELTING POINTS

| | % C | | % H | | % halogen | | % P (As) | | | Mol wt | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Mp, °C | Calcd | Found | (Molarity) | Solvent |
| MP | 83.5 | 83.0 | 6.8 | 6.4 | | | | | | | | | |
| $CuI(AA)_2$ | 41.7 | 41.7 | 4.8 | 5.0 | 20.0 | 19.8 | 23.6 | 23.7 | 98–99 | 635 | 528 | (0.0108) | $CHCl_3$ |
| | | | | | | | | | | | 600 | (0.0406) | $CHCl_3$ |
| | | | | | | | | | | | 630 | (0.104) | $CHCl_3$ |
| | | | | | | | | | | | 693 | (0.0396) | Acetone |
| | | | | | | | | | | | 831 | (0.0942) | Acetone |
| $[CuCl \cdot AP]_2$ | 62.8 | 62.8 | 4.8 | 4.8 | 8.8 | 9.0 | 7.7 | 7.9 | 257–258 | 803 | 676 | (0.0205) | $CHCl_3$ |
| $[CuBr \cdot AP]_2$ | 56.6 | 56.7 | 4.3 | 4.4 | 17.9 | 17.7 | 7.0 | 7.2 | 214–216 | 892 | 695 | (0.0211) | $CHCl_3$ |
| | | | | | | | | | | | 807 | (0.0439) | $CHCl_3$ |
| $[CuI \cdot AP]_2$ | 51.2 | 51.2 | 3.9 | 3.8 | 25.8 | 25.7 | 6.3 | 6.1 | 175–176 | 986 | 845 | (0.0050) | $CHCl_3$ |
| | | | | | | | | | | | 910 | (0.0200) | $CHCl_3$ |
| | | | | | | | | | | | 965 | (0.0434) | $CHCl_3$ |
| $[CuI \cdot MP]_2$ | 52.1 | 51.8 | 4.2 | 4.7 | 25.1 | 25.6 | | | 183–185 | | | | |
| $AgNO_3AA$ | 33.7 | 33.4 | 3.9 | 4.0 | 3.6 | 3.6[a] | 19.1 | 19.0 | 70–71 | 392 | 580 | (0.0468) | $CHCl_3$ |
| | | | | | | | | | | | 618 | (0.166) | $CHCl_3$ |
| | | | | | | | | | | | 439 | (0.0312) | Acetone |
| | | | | | | | | | | | 495 | (0.0898) | Acetone |
| $AgNO_3(AP)$ | 53.4 | 53.2 | 4.0 | 3.9 | 3.0 | 2.8[a] | 6.6 | 6.7 | 166–168 | 472 | 552 | (0.0220) | $CHCl_3$ |
| | | | | | | | | | | | 768 | (0.0589) | $CHCl_3$ |
| $AgCl(AP)_2$ | 67.5 | 67.5 | 5.1 | 5.1 | 4.7 | 5.2 | 8.3 | 7.7 | 155–156 | 748 | 581 | (0.0102) | $CHCl_3$ |
| | | | | | | | | | | | 658 | (0.0401) | $CHCl_3$ |
| $AgBr(AP)_2$ | 63.6 | 63.9 | 4.8 | 5.1 | 10.1 | 9.7 | 7.8 | 7.6 | 130–131 | 793 | 630 | (0.0106) | $CHCl_3$ |
| | | | | | | | | | | | 690 | (0.0437) | $CHCl_3$ |
| $AgI(AP)_2$ | 60.0 | 59.7 | 4.6 | 4.3 | 15.1 | 14.6 | | | 93–94 | 840 | 672 | (0.0105) | $CHCl_3$ |
| AgI(AP) | 46.9 | 47.0 | 3.5 | 3.5 | 23.6 | 24.6 | 5.8 | 5.5 | 96–97 | | | | |

[a] Nitrogen analysis.

prepared by the literature method,[11] and the silver halides were freshly prepared from silver nitrate solution and the appropriate halogen acids. All other chemicals were commercially available reagent grade quality.

**o-(2-Methallyl)phenyldiphenylphosphine.**—This was prepared similarly to *o*-allylphenyldiphenylphosphine.[10] The mono-Grignard reagent of *o*-bromochlorobezene was treated with 2-methallyl chloride to give *o*-(2-methallyl)chlorobenzene. The Grignard reagent of this compound, prepared in dry tetrahydrofuran, was treated with chlorodiphenylphosphine in the same solvent. The reaction was worked up[10] to give a 45% yield of the required ligand, which was a white solid melting just below room temperature.

**Di-μ-chloro-bis(o-allylphenyldiphenylphosphine)dicopper(I), $[CuCl \cdot AP]_2$.**—A solution of *o*-allylphenyldiphenylphosphine (1.53 g, 5.0 mmoles) in 20 ml of ethanol was added slowly (30 min) to a stirred solution of copper(I) chloride (0.5 g, 5 mmoles) in 20 ml of a saturated aqueous solution of potassium chloride at room temperature. After stirring for 1 hr more, the white precipitate was filtered and washed successively with potassium chloride solution, water, and alcohol. The solid (1.55 g, 75%) was recrystallized from ethanol to give colorless plates of the complex $[CuCl \cdot AP]_2$.

The complexes $[CuBr \cdot AP]_2$, $[CuI \cdot AP]_2$, $[CuI \cdot MP]_2$, and $CuI(AA)_2$ were prepared similarly from the appropriate copper(I) halide dissolved in potassium halide solution and the ligand.

**Iodo(o-allylphenyldiphenylphosphine)silver(I), AgI(AP).**—A solution of *o*-allylphenyldiphenylphosphine (1.2 g, 4 mmoles) in 40 ml of ethanol was added slowly (1 hr) to a stirred solution of silver iodide (1.0 g, 4.3 mmoles) in 40 ml of saturated aqueous potassium iodide at room temperature. After stirring for 1 hr more, the white precipitate was filtered and washed successively with potassium iodide solution, water, alcohol, and ether. It was then reprecipitated from acetone solution at about 10° by addition of ether; yield, 1.3 g (60%).

**Iodobis(o-allylphenyldiphenylphosphine)silver(I), $AgI(AP)_2$.**—The complex AgI·AP (1.3 g, 2.4 mmoles) was recrystallized from 200 ml of ethanol containing *o*-allylphenyldiphenylphosphine (0.85 g, 2.8 mmoles) to give white crystals of the complex $AgI(AP)_2$ (0.83 g, 50%).

The complexes $AgCl(AP)_2$ and $AgBr(AP)_2$ were prepared similarly by reaction between the silver halide and the ligand in either a 1:1 or a 1:2 mole ratio.

**Nitrato(o-allylphenyldimethylarsine)silver(I), $AgNO_3 \cdot AA$.**—A solution of *o*-allylphenyldimethylarsine (0.75 g, 3.4 mmoles) in 15 ml of acetone was added slowly (30 min) to a stirred solution of silver nitrate (1.7 g, 10 mmoles) in 40 ml of 1:1 aqueous acetone at room temperature. Slow evaporation of the filtered solution gave colorless crystals of the complex $AgNO_3 \cdot AA$ (0.95 g, 70%).

The complex $AgNO_3(AP)$ was prepared similarly (50% yield).

## Results

**Copper(I) Complexes.**—Copper(I) iodide reacts with *o*-allylphenyldimethylarsine (AA) to give a diamagnetic complex of empirical formula $CuI(C_{11}H_{15}As)_2$, which is nonconducting in nitrobenzene and monomeric in chloroform; the complex seems to be slightly associated in acetone. The infrared spectrum shows a band at *ca.* 1640 cm$^{-1}$ due to an uncoordinated C=C stretching vibration (Table II), and the $^1$H nmr spectrum is very similar to that of the ligand (Table III). It seems likely that only the arsenic atom of the ligand is attached to the metal, and that the complex contains three-coordinate copper(I) (structure I) both in the solid state and in solution. A similar structure has been proposed for complexes of formula CuX(ligand)$_2$ formed by 2-phenylisophosphindoline, which, by contrast with our compound, are associated in dichloromethane.[12] Attempts to prepare the chloro and bromo analogs of $CuX(AA)_2$ have been unsuccessful.

*o*-Allylphenyldiphenylphosphine (AP) reacts with copper(I) halides to give a series of isomorphous complexes of empirical formula $CuXC_{21}H_{19}P$ (X = Cl, Br, or

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[11] R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

[12] J. W. Collier, A. R. Fox, I. G. Hinton, and F. G. Mann, *J. Chem. Soc.*, 1819 (1964).

Table II

Infrared Spectra (1700–650 $cm^{-1}$) of AA, AP, MP, and Their Complexes with Cu(I) and Ag(I)[c]

| Assignment | AA | CuI(AA)$_2$ | AgNO$_3$·AA | AP | [CuBr·AP]$_2$ | AgI(AP) | AgI(AP)$_2$ | AgNO$_3$(AP) | MP | [CuI·MP]$_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| C=C str | 1640 w | 1642 w | 1590 m[a] | 1639 w | 1562 w[a] | 1640 w | 1640 w | 1631 w | 1653 w | 1575 w[a] |
|  | 1590 w | 1590 w |  | 1585 w | 1587 w | 1587 w | 1587 w | 1585 w | 1587 w | 1587 w |
| Arom | 1570 vw | 1562 vw | 1481 w, sh | 1562 vw |  | 1562 vw | 1560 vw | 1560 vw | 1570 vw |  |
| ring | 1481 w, sh | 1471 m | 1471 w, sh | 1493 vw, sh | 1484 w | 1493 vw, sh | 1490 vw, sh | 1493 vw, sh | 1484 w | 1484 w |
| C—C | 1473 w |  |  | 1479 w | 1471 w | 1479 w | 1479 w | 1477 w | 1471 w | 1466 w |
| str | 1447 m, sh | 1445 m, sh | 1447 m, sh | 1466 w |  | 1468 w | 1466 w | 1466 w |  |  |
| Aliph | 1437 m |  | 1437 m | 1437 m | 1437 m | 1435 m | 1435 m | 1433 m | 1437 m | 1437 m |
| C—H def | 1429 m, sh | 1429 m | 1414 m, sh[b] | 1429 w, sh | 1425 w, sh | 1429 w, sh | 1429 w, sh |  |  |  |
|  |  |  | 1383 s[b] | 1410 vw, sh | 1406 vw, sh |  |  | 1376 s[b] | 1377 w |  |
| Arom and | 1302 vw | 1312 vw | 1351 s[b] | 1323 vw | 1330 vw | 1332 vw | 1330 vw | 1339 s[b] | 1330 vw | 1333 vw |
| olef C—H def |  |  | 1341 s[b] | 1307 vw | 1309 w | 1311 w | 1309 w | 1307 s[b] | 1309 vw | 1311 vw |
|  |  |  |  |  |  |  |  | 1266 m, sh[b] |  |  |
|  | 997 m | 996 w | 1008 w | 993 m | 997 w | 996 m | 997 m | 1007 m | 1000 vw | 998 vw |
|  | 917 s | 922 m | 950 w |  | 980 w |  |  | 1000 m |  |  |
| Olef |  |  |  |  |  |  |  |  |  |  |
| C—H out of | 891 m | 912 m | 936 w | 911 m, sh | 914 m | 915 m | 916 m | 933 m, sh |  |  |
| plane def |  | 893 m | 922 w | 908 m | 909 m, sh | 908 w, sh | 907 w, sh | 920 m | 911 vw, sh |  |
|  |  |  | 890 w | 899 w, sh | 901 w, sh |  |  |  | 893 m | 891 m |
|  | 848 m | 855 m | 884 w |  | 871 w |  |  |  |  | 877 w |
|  |  |  | 870 w |  | 851 w |  |  |  |  |  |
| Arom |  |  | 821 w[b] |  | 819 w |  |  | 814 m[b] |  |  |
| C—H out |  |  | 816 w[b] |  |  |  |  |  |  | 762 s |
| of plane def | 752 s | 752 s | 746 m | 746 s | 745 s | 745 s | 746 s | 752 s | 746 s | 752 s |
|  | 734 m |  | 738 w | 718 m | 719 m | 719 w | 723 w | 741 m, sh | 721 m | 742 s |
|  |  |  |  |  |  |  |  | 722 w |  | 729 w |
|  |  |  |  |  |  |  |  | 704 m, sh |  |  |
|  |  |  |  | 696 s | 692 s | 692 s | 693 s | 696 s | 696 s | 690 s |
|  |  |  |  |  |  |  |  | 673 m, sh | 671 w, sh | 675 w, sh |

[a] Band due to C=C stretch probably overlaps aromatic absorption. [b] Absorption due to $NO_3^-$. [c] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

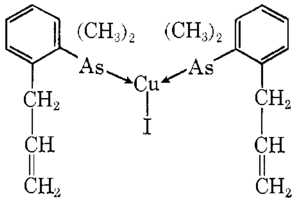
Table III

Proton Nmr Data for the Ligands AA, AP, MP, and Their Complexes with Copper(I) and Silver(I)

|  | Chemical shifts,[a] ppm |  |  |  |  | Spin–spin coupling constants, cps |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $H_1$[b] | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $J_{12}$ | $J_{13}$ | $J_{14}$ | $J_{23}$ |
| AA | 4.11 | 5.05 | 5.11 | 6.41 | 8.98 | 10.2 | 16.9 | 6.25 | 1.7 |
| CuI(AA)$_2$ | 3.89 | 4.85[c] | 4.85[c] | 6.24 | 8.60 | 10.7 | 17.2 | 6.4 |  |
| AgNO$_3$·AA | 3.85 | 4.81 | 5.11 | 6.31 | 8.40 | 10.5 | 17.5 | 5.3 | 1.7 |
| AP | 4.15 | 5.07[d] | 5.05[d] | 6.20 |  | 9.0 | 18.0 | 6.7 | 2.0 |
| [CuBr·AP]$_2$ | 4.34 | 5.20[c] | 5.20[c] | 6.50 |  | 10.7 | 16.6 | 6.25 |  |
| AgNO$_3$(AP) | 3.90 | 4.72 | 5.03 | 6.59 |  | 10.5 | 17.0 | 5.0 | 2.0 |
| MP | 8.4[e] | 5.25 | 5.44 | 6.42 |  |  |  |  |  |
| [CuI·MP]$_2$ | 8.4[e] | 5.08 | 5.24 | 6.53 |  |  |  |  |  |

[a] Chemical shift values ($\tau$) relative to TMS as the internal standard in $CDCl_3$. [b] Protons are numbered as shown in the Introduction. Each spectrum shows absorption in the region 2.5–3.0 ppm due to aromatic protons. [c] Small splitting insufficiently resolved to justify analysis. [d] The reverse assignment is also possible. [e] $CH_3$ group.

I) which are dimeric in chloroform and nonconducting in nitrobenzene. The $^1H$ nmr spectra (Table III) are very similar to that of the ligand, showing that no isomerization has occurred. The infrared spectra of the complexes show no band at *ca.* 1640 $cm^{-1}$ assignable to a free C=C stretching frequency, but a very weak band at 1560 $cm^{-1}$ which appears in the spectrum of the ligand is considerably more intense in the spectra of the complexes, which suggests that it may be due to the coordinated C=C stretching frequency. The band at 1640 $cm^{-1}$ in the spectrum of *o*-(2-methallyl)-phenyldiphenylphosphine(MP) is more intense than that in the ligand (AP), presumably owing to the reduced symmetry about the double bond, but this band is completely absent from the spectrum of the complex [CuBr(MP)]$_2$, which also shows enhanced intensity in a band at 1560 $cm^{-1}$. The copper(I) complexes are therefore formulated as tetrahedrally coordinated dimers, both in the solid state and in solution, the ligands behaving as bidentate chelate groups (structures II and III). The shift of the C=C frequency on coordination (80 $cm^{-1}$) is of the same order as that observed in



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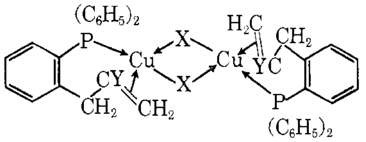
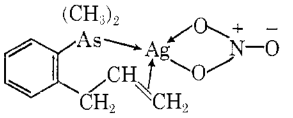
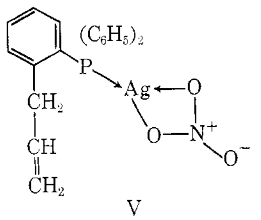


II, X = Cl, Br, I; Y = H
III, X = Br; Y = $CH_3$



IV



V

copper(I) complexes of unsaturated nitriles,[13] cyclic olefins,[13-15] and 2-allylpyridine.[5]

**Silver(I) Complexes.**—All attempts to prepare silver halide complexes of *o*-allylphenyldimethylarsine (AA) have been unsuccessful. However, the corresponding phosphine (AP) reacts with silver iodide to give a colorless compound of empirical formula $AgIC_{21}H_{19}P$ whose solutions in organic solvents are nonconducting and readily deposit silver iodide. On recrystallization from solvents containing an equimolar quantity of free ligand, a 2:1 adduct $AgI(C_{21}H_{19}P)_2$ is obtained. Silver chloride and bromide react directly with the ligand to give similar 2:1 adducts which are isomorphous with each other, but not with the iodide. In chloroform solution, the 2:1 adducts are essentially monomeric, though slightly dissociated. The infrared spectra of all of the complexes show a band at *ca.* 1640 $cm^{-1}$ due to the free C=C stretching frequency so that only the phosphorus atom is coordinated. Therefore, the 2:1 adducts probably contain three-coordinate silver and are analogous to other tertiary phosphine complexes of formula $AgX(ligand)_2$,[16] but the structure of the 1:1 adduct with silver iodide is unknown; it may be tetrameric in the solid state like the corresponding complexes with trialkylphosphines and trialkylarsines.[17]

*o*-Allylphenyldimethylarsine (AA) reacts with silver nitrate to give a compound of empirical formula $AgNO_3$-$C_{11}H_{15}As$ which is essentially monomeric in chloroform, though at higher concentration the compound is obviously associated; in acetone virtually no association is evident. The complex is nonconducting in acetone and nitrobenzene.

The $^1H$ nmr spectrum clearly shows the presence of the allyl group, although some of the signals are shifted compared with those of the free ligand (Table III). The infrared spectrum of the complex shows no band at 1640 $cm^{-1}$, and a very weak band at 1590 $cm^{-1}$ in the spectrum of the free ligand shows enhanced intensity in the spectrum of the complex; this is tentatively assigned to the C=C frequency modified by coordination. Similar frequency shifts have been observed in other silver–olefin complexes.[5,18,19]

The corresponding phosphine (AP) also forms a monomeric, nonconducting, 1:1 adduct with silver nitrate, whose $^1H$ nmr spectrum resembles that of the complex $AgNO_3\cdot AA$. Surprisingly, however, the infrared spectrum of the phosphine complex $AgNO_3(AP)$ shows a band at 1640 $cm^{-1}$, showing that the double bond is not coordinated. The infrared spectra of both $AgNO_3\cdot AA$ and $AgNO_3(AP)$ are too complicated for any firm conclusions to be drawn about the type of bonding of the nitrate group. Since the compounds are nonconducting in solution, however, it is unlikely that they are ionic in the solid state. Also, the number of bands assigned to nitrate absorption, and their frequency range, may indicate the presence of monodentate and/or bidentate nitrate groups.[20] By analogy with the structure of the complexes (cyclooctatetraene)-$AgNO_3$[21] and (norbornadiene)$\cdot 2AgNO_3$,[22] it is likely that, in the solid state, $AgNO_3\cdot AA$ and $AgNO_3(AP)$ contain chains of silver ions connected by bridging nitrate groups. Presumably, each silver ion in $AgNO_3\cdot AA$ is tetrahedrally coordinated *via* an arsenic atom and a double bond of the ligand and two oxygen atoms from different nitrate groups, while $AgNO_3(AP)$ contains three-coordinate silver, the double bond being uncoordinated. In solution, $AgNO_3\cdot AA$ may retain tetrahedrally coordinated silver, if the nitrate group acts as a bidentate chelate group (structure IV), and similarly, in solution, $AgNO_3(AP)$ may contain three-coordinate silver, with a bidentate chelate nitrate group (structure V). An alternative possibility, which receives a small measure of support from the similarity of the $^1H$ nmr spectra of $AgNO_3\cdot AA$ and $AgNO_3(AP)$, is that in solution the double bond of AP coordinates to silver to complete the tetrahedral coordination.

**Proton Magnetic Resonance Spectra.**—The chemical shifts and coupling constants of the ligands and complexes are given in Table III, the protons being numbered as shown in the Introduction. The hope that these data would provide an additional criterion for coordination of the olefinic double bond in the complexes was not fulfilled. In general, the nmr spectra of ligands and complexes are very similar, and there are no systematic changes on coordination. For example, in both $CuI(AA)_2$ and $AgNO_3\cdot AA$, the vinyl proton resonances due to $H_1$ and $H_2$ appear at lower field than in the free ligand, even though the ligand is monodentate in the first case and bidentate in the second. In the case of the chelate complex $[CuBr\cdot AP]_2$, all the olefinic proton resonances are shifted slightly upfield compared with those of the ligand, whereas in the case of the chelate complex $[CuI\cdot MP]_2$, the reverse occurs. It may be noted that there is a downfield shift of olefinic proton resonance on coordination in complexes of the type $AgBF_4\cdot 2(olefin)$,[19] but in most other olefin complexes, an upfield shift is observed.[23]

## Discussion

The preparative and infrared spectroscopic results support the conclusions drawn by previous workers[2,5] that copper(I)–olefin complexes are more stable than silver(I)–olefin complexes. Thus, neither *o*-allylphenyldimethylarsine (AA) nor *o*-allylphenyldiphenylphosphine (AP) forms chelate complexes with silver halides,

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whereas AP forms chelate complexes with copper(I) halides. The shift in C=C stretching frequency on complexing, $\Delta\nu$(C=C), which provides a rough measure of metal–olefin bond strength, is approximately 50 $cm^{-1}$ for $AgNO_3 \cdot AA$ and approximately 80 $cm^{-1}$ for $[CuX \cdot AP]_2$. Previous results[2,5,15,18,19] indicate, as would be expected, that olefin complexes of copper(I) and silver(I) are formed more readily if poorly coordinating anions, such as $BF_4^-$, $ClO_4^-$, or $NO_3^-$, are present in place of halide ions. It is surprising, therefore, that AA, but not AP, forms a chelate complex with silver nitrate, since in the case of the copper halides discussed above, and in the case of palladium(II),[9] AP is clearly the better chelate ligand. Preliminary attemps to prepare chelate complexes of AP with $AgBF_4$ have also been unsuccessful. Experiments using a range of related olefinic tertiary phosphines and arsines will be required to provide an answer to this problem.

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# Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. VII.[1] Chelate Monoolefin Complexes of Platinum(II) and Palladium(II)

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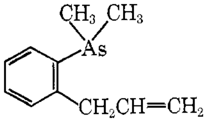
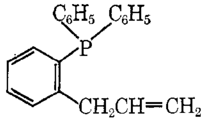
The ligands *o*-allylphenyldimethylarsine (AA), *o*-$CH_2{=}CHCH_2C_6H_4As(CH_3)_2$, and *o*-allylphenyldiphenylphosphine (AP), *o*-$CH_2{=}CHCH_2C_6H_4P(C_6H_5)_2$, form chelate complexes of formula $MX_2$(ligand) (M = Pt, Pd; X = Cl, Br), in which both the group V atom and the double bond are coordinated to the metal. The reactions of these compounds with iodide ion and with thiocyanate ion lead to a variety of compounds in which the double bond may or may not be coordinated to the metal. These studies, together with the infrared spectra of the complexes, suggest that metal–olefin bonding is stronger for platinum(II) than for palladium(II), in agreement with previous work. The phosphine AP forms chelate complexes more readily than does the arsine AA.

## Introduction

Olefinic tertiary phosphines and arsines containing the 4-pentenyl group, of general formula $CH_2{=}CH(CH_2)_3P(As)R_2$ (R = $CH_3$ or $C_6H_5$), form chelate, monomeric monoolefin complexes with platinum(II) of formula $PtX_2$(ligand) (X = Cl, Br, or I), but with palladium(II) dimeric complexes exemplified by $[PdCl_2(ligand)]_2$ are formed, in which the double bond is not coordinated to the metal.[2] We have previously briefly reported the preparation of chelate derivatives of formula $PtBr_2$(ligand) with *o*-allylphenyldimethylarsine (AA)[3] and *o*-allylphenyldiphenylphosphine (AP),[4] and now we compare the chelating tendencies of these two ligands with platinum(II) and palladium(II).


AA


AP

## Experimental Section

**Starting Materials.**—Tetrahydrofuran was distilled from sodium–benzophenone and stored over sodium. All other solvents and chemicals were of reagent grade quality and were used without purification.

*o*-Allylphenyldimethylarsine (AA) and *o*-allylphenyldiphenylphosphine (AP) were prepared as described previously.[3,4] They are referred to as "the arsine" and "the phosphine" throughout the Experimental Section.

**Measurements.**—Infrared spectra, proton nmr spectra, melting points, molecular weights, conductances, and X-ray powder data were measured as described previously.[1] Magnetic susceptibilities were measured at room temperature on powdered samples using the Gouy method, following the procedure of Figgis.[5] Ultraviolet and visible spectra were recorded on a Unicam SP 800 spectrophotometer using 1-cm silica cells.

Microanalyses were carried out by the microanalytical laboratory of this department, by Messrs Weiler and Strauss, Oxford, and by Alfred Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany. Platinum and palladium in the tertiary arsine complexes were determined by ignition to the metal after moistening with a few drops of concentrated sulfuric acid.

**Dichloro(*o*-allylphenyldiphenylphosphine)platinum(II), $Pt Cl_2AP$.**—A solution of the phosphine (2.5 g, 8.3 mmoles) in 40 ml of chloroform was added slowly (1 hr) to a stirred suspension of anhydrous platinum(II) chloride (2.2 g, 8.3 mmoles) in 30 ml of chloroform at room temperature. The mixture was refluxed

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