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Structural Studies on Silver(I) Complexes with 2,11-Bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene (1): [Ag(1)Cl], [Ag(1)(SnCl$_3$)], [Ag(1)(NO$_3$)], and [Ag(1)(ClO$_4$)]

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X-ray crystal structures of [Ag(**1**)X] (**1** = 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene; X = Cl (**2**), SnCl$_3$ (**3**), NO$_3$ (**4**), and ClO$_4$ (**5**)) are reported. The crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 9.4$ Å, $b = 17.2$ Å, $c = 22.1$ Å, and $\beta = 106.15°$. The crystals of **3** are monoclinic, space group $C2/c$, with $Z = 8$ in a unit cell of dimensions $a = 21.88$ Å, $b = 21.75$ Å, $c = 23.61$ Å, and $\beta = 135.91°$. The crystals of **4** are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 9.498$ (1) Å, $b = 17.659$ (2) Å, $c = 21.816$ (3) Å, and $\beta = 98.31$ (1)°. The crystals of **5** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 15.435$ (3) Å, $b = 13.129$ (3) Å, $c = 18.927$ (3) Å, and $\beta = 100.39$ (1)°. The Ag atom in **2** shows a distorted trigonal coordination to two P atoms and one Cl atom. The Ag atom in **3**–**5** is formally four-coordinate with slightly different Ag–Cl or Ag–O bonds to the chelating anions. The P–Ag–P angle increases from 140.7° in **2** to 151.5° in **5**, the bonds to the phosphine tend to become shorter and those to the anion longer, and the coupling constant $^1J(^{107}\text{Ag},^{31}\text{P})$ increases in this series.

Introduction

The diphosphine ligand 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene (**1**)[2] seems well suited for the preferential formation of mononuclear two- and three-coordinate species of the type [M(**1**)]$^+$X$^-$ or [M(**1**)X] with M = Cu, Ag, Au. An X-ray study of the chloride salts showed that the metal centers are three-coordinate with P–M–P angles of 132, 141, and 176°, respectively, and that the widening of this angle is accompanied by an increase of the ionic character of the M–Cl bond.[3] Molecular weight, conductivity, and NMR studies in solution suggested that [Ag(**1**)X] complexes are noticeably dissociated in acetonitrile and nitromethane solutions for X = NO$_3^-$ and BF$_4^-$ but not dissociated if X = Cl$^-$.[4]

The X-ray structures of the complexes [Ag(**1**)X] with X = SnCl$_3^-$, NO$_3^-$, ClO$_4^-$ are described in this paper. Single crystals of [Ag(**1**)(BF$_4$)] could not be obtained due to the formation of the monofluoro-bridged complex [(**1**)Ag(μ-F)Ag(**1**)][BF$_4$] during crystal growth.[5] The structure determination of [Ag(**1**)Cl], reported in a preliminary communication,[3] is fully presented in this paper. The nature of the Ag–X interaction, its influence on the coordination of the metal, and its possible relevance for the interpretation of solution data are discussed.

Experimental Section

Preparation of [Ag(1)Cl] (2) and [Ag(1)(NO$_3$)] (4). These were carried out as described elsewhere.[2,4]

Preparation of [Ag(1)(ClO$_4$)] (5). A 1.5-g (6.6-mmol) quantity of AgClO$_4$·H$_2$O and 2.25 g (3.6 mmol) of **1** were suspended in 70 mL of CH$_2$Cl$_2$, and the suspension was stirred overnight. The solution was filtered off, and the solvent was reduced to a small volume under N$_2$, filtered over a short silica gel column, and then allowed to diffuse slowly under an N$_2$ atmosphere. Anal. Calcd: C, 63.51; H, 4.12; P, 7.44. Found: C, 63.51; H, 4.00; P, 7.50. ^{31}P NMR data: a doublet of doublets centered at 10.50 ppm; $^1J(^{107}\text{Ag},^{31}\text{P}) = 507$ Hz, $^1J(^{109}\text{Ag},^{31}\text{P}) = 585$ Hz.

The compounds [Ag$_2$Cl$_2$(Ph$_2$P(CH$_2$)$_5$PPh$_2$)] (**6**) and [Ag$_2$Cl$_2$(Ph$_2$P(CH$_2$)$_2$S(CH$_2$)$_2$PPh$_2$)] (**7**), kindly provided by Dr. B. Aurivillius, were those from which the single crystals were selected from the X-ray study.[18,19] Their ^{31}P NMR data are as follows: **6**, δ 3.50, $^1J(^{107}\text{Ag},^{31}\text{P}) = 390$ Hz, $^1J(^{109}\text{Ag},^{31}\text{P}) = 450$ Hz; **7**, δ 2.79, $^1J(^{107}\text{Ag},^{31}\text{P}) = 381$ Hz, $^1J(^{109}\text{Ag},^{31}\text{P}) = 438$ Hz.

Preparation of [Ag(1)(SnCl$_3$)] (3). A 130-mg (0.17-mmol) amount of [Ag(**1**)Cl] (**2**) was dissolved in 10 mL of CH$_2$Cl$_2$ and mixed with 50 mg (0.33 mmol) of SnCl$_2$·2H$_2$O dissolved in 5 mL of (CH$_3$)$_2$CO. After 4 h a few crystals and a white precipitate had formed. The crystals were carefully separated from the precipitate and dried. Anal. Calcd: C, 54.90; H, 3.57; Cl, 10.98. Found: C, 55.19; H, 3.58; Cl, 11.11. ^{31}P NMR data: δ 8.46, $^1J(^{107}\text{Ag},^{31}\text{P}) = 418$ Hz, $^1J(^{109}\text{Ag},^{31}\text{P}) = 481$ Hz.

Crystallization of [Ag(1)Cl] (2), [Ag(1)(NO$_3$)] (4), and [Ag(1)(ClO$_4$)] (5). Single crystals, in the form of colorless monoclinic prisms, were grown from acetonitrile, benzonitrile, and dichloromethane solutions, respectively. X-ray diffraction photographs showed them to be suitable for diffraction analysis.

^{31}P NMR Spectra. These were measured on a Bruker HX 90 spectrometer operating at 36.43 MHz. Chemical shifts are given relative to external H$_3$PO$_4$. A positive sign indicates a shift to low field of the resonance. The spectra were measured at temperatures between 0 and −10 °C. CDCl$_3$ was used as a solvent.

Collection and Reduction of X-ray Intensity Data. A summary of crystal data, together with various details concerning intensity measurements, is given in Table I. Intensities of standard reflections, monitored periodically for each compound, remained constant throughout data collection.

Due to the large size of the crystal of **3** certain intense low-angle reflections were presumed to be affected by dead-time losses in the counting chain. Accordingly, all reflections with $\theta < 12°$ were remeasured with reduced X-ray power. The reflections, which showed medium intensity in both data sets, were used to scale the attenuated data to the unattenuated data by a least-squares process.

The collected intensities were processed to give structure factor amplitudes with standard deviations.[6]

Solution and Refinement of the Structures. The four structures were solved by the usual combination of the Patterson and Fourier methods and were refined by least-squares procedures.

[Ag(1)Cl] (2). Least-squares refinement was performed in three large nonoverlapping blocks: $w^{-1} = 1 + 0.00049(F - 20)$; X-RAY 72 extinction factor $g = 0.0055$ (3). Hydrogen atoms were included in the model at fixed, calculation positions (d(C–H) = 1.0 Å) with a fixed isotropic temperature coefficient ($B = 5.0$ Å^2). Anisotropic

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(6) Standard deviations $\sigma(F)$ for **2** and **3** were calculated according to $\sigma(F) = \sigma(I)/2F$, with I = (scan counts) − 2(background counts) and $\sigma^2(I) = (I + 0.001I)^2$. The procedure of data reduction for **4** and **5** is described in: Bachechi, F.; Zambonelli, L.; Marcotrigiano, G. *J. Cryst. Mol. Struct* **1977**, *7*, 11. Values of $p = 0.004$ and 0.001 for **4** and **5** respectively were used.

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Table I. Summary of Crystal Data and Intensity Collection Details for the Compounds [Ag(1)X][a]

	X = Cl, **2**	X = $SnCl_3$, **3**	X = NO_3, **4**	X = ClO_4, **5**
formula	$C_{44}H_{34}AgClP_2$	$C_{44}H_{34}AgCl_3P_2Sn$	$C_{44}H_{34}AgNO_3P_2$	$C_{44}H_{34}AgClO_4P_2$
fw	768.027	957.623	794.579	832.024
a, Å	9.4	21.88	9.498 (1)	15.435 (3)
b, Å	17.2	21.75	17.659 (2)	13.129 (3)
c, Å	22.1	23.61	21.816 (3)	18.927 (3)
β, deg	106.15	135.91	98.34 (1)	100.39 (1)
V, Å^3	3478	7818	3620 (1)	3773 (1)
Z	4	8	4	4
density, g cm^{-3} calcd	1.466	1.627	1.458	1.465
obsd	. . .	1.62 (1)	1.46 (1)	1.46 (1)
space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$
cryst dimens, mm^3	0.40 × 0.40 × 0.50	. . .	0.20 × 0.20 × 0.30	0.15 × 0.20 × 0.35
diffractometer	Hilger and Watts Y290	Hilger and Watts Y290	Syntex $P2_1$	Syntex $P2_1$
radiation	Mo Kα (graphite monochrom)	Mo Kα (graphite monochrom)	Cu Kα (graphite monochrom)	Mo Kα (graphite monochrom)
μ, cm^{-1}	7.7	14.47	14.06	7.24
scan mode	$2\theta/\omega$	ω	ω	ω
scan range, deg	1.0	1.04	0.9	0.9
bkgd counts	$^1/_4$ of scan time at each end of scan range		$^1/_4$ of scan time at ±0.5° from the center of scan range	
2θ limits, deg	1–54	1–48	3–116	3–56
total no. of observns	7584	6315 ($h,k,\pm l$)	5320 ($h,k,\pm l$)	9639 ($h,k,\pm l$)
no. of unique data, $F_o^2 > \sigma(F_o^2)$	6179	4485	3641	2921
final no. of variables	213	241	172	235
final R, R_w	0.045, 0.054	0.046, 0.048	0.062, 0.069	0.069, 0.070

[a] Crystals of [Ag(1)Cl] (**2**) and [Ag(1)(NO_3)] (**4**) are isomorphous. However, while the structure of **2** was solved in the standard space group $P2_1/c$ ($\beta = 106.15°$), the structure of **4** was solved with use of the nonstandard space group $P2_1/n$, which provides a β angle of 98.34° and near-orthogonality of the crystallographic coordinate system, thus aiding in the least-squares refinement process. When it is transformed to the space group $P2_1/n$, the cell of **2** becomes $a = 9.457$ Å, $b = 17.255$ Å, $c = 21.561$ Å, and $\beta = 98.73°$.

temperature factors were determined only for atoms heavier than C. A final difference Fourier synthesis showed eight regions of difference electron density (average height 0.6 e Å^{-3}), which could be ascribed to the neglect of anisotropic vibrations of carbon atoms. Atomic scattering factors for neutral Ag, Cl, and P were taken from ref 7 with real and imaginary components of anomalous dispersion taken from ref 8; for neutral C and H these were taken from ref 7 and 9, respectively. Calculations were performed with the X-RAY 72 system of programs[10] on the CDC 6500 computer of the ETH, Zürich.

[Ag(1)($SnCl_3$)] (3). Least-squares refinement was performed by the block-diagonal approximation: $w = 1/\sigma^2(F)$; no extinction correction. Hydrogen atoms were included in the model at fixed, calculated positions (d(C–H) = 1.02 Å, B = 5.5 Å^2). Anisotropic temperature factors were determined only for atoms heavier than C. Atomic scattering factors for neutral Ag, Sn (Thomas–Fermi–Dirac statistical model), Cl, and P including anomalous dispersion effects were taken from ref 11a; for neutral C and H these were taken from ref 11b. Calculations were performed with the X-RAY 72 system of programs[10] on the CDC 6500 computer of the ETH, Zürich.

[Ag(1)(NO_3)] (4). In the final cycles of least squares ($w = (\sin \theta)/\lambda$; block-diagonal approximation), each phenyl ring was treated as a rigid body restricted to its idealized geometry (6/*mmm* symmetry, d(C–C) = 1.392 Å, d(C–H) = 1.0 Å) with one overall isotropic thermal parameter per phenyl ring. Anisotropic thermal parameters were used for atoms heavier than carbon. The fixed contribution of the hydrogen atoms was included into the calculations with idealized positions and isotropic thermal parameters of the nearest carbon atoms. Scattering factors and anomalous dispersion terms were taken from ref 11b. The calculations were performed with use of local programs on the Univac 1110 of the University of Rome[12] and on the HP 21MX minicomputer of the CNR Research Area of Rome.[13]

[Ag(1)(ClO_4)] (5). During the final cycles of full-matrix least-squares refinement the non-carbon non-hydrogen atoms were allowed to vibrate anisotropically. Each phenyl ring was treated as a rigid body restricted to its idealized geometry (6/*mmm* symmetry, d(C–C) = 1.395 Å, d(C–H) = 0.96 Å) with an individual isotropic thermal parameter for each carbon atom. The fixed contribution of the hydrogen atoms was included into the calculations with idealized positions and isotropic thermal parameters of the nearest carbon atoms; $w = 1/[\sigma^2(F_o) + b(F_o^2)]$. The constant b (=0.0009) was chosen so as to minimize the dispersion of $\langle w(|F_o| - |F_c|)^2\rangle$ over ranges of reflections.

During refinement abnormally high temperature factors for carbon atoms C(39)–C(44) of one phenyl group bound to P(2) were observed; furthermore, the atom C(41) was too close to its equivalent at $1 - x$, $-y$, $1 - z$. Zonal Fourier difference maps revealed evidence of disorder for this phenyl ring. In the final model two distinct rigid bodies were assumed for this phenyl ring and both were refined with half-occupation. A successive Fourier difference map showed no significant residual electron density.

Scattering factors and anomalous dispersion terms were taken from ref 11a. The calculations were performed on the IBM 370 computer of the CNUCE (Pisa, Italy), with the SHELX 76 system of programs,[14] and on the HP 21MX minicomputer of the CNR Research Area of Rome, with local programs.[13]

Crystallographic Data. The following data are tabulated: (1) the final values of all refined atomic coordinates (Table II); (2) the positional and thermal parameters for all non-hydrogen atoms (Table S-I), the hydrogen parameters (Table S-II), and the structure amplitudes (Table S-III) (Tables S-I–S-III are deposited as supplementary material).

Results and Discussion

Selected interatomic distances and interbond angles for the four species are compared in Table III. Perspective views of the molecules are shown in Figures 1–4. The crystals of the three complexes are composed of discrete molecular units with no close intermolecular contacts.

[Ag(1)Cl] (2). Ag is bonded to two P and one Cl atom; it deviates 0.07 Å from the plane of the these three atoms. The

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Table II. Positional Parameters for the Non-Hydrogen Atoms in Complexes [Ag(**1**)X] (X = Cl, $SnCl_3$, NO_3, and ClO_4) (Estimated Standard Deviations in the Least Significant Figure(s) Given in Parentheses)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
			[Ag(**1**)Cl]				
Ag	0.13771 (3)	0.28505 (2)	0.28972 (1)	C(21)	0.4370 (4)	0.1765 (2)	0.3855 (2)
Cl	0.32598 (13)	0.34638 (7)	0.24397 (6)	C(22)	0.4282 (4)	0.1007 (2)	0.4049 (2)
P(1)	0.30220 (9)	0.24958 (5)	0.39264 (4)	C(23)	0.5274 (5)	0.0448 (3)	0.3970 (2)
P(2)	−0.11993 (9)	0.28626 (5)	0.23290 (4)	C(24)	0.6375 (5)	0.0648 (3)	0.3700 (2)
C(1)	0.2286 (4)	0.4367 (2)	0.4204 (2)	C(25)	0.6462 (5)	0.1393 (3)	0.3503 (2)
C(2)	0.3469 (4)	0.3944 (2)	0.4554 (2)	C(26)	0.5471 (5)	0.1956 (2)	0.3575 (2)
C(3)	0.4071 (5)	0.4132 (3)	0.5194 (2)	C(27)	0.2381 (4)	0.2100 (2)	0.4560 (2)
C(4)	0.3580 (5)	0.4763 (3)	0.5443 (2)	C(28)	0.0986 (5)	0.1771 (3)	0.4416 (2)
C(5)	0.2107 (5)	0.5962 (3)	0.5314 (2)	C(29)	0.0524 (6)	0.1382 (3)	0.4875 (3)
C(6)	0.1165 (5)	0.6453 (3)	0.4935 (2)	C(30)	0.1424 (6)	0.1333 (3)	0.5469 (3)
C(7)	−0.0686 (5)	0.6756 (3)	0.3932 (2)	C(31)	0.2795 (5)	0.1671 (3)	0.5631 (2)
C(8)	−0.1593 (5)	0.6543 (3)	0.3377 (2)	C(32)	0.3291 (5)	0.2052 (3)	0.5173 (2)
C(9)	−0.2763 (5)	0.5493 (3)	0.2661 (2)	C(33)	−0.2124 (4)	0.1936 (2)	0.2156 (2)
C(10)	−0.2964 (5)	0.4727 (2)	0.2523 (2)	C(34)	−0.3650 (4)	0.1886 (2)	0.1897 (2)
C(11)	−0.2058 (4)	0.4173 (2)	0.2908 (2)	C(35)	−0.4344 (4)	0.1174 (2)	0.1820 (2)
C(12)	−0.0911 (4)	0.4412 (2)	0.3405 (2)	C(36)	−0.3546 (5)	0.0502 (3)	0.2004 (2)
C(13)	0.1693 (4)	0.5003 (2)	0.4460 (2)	C(37)	−0.2038 (5)	0.0546 (3)	0.2258 (2)
C(14)	0.2436 (4)	0.5230 (2)	0.5081 (2)	C(38)	−0.1323 (4)	0.1259 (2)	0.2333 (2)
C(15)	−0.0649 (4)	0.5204 (2)	0.3558 (2)	C(39)	−0.1600 (4)	0.3419 (2)	0.1603 (2)
C(16)	−0.1650 (4)	0.5754 (2)	0.3187 (2)	C(40)	−0.2466 (5)	0.3159 (3)	0.1022 (2)
C(17)	0.0468 (4)	0.5472 (2)	0.4105 (2)	C(41)	−0.2725 (5)	0.3643 (3)	0.0504 (2)
C(18)	0.0326 (5)	0.6228 (3)	0.4321 (2)	C(42)	−0.2146 (5)	0.4380 (3)	0.0554 (2)
C(19)	0.4198 (4)	0.3326 (2)	0.4265 (2)	C(43)	−0.1236 (5)	0.4627 (3)	0.1119 (2)
C(20)	−0.2361 (4)	0.3325 (2)	0.2775 (2)	C(44)	−0.0961 (5)	0.4143 (2)	0.1638 (2)
			[Ag(**1**)($SnCl_3$)]				
Sn	0.40511 (3)	0.19963 (2)	0.45631 (3)	C(20)	0.0662 (5)	0.0981 (3)	0.1095 (4)
Ag	0.23509 (3)	0.22297 (2)	0.22070 (3)	C(21)	0.1728 (5)	0.3691 (3)	0.1364 (4)
Cl(1)	0.38804 (10)	0.16323 (8)	0.34356 (10)	C(22)	0.0994 (5)	0.3842 (3)	0.0548 (4)
Cl(2)	0.29142 (12)	0.28121 (9)	0.36753 (11)	C(23)	0.0373 (5)	0.4250 (4)	0.0354 (5)
Cl(3)	0.52616 (13)	0.26724 (10)	0.50701 (12)	C(24)	0.0477 (6)	0.4508 (4)	0.0942 (5)
P(1)	0.25147 (11)	0.30986 (8)	0.16854 (10)	C(25)	0.1208 (6)	0.4376 (4)	0.1747 (6)
P(2)	0.12406 (11)	0.15652 (8)	0.19040 (10)	C(26)	0.1836 (5)	0.3958 (4)	0.1957 (5)
C(1)	0.2655 (5)	0.1803 (3)	0.0930 (4)	C(27)	0.3544 (5)	0.3532 (3)	0.2381 (4)
C(2)	0.2887 (4)	0.2402 (3)	0.0994 (4)	C(28)	0.4237 (5)	0.3316 (4)	0.3166 (5)
C(3)	0.3704 (5)	0.2539 (4)	0.1282 (5)	C(29)	0.4998 (6)	0.3666 (4)	0.3709 (5)
C(4)	0.4214 (5)	0.2062 (4)	0.1442 (5)	C(30)	0.5073 (6)	0.4217 (4)	0.3476 (5)
C(5)	0.4524 (5)	0.0963 (4)	0.1524 (5)	C(31)	0.4398 (6)	0.4427 (4)	0.2710 (6)
C(6)	0.4304 (5)	0.0383 (4)	0.1439 (5)	C(32)	0.3618 (5)	0.4085 (4)	0.2145 (5)
C(7)	0.3365 (5)	−0.0433 (4)	0.1191 (5)	C(33)	0.1687 (5)	0.1113 (3)	0.2788 (4)
C(8)	0.2682 (5)	−0.0638 (4)	0.1036 (5)	C(34)	0.1399 (6)	0.1172 (4)	0.3145 (6)
C(9)	0.1504 (5)	−0.0449 (4)	0.0930 (5)	C(35)	0.1817 (7)	0.0810 (5)	0.3848 (7)
C(10)	0.1034 (5)	−0.0063 (4)	0.0962 (5)	C(36)	0.2502 (6)	0.0428 (4)	0.4168 (6)
C(11)	0.1219 (5)	0.0569 (3)	0.1093 (4)	C(37)	0.2757 (5)	0.0375 (4)	0.3799 (5)
C(12)	0.1856 (4)	0.0799 (3)	0.1159 (4)	C(38)	0.2360 (5)	0.0711 (4)	0.3108 (5)
C(13)	0.3194 (4)	0.1298 (3)	0.1156 (4)	C(39)	0.0348 (5)	0.2023 (3)	0.1608 (4)
C(14)	0.3992 (5)	0.1448 (4)	0.1387 (4)	C(40)	−0.0513 (6)	0.1822 (4)	0.1063 (5)
C(15)	0.2335 (4)	0.0430 (3)	0.1094 (4)	C(41)	−0.1168 (6)	0.2217 (4)	0.0845 (6)
C(16)	0.2157 (5)	−0.0219 (3)	0.1003 (4)	C(42)	−0.0965 (6)	0.2786 (4)	0.1157 (5)
C(17)	0.3014 (4)	0.0654 (3)	0.1161 (4)	C(43)	−0.0131 (6)	0.3000 (5)	0.1679 (6)
C(18)	0.3556 (5)	0.0235 (4)	0.1263 (5)	C(44)	0.0534 (6)	0.2611 (4)	0.1899 (5)
C(19)	0.2300 (5)	0.2925 (4)	0.0792 (5)				
			[Ag(**1**)(ClO_4)]				
Ag	1947 (1)	2131 (1)	3468 (0)	C(22)	−926 (5)	1804 (6)	2959 (3)
P(1)	563 (2)	3006 (2)	3437 (2)	C(23)	−1630 (5)	1186 (6)	3057 (3)
P(2)	3124 (2)	1545 (2)	2898 (2)	C(24)	−1769 (5)	964 (6)	3749 (3)
Cl	2298 (2)	1819 (3)	5234 (2)	C(25)	−1203 (5)	1361 (6)	4343 (3)
O(1)	2009 (10)	1057 (10)	4726 (6)	C(26)	−498 (5)	1979 (6)	4246 (3)
O(2)	2675 (7)	2619 (8)	4897 (6)	C(27)	168 (5)	3667 (6)	2600 (3)
O(3)	1576 (8)	2230 (12)	5490 (8)	C(28)	615 (5)	3541 (6)	2028 (3)
O(4)	2876 (9)	1438 (10)	5791 (6)	C(29)	319 (5)	4038 (6)	1378 (3)
C(1)	1951 (7)	4910 (10)	3959 (7)	C(30)	−424 (5)	4661 (6)	1300 (3)
C(2)	1085 (8)	4934 (10)	4032 (6)	C(31)	−871 (5)	4787 (6)	1873 (3)
C(3)	660 (9)	5885 (10)	4031 (7)	C(32)	−575 (5)	4290 (6)	2523 (3)
C(4)	1095 (11)	6742 (7)	4021 (39)	C(33)	2814 (6)	536 (6)	2257 (5)
C(5)	2492 (11)	7679 (14)	4063 (8)	C(34)	2913 (6)	−484 (6)	2462 (5)
C(6)	3326 (14)	7674 (18)	4086 (10)	C(35)	2647 (6)	−1251 (6)	1960 (5)
C(7)	4771 (16)	6746 (19)	4143 (12)	C(36)	2282 (6)	−998 (6)	1253 (5)
C(8)	5222 (15)	5923 (19)	4089 (11)	C(37)	2183 (6)	22 (6)	1048 (5)
C(9)	5234 (12)	4202 (14)	3533 (9)	C(38)	2449 (6)	789 (6)	1550 (5)
C(10)	4826 (11)	3429 (14)	3115 (9)	C(39)	4097 (12)	926 (17)	3459 (9)
C(11)	3901 (10)	3449 (12)	2900 (8)	C(40)	4148 (12)	947 (17)	4202 (9)
C(12)	3437 (8)	4199 (10)	3175 (6)	C(41)	4893 (12)	568 (17)	4653 (9)
C(13)	2434 (10)	5821 (6)	3906 (31)	C(42)	5588 (12)	168 (17)	4361 (9)
C(14)	1995 (9)	6740 (10)	3987 (7)	C(43)	5538 (12)	147 (17)	3618 (9)

Table II (*Continued*)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
C(15)	3835 (9)	4979 (11)	3605 (7)	C(44)	4792 (12)	526 (17)	3167 (9)
C(16)	4769 (11)	4999 (14)	3757 (9)	C(45)	4167 (10)	1252 (18)	3400 (10)
C(17)	3341 (9)	5833 (12)	3855 (7)	C(46)	4429 (10)	1742 (18)	4058 (10)
C(18)	3823 (14)	6741 (15)	4042 (10)	C(47)	5307 (10)	1703 (18)	4402 (10)
C(19)	590 (8)	3985 (12)	4147 (7)	C(48)	5924 (10)	1173 (18)	4088 (10)
C(20)	3483 (11)	2629 (12)	2409 (8)	C(49)	5662 (10)	683 (18)	3430 (10)
C(21)	−360 (5)	2200 (6)	3554 (3)	C(50)	4784 (10)	723 (18)	3086 (10)
			[$Ag(1)(NO_3)$]				
Ag	1638 (1)	2080 (0)	2955 (0)	C(20)	5088 (9)	1482 (5)	2763 (4)
P(1)	871 (2)	2456 (1)	3923 (1)	C(21)	−554 (5)	3173 (3)	3833 (3)
P(2)	3534 (2)	1969 (1)	2336 (1)	C(22)	−258 (5)	3925 (3)	3993 (3)
N	−978 (6)	1355 (3)	2371 (3)	C(23)	−1341 (6)	4463 (2)	3909 (3)
O(1)	−112 (13)	1043 (5)	2717 (5)	C(24)	−2719 (5)	4248 (3)	3666 (3)
O(2)	−842 (14)	1992 (7)	2312 (6)	C(25)	−3015 (5)	3495 (3)	3507 (3)
O(3)	−1985 (10)	1016 (6)	2044 (5)	C(26)	−1932 (6)	2958 (2)	3590 (3)
C(1)	1851 (9)	621 (5)	5254 (4)	C(27)	2157 (6)	2856 (4)	4535 (2)
C(2)	1044 (9)	1062 (5)	4581 (4)	C(28)	3424 (6)	3145 (4)	4381 (2)
C(3)	1084 (10)	917 (6)	5224 (5)	C(29)	4364 (5)	3527 (4)	4825 (3)
C(4)	1814 (11)	327 (6)	5490 (5)	C(30)	4038 (6)	3620 (4)	5422 (2)
C(5)	3163 (11)	−863 (6)	5421 (5)	C(31)	2771 (6)	3331 (4)	5575 (2)
C(6)	3705 (12)	−1362 (7)	5074 (5)	C(32)	1830 (5)	2949 (4)	5132 (3)
C(7)	4513 (12)	−1753 (6)	4080 (5)	C(33)	4323 (5)	2865 (2)	2155 (3)
C(8)	4829 (11)	−1610 (6)	3525 (5)	C(34)	5617 (5)	2900 (2)	1927 (3)
C(9)	5221 (10)	−650 (5)	2745 (4)	C(35)	6242 (4)	3599 (3)	1845 (3)
C(10)	5294 (10)	82 (5)	2559 (4)	C(36)	5573 (6)	4263 (2)	1990 (3)
C(11)	4850 (8)	667 (5)	2929 (4)	C(37)	4278 (5)	4228 (2)	2217 (3)
C(12)	4219 (8)	482 (5)	3435 (4)	C(38)	3654 (4)	3530 (3)	2300 (3)
C(13)	2686 (9)	9 (5)	4535 (4)	C(39)	3125 (7)	1436 (3)	1613 (2)
C(14)	2585 (9)	−162 (5)	5161 (4)	C(40)	3513 (7)	1672 (3)	1052 (3)
C(15)	4092 (9)	−276 (5)	3631 (4)	C(41)	3236 (7)	1210 (3)	531 (2)
C(16)	4697 (10)	−844 (5)	3282 (4)	C(42)	2571 (7)	513 (3)	571 (2)
C(17)	3561 (9)	−479 (5)	4197 (4)	C(43)	2184 (7)	277 (3)	1132 (3)
C(18)	3906 (11)	−1198 (6)	4452 (5)	C(44)	2461 (7)	738 (3)	1653 (2)
C(19)	42 (9)	1654 (5)	4278 (4)				

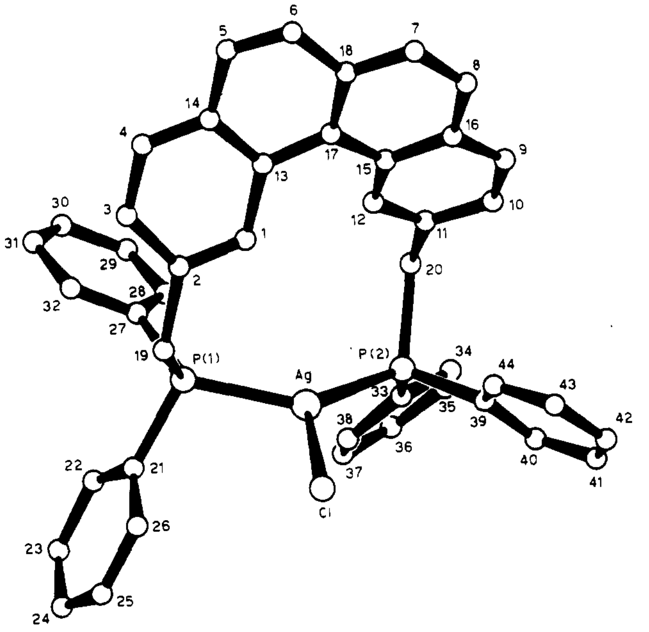

Figure 1. Perspective view of the complex [Ag(1)Cl].

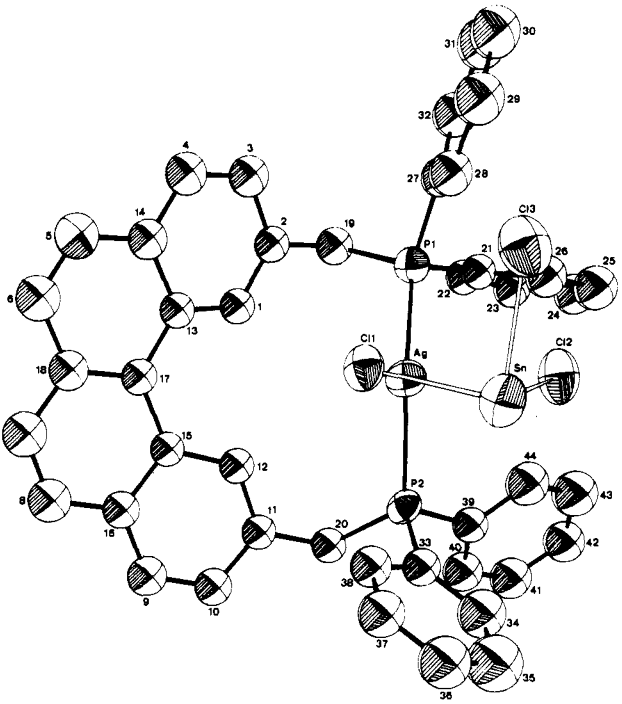

Figure 2. Perspective view of the complex [$Ag(1)(SnCl_3)$].

two Ag–P bond lengths fall in a normal range[15] but are significantly different (0.043 (2) Å). The shorter Ag–P bond is involved in the larger P–Ag–Cl angle (120.7 (1)°) and the longer one in the smaller angle (98.3 (1)°). The driving force for this correlated distortion in bond lengths and bond angles from a symmetric arrangement seems to be related to the observation that Cl faces C(39) but lies in between C(19) and C(21) (Figure 1).

[$Ag(1)(SnCl_3)$] (3). Ag is bonded to two P and one Cl atom; it deviates 0.12 Å from the plane defined by these three atoms. A second Cl atom is 3 Å from Ag, ~0.3 Å further away than

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(15) A search in the Cambridge Crystallographic Data File[16] revealed 16 structures containing the fragment P–Ag–P with no further P atoms coordinating. In all but one of the cases for which atomic coordinates are available (11), Ag is (distorted) four-coordinate and in one case three-coordinate. The range of Ag–P distances is 2.41–2.48 Å.

(16) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. D.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 233.

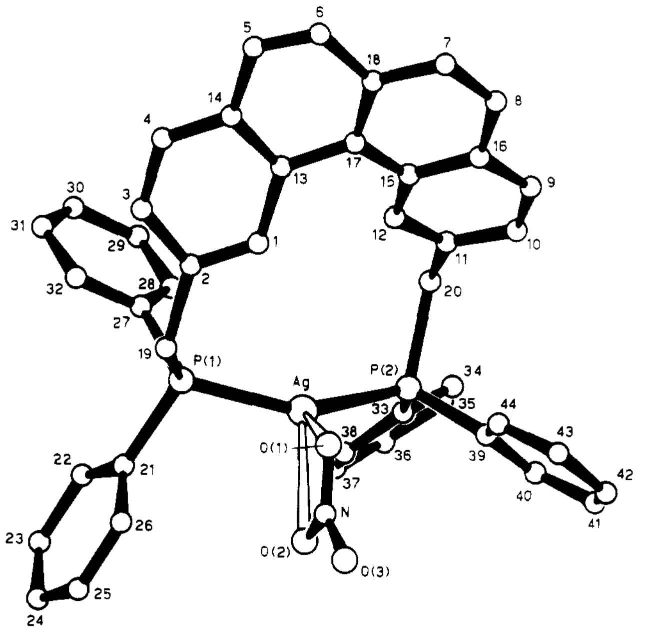


Figure 3. Perspective view of the complex $[Ag(\mathbf{1})(NO_3)]$.

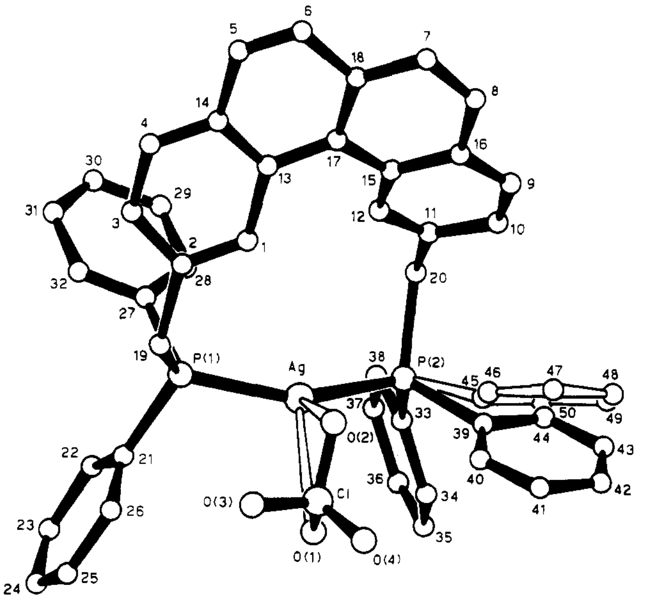


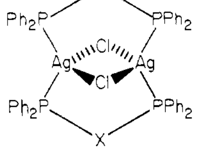
Figure 4. Perspective view of the complex $[Ag(\mathbf{1})(ClO_4)]$. The disordered phenyl group is shown in the positions of the model used.

the closer Cl. The two Ag–P bond lengths are normal[15] but again significantly different (0.032 (6) Å). Analogously to the case for **2**, the shorter Ag–P bond is involved in the larger P–Ag–Cl angle and vice versa, with angles of 113.5 (1) and 103 (1)°. The effect is smaller than in **2**; the driving force is not obvious.

$[Ag(1)(NO_3)]$ (4). Ag is bonded to two P atoms and to two O atoms of the nitrate group in a distorted-tetrahedral arrangement. The two Ag–O bonds (2.476 (12) and 2.565 (14) Å) differ by only ~4σ; i.e., the nitrate group may be considered as a symmetrical, bidentate ligand.[17] The noncoordinating N–O(3) bond is ~0.1 Å longer than the other two nitrogen–oxygen bonds, which are not significantly different. The nitrate group is planar, and its plane, which nearly contains Ag, is almost perpendicular to the plane through Ag and P(1), which nearly contains N and O(3). The angles between the Ag–P(1) and Ag–P(2) directions and the NO_3 plane are 97 and 114°, reflecting the fact that the nitrate group is facing the C(39)–C(44) phenyl group. The two Ag–P bonds (2.424 (2) and 2.410 (2) Å) differ by only 4σ.[15]

$[Ag(1)(ClO_4)]$ (5). Analogously to the case for **4**, Ag is bonded to two P atoms and to two of the four O atoms of the perchlorate group in a distorted-tetrahedral arrangement. The two Ag–O bonds (2.753 (12) and 2.808 (12) Å) differ by only 3σ. The ClO_4^- group maintains its regular tetrahedral arrangement with an average Cl–O bond length of 1.391 (11) Å and O–Cl–O angle of 109.5 (7)°. The plane through Ag, O(1), and O(2) is nearly perpendicular to the plane through Ag, P(1), and P(2), which contains also Cl, O(3), and O(4). As a consequence of the vicinity of the perchlorate group to the phenyl C(39)–C(44) atoms (or C(45)–C(50) if the disorder is considered) the plane through Ag, O(1), and O(2) makes unequal angles with the Ag–P(1) and Ag–P(2) directions of 99 and 110°. The two Ag–P bonds are nearly equivalent (2.417 (3) and 2.401 (3) Å).[15]

Comparison of the Structures. We include compounds **6**[18] and **7**[19] in the comparison since their phosphine ligands are



6, X = $-CH_2CH_2CH_2CH_2CH_2-$
7, X = $-CH_2CH_2SCH_2CH_2-$

of the type Ph_2PCH_2R, i.e. electronically similar to **1**. The resulting set of six compounds may be divided into three groups: (a) the binuclear compounds **6** and **7** with two additional Cl ligands, (b) the mononuclear compounds **2** and **3** with one or two additional Cl ligands, and (c) the mononuclear compounds **4** and **5** with two additional O ligands. Averaged coordination geometries (or ranges of values) are given in Table IV for the three groups. Ag–P bond lengths decrease with increasing P–Ag–P angle. As far as the Ag–Cl and Ag–O bonds are concerned, the situation is less clear since large ranges of distances are observed and comparison is between different ligand atoms. If we increase the Ag–O distances by 0.33 Å to account for the difference in O and Cl covalent radii,[20] we find, at least qualitatively, that the Ag–Cl (Ag–O) distances tend to increase and that the Cl–Ag–Cl (O–Ag–O) angles tend to decrease as the angle P–Ag–P increases. Note that **4** and **5** with the very weakly coordinating NO_3^- and ClO_4^- anions show the largest P–Ag–P angles. In **3** the two coordinating chlorides are bonded mainly to Sn, coordinating only weakly to Ag (Table III); the P–Ag–P angle is still relatively large. Finally, in **6** and **7** the two coordinating Cl atoms are shared equally by two Ag atoms and the P–Ag–P angle is the smallest. When they are taken together, these observations seem to substantiate the earlier conclusion[3] that the P–Ag–P angle may be taken as a qualitative and relative measure of the ionic nature in the Ag–Cl and Ag–O interactions.

In this context **2** is somewhat exceptional: in view of the fact that Cl is bonded only to one Ag, the P–Ag–P angle is quite large. This observation is corroborated by comparison with the P–M–P angles in $[CuBr(PPh_3)_2]$ (126.0°)[21] or $[AuCl(PPh_3)_2]$ (132.1°).[22] Whether the large P–Ag–P angle

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Table III. Selection of Interatomic Distances (Å) and Interbond Angles (deg) in Complexes **2-5**

	2 (Y = Cl)	**3** (X = Sn, Y = Cl)	**4** (X = N, Y = O)	**5** (X = Cl, Y = O)
Distances				
Ag-P(1)	2.455 (1)	2.419 (3)	2.424 (2)	2.417 (3)
Ag-P(2)	2.412 (1)	2.451 (3)	2.410 (2)	2.401 (3)
Ag-Y(1)	2.512 (1)	2.713 (2)	2.476 (12)	2.753 (12)
Ag-Y(2)		3.000 (3)	2.565 (14)	2.808 (12)
X-Y(1)		2.534 (3)	1.170 (15)	1.404 (13)
X-Y(2)		2.498 (3)	1.143 (14)	1.410 (11)
X-Y(3)		2.461 (3)	1.258 (13)	1.399 (14)
X-Y(4)				1.348 (14)
P(1)-C(19)	1.841 (4)	1.842 (12)	1.846 (9)	1.855 (15)
P(1)-C(21)	1.832 (4)	1.822 (8)	1.842 (6)	1.820 (8)
P(1)-C(27)	1.813 (4)	1.828 (6)	1.817 (6)	1.812 (7)
P(2)-C(20)	1.852 (4)	1.842 (7)	1.840 (9)	1.837 (16)
P(2)-C(33)	1.812 (4)	1.830 (9)	1.820 (5)	1.801 (10)
P(2)-C(39)	1.822 (4)	1.825 (10)	1.830 (6)	1.863 (20)
P(2)-C(45)				1.758 (18)
C(2)-C(19)	1.506 (5)	1.513 (12)	1.501 (13)	1.497 (19)
C(11)-C(20)	1.504 (5)	1.514 (14)	1.509 (12)	1.490 (23)
Angles				
P(1)-Ag-P(2)	140.7 (1)	142.2 (1)	148.6 (1)	151.5 (1)
P(1)-Ag-Y(1)	98.3 (1)	113.5 (1)	96.2 (3)	99.1 (3)
P(1)-Ag-Y(2)		99.8 (1)	97.2 (3)	96.5 (2)
P(2)-Ag-Y(1)	120.7 (1)	103.5 (1)	110.8 (3)	108.3 (3)
P(2)-Ag-Y(2)		94.9 (1)	113.0 (3)	107.6 (2)
Y(1)-Ag-Y(2)		78.4 (1)	46.0 (4)	48.6 (4)
Ag-Y(1)-X		96.4 (1)	100.1 (7)	100.7 (6)
Ag-Y(2)-X		90.3 (1)	96.2 (9)	98.1 (6)
Y(1)-X-Y(2)		92.0 (1)	117.1 (10)	109.0 (7)
Y(1)-X-Y(3)		89.6 (1)	123.2 (9)	109.7 (9)
Y(1)-X-Y(4)				110.9 (8)
Y(2)-X-Y(3)		93.4 (1)	119.6 (10)	106.7 (8)
Y(2)-X-Y(4)				111.2 (8)
Y(3)-X-Y(4)				109.2 (9)
Ag-P(1)-C(19)	109.9 (2)	114.4 (3)	110.9 (3)	114.0 (5)
Ag-P(1)-C(21)	111.5 (2)	108.9 (4)	113.9 (2)	115.4 (3)
Ag-P(1)-C(27)	123.6 (2)	118.9 (3)	119.5 (2)	113.9 (3)
C(19)-P(1)-C(21)	102.4 (2)	106.3 (4)	102.7 (3)	103.3 (5)
C(19)-P(1)-C(27)	105.8 (2)	105.7 (5)	105.8 (4)	105.2 (5)
C(21)-P(1)-C(27)	101.5 (2)	101.2 (4)	102.5 (3)	103.8 (4)
Ag-P(2)-C(20)	112.8 (2)	120.6 (4)	111.4 (3)	197.4 (5)
Ag-P(2)-C(33)	117.4 (1)	112.3 (3)	114.6 (2)	114.1 (3)
Ag-P(2)-C(39)	113.4 (1)	110.7 (3)	116.3 (2)	118.8 (5)
Ag-P(2)-C(45)				121.4 (6)
C(20)-P(2)-C(33)	99.8 (2)	102.6 (4)	101.0 (3)	107.3 (6)
C(20)-P(2)-C(39)	103.7 (2)	103.3 (4)	104.5 (4)	109.8 (8)
C(20)-P(2)-C(45)				96.4 (9)
C(33)-P(2)-C(39)	108.0 (2)	106.2 (5)	107.6 (3)	98.7 (7)
C(33)-P(2)-C(45)				108.0 (8)
C(39)-P(2)-C(45)				14.2 (10)
C(2)-C(19)-P(1)	115.4 (3)	109.4 (6)	115.9 (6)	114.6 (9)
C(11)-C(20)-P(2)	114.5 (3)	117.1 (5)	115.5 (6)	112.5 (11)
Relevant Torsion Angles in the 12-Membered Ring				
C(1)-C(2)-C(19)-P(1)	−63.0 (5)	84.2	−64.8 (10)	−57.6 (14)
C(2)-C(19)-P(1)-Ag	78.3 (3)	−55.8	75.1 (7)	73.0 (9)
C(12)-C(11)-C(20)-P(2)	−82.0 (5)	−48.7	−81.4 (9)	−84.5 (16)
C(11)-C(10)-P(2)-Ag	64.2 (3)	48.0	64.4 (7)	66.7 (12)
C(19)-P(1)···P(2)-C(20)	−72.5 (2)	−1.1	−69.3 (4)	−75.2 (7)

Table IV. Averaged Coordination Geometries (or Ranges) and $^1J(^{107}Ag,^{31}P)$ Coupling Constants for Silver Phosphine Complexes

	d(Ag-P), Å	α(P-Ag-P), deg	d(Ag-X), Å	α(X-Ag-X), deg	$^1J(^{107}Ag,^{31}P)$, Hz
6, **7** (X = Cl)	2.483 (15)	123.5 (5.6)	2.671 (26)	90.0 (1.2)	399,[a] 381[a]
2, **3** (X = Cl)	2.434 (22)	141.5 (1.0)	2.5-3.0	. . ., 78.4	411,[a] 418[4]
4, **5**	2.413 (10)	150.0 (1.5)	2.5-2.8	46.0, 48.6	461,[4] 507[a]

[a] This paper.

in **2** is due mainly to the influence of **1**, which is known to favor large P–M–P angles, or to an as yet unknown electronic property intrinsic to P–Ag–P cannot be decided from the available data.

The ligand conformations of **2**, **4**, and **5** on the one hand and of **3** on the other are different (Table III, Figures 1–4). It has been observed that the conformation observed for **2**, **4**, and **5** is favored for P–Ag–P angles smaller than 150° and that the conformation of **3** is preferred for P–Ag–P angles larger than 150°.[23] In view of the present results this rule has to be modified slightly: in the range of P–Ag–P angles

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between 140 and 155° both conformations are possible when ligand **1** is used.

NMR Coupling Constants. Table IV shows NMR coupling constants between Ag and P ($^1J(^{107}Ag,^{31}P)$). Their changes are correlated to changes in structure: The coupling constants increase with decreasing Ag–P distance, increasing P–Ag–P angle, and decreasing nucleophilicity of the coordinating atom in the counterion. The trend is entirely analogous to results found for HgX_2L_2 compounds[24] (L stands for a variety of mono- and bidentate phosphine ligands, and X stands for a variety of anions). The trend in the coupling constants indicates an increase in the involvement of 5s orbitals of Ag in the bonding to P; the decrease in Ag–P distances suggests a concomitant strengthening of the Ag–P bond. The structures and coupling constants of **6** and **7** (Table IV) may also serve to explain data for $[AgCl(P(p\text{-}Tol)_3)_2]$ (**8**) and $[Ag_2Cl_2(PPh_3)_4]$ (**9**). The molecular weight of **8** determined from freezing point depression in benzene (at $\sim$5 °C) indicates a monomeric structure.[25] The Ag–P coupling constant of 378 Hz determined at −80 °C[25] indicates a dimeric structure if it is compared to the values for **6** and **7** (399, 381 Hz). Indeed the crystal structure of **9** shows dimeric units[26] analogous to those observed for **6** and **7**. It would thus seem that at low temperature **8** associates into entropically more favorable dimers.

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Registry No. **2**, 59296-63-8; **3**, 86064-92-8; **4**, 86064-93-9; **5**, 86064-94-0; **6**, 60452-81-5; **7**, 52641-45-9.

Supplementary Material Available: Listings of positional and thermal parameters for all non-hydrogen atoms (Table S-I), calculated atomic coordinates for the hydrogen atoms (Table S-II), and calculated and observed amplitudes (Table S-III) (145 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Higher Oxidation States. 5.[1] Reaction of Palladium(II) Iodo Complexes with Molecular Iodine and Crystal and Molecular Structure of Diiodo(*cis*-1,2-bis(diphenylphosphino)ethylene)palladium(II)–Diiodine (1/1)

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The reactions of $[Pd(L\text{–}L)I_2]$ (L–L = $Me_2As(CH_2)_3AsMe_2$ (**1**), *cis*-$Ph_2PCH{=}CHPPh_2$ (**2**), *o*-$C_6H_4(SPh)_2$ (**3**)) with iodine produces the palladium(II) polyiodides $[Pd(L\text{–}L)I_4]$ (L–L = **1**, **2**) and $[Pd(L\text{–}L)I_3]$ (L–L = **3**). Similarly $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2I_2]$ is converted into $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2(I_3)_2]$. The crystal and molecular structure of $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_4]$ has been determined by X-ray diffraction (orthorhombic, space group *Pcab*, a = 16.424 (3) Å, b = 17.955 (6) Å, c = 20.545 (2) Å, Z = 8). The palladium atom is four-coordinate (P_2I_2 donor set, Pd–P = 2.252 (3), 2.244 (3) Å, Pd–I = 2.660 (1), 2.652 (1) Å) in a square-planar arrangement with adjacent groups being linked by I_2 molecules (I···I–I···I, I–I = 2.745 (1) Å, I···I = 3.527 (1), 3.483 (1) Å) to form approximately linear I_4 groups. The results are compared with the reactions of $[Pd(L\text{–}L)Cl_2]$ and $[Pd(L\text{–}L)Br_2]$ with the corresponding halogens, which in some cases lead to palladium(IV) complexes.

Introduction

We have recently reported[1,2] the synthesis and properties of a range of palladium(IV) chloro complexes containing neutral ligands, e.g. $[R_4N][PdLCl_5]$ (L = NMe_3, P-*n*-Pr_3, SMe_2), $[Pd(L\text{–}L)Cl_4]$ (L–L = $Me_2PCH_2CH_2PMe_2$, 2,2′-bipyridyl, $Ph_2PCH_2CH_2PPh_2$), and *trans*-$[Pd(L\text{–}L)_2Cl_2](ClO_4)_2$ (L–L = $Me_2PCH_2CH_2PMe_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$). A more restricted set of bromo complexes were also characterized, e.g. $[Pd(L\text{–}L)Br_4]$ (L–L = alkyldiphosphine or -diarsine).[1] Since the only established palladium(IV) iodo complex is the very recently reported[3] Cs_2PdI_6, the formation of iodopalladium(IV) complexes containing neutral ligands would be unexpected. However, a preliminary survey revealed that some $[Pd(L\text{–}L)I_2]$ reacted readily with molecular iodine, and hence a more detailed study was undertaken.

The reactions of platinum(II) iodo complexes of group 5B donor ligands with iodine gives products that depending upon the ligand and the conditions belong to one of the following classes: (i) platinum(IV) iodides, e.g. $[Pt(PMe_3)_2I_4]$[4] and $[Pt(Ph_2PCH_2CH_2PPh_2)I_4]$;[5] (ii) platinum(IV) polyiodides, e.g. $[Pt(o\text{-phenanthroline})I_6]$;[6] (iii) mixed-valence class 2 compounds $[Pt(H_2NCH_2CH_2NH_2)_2][Pt(H_2NCH_2CH_2NH_2)_2I_2](ClO_4)_4$;[7] (iv) platinum(II) polyiodides, e.g. $[Pt(dimethylimidazole)_4](I_3)_2$[8] and $[Pt(TAAB)]I_8$[9] (TAAB = tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine). Several reports of palladium(II) polyiodides, e.g. $[Pd(TAAB)]I_8$,[9] $[Pd(NH_3)_4]I_8$,[10] and "partially oxidized" materials,[11,12] e.g.

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