

[PdL(bpy)](hfac) exhibits two methine signals at 5.97 and 5.27 ppm, of which the former is assigned to CH in L by reference to the chemical shift of CH in HL. The methine proton of the hfac anion in [Pd(*n*-PrNH<sub>2</sub>)<sub>4</sub>](hfac)<sub>2</sub> and [Pd(py)<sub>4</sub>](hfac)<sub>2</sub> resonates at 5.89 and 5.97 ppm, respectively, in CDCl<sub>3</sub>.<sup>3</sup> The value of 5.27 ppm in the present case lies at a remarkably high field. The difference of solvent might be responsible for this discrepancy. These <sup>1</sup>H NMR data alone may not exclude the possibility of [Pd(hfac)(bpy)]L, but the IR spectra clearly deny the latter since the 1610-cm<sup>-1</sup> band characteristic of the chelated hfac ligand in [Pd(hfac)(bpy)](hfac) disappeared after the reaction with HL, whereas the 1670-cm<sup>-1</sup> band for the hfac anion in the outer sphere is retained.

The proposed structures of the dinuclear complexes in Figure 1 are well reconciled with the IR and <sup>1</sup>H NMR data, and the insoluble trinuclear complexes ML<sub>2</sub> are also presumed to have similar structures. Metal complexes containing a β-diketonate dianion which have been reported so far are TeCl<sub>2</sub>(C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>),<sup>4</sup> Te(C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>),<sup>4</sup> and Te(C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>).<sup>5</sup> In these complexes the dianion is chelating to the tellurium(IV) or -(II) atom via the two terminal carbon atoms. The role of the pentanedionate anion in the present compound connecting two metal atoms

via the terminal carbon and two oxygen atoms is a novel one and is expected to be found in the future among various compounds of metals other than palladium(II) and of β-dicarbonyl ligands other than 2,4-pentanedione.

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**Registry No.** CuL<sub>2</sub>, 67360-75-2; VOL<sub>2</sub>, 67360-76-3; PdL<sub>2</sub>, 67360-77-4; Be(acac)L, 67360-78-5; Pd(acac)L, 67360-79-6; Pd(tfac)L, 67360-80-9; [CuL(bpy)]ClO<sub>4</sub>, 67360-82-1; [PdL(bpy)](hfac), 67360-84-3; HL, 59588-96-4; Cu(acac)<sub>2</sub>, 13395-16-9; VO(acac)<sub>2</sub>, 3153-26-2; Pd(tfac)<sub>2</sub>, 63742-52-9; Be(acac)<sub>2</sub>, 10210-64-7; Pd(acac)<sub>2</sub>, 14024-61-4; [Cu(acac)(bpy)]ClO<sub>4</sub>, 67360-85-4; [Pd(hfac)(bpy)](hfac), 65353-89-1.

### References and Notes

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## Tri-*tert*-butylphosphine Complexes of Silver(I). Preparation, Characterization, and Spectral Studies<sup>1</sup>

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Tri-*tert*-butylphosphine reacts with silver salts to form complexes of the types [(*t*-Bu)<sub>3</sub>P]<sub>2</sub>AgX and (*t*-Bu)<sub>3</sub>PAgX. The 2:1 complexes have been isolated for X = ClO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, and NO<sub>3</sub> and the 1:1 complexes have been isolated for X = Cl, Br, I, CN, SCN, CH<sub>3</sub>CO<sub>2</sub>, and NO<sub>3</sub>. <sup>1</sup>H and <sup>31</sup>P NMR and vibrational spectral measurements as well as the conductance measurements show that the 2:1 complexes contain the linear cation [(*t*-Bu)<sub>3</sub>P-Ag-P(*t*-Bu)<sub>3</sub>]<sup>+</sup> whereas the 1:1 complexes are nonionic compounds. Molecular weight measurements in 1,2-dichloroethane or chloroform show that the complexes (*t*-Bu)<sub>3</sub>PAgX, where X = Cl, CH<sub>3</sub>CO<sub>2</sub>, and NO<sub>3</sub>, are monomers whereas the bromo complex (*t*-Bu)<sub>3</sub>PAgBr is a dimer; the thiocyanato complex (*t*-Bu)<sub>3</sub>PAgBr has a degree of association of 1.5. Vibrational spectral data indicate that the acetato complex has a three-coordinate structure whereas the nitrate complex has a two-coordinate structure. The cyano and the thiocyanato complexes appear to contain bridging CN and SCN groups, respectively. The Ag-P stretching frequencies for the complexes occur in the 85–115-cm<sup>-1</sup> region. In contrast to the earlier reported silver(I) complexes of tertiary phosphines, the tri-*tert*-butylphosphine complexes do not undergo rapid phosphine exchange at room temperature as shown by the silver-phosphorus spin-spin coupling observed in their <sup>31</sup>P NMR spectra at ambient temperatures. The <sup>1</sup>J(Ag-P) values for the neutral complexes follow the order NO<sub>3</sub> > CH<sub>3</sub>CO<sub>2</sub> > Cl > SCN > Br > I > CN.

### Introduction

A variety of silver(I) complexes of triarylphosphines<sup>2-11</sup> and mixed alkyl-aryl tertiary phosphines<sup>6,11,12</sup> are known. However, most of the known silver(I) complexes of trialkylphosphines<sup>11,13-19</sup> are of 1:1 stoichiometry and these complexes are indicated to have associated structures in which silver atoms are tetrahedrally coordinated. Structures of four such complexes have been determined by crystallographic studies;<sup>16,18,19</sup> the complex (*n*-Pr)<sub>3</sub>PAgSCN<sup>16</sup> is a polymer whereas the complexes Et<sub>3</sub>PAgCl,<sup>19</sup> Et<sub>3</sub>PAgBr,<sup>19</sup> and Et<sub>3</sub>PAgI<sup>18</sup> are tetramers with "cubanelike" structures. The silver(I) halide complexes of triethylphosphine<sup>13</sup> as well as the trimethylphosphine complexes Me<sub>3</sub>PAgI<sup>17</sup> and Me<sub>3</sub>PAgNO<sub>3</sub><sup>17</sup> also exist as tetramers in benzene solutions. Tetrameric structures have also been established for the 1:1 triphenylphosphine complexes of silver(I) halides by X-ray diffraction

studies.<sup>7-10</sup> Nonionic, three- or four-coordinate complexes<sup>5,8</sup> of the types (R<sub>3</sub>P)<sub>2</sub>AgX and (R<sub>3</sub>P)<sub>3</sub>AgX as well as the cationic complexes<sup>2,5</sup> of the types (R<sub>3</sub>P)<sub>4</sub>Ag<sup>+</sup>, (R<sub>3</sub>P)<sub>3</sub>Ag<sup>+</sup>, and (R<sub>3</sub>P)<sub>2</sub>Ag<sup>+</sup>, where R = phenyl or *p*-tolyl, have also been reported.

To date little work has been reported on silver(I) complexes of sterically hindered phosphines. In continuation of our work on metal complexes of sterically hindered phosphines,<sup>20-25</sup> we have investigated reactions of tri-*tert*-butylphosphine with a variety of silver(I) salts. The results of this investigation show that in contrast to less bulky phosphines, tri-*tert*-butylphosphine forms complexes which with one possible exception contain only two- or three-coordinate silver.

### Experimental Section

**General Procedures.** Tri-*tert*-butylphosphine was prepared by the method reported<sup>21</sup> previously. It was manipulated either in a glovebox

Table I. Analytical, Conductance, and Molecular Weight Data

compound	mp, °C	% C		% H		molar conductance <sup>a</sup>		mol wt	
		calcd	found	calcd	found	in CH <sub>2</sub> Cl <sub>2</sub>	in CH <sub>2</sub> NO <sub>2</sub>	calcd	found
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgClO <sub>4</sub>	228 dec	47.10	46.92	8.80	9.15	69.50	96.20		
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgBF <sub>4</sub>	213 dec	48.10	48.34	9.02	9.25	72.40	101.00		
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgPF <sub>6</sub>	219 dec	43.80	43.63	8.22	8.20	66.70	92.00		
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgNO <sub>3</sub>	260 dec	50.18	50.05	9.41	9.46	52.65	71.60		
( <i>t</i> -Bu) <sub>3</sub> PAgCl	254 dec	41.70	41.87	7.81	8.15	00.75	3.70	345.4	369 <sup>c,d</sup>
( <i>t</i> -Bu) <sub>3</sub> PAgBr	251 dec	36.94	37.14	6.93	7.14	00.34	<i>b</i>	398.9	720 <sup>c,d</sup>
( <i>t</i> -Bu) <sub>3</sub> PAgI	240 dec	32.97	32.71	6.18	6.01	00.94	<i>b</i>	436.8	<i>b</i>
( <i>t</i> -Bu) <sub>3</sub> PAgCN	205 dec	46.40	46.38	8.03	8.36	00.70	14.00	335.9	<i>b</i>
( <i>t</i> -Bu) <sub>3</sub> PAgSCN	225 dec	42.40	42.46	7.34	7.82	00.85	13.10	367.9	544 <sup>c,d</sup>
( <i>t</i> -Bu) <sub>3</sub> PAg(O <sub>2</sub> CCH <sub>3</sub> )	160 dec	45.54	45.55	8.13	8.35	00.73	5.42	368.9	363 <sup>d</sup>
( <i>t</i> -Bu) <sub>3</sub> PAgNO <sub>3</sub>	237 dec	38.72	38.64	7.26	7.49	00.72	23.50	371.9	371 <sup>d</sup>

<sup>a</sup> In ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> for ~10<sup>-3</sup> M solutions at 25 °C. <sup>b</sup> Compound not sufficiently soluble. <sup>c</sup> In CHCl<sub>3</sub> at ~10<sup>-2</sup> M concentration. <sup>d</sup> In 1,2-dichloroethane at ~10<sup>-2</sup> M concentration.

Table II. <sup>1</sup>H and <sup>31</sup>P NMR Data<sup>a</sup>

compound	<sup>1</sup> H NMR data		<sup>31</sup> P NMR data		
	δ, <sup>b</sup> ppm	<sup>3</sup> J(P-H) + <sup>5</sup> J(P-H), Hz	<sup>1</sup> J( <sup>109</sup> Ag- <sup>31</sup> P), Hz	<sup>1</sup> J( <sup>107</sup> Ag- <sup>31</sup> P), Hz	δ, <sup>c</sup> ppm
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgClO <sub>4</sub>	1.48 <sup>d</sup>	14.0	503	442	79.73
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgBF <sub>4</sub>	1.25 <sup>d</sup>	14.0	508	444	80.06
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgPF <sub>6</sub>	1.28 <sup>d</sup>	14.0	509	437	79.86
[( <i>t</i> -Bu) <sub>3</sub> P] <sub>2</sub> AgNO <sub>3</sub>	1.46 <sup>d</sup>	14.0	510	442	79.76
( <i>t</i> -Bu) <sub>3</sub> PAgCl	1.39 <sup>e</sup>	13.0	686	593	82.47
( <i>t</i> -Bu) <sub>3</sub> PAgBr	1.42 <sup>e</sup>	13.0	649	561	73.78
( <i>t</i> -Bu) <sub>3</sub> PAgI	1.38 <sup>e</sup>	15.0	623	540	74.48
( <i>t</i> -Bu) <sub>3</sub> PAgCN	1.38 <sup>e</sup>	14.0	576	498	79.75
( <i>t</i> -Bu) <sub>3</sub> PAgSCN	1.38 <sup>e</sup>	14.0	661	568	79.51
( <i>t</i> -Bu) <sub>3</sub> PAg(O <sub>2</sub> CCH <sub>3</sub> ) <sup>f</sup>	1.41 <sup>e</sup>	13.0	735	635	83.35
( <i>t</i> -Bu) <sub>3</sub> PAgNO <sub>3</sub>	1.26 <sup>e</sup>	13.5	786	683	86.34

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature. <sup>b</sup> Downfield from Me<sub>4</sub>Si; δ for free phosphine in CH<sub>2</sub>Cl<sub>2</sub> = 1.24 ppm; <sup>3</sup>J(P-H) = 10.0 Hz. <sup>c</sup> Positive shifts are downfield from a H<sub>3</sub>PO<sub>4</sub> external standard. δ for free phosphine in CH<sub>2</sub>Cl<sub>2</sub> = 60.70 ppm. <sup>d</sup> 1:2:1 triplet. <sup>e</sup> 1:1 doublet. <sup>f</sup> δ<sub>CH<sub>3</sub>CO<sub>2</sub></sub> = 1.85.

under an atmosphere of oxygen-free dry nitrogen or in a conventional vacuum system. Reagent grade silver salts were used for the preparation of the complexes. All solvents were dried by standard methods and were stored over molecular sieves. Elemental analyses were performed by M.H.W. Laboratories, Garden City, Mich. Molecular weights were determined by vapor-phase osmometry measurements either in this department (using a Hitachi Perkin-Elmer 115 vapor-phase osmometer) or at the Galbraith Laboratories, Knoxville, Tenn. Conductance measurements were made with a Yellow Springs Instrument Model 31 conductivity bridge using a conductivity cell with platinized platinum electrodes. Infrared spectra were recorded either on a Beckman IR-12 spectrophotometer (4000–400-cm<sup>-1</sup> region) or on a Perkin-Elmer 180 spectrophotometer (400–130-cm<sup>-1</sup> region). Solid samples were prepared as mulls in Nujol or Halocarbon oil. Sealed KBr cells were used to measure the spectra in solution. Raman spectra were measured with a Jarrell-Ash spectrophotometer using the 5145-Å exciting line of an argon ion laser. <sup>31</sup>P NMR spectra were obtained with a Bruker 60 Fourier transform spectrometer and <sup>1</sup>H NMR spectra were recorded on a Varian A-60 spectrometer. Analytical, conductance, and molecular weight data are recorded in Table I. NMR data are shown in Table II.

**Preparation of the Complexes.** (a) [(*t*-Bu)<sub>3</sub>P]<sub>2</sub>AgX (X = ClO<sub>4</sub>, Br, PF<sub>6</sub>, and NO<sub>3</sub>). Finely powdered silver(I) salt (1 mmol) was suspended in ~25 mL of dichloromethane and tri-*tert*-butylphosphine (4–5 mmol) was added dropwise with constant stirring. The mixture was stirred for several hours to give a clear solution which was concentrated under vacuum to ~5 mL. Upon adding light petroleum ether to the concentrated solution, the complexes [(*t*-Bu)<sub>3</sub>P]<sub>2</sub>AgX were precipitated in almost quantitative yield. They were recrystallized from a mixture of dichloromethane and light petroleum ether.

(b) (*t*-Bu)<sub>3</sub>PAgX. Complexes where X = Cl, Br, I, CN, and SCN were prepared by adding tri-*tert*-butylphosphine (2 mmol) dropwise with continuous stirring to a suspension of silver(I) salt (1 mmol) in ~25 mL of dichloromethane. After the mixture was stirred for 24 h, a clear solution was obtained which was concentrated in vacuo until it became turbid. When light petroleum ether was added to the turbid solution, complexes (*t*-Bu)<sub>3</sub>PAgX were precipitated in almost 100%

yield. (*t*-Bu)<sub>3</sub>PAgNO<sub>3</sub> was prepared in a similar manner from the reaction of (*t*-Bu)<sub>3</sub>P and AgNO<sub>3</sub> in 1:1 mole ratio. In each case, recrystallization from a mixture of dichloromethane and light petroleum ether afforded a white crystalline solid. (*t*-Bu)<sub>3</sub>PAg(O<sub>2</sub>CCH<sub>3</sub>) was prepared from the reaction of tri-*tert*-butylphosphine with a suspension of silver(I) acetate (1 mmol) in 25 mL of benzene. After the mixture was stirred for 2 h, a clear solution was formed which was evaporated in vacuo to give a viscous product which was diluted with petroleum ether to precipitate the complex. It was recrystallized from an ice-cold solution in a mixture of benzene and hexane.

### Results and Discussion

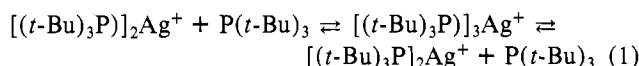
Tri-*tert*-butylphosphine reacts with silver(I) salts to form cationic complexes of the type [(*t*-Bu)<sub>3</sub>PAgP(*t*-Bu)<sub>3</sub>]X, X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, and neutral complexes of the type (*t*-Bu)<sub>3</sub>PAgX, X = Cl, Br, I, CN, SCN, O<sub>2</sub>CCH<sub>3</sub>, and NO<sub>3</sub>. All these complexes are white crystalline air-stable solids which decompose upon melting. The complexes (*t*-Bu)<sub>3</sub>PAgI and (*t*-Bu)<sub>3</sub>PAgCN are sparingly soluble in dichloromethane; other complexes dissolve readily in dichloromethane or chloroform. The (*t*-Bu)<sub>3</sub>PAg(O<sub>2</sub>CCH<sub>3</sub>) is also soluble in benzene.

**Cationic Complexes.** As shown by the data in Table I, the molar conductances for the cationic complexes in dichloromethane and in nitromethane are in good agreement with those reported for 1:1 electrolytes.<sup>5,26</sup> The infrared and Raman spectral data clearly show that the perchlorate, tetrafluoroborate, and the hexafluorophosphate complexes contain the unperturbed anions,<sup>27</sup> in the solid state. In the case of the nitrate complex some perturbation of the D<sub>3h</sub> symmetry of the nitrate ion is indicated as shown by the splitting of the antisymmetric NO stretching mode into two bands (1380 and 1305 cm<sup>-1</sup>). However, the observed splitting is significantly smaller than that reported<sup>27</sup> for coordinated nitrate ligand. In the region of the symmetric NO stretching frequency, only

a very weak infrared band is observed at 1040  $\text{cm}^{-1}$  and the Raman spectrum of the complex shows a very strong band at 1042  $\text{cm}^{-1}$ . Therefore, the spectral data for the complex are consistent with an ionic structure, in the solid state.

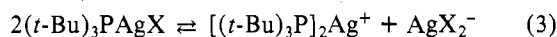
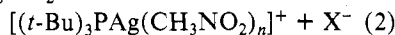
The Raman spectra of the four complexes, in the solid state, show a medium to strong band at ca. 95  $\text{cm}^{-1}$ . Since this band is also observed in the Raman spectra of methanol solutions of the perchlorate and the nitrate complexes, it cannot be due to a lattice vibration. We assign this band to the symmetric Ag–P stretching frequency of the linear  $[(t\text{-Bu})_3\text{P}Ag\text{P}(t\text{-Bu})_3]^+$  cation. Although no values for Ag–P stretching frequencies are reported in the literature, the proposed assignment for the Ag–P stretching frequency is reasonable in view of the fact that the Cd–P stretching frequencies<sup>22</sup> for the tri-*tert*-butylphosphine complexes of cadmium(II) halides are indicated to occur in the 128–104- $\text{cm}^{-1}$  region.

The  $^1\text{H}$  NMR spectra of each of the complexes, at ambient temperatures, show a 1:2:1 triplet downfield from the 1:1 doublet observed for free phosphine. The observed triplet arises from a large value for  $^2J(\text{P}-\text{P})$  and is indicative of the presence of linear  $[(t\text{-Bu})_3\text{P}Ag\text{P}(t\text{-Bu})_3]^+$  species in solution. The  $^{31}\text{P}$  NMR spectrum for each complex, at ambient temperature, consists of two doublets arising from  $^{109}\text{Ag}-^{31}\text{P}$  and  $^{107}\text{Ag}-^{31}\text{P}$  spin–spin coupling. Ratios of  $^1J(^{109}\text{Ag}-^{31}\text{P})/^1J(^{107}\text{Ag}-^{31}\text{P})$  for all the complexes are in good agreement with the theoretical ratio of 1.149. The chemical shifts as well as the silver–phosphorus coupling constants for the cationic complexes are invariant within experimental error. The observation of the silver–phosphorus spin–spin coupling in the  $^{31}\text{P}$  NMR spectra for these complexes at ambient temperatures is in marked contrast with the solution behavior of silver(I) complexes of other tertiary phosphines which are known to undergo fast ligand exchange<sup>5,6</sup> above  $-70^\circ\text{C}$ .  $^{31}\text{P}$  NMR spectra of samples containing 0.5 mmol of complex and 0.1 mmol of free phosphine consisted of two doublets due to the complex and a singlet due to the free phosphine. However, the  $^{31}\text{P}$  NMR spectra of 0.2 M solutions containing an equimolar mixture of phosphine and complex showed a single peak indicating rapid phosphine exchange. Separate signals due to the free phosphine and the linear complex  $[(t\text{-Bu})_3\text{P}Ag\text{P}(t\text{-Bu})_3]^+$  were observed at  $-90^\circ\text{C}$ . These results show that the phosphine exchange observed in the presence of free phosphine occurs through an  $\text{S}_{\text{N}}2$  mechanism (eq 1). However, complexes



containing more than 2 mol of phosphine/mol of silver are not isolable. This is certainly due to the very large steric requirement<sup>20,25,29</sup> of tri-*tert*-butylphosphine since stable tetrahedral or trigonal-planar cationic complexes of silver(I) have been isolated with less bulky phosphines such as triphenylphosphine<sup>2</sup> or tri-*p*-tolylphosphine.<sup>5</sup>

**Neutral Complexes.** Conductance data (Table I) show that most of the  $(t\text{-Bu})_3\text{P}Ag\text{X}$  complexes are not ionized in dichloromethane or nitromethane. However, the complexes  $(t\text{-Bu})_3\text{P}Ag\text{CN}$ ,  $(t\text{-Bu})_3\text{P}Ag\text{SCN}$ , and  $(t\text{-Bu})_3\text{P}Ag\text{NO}_3$  have some conductance in nitromethane. This may be either due to the ionization according to eq 2 or due to the disproportionation represented by eq 3. The 0.01 M solutions of these  $(t\text{-Bu})_3\text{P}Ag\text{X} + n\text{CH}_3\text{NO}_2 \rightleftharpoons$



complexes in nitromethane are essentially nonconducting. Therefore ionic species are formed only at lower concentration. This is also supported by  $^{31}\text{P}$  NMR measurements which did not provide any evidence for the presence of any species other than the neutral  $(t\text{-Bu})_3\text{P}Ag\text{X}$  species (vide infra).

The complexes  $(t\text{-Bu})_3\text{P}Ag\text{Cl}$ ,  $(t\text{-Bu})_3\text{P}Ag(\text{O}_2\text{CCH}_3)$ , and  $(t\text{-Bu})_3\text{P}Ag\text{NO}_3$  behave as monomeric molecular species in 1,2-dichloroethane. The complex  $(t\text{-Bu})_3\text{P}Ag\text{Br}$  is a dimer in 1,2-dichloroethane and chloroform whereas the degree of association for the complex  $(t\text{-Bu})_3\text{P}Ag\text{SCN}$  in chloroform or 1,2-dichloroethane is  $\sim 1.5$ . Molecular weights of the iodo and the cyano complexes could not be measured due to their insufficient solubility in a suitable solvent.

The  $^1\text{H}$  NMR spectra of all the  $(t\text{-Bu})_3\text{P}Ag\text{X}$  complexes show a 1:1 doublet downfield from the doublet observed for free phosphine. The  $^{31}\text{P}$  NMR spectra, at ambient temperatures, show two well-resolved doublets similar to those observed for the cationic complexes. Thus, the neutral complexes, like the cationic complexes, are also nonlabile. As can be seen by the data in Table II, the  $^{31}\text{P}$  NMR chemical shifts and the phosphorus–silver spin–spin coupling constants for the  $(t\text{-Bu})_3\text{P}Ag\text{X}$  complexes show a marked dependence on the anionic ligand X. This is indeed expected if the counteranion X is bonded to silver. The coupling constants decrease in the order  $\text{NO}_3 > \text{O}_2\text{CCH}_3 > \text{Cl} > \text{SCN} > \text{Br} > \text{I} > \text{CN}$ , reflecting variations in the strength of the Ag–P bond in the  $(t\text{-Bu})_3\text{P}Ag\text{X}$  complexes.

The  $^{31}\text{P}$  NMR spectra of  $(t\text{-Bu})_3\text{P}Ag\text{Cl}$ ,  $(t\text{-Bu})_3\text{P}Ag\text{CN}$ , and  $(t\text{-Bu})_3\text{P}Ag\text{SCN}$ , for nitromethane solutions, in the 0.1–0.01 M concentration range, were identical with those observed for dichloromethane solutions. Therefore the possibility of ionization or disproportionation of the complexes in this concentration range can be ruled out.

An equimolar mixture of  $(t\text{-Bu})_3\text{P}Ag\text{NO}_3$  and  $(t\text{-Bu})_3\text{P}$  gave a  $^{31}\text{P}$  NMR spectrum identical with that of the cationic complex  $[(t\text{-Bu})_3\text{P}]_2\text{AgNO}_3$  showing that the 1:1 complex readily reacts with another phosphine molecule to form the 1:2 cationic complex. Addition of another equivalent of phosphine to the above solution caused the collapse of the two doublets of the cationic complex in the ambient-temperature  $^{31}\text{P}$  NMR spectrum. However, the  $^{31}\text{P}$  NMR spectral measurement at  $-90^\circ\text{C}$  showed the presence of only the cationic species  $[(t\text{-Bu})_3\text{P}Ag\text{P}(t\text{-Bu})_3]^+$  and free phosphine. The reactivity of the chloro, bromo, and the iodo complexes toward free phosphine was also examined by  $^{31}\text{P}$  NMR spectral measurements. The  $^{31}\text{P}$  NMR spectra of the complexes containing 2 equiv of excess phosphine showed a single peak at ambient temperatures. The spectra at  $-90^\circ\text{C}$ , however, showed characteristic peaks due to the cationic complex  $[(t\text{-Bu})_3\text{P}Ag\text{P}(t\text{-Bu})_3]^+$  and free phosphine. From these results it is clear that the cationic complexes  $[(t\text{-Bu})_3\text{P}]_2\text{AgX}$  are also readily formed in solution when  $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ .

The infrared spectra of the chloro, bromo and the iodo complexes, in the solid state, in the 4000–130- $\text{cm}^{-1}$  region do not show any band other than the bands observed for the phosphine. A medium-intensity band is observed in the Raman spectra of these compounds and the position of this band shifts from 114 to 90  $\text{cm}^{-1}$  in going from the chloro to the iodo complex. By comparison with the Cd–P stretching frequencies<sup>22</sup> for the 1:1 tri-*tert*-butylphosphine complexes of cadmium(II) halides, the observed Raman bands are assigned to the silver–phosphorus stretching frequency. The infrared spectrum of the cyano complex shows bands at 2155 (s), 425 (ms), and 310 (m)  $\text{cm}^{-1}$  which are not present in the spectra of the halide complexes. These bands are similar to those observed for the infrared spectrum<sup>30</sup> of the  $\text{Ag}(\text{CN})_2^-$  ion and can be assigned to the antisymmetric  $\text{C}\equiv\text{N}$  stretching, Ag–CN stretching, and the Ag–CN bending frequencies, respectively. The Raman spectrum of the cyano complex shows a medium band at 85  $\text{cm}^{-1}$  similar to that observed for the halide complexes and additional bands at 2165 (s) and 252  $\text{cm}^{-1}$ . The 85- $\text{cm}^{-1}$  band is assigned to the silver–phosphorus stretching frequency and the bands at 2165 and 252  $\text{cm}^{-1}$  can

be assigned to the symmetric  $C\equiv N$  stretching<sup>30</sup> and Ag—CN bending<sup>30</sup> frequencies. The CN stretching frequencies for the complex are about  $20\text{-cm}^{-1}$  higher than those reported<sup>30</sup> for the complex  $Ag(CN)_2^-$  which contains two terminally bonded cyanide groups. Since the CN stretching frequency for the bridging cyanide<sup>31</sup> is  $20\text{-}40\text{ cm}^{-1}$  higher than that for the terminally bonded cyanide, the complex  $(t\text{-Bu})_2\text{P}AgCN$  contains bridging cyanide. Satisfactory Raman spectra could not be obtained for the thiocyanato, acetato, and nitrate complexes. The infrared spectrum of the thiocyanato complexes shows two well-resolved bands at  $2105$  and  $2070\text{ cm}^{-1}$  and a shoulder at  $2030\text{ cm}^{-1}$  due to the CN stretching frequency. In the CS stretching frequency region, a weak band is observed at  $703\text{ cm}^{-1}$  which can be assigned unambiguously to the CS stretching frequency since phosphine does not give rise to any infrared absorption in the  $650\text{-}750\text{-cm}^{-1}$  region. In the low-frequency region, a weak band at  $445\text{ cm}^{-1}$  and a medium band at  $423\text{ cm}^{-1}$  are observed due to the SCN bending frequency. Thus the infrared data are consistent<sup>32</sup> with the presence of bridging SCN. The infrared spectrum of the complex in dichloromethane, showed two strong well-resolved bands at  $2109$  and  $2075\text{ cm}^{-1}$  in the  $\nu(CN)$  spectral region. Since the molecular weight measurements in dichloromethane and chloroform show a degree of association of  $\sim 1.5$ , it is most likely that the compound has a three-coordinate dimeric structure in the solid state. The observed  $CO_2$  stretching frequencies ( $1560$  and  $1396\text{ cm}^{-1}$ ) for the acetato complex, in the solid state, are similar to those reported<sup>27</sup> for a free acetate ion and these frequencies are not significantly altered in dichloromethane. In view of the molecular nature of the complex, it is evident that the acetate is bidentately bonded<sup>27</sup> to the silver in the solid state as well as in solution. The  $CO_2$  stretching frequencies for  $(t\text{-Bu})_3\text{P}Ag(O_2CCH_3)$  are very similar to those observed for  $(t\text{-Bu})_3\text{P}Hg(O_2CCH_3)_2$ <sup>25</sup> which has been shown by X-ray diffraction study to contain acetates functioning as asymmetrical bidentate ligands. Thus, the acetato complex can be assigned a monomeric three-coordinate structure. The far-infrared spectrum of the complex, in the solid state, shows a broad band of medium intensity at ca.  $208\text{ cm}^{-1}$  which can be assigned to the antisymmetric silver-oxygen stretching frequency. The observed infrared frequencies due to the nitrate group ( $1470$ ,  $1260$ ,  $1000$ , and  $706\text{ cm}^{-1}$ ) for the nitrate complex indicate that the nitrate is coordinated to the silver atom. The silver-oxygen stretching frequency for the nitrate complex occurs at  $240\text{ cm}^{-1}$  which is significantly higher than the silver-oxygen stretching frequency for the acetato complex. Since acetate is a better coordinating anion than nitrate, the higher silver-oxygen stretching frequency for the nitrate complex is indicative of a lower coordination number of silver in the nitrate complex. The  $1470\text{-cm}^{-1}$  band in the nitrate complex remained unaltered when the spectrum was measured in chloroform indicating that the structure of the complex is not changed in going from the solid state to solution. Thus, the infrared data for the nitrate complex are in accord with a two-coordinate structure.

In summary, in contrast to less bulky tertiary phosphines, tri-*tert*-butylphosphine forms only 1:1 and 2:1 complexes with silver(I). Although definitive conclusions about their structures must await single-crystal X-ray diffraction studies, results of the present study indicate that with the possible exception of the iodo complex all the complexes contain two- or three-coordinate silver in solution as well as in the solid state. As compared with complexes of other phosphines, the tri-*tert*-butylphosphine complexes of silver(I) are nonlabile and ligand exchange in these complexes seems to occur via an associative process.

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**Registry No.**  $[(t\text{-Bu})_3\text{P}]_2\text{AgClO}_4$ , 67530-52-3;  $[(t\text{-Bu})_3\text{P}]_2\text{AgBF}_4$ , 67530-53-4;  $[(t\text{-Bu})_3\text{P}]_2\text{AgPF}_6$ , 67530-54-5;  $[(t\text{-Bu})_3\text{P}]_2\text{AgNO}_3$ , 67530-55-6;  $(t\text{-Bu})_3\text{P}AgCl$ , 66862-82-6;  $(t\text{-Bu})_3\text{P}AgBr$ , 67530-56-7;  $(t\text{-Bu})_3\text{P}AgI$ , 67530-57-8;  $(t\text{-Bu})_3\text{P}AgCN$ , 67530-58-9;  $(t\text{-Bu})_3\text{P}AgSCN$ , 67530-59-0;  $(t\text{-Bu})_3\text{P}Ag(O_2CCH_3)$ , 67577-00-8;  $(t\text{-Bu})_3\text{P}AgNO_3$ , 67542-40-9.

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