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Silver Complexes Containing an Ag_4O_8 Core Imposed by Multidentate Ligands Having Fixed Geometry. Crystal Structure of [Bis(1,8-naphthalenedicarboxylato)][tetrakis(triphenylphosphine)silver(I)]–Dibenzene

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Reactions of (1,8-naphthalenedicarboxylato)disilver(I), $(C_{12}H_6O_4)Ag_2$, with phosphines yielded the products $(C_{12}H_6O_4)_2(LAg)_4$, where L = triphenylphosphine or tri-*p*-tolylphosphine and 2L = bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe). An X-ray crystallographic study revealed the molecular structure of [bis(1,8-naphthalenedicarboxylato)][tetrakis(triphenylphosphine)silver(I)]–dibenzene, $(C_{12}H_6O_4)_2(Ph_3PAg)_4{\cdot}2C_6H_6$: space group $P\bar{1}$ with unit cell dimensions $a = 11.804$ (4) Å, $b = 18.390$ (4) Å, $c = 22.046$ (1) Å, $\alpha = 103.23$ (7)°, $\beta = 95.81$ (3)°, $\gamma = 90.08$ (7)°, $V = 4.633 \times 10^3$ Å^3, and $Z = 2$. The crystal structure was solved for the heavy atoms by direct methods and completed by standard Fourier techniques. Block-diagonal least-squares refinement with 8664 observed diffractometer data converged to $R_F = 0.055$ ($R_w = 0.054$). The coordination geometry is different for each of the four silver atoms, each of which is bonded to one phosphine and positioned against a core of eight oxygen atoms. The four shortest Ag–Ag distances are in the range of 3.672–3.961 Å while the Ag–P distances amount to 2.378 (5), 2.346 (5), 2.341 (5), and 2.363 (4) Å. The carboxylato groups act as monodentate, chelating, or bridging ligands. The coordination is interpreted in terms of a weak ionic interaction between the oxygen atoms and the Ph_3PAg^+ ions containing a strong covalent P–Ag bond. Molecular weight determinations together with ^{31}P NMR data show that the tetranuclear structure is retained in solution. The ^{31}P resonances of the four Ph_3PAg units are isochronous ($J(^{31}P-^{107}Ag) = 650$ Hz) pointing to the occurrence of an intramolecular process which renders these groups equivalent. A process involving intermolecular exchange with excess phosphine at low temperature could be excluded. In order to obtain additional information concerning J(Ag–P) in these compounds, the ^{31}P NMR spectra of novel dppm$(AgOAc)_2$ ($J(^{31}P-^{107}Ag) = 680$ Hz) and dppe$(AgOAc)_2$ ($J(^{31}P-^{107}Ag) = 663$ Hz) were recorded.

Introduction

Much interest exists in the synthesis of polynuclear compounds using multidentate ligands which can hold metal centers in close proximity. Bidentate ligands in which the donor atoms are separated by only one other atom have been shown to be good building blocks for dimers such as 2,4,6-substituted methoxyphenyl groups in $Cr_2[2,4,6\text{-}(MeO)_3C_6H_2]_4$[1] and $V_2[2,6\text{-}(MeO)_2C_6H_3]_4$[2] or for clusters such as 2-(dimethylamino)phenyl in $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$[3] and 2-(dimethylaminomethyl)phenyl in $(5\text{-}Me\text{-}2\text{-}(Me_2NCH_2)\text{-}C_6H_3)_4Cu_4$.[4] The carboxylato group represents a second type of ligand which can lead to the formation of polynuclear compounds.[5] A common structure for the metal 1B carboxylates appears to be a planar tetranuclear core of which the trans edges are bridged by almost parallel-positioned carboxylato groups.[6,7] The Pt compound $[Pt(OAc)_2]_4$[8] has been reported to have the same structural feature. In principle, ligand systems consisting of two or more of the building blocks mentioned above connected to a rigid skeleton might then lead to polynuclear species in which more than two metal centers are in close proximity. An example is 1,8-naphthalenedicarboxylic acid, in which steric constraint in the skeleton favors parallel-positioned carboxylato groups and thus can be considered as a good building block for the synthesis of polynuclear compounds $M_4(O_4C_{12}H_6)_2$. We started our investigation with the synthesis of compounds $M_4(O_4C_{12}H_6)_2$ in which M represents a group 1B metal, because metal 1B carboxylates have proven to be good starting materials for other transition-metal carboxylates, e.g., $[Rh(OAc)(CO)_2]_2$[9] and $[Pt(O_2CCF_3)_2(PPh_3)_2]$,[10] by metathetical reactions with halogeno complexes, and the Pt–Pt bonded complex $[Pt^{III}Me_2(OAc)(SEt_2)]_2$,[11] by one-electron oxidation.

In this paper we report (i) the synthesis and characterization of complexes of the stoichiometry $(C_{12}H_6O_4)_2(LAg)_4$, (ii) a comparison of the structure of $(C_{12}H_6O_4)_2(Ph_3PAg)_4$ in the solid state (by X-ray analysis) and in solution (^{31}P NMR spectroscopy), and (iii) the structure of some related silver acetate–phosphine complexes in order to obtain more information about the interaction of bidentate phosphine ligands with silver carboxylate complexes.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Solvents were dried prior to use. ^1H NMR and ^{31}P NMR spectra were recorded on Varian T-60 and XL-100 spectrometers and the IR spectra were taken on a Beckman 4250 instrument. Molecular weights were determined with a Hewlett-Packard vapor-pressure osmometer, Model 320 B. Elemental analyses were carried out at the Institute for Organic Chemistry, Utrecht.

Preparation of the Compounds. The starting compound $(C_{12}H_6O_4)Ag_2$ was obtained upon addition of $C_{12}H_6O_4K_2$ to a solution of silver nitrate in water. The product was filtered off, washed with ethanol and ether, and vacuum-dried.[12]

$(C_{12}H_6O_4)_2(Ph_3PAg)_2$. $(C_{12}H_6O_4)Ag_2$ (0.45 g, 1 mmol) was added to a solution of PPh_3 (1.05 g, 4 mmol) in benzene (15 mL) and stirred for 4 h. The white precipitate, which was obtained upon addition of hexane (15 mL) to the colorless solution, was filtered off and vacuum-dried; yield 0.9 g (93%) of $(C_{12}H_6O_4)_2(Ph_3PAg)_4$; ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$) δ 7.40, and 7.10 (m). Anal. Calcd for $C_{24}H_{18}AgO_2P$: C, 60.50; H, 3.78; P, 6.51; mol wt 1904. Found: C, 60.50; H, 3.96; P, 6.51; mol wt (in $CHCl_3$, 26 °C) 1480 (10 g/L), 1640 (20 g/L), 1800 (40 g/L). Slow crystallization by diffusion of hexane into the benzene solution afforded colorless crystals containing benzene solvent molecules. Anal. Calcd for $C_{27}H_{21}AgO_2P$ $[(C_{12}H_6O_4)_2(Ph_3PAg)_4{\cdot}2C_6H_6]$: C, 62.79; H, 4.07; P, 6.01. Found: C, 62.68; H, 4.16; P, 6.04.

$(C_{12}H_6O_4)((p\text{-tol})_3PAg)_2{\cdot}C_6H_6$. $(C_{12}H_6O_4)Ag_2$ (0.45 g, 1 mmol) was added to a solution of $P(p\text{-tol})_3$ (1.00 g, 3.3 mmol) in benzene (20 mL) and stirred for 6 h. The white precipitate, which was obtained upon addition of hexane (25 mL) to the colorless solution, was filtered off and vacuum-dried; yield 1.0 g (95%); ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$) δ 2.17 (s, 9 CH_3), 7.10 (m, 15.6 aryl H). Anal. Calcd for $C_{51}H_{51}Ag_2O_4P_2$: C, 61.00; H, 5.09; P, 5.98. Found: C, 62.34; H, 4.81; P, 6.25.

$(C_{12}H_6O_4)_2(Ph_2PCH_2CH_2PPh_2)_2Ag_4$. $(C_{12}H_6O_4)Ag_2$ (0.45 g, 1 mmol) was added to a solution of 1,2-bis(diphenylphosphino)ethane (1.09, 2.5 mmol) in benzene (20 mL) and stirred for 20 h. The white precipitate was filtered off, washed with hexane, and vacuum-dried; yield 0.6 g (80%); ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$) δ 2.30 (J(P–H) = 7 Hz, d, 2 CH_2), 7.30 (m, 18 aryl H). Anal. Calcd: C,

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54.94; H, 4.10; P, 7.23. Found: C, 55.46; H, 4.0; P, 8.40.

$(C_{12}H_6O_4)_2(Ph_2PCH_2PPh_2)_2Ag_4$. $(C_{12}H_6O_4)Ag_2$ (0.45 g, 1 mmol) was added to a solution of bis(diphenylphosphino)methane (0.8 g, 2.0 mmol) in benzene (15 mL) and stirred for 20 h. The white precipitate was filtered off, washed with hexane, and vacuum-dried; yield 0.65 g (85%). Insolubility of the product hampered physicochemical measurements in solution. Anal. Calcd for $C_{37}H_{28}Ag_2O_4P_2$: C, 54.68; H, 3.45; P, 7.39. Found: C, 56.11; H, 4.17; P, 6.97.

$(H_3CCO_2)_2Ag_2(Ph_2PCH_2CH_2PPh_2)$. $(H_3CCO_2)Ag$ (0.17 g, 1 mmol) was added to a solution of 1,2-bis(diphenylphosphino)ethane (0.8 g, 2 mmol) in benzene (20 mL) and stirred for 6 h. The almost clear solution was filtered and hexane (25 mL) was added. The white precipitate was filtered off and vacuum-dried; yield 0.3 g (85%); ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$) δ 2.00 (s, 3.2 CH_3), 2.43 (J(P–H) = 6 Hz, d, 2 CH_2), 7.38 (m, 13 aryl H). Anal. Calcd: C, 50.00; H, 4.17; P, 8.34; mol wt 730. Found: C, 49.33; H, 4.18; P, 8.15; mol wt (in $CHCl_3$, 26 °C) 727.

$(H_3CCO_2)_2Ag_2(Ph_2PCH_2PPh_2)$. $(H_3CCO_2)Ag$ (0.17 g, 1 mmol) was added to a solution of bis(diphenylphosphino)methane (0.8 g, 2.0 mmol) in benzene (15 mL) and stirred for 20 h. The white precipitate, which was obtained upon addition of hexane (20 mL), was filtered off and vacuum-dried; yield 0.25 g (70%); ^1H NMR ($CDCl_3$, internal $Si(CH_3)_4$) δ 1.91 (s, 2.9 CH_3), 3.22 (J(P–H) = 10 Hz, t, 1.2 CH_2) 7.2, 7.4 (m, 12 aryl H). Anal. Calcd: C, 48.60; H, 3.91; P, 8.38. Found: C, 46.54; H, 4.53; P, 8.44.

Crystallographic Data. Crystal data for $(C_{12}H_6O_4)_2(Ph_3PAg)_4\cdot 2C_6H_6$: triclinic, space group $P\bar{1}$, a = 11.804 (4) Å, b = 18.390 (4) Å, c = 22.046 (1) Å, α = 103.23 (7)°, β = 95.81 (3)°, γ = 90.08 (7)°, $V = 4.6330 \times 10^3$ Å^3, Z = 2, ρ(obsd) = 1.47 ± 0.01 g cm^{-3} ($H_2O/ZnCl_2$ by flotation), ρ(calcd) = 1.480 g cm^{-3}, mol wt 2065.22; μ(Mo Kα) = 9.4 cm^{-1}, $F(000)$ = 2088 electrons.

A transparent colorless crystal of bis[1,8-naphthalenedicarboxylato][tetrakis(triphenylphosphine)silver(I)]-dibenzene measuring 0.11 × 0.20 × 0.22 mm was mounted on a thin-walled glass capillary, approximately parallel to the b axis. The quality of the crystal was examined by preliminary Weissenberg photographs. The relatively high-temperature movement of parts of the molecule was reflected in a fast drop of the intensities beyond (sin θ)/λ = 0.5 Å^{-1}. The crystal was transferred to an Enraf-Nonius CAD4 computer-controlled diffractometer for data collection. Accurate values of the unit cell parameters and the crystal orientation matrix were determined at ambient temperature from a least-squares treatment of the angular settings of 22 carefully centered reflections (Mo Kα radiation; λ 0.71069 Å).[13] The standard deviations in the lattice parameters were obtained from the comparison of the deviations from integer values of the indexes, calculated with the orientational matrix, for the angular settings of the orientation reflections as described by Duisenberg.[14]

Collection and Refinement of the Intensity Data. Intensity data were collected with the CAD4 diffractometer equipped with a scintillation counter in the ω-scan mode using graphite-monochromatized Mo Kα radiation. The applied scan angle was $\Delta\omega = 1.70 + 0.35 \tan\theta$. The background was measured in an additional scan area of $\Delta\omega/4°$ on both sides of the main scan and with the same scan speed. The intensity of every reflection was measured at the highest possible speed and then, if necessary, at a speed designed to achieve I(net) > 3$\sigma(I)$. A maximum of 120 s was placed on the measurement time. The vertical and horizontal detector apertures were 3 and 2.0 + 0.70 tan θ mm, respectively, and the distance from the crystal to the aperture was 174 mm. An attenuator would have been automatically inserted if a preliminary scan indicated a count rate greater than 50 000 counts/s[13] but it was not necessary. Two reflections (005 and $2\bar{2}\bar{3}$) were used as standard reflections and their intensities were monitored after every 0.5 h of X-ray exposure time.

A total of 9251 reflections were collected within the limiting sphere up to θ = 20°. The net intensity was calculated with

$$I(\text{net}) = (\text{scale})(S - 2(L + R))/\text{npi}$$

where $(L + R)$ is the total background count, S the scan count, npi the ratio of the maximum possible scan speed to the applied scan speed, and (scale) a function of the time taking into account short- and long-range fluctuations in the intensity, by interpolation in a polynomial of the third degree through eight neighboring measurement values of the standard reflections, in order to smooth out very short-term fluctuations in the intensity of the standard reflections. The long-term variation indicated an approximately linear isotropic decay (47%) of the crystal during the measurement time. The standard deviation in the net intensity was calculated with

$$\sigma(I) = \frac{\text{scale}}{\text{npi}}(S + 4(L + R))^{1/2}$$

The equivalent reflections were averaged with

$$\bar{I} = \sum_i (I_i/\sigma_i^2)/\sum(1/\sigma_i^2)$$

$$\sigma(\bar{I}) = [1/\sum_i(1/\sigma_i^2)]^{1/2}$$

where I_i and σ_i are the intensity and the standard deviation of the ith equivalent diffraction. The resulting unique set contained 8664 reflections of which 5034 had intensities above background ($I > 2\sigma(I)$). The data were corrected for Lorentz and polarization factors (Lp). The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by

$$\sigma(F) = [(I + \sigma(I))/Lp]^{1/2} - (I/Lp)^{1/2}$$

Solution and Refinement of the Structure. Direct methods were used to locate the positions of the silver atoms. The other nonhydrogen atoms were found by subsequent iterative Fourier methods. The structure was refined by block-diagonal least-squares techniques assuming anisotropic thermal motion for all atoms. Unit weights were applied in the preliminary stages of the refinement. The structure refinement converged to R_F = 0.053 and R_{wF} = 0.058.[15] Refinement was continued after the introduction of weights on the basis of counting statistics, with a weight factor of $w^{-1} = \sigma^2(F_o) + 0.0003F_o^2$. The final R values for 8664 observed reflections are R_F = 0.055 and R_{wF} = 0.054. A total of 1118 parameters including one scale factor were varied. All shifts were within their standard deviation when refinement was stopped. The final positional and thermal parameters are tabulated in Table I. The average deviation in an observation of unit weight, defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.34 as compared to the ideal value of 1. The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon F_o or upon (sin θ)/λ, thereby indicating a correctly chosen weighting scheme. A final electron density difference Fourier synthesis revealed no significant residual features higher than 0.48×10^{-6} e Å^{-3}. Scattering factors for all atoms were taken from ref 16. Anomalous dispersion corrections for Ag and P were taken from a compilation of Rietveld.[17] All computer calculations were performed on a CDC Cyber 73 computer at the computer center of the University of Utrecht. Programs used in this structure determination included the local programs CAD4 TAPE (for handling of the diffractometer output, by D. Kaas), ASYM (averaging to the unique data set by A. L. Spek), the MULTAN 77 system,[18] ORTEP (thermal ellipsoid drawing by C. K. Johnson),[19] and an extended version of the X-ray System Version of 1976 (Stewart;[20] implemented by the Dutch X-ray System Group) for most of the other calculations.

Results and Discussion

Description of the Structure of $(Ph_3PAg)_4(O_4C_{12}H_6)_2\cdot 2C_6H_6$. The crystal structure of $(Ph_3PAg)_4(O_4C_{12}H_6)_2\cdot 2C_6H_6$ consists of two discrete tetranuclear molecules per unit cell which are mutually separated by normal van der Waals distances. The four molecules of benzene occupy interstitial sites in the crystal structure. The molecular structure along with the thermal vibrational ellipsoids and the adopted numbering scheme is shown in an ORTEP drawing[19] (Figure 1). Interatomic distances and bond angles about silver and phosphorus are listed in Table II.

The carboxylic groups of the two naphthalenedicarboxylato ligands are positioned in close proximity, thus forming a core of eight oxygen atoms. Figure 2, in which the phenyl rings are omitted for clarity, shows that the silver atoms interact with only seven of the oxygen atoms [Ag–O = 2.249 (9)–2.628 (9)Å], while the shortest Ag–O distance for O(601) amounts to 2.90 (1) Å. This figure furthermore shows that the planes through the naphthalene rings are not orthogonal but make a dihedral angle of 76.5° while the angle between the axis through the central C–C bonds amounts to 20.8°. The four silver atoms are positioned in a butterfly arrangement with

Table I. List of Atomic Parameters[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	0.8126 (1)	0.18762 (7)	0.33021 (6)	0.073 (1)	0.0630 (8)	0.0787 (9)	−0.0051 (8)	−0.0152 (8)	0.0432 (7)
Ag(2)	0.6436 (1)	0.36998 (6)	0.23019 (5)	0.0549 (9)	0.0632 (8)	0.0606 (8)	0.0073 (7)	0.0071 (7)	0.0359 (6)
Ag(3)	0.5668 (1)	0.31436 (6)	0.37071 (5)	0.0556 (9)	0.0700 (8)	0.0485 (7)	0.0053 (7)	0.0204 (7)	0.0193 (6)
Ag(4)	0.7084 (1)	0.17095 (6)	0.15093 (5)	0.071 (1)	0.0641 (8)	0.0417 (7)	0.0006 (8)	0.0110 (7)	0.0074 (6)
P(1)	0.8909 (4)	0.1125 (2)	0.3978 (2)	0.050 (3)	0.048 (3)	0.058 (3)	0.003 (2)	0.000 (2)	0.027 (2)
P(2)	0.6276 (3)	0.4705 (2)	0.1810 (2)	0.043 (3)	0.055 (3)	0.055 (3)	0.005 (2)	0.005 (2)	0.026 (2)
P(3)	0.4790 (3)	0.3143 (2)	0.4613 (2)	0.032 (3)	0.054 (3)	0.047 (2)	0.006 (2)	0.009 (2)	0.017 (2)
P(4)	0.7256 (4)	0.1479 (2)	0.0424 (2)	0.080 (4)	0.066 (3)	0.041 (2)	0.008 (3)	0.007 (2)	0.008 (2)
C(111)	1.032 (1)	0.0745 (7)	0.3829 (5)	0.06 (1)	0.07 (1)	0.030 (8)	0.012 (9)	0.012 (8)	0.008 (7)
C(112)	1.111 (1)	0.1228 (8)	0.3678 (6)	0.08 (1)	0.06 (1)	0.06 (1)	−0.02 (1)	0.025 (9)	0.004 (8)
C(113)	1.225 (2)	0.1001 (9)	0.3585 (7)	0.09 (2)	0.09 (1)	0.08 (1)	0.01 (1)	0.02 (1)	0.00 (1)
C(114)	1.250 (1)	0.026 (1)	0.3637 (6)	0.04 (1)	0.16 (2)	0.041 (9)	−0.01 (1)	0.002 (9)	0.01 (1)
C(115)	1.169 (1)	−0.0234 (8)	0.3772 (7)	0.05 (1)	0.09 (1)	0.07 (1)	0.03 (1)	0.001 (9)	0.021 (9)
C(116)	1.057 (1)	0.0013 (7)	0.3882 (6)	0.07 (1)	0.043 (9)	0.07 (1)	0.011 (9)	0.005 (9)	0.012 (8)
C(121)	0.804 (1)	0.0302 (6)	0.3962 (6)	0.05 (1)	0.020 (8)	0.07 (1)	0.007 (8)	0.017 (8)	0.019 (7)
C(122)	0.798 (1)	0.0014 (7)	0.4497 (7)	0.05 (1)	0.049 (9)	0.10 (1)	0.002 (9)	0.021 (9)	0.053 (9)
C(123)	0.731 (1)	−0.0623 (7)	0.4453 (6)	0.05 (1)	0.06 (1)	0.07 (1)	0.017 (9)	0.018 (9)	0.022 (8)
C(124)	0.671 (1)	−0.0979 (7)	0.3886 (7)	0.04 (1)	0.042 (9)	0.11 (1)	0.015 (9)	0.02 (1)	0.013 (9)
C(125)	0.675 (1)	−0.0688 (8)	0.3324 (7)	0.07 (1)	0.07 (1)	0.09 (1)	0.00 (1)	0.01 (1)	0.009 (9)
C(126)	0.743 (1)	−0.0030 (7)	0.3387 (7)	0.05 (1)	0.05 (1)	0.09 (1)	−0.007 (9)	0.01 (1)	0.000 (9)
C(131)	0.909 (1)	0.1617 (7)	0.4810 (6)	0.04 (1)	0.040 (9)	0.07 (1)	0.004 (8)	0.007 (8)	0.029 (7)
C(132)	0.998 (1)	0.1404 (7)	0.5220 (6)	0.05 (1)	0.06 (1)	0.053 (9)	0.004 (9)	0.003 (8)	0.026 (8)
C(133)	1.011 (1)	0.1768 (7)	0.5852 (6)	0.08 (1)	0.045 (9)	0.06 (1)	0.00 (1)	0.01 (1)	0.012 (8)
C(134)	0.937 (1)	0.2335 (8)	0.6078 (6)	0.07 (1)	0.06 (1)	0.07 (1)	−0.02 (1)	0.00 (1)	0.001 (9)
C(135)	0.847 (1)	0.2532 (8)	0.5665 (7)	0.04 (1)	0.08 (1)	0.09 (1)	−0.03 (1)	0.01 (1)	0.01 (1)
C(136)	0.834 (1)	0.2167 (7)	0.5023 (7)	0.04 (1)	0.047 (9)	0.09 (1)	−0.009 (9)	0.018 (9)	0.014 (8)
C(211)	0.729 (1)	0.4682 (7)	0.1227 (6)	0.05 (1)	0.07 (1)	0.050 (9)	0.008 (9)	0.000 (8)	0.033 (8)
C(212)	0.733 (1)	0.3983 (8)	0.0802 (6)	0.08 (1)	0.06 (1)	0.06 (1)	0.02 (1)	0.029 (9)	0.018 (8)
C(213)	0.819 (1)	0.3916 (8)	0.0385 (7)	0.08 (1)	0.09 (1)	0.09 (1)	0.01 (1)	0.02 (1)	0.05 (1)
C(214)	0.889 (1)	0.4529 (9)	0.0380 (7)	0.09 (2)	0.11 (1)	0.06 (1)	0.02 (1)	0.03 (1)	0.04 (1)
C(215)	0.879 (1)	0.5218 (9)	0.0781 (7)	0.05 (1)	0.14 (1)	0.06 (1)	0.00 (1)	0.009 (9)	0.04 (1)
C(216)	0.796 (1)	0.5310 (9)	0.1221 (7)	0.07 (1)	0.09 (1)	0.09 (1)	−0.01 (1)	0.02 (1)	0.04 (1)
C(221)	0.487 (1)	0.4695 (8)	0.1380 (6)	0.03 (1)	0.08 (1)	0.06 (1)	0.004 (9)	0.004 (8)	0.028 (8)
C(222)	0.468 (1)	0.4984 (8)	0.0843 (6)	0.06 (1)	0.09 (1)	0.06 (1)	0.03 (1)	0.010 (9)	0.039 (9)
C(223)	0.353 (1)	0.490 (1)	0.0536 (7)	0.06 (1)	0.15 (2)	0.07 (1)	0.03 (1)	0.00 (1)	0.04 (1)
C(224)	0.269 (1)	0.453 (1)	0.0734 (8)	0.05 (1)	0.12 (2)	0.11 (1)	0.02 (1)	0.02 (1)	0.04 (1)
C(225)	0.290 (1)	0.4216 (9)	0.1261 (7)	0.06 (1)	0.12 (1)	0.10 (1)	0.02 (1)	−0.01 (1)	0.04 (1)
C(226)	0.402 (1)	0.4318 (7)	0.1591 (6)	0.04 (1)	0.06 (1)	0.08 (1)	0.007 (9)	0.007 (9)	0.013 (8)
C(231)	0.649 (1)	0.5634 (7)	0.2308 (6)	0.05 (1)	0.05 (1)	0.07 (1)	0.009 (9)	0.019 (9)	0.028 (8)
C(232)	0.588 (2)	0.6241 (8)	0.2193 (8)	0.15 (2)	0.04 (1)	0.11 (1)	0.02 (1)	0.01 (1)	0.01 (1)
C(233)	0.620 (2)	0.6951 (9)	0.2613 (9)	0.14 (2)	0.08 (1)	0.15 (2)	0.03 (1)	0.01 (2)	0.03 (1)
C(234)	0.705 (2)	0.7042 (9)	0.3108 (9)	0.12 (2)	0.07 (1)	0.15 (2)	0.01 (1)	0.01 (2)	0.01 (1)
C(235)	0.761 (1)	0.6426 (9)	0.3215 (7)	0.07 (1)	0.10 (1)	0.08 (1)	0.01 (1)	0.01 (1)	0.00 (1)
C(236)	0.735 (1)	0.5714 (8)	0.2815 (7)	0.08 (1)	0.07 (1)	0.07 (1)	0.00 (1)	0.01 (1)	0.014 (9)
C(311)	0.326 (1)	0.3105 (6)	0.4517 (6)	0.04 (1)	0.027 (8)	0.061 (9)	0.000 (8)	0.007 (8)	0.003 (7)
C(312)	0.271 (1)	0.3277 (7)	0.3960 (6)	0.05 (1)	0.05 (1)	0.07 (1)	0.009 (9)	−0.007 (9)	0.009 (8)
C(313)	0.153 (1)	0.3293 (7)	0.3881 (7)	0.04 (1)	0.043 (9)	0.09 (1)	−0.002 (8)	0.002 (9)	0.017 (8)
C(314)	0.087 (1)	0.3127 (7)	0.4327 (7)	0.04 (1)	0.05 (1)	0.09 (1)	0.009 (9)	−0.001 (9)	−0.008 (8)
C(315)	0.142 (1)	0.2913 (7)	0.4870 (7)	0.06 (1)	0.05 (1)	0.09 (1)	−0.014 (9)	0.02 (1)	0.011 (9)
C(316)	0.263 (1)	0.2907 (7)	0.4962 (6)	0.016 (9)	0.07 (1)	0.06 (1)	−0.006 (8)	0.017 (8)	0.009 (8)
C(321)	0.519 (1)	0.3929 (6)	0.5280 (5)	0.04 (1)	0.025 (8)	0.030 (7)	0.001 (7)	0.007 (7)	0.008 (6)
C(322)	0.635 (1)	0.4151 (7)	0.5375 (7)	0.03 (1)	0.05 (1)	0.09 (1)	−0.021 (9)	−0.010 (9)	0.021 (9)
C(323)	0.667 (1)	0.4743 (8)	0.5922 (7)	0.05 (1)	0.06 (1)	0.08 (1)	−0.01 (1)	−0.002 (9)	−0.003 (9)
C(324)	0.592 (1)	0.5099 (7)	0.6305 (7)	0.08 (1)	0.04 (1)	0.08 (1)	0.00 (1)	0.03 (1)	0.007 (8)
C(325)	0.478 (1)	0.4881 (8)	0.6182 (7)	0.09 (1)	0.06 (1)	0.08 (1)	0.00 (1)	0.03 (1)	0.017 (9)
C(326)	0.437 (1)	0.4281 (7)	0.5655 (6)	0.07 (1)	0.06 (1)	0.047 (9)	0.009 (9)	0.034 (9)	0.005 (8)
C(331)	0.519 (1)	0.2319 (7)	0.4902 (5)	0.03 (1)	0.050 (9)	0.045 (8)	0.001 (8)	0.002 (7)	0.019 (7)
C(332)	0.518 (1)	0.1650 (7)	0.4446 (6)	0.02 (1)	0.038 (9)	0.08 (1)	−0.007 (8)	0.013 (8)	0.014 (8)
C(333)	0.547 (1)	0.0975 (8)	0.4653 (7)	0.04 (1)	0.09 (1)	0.09 (1)	0.00 (1)	0.03 (1)	0.03 (1)
C(334)	0.576 (1)	0.1004 (8)	0.5280 (7)	0.04 (1)	0.08 (1)	0.10 (1)	−0.01 (1)	0.01 (1)	0.04 (1)
C(335)	0.575 (1)	0.1671 (8)	0.5726 (7)	0.04 (1)	0.09 (1)	0.09 (1)	−0.01 (1)	0.01 (1)	0.05 (1)
C(336)	0.544 (1)	0.2354 (8)	0.5549 (6)	0.020 (9)	0.08 (1)	0.07 (1)	0.003 (8)	0.000 (8)	0.045 (8)
C(411)	0.623 (1)	0.2009 (7)	0.0038 (6)	0.06 (1)	0.05 (1)	0.046 (9)	0.006 (9)	−0.003 (8)	0.008 (7)
C(412)	0.538 (1)	0.2372 (8)	0.0381 (7)	0.06 (1)	0.08 (1)	0.11 (1)	0.02 (1)	0.00 (1)	0.02 (1)
C(413)	0.459 (2)	0.2804 (9)	0.0112 (8)	0.10 (2)	0.10 (1)	0.11 (1)	0.02 (1)	−0.02 (1)	0.03 (1)
C(414)	0.471 (2)	0.290 (1)	−0.0493 (8)	0.10 (2)	0.11 (2)	0.12 (2)	0.00 (1)	−0.01 (1)	0.05 (1)
C(415)	0.554 (2)	0.256 (1)	−0.0809 (8)	0.09 (2)	0.16 (2)	0.10 (1)	0.00 (1)	0.00 (1)	0.06 (1)
C(416)	0.635 (2)	0.2092 (9)	−0.0571 (7)	0.10 (2)	0.13 (2)	0.05 (1)	0.02 (1)	−0.01 (1)	0.04 (1)
C(421)	0.864 (1)	0.1753 (8)	0.0230 (8)	0.06 (1)	0.09 (1)	0.06 (1)	0.04 (1)	0.022 (9)	0.009 (9)
C(422)	0.930 (1)	0.2247 (9)	0.0720 (8)	0.07 (1)	0.08 (1)	0.12 (1)	−0.01 (1)	0.04 (1)	0.02 (1)
C(423)	1.039 (1)	0.252 (1)	0.0572 (9)	0.07 (1)	0.11 (1)	0.16 (2)	0.02 (1)	0.06 (1)	0.06 (1)
C(424)	1.070 (2)	0.230 (1)	−0.0044 (9)	0.13 (2)	0.14 (2)	0.15 (2)	0.05 (2)	0.08 (2)	0.09 (1)
C(425)	1.001 (2)	0.176 (1)	−0.0492 (8)	0.11 (2)	0.18 (2)	0.10 (2)	0.05 (2)	0.04 (1)	0.03 (1)
C(426)	0.897 (2)	0.151 (1)	−0.0369 (7)	0.10 (2)	0.20 (2)	0.06 (1)	0.05 (2)	0.04 (1)	0.04 (1)
C(431)	0.704 (2)	0.0517 (7)	−0.0032 (6)	0.17 (2)	0.05 (1)	0.039 (9)	0.02 (1)	0.02 (1)	0.000 (8)
C(432)	0.602 (2)	0.0289 (8)	−0.0392 (6)	0.17 (2)	0.09 (1)	0.04 (1)	−0.06 (1)	0.04 (1)	−0.019 (9)
C(433)	0.587 (2)	−0.051 (1)	−0.0706 (7)	0.19 (2)	0.12 (2)	0.05 (1)	−0.03 (2)	0.06 (1)	0.01 (1)

Table I (*Continued*)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(434)	0.673 (2)	−0.097 (1)	−0.0629 (8)	0.21 (3)	0.14 (2)	0.08 (1)	−0.04 (2)	0.00 (2)	0.03 (1)
C(435)	0.776 (3)	−0.074 (1)	−0.031 (1)	0.35 (4)	0.07 (1)	0.15 (2)	0.07 (2)	0.01 (2)	0.03 (1)
C(436)	0.798 (2)	0.005 (1)	0.0023 (9)	0.26 (3)	0.08 (1)	0.09 (1)	0.06 (2)	−0.04 (2)	−0.01 (1)
O(501)	0.5989 (8)	0.1841 (4)	0.3090 (4)	0.064 (8)	0.037 (5)	0.051 (6)	−0.005 (5)	−0.009 (5)	0.009 (5)
O(502)	0.6858 (8)	0.1159 (5)	0.2302 (4)	0.060 (8)	0.063 (7)	0.064 (6)	0.021 (6)	0.016 (6)	0.034 (5)
O(503)	0.4709 (8)	0.3236 (5)	0.2681 (4)	0.056 (7)	0.057 (6)	0.054 (6)	0.013 (6)	0.001 (5)	0.026 (5)
O(504)	0.5328 (8)	0.2411 (5)	0.1903 (4)	0.046 (7)	0.064 (6)	0.066 (6)	0.019 (6)	0.011 (6)	0.030 (5)
C(501)	0.598 (1)	0.1359 (6)	0.2578 (5)	0.06 (1)	0.034 (8)	0.045 (8)	0.018 (8)	0.002 (8)	0.021 (7)
C(502)	0.485 (1)	0.0951 (7)	0.2317 (5)	0.05 (1)	0.07 (1)	0.033 (8)	−0.008 (9)	0.006 (8)	0.001 (7)
C(503)	0.495 (1)	0.0168 (7)	0.2197 (6)	0.10 (1)	0.05 (1)	0.06 (1)	−0.03 (1)	0.00 (1)	0.007 (8)
C(504)	0.392 (2)	−0.0277 (9)	0.2035 (7)	0.11 (2)	0.09 (1)	0.06 (1)	−0.02 (1)	0.00 (1)	0.01 (1)
C(505)	0.287 (2)	0.0041 (9)	0.2007 (7)	0.14 (2)	0.08 (1)	0.07 (1)	−0.05 (1)	0.00 (1)	0.02 (1)
C(506)	0.278 (1)	0.0823 (9)	0.2102 (7)	0.07 (1)	0.10 (1)	0.06 (1)	−0.04 (1)	−0.01 (1)	0.022 (9)
C(507)	0.170 (1)	0.116 (1)	0.2073 (7)	0.06 (1)	0.15 (2)	0.08 (1)	−0.02 (1)	0.01 (1)	0.03 (1)
C(508)	0.162 (1)	0.195 (1)	0.2197 (7)	0.04 (1)	0.13 (2)	0.08 (1)	0.00 (1)	0.01 (1)	0.02 (1)
C(509)	0.260 (1)	0.2415 (9)	0.2304 (6)	0.01 (1)	0.13 (1)	0.06 (1)	0.01 (1)	−0.003 (8)	0.02 (1)
C(510)	0.366 (1)	0.2105 (7)	0.2308 (6)	0.05 (1)	0.037 (8)	0.052 (9)	−0.029 (8)	0.000 (8)	0.008 (7)
C(511)	0.465 (1)	0.2597 (7)	0.2308 (6)	0.05 (1)	0.052 (9)	0.042 (8)	0.023 (9)	0.011 (8)	0.005 (7)
C(512)	0.378 (1)	0.1314 (8)	0.2249 (5)	0.06 (1)	0.09 (1)	0.018 (8)	−0.02 (1)	−0.007 (8)	0.007 (7)
O(601)	0.8058 (8)	0.3390 (6)	0.4163 (4)	0.054 (8)	0.135 (9)	0.066 (7)	0.019 (7)	0.018 (6)	0.068 (7)
O(602)	0.7106 (7)	0.3657 (5)	0.3326 (4)	0.034 (7)	0.089 (7)	0.040 (5)	0.000 (6)	0.000 (5)	0.026 (5)
O(603)	0.9097 (8)	0.2698 (5)	0.2901 (4)	0.045 (7)	0.061 (6)	0.065 (6)	0.006 (6)	0.007 (5)	0.031 (5)
O(604)	0.7979 (8)	0.2831 (5)	0.2054 (4)	0.059 (8)	0.064 (7)	0.052 (6)	0.011 (6)	−0.001 (5)	0.012 (5)
C(601)	0.797 (1)	0.3744 (7)	0.3735 (6)	0.03 (1)	0.07 (1)	0.042 (8)	0.011 (9)	0.010 (8)	0.008 (7)
C(602)	0.887 (1)	0.4326 (7)	0.3719 (5)	0.016 (9)	0.051 (9)	0.053 (9)	0.021 (8)	0.005 (7)	0.012 (7)
C(603)	0.906 (1)	0.4858 (8)	0.4286 (7)	0.06 (1)	0.06 (1)	0.07 (1)	0.02 (1)	−0.01 (1)	−0.012 (9)
C(604)	0.980 (1)	0.5480 (9)	0.4317 (8)	0.06 (1)	0.08 (1)	0.11 (1)	0.01 (1)	−0.01 (1)	0.02 (1)
C(605)	1.029 (1)	0.5573 (7)	0.3804 (7)	0.06 (1)	0.04 (1)	0.12 (1)	0.012 (9)	0.00 (1)	0.009 (9)
C(606)	1.009 (1)	0.5016 (7)	0.3227 (7)	0.04 (1)	0.047 (9)	0.09 (1)	−0.007 (8)	−0.003 (9)	0.023 (8)
C(607)	1.055 (1)	0.5138 (8)	0.2684 (8)	0.07 (1)	0.08 (1)	0.11 (1)	0.00 (1)	0.01 (1)	0.04 (1)
C(608)	1.035 (1)	0.4629 (9)	0.2116 (8)	0.06 (1)	0.09 (1)	0.13 (2)	0.01 (1)	0.03 (1)	0.06 (1)
C(609)	0.969 (1)	0.3941 (8)	0.2056 (6)	0.03 (1)	0.11 (1)	0.08 (1)	0.01 (1)	0.032 (9)	0.05 (1)
C(610)	0.925 (1)	0.3803 (6)	0.2586 (6)	0.018 (9)	0.039 (9)	0.061 (9)	−0.002 (7)	−0.005 (7)	0.019 (7)
C(611)	0.870 (1)	0.3059 (7)	0.2523 (6)	0.04 (1)	0.048 (9)	0.057 (9)	0.020 (8)	0.021 (8)	0.016 (7)
C(612)	0.939 (1)	0.4357 (7)	0.3174 (6)	0.017 (9)	0.049 (9)	0.07 (1)	0.000 (8)	−0.007 (8)	0.024 (8)
C(701)	0.270 (2)	0.638 (1)	0.215 (1)	0.10 (2)	0.13 (2)	0.21 (2)	0.01 (2)	0.04 (2)	0.04 (2)
C(702)	0.299 (2)	0.702 (1)	0.263 (1)	0.15 (3)	0.21 (3)	0.18 (2)	0.01 (2)	−0.02 (2)	0.09 (2)
C(703)	0.262 (2)	0.775 (1)	0.253 (1)	0.19 (3)	0.18 (2)	0.15 (2)	0.01 (2)	0.02 (2)	0.01 (2)
C(704)	0.192 (2)	0.777 (1)	0.202 (1)	0.18 (3)	0.16 (2)	0.17 (2)	−0.04 (2)	0.00 (2)	0.01 (2)
C(705)	0.159 (2)	0.714 (1)	0.157 (1)	0.17 (3)	0.16 (2)	0.20 (2)	0.00 (2)	0.01 (2)	0.09 (2)
C(706)	0.200 (2)	0.647 (1)	0.165 (1)	0.16 (2)	0.17 (2)	0.16 (2)	0.01 (2)	0.03 (2)	0.02 (2)
C(801)	0.248 (2)	0.114 (1)	0.855 (1)	0.30 (3)	0.19 (3)	0.18 (2)	0.12 (2)	0.18 (2)	0.08 (2)
C(802)	0.228 (2)	0.173 (1)	0.834 (1)	0.12 (2)	0.32 (3)	0.12 (2)	−0.03 (2)	0.06 (2)	0.05 (2)
C(803)	0.134 (2)	0.168 (1)	0.793 (1)	0.15 (3)	0.29 (2)	0.12 (2)	−0.05 (2)	0.06 (2)	0.01 (2)
C(804)	0.077 (2)	0.107 (2)	0.775 (1)	0.18 (2)	0.22 (3)	0.16 (2)	−0.10 (2)	0.10 (2)	−0.05 (2)
C(805)	0.092 (2)	0.042 (1)	0.793 (1)	0.20 (3)	0.24 (3)	0.19 (3)	−0.03 (2)	0.16 (3)	−0.06 (2)
C(806)	0.200 (2)	0.045 (1)	0.838 (1)	0.18 (3)	0.14 (2)	0.26 (3)	0.05 (2)	0.16 (3)	0.01 (2)

[a] The temperature factor has the form of exp(−T), where $T = 2\pi^2 \Sigma_{ij} h_i h_j U_{ij} a^*_i a^*_j$, for anisotropic atoms. a^*_i are reciprocal axial lengths and h_i are Miller indices. The esd of the last significant digit is given in parentheses.

the four shortest Ag–Ag distances ranging from 3.672 (2) to 3.961 (2) Å (see Table III).

The structure contains two interesting structural features: (i) the different coordination geometry of each of the four silver atoms and (ii) the type of coordination behavior of the naphthalenecarboxylato ligand as a consequence of the constraint of the aromatic ring system.

Coordination of Silver. The four independent silver atoms are surrounded by one phosphorus and either three or four oxygen atoms; see Figure 4. The geometry of the phosphorus atoms is slightly distorted from tetrahedral, which is normally found for triphenylphosphine–metal 1B complexes.[21] The Ag–P distances, which are somewhat shorter than the sum of the single-bond covalent radii (2.44 Å[22]), are comparable to the Ag–P distance in $AgNO_3 \cdot PPh_3$ (2.369 (6) Å)[21] and shorter than the Ag–P distance found in other (triphenylphosphine)silver(I) compounds: $(PPh_3)_4Ag_4I_4$, 2.455 (5) Å;[23] $[(Ph_3P)_2AgNCS]_2$, 2.455 (3), 2.503 (5) Å;[24] $[(Ph_3P)_2Ag]_2Ni(S_2C{=}C(CN)_2)$, 2.465 (3) Å.[25] The Ag–O bond distances, which are comparable to those observed in ionic silver complexes with oxyanions (nitrate,[21,27] chlorite[28]), are rather long as compared with the distances in other (carboxylato)silver complexes. This combination of longer Ag–O distances and short Ag–P distance is found in complexes such as $AgNO_3 \cdot PPh_3$[21] and can be interpreted in terms of a weak ionic interaction of Ph_3PAg cationic units containing a strong covalent Ag–P bond with the other oxygen-containing ligands. That the interaction between silver and oxygen must be weak is illustrated by the invariancy of the C–O distances even for the uncoordinated oxygen atom O(601). The bonding in the present complex can be regarded to involve overlap of an sp^3 hybrid orbital on phosphorus with a $d_{z^2}sp_z$-type hybrid orbital on silver having much s character. ^{31}P NMR spectroscopic data support this view (vide infra).

An interesting aspect of the coordination about silver is the different mode of interaction of each of the silver atoms with the oxygen-containing ligands (Figure 3). The coordination of the carboxylato groups with Ag(1) is comparable with the coordination of the NO_3 ions with silver in $AgNO_3 \cdot PPh_3$:[21] both contain one chelating and one monodentate ligand. For metal 1B carboxylates $(Ph_3P)_2Cu(O_2CCH_3)$[29] is the only precedent for which the presence of a chelating carboxylato group has been established, while for $(Ph_3P)_2Ag(O_2CR)$[30] chelation is proposed. Chelation also occurs at Ag(2). Furthermore, Ag(2) is coordinated by two monodentate carboxylato groups of the second naphthalenedicarboxylato

Table II. Bond Distances (A) and Bond Angles (deg) for $(C_{12}H_6O_4)_2(AgPPh_3)_4 \cdot 2C_6H_6$[a]

	Distances from the Silver Atoms		
Ag(1)-P(1)	2.378 (5)	Ag(3)-P(3)	2.342 (4)
Ag(1)-O(501)	2.516 (9)	Ag(3)-O(501)	2.519 (8)
Ag(1)-O(502)	2.614 (8)	Ag(3)-O(503)	2.466 (9)
Ag(1)-O(603)	2.278 (9)	Ag(3)-O(602)	2.264 (9)
Ag(2)-P(2)	2.346 (5)	Ag(4)-P(4)	2.363 (4)
Ag(2)-O(503)	2.500 (9)	Ag(4)-O(502)	2.249 (9)
Ag(2)-O(504)	2.628 (9)	Ag(4)-O(504)	2.564 (9)
Ag(2)-O(602)	2.334 (8)	Ag(4)-O(604)	2.328 (8)
Ag(4)-O(604)	2.445 (9)		
	Distances from the Phosphorus Atoms		
P(1)-C(111)	1.85 (2)	P(3)-C(311)	1.79 (1)
P(1)-C(121)	1.82 (1)	P(3)-C(321)	1.83 (1)
P(1)-C(131)	1.84 (1)	P(3)-C(331)	1.82 (1)
P(2)-C(211)	1.84 (2)	P(4)-C(411)	1.82 (2)
P(2)-C(221)	1.82 (1)	P(4)-C(421)	1.83 (2)
P(2)-C(231)	1.81 (1)	P(4)-C(431)	1.83 (1)
	Distances within Naphthalenedicarboxylic Ligands		
O(501)-C(501)	1.27 (1)	O(601)-C(601)	1.26 (2)
O(502)-C(501)	1.26 (2)	O(602)-C(601)	1.27 (2)
O(503)-C(511)	1.27 (1)	O(603)-C(611)	1.24 (2)
O(504)-C(511)	1.25 (2)	O(604)-C(611)	1.26 (1)
C(501)-C(502)	1.52 (2)	C(601)-C(602)	1.52 (2)
C(502)-C(503)	1.41 (2)	C(602)-C(603)	1.40 (2)
C(502)-C(512)	1.44 (2)	C(602)-C(612)	1.42 (2)
C(503)-C(504)	1.43 (2)	C(603)-C(604)	1.42 (2)
C(504)-C(505)	1.37 (3)	C(604)-C(605)	1.37 (3)
C(505)-C(506)	1.41 (2)	C(605)-C(606)	1.44 (2)
C(506)-C(507)	1.42 (2)	C(606)-C(607)	1.43 (2)
C(506)-C(512)	1.45 (2)	C(606)-C(612)	1.45 (2)
C(507)-C(508)	1.42 (3)	C(607)-C(608)	1.38 (2)
C(508)-C(509)	1.41 (2)	C(608)-C(609)	1.45 (2)
C(509)-C(510)	1.38 (2)	C(609)-C(610)	1.40 (2)
C(510)-C(511)	1.48 (2)	C(610)-C(611)	1.49 (2)
C(510)-C(512)	1.44 (2)	C(610)-C(612)	1.45 (2)
	Angles around Silver Atoms		
P(1)-Ag(1)-O(501)	116.3 (2)	O(504)-Ag(2)-O(604)	77.8 (3)
P(1)-Ag(1)-O(502)	115.4 (2)	O(602)-Ag(2)-O(604)	82.2 (3)
P(1)-Ag(1)-O(603)	126.6 (3)	P(3)-Ag(3)-O(501)	112.3 (2)
O(501)-Ag(1)-O(502)	51.7 (3)	P(3)-Ag(3)-O(503)	126.5 (2)
O(501)-Ag(1)-O(603)	116.9 (3)	P(3)-Ag(3)-O(602)	144.2 (2)
O(502)-Ag(1)-O(603)	101.0 (3)	O(501)-Ag(3)-O(503)	80.9 (3)
P(2)-Ag(2)-O(503)	119.3 (2)	O(501)-Ag(3)-O(602)	93.7 (3)
P(2)-Ag(2)-O(504)	125.2 (2)	O(503)-Ag(3)-O(602)	80.2 (3)
P(2)-Ag(2)-O(602)	130.9 (2)	P(4)-Ag(4)-O(502)	143.9 (2)
P(2)-Ag(2)-O(604)	117.9 (3)	P(4)-Ag(4)-O(504)	117.3 (2)
O(503)-Ag(2)-O(504)	50.8 (3)	P(4)-Ag(4)-O(604)	112.0 (3)
O(503)-Ag(2)-O(602)	78.1 (3)	O(502)-Ag(4)-O(504)	81.9 (3)
O(503)-Ag(2)-O(604)	118.1 (3)	O(502)-Ag(4)-O(604)	100.7 (3)
O(504)-Ag(2)-O(602)	101.8 (3)	O(504)-Ag(4)-O(604)	81.2 (3)
	Angles around Phosphorus Atoms		
Ag(1)-P(1)-C(111)	116.3 (5)	Ag(3)-P(3)-C(311)	115.7 (4)
Ag(1)-P(1)-C(121)	113.9 (5)	Ag(3)-P(3)-C(321)	115.5 (4)
Ag(1)-P(1)-C(131)	113.4 (4)	Ag(3)-P(3)-C(331)	109.9 (4)
C(111)-P(1)-C(121)	103.7 (6)	C(311)-P(3)-C(321)	105.5 (6)
C(111)-P(1)-C(131)	104.2 (6)	C(311)-P(3)-C(331)	104.5 (6)
C(121)-P(1)-C(131)	104.0 (6)	C(321)-P(3)-C(331)	104.5 (5)
Ag(2)-P(2)-C(211)	113.6 (5)	Ag(4)-P(4)-C(411)	111.2 (4)
Ag(2)-P(2)-C(221)	110.7 (6)	Ag(4)-P(4)-C(421)	114.3 (4)
Ag(2)-P(2)-C(231)	117.0 (5)	Ag(4)-P(4)-C(431)	117.5 (5)
C(211)-P(2)-C(221)	105.2 (6)	C(411)-P(4)-C(421)	104.6 (7)
C(211)-P(2)-C(231)	103.4 (6)	C(411)-P(4)-C(431)	104.4 (7)
C(221)-P(2)-C(231)	106.0 (6)	C(421)-P(4)-C(431)	103.5 (8)
	Angles around Oxygen Atoms		
Ag(1)-O(501)-Ag(3)	97.1 (3)	Ag(2)-O(504)-C(511)	90.8 (7)
Ag(1)-O(501)-C(501)	93.5 (8)	Ag(4)-O(504)-C(511)	151.0 (9)
Ag(3)-O(501)-C(501)	151.7 (8)	Ag(2)-O(602)-Ag(3)	106.0 (3)
Ag(1)-O(502)-Ag(4)	108.8 (3)	Ag(2)-O(602)-C(601)	145.8 (9)
Ag(1)-O(502)-C(501)	89.1 (6)	Ag(3)-O(602)-C(601)	107.8 (8)
Ag(4)-O(502)-C(501)	114.0 (8)	Ag(1)-O(603)-C(611)	126.4 (9)
Ag(2)-O(503)-Ag(3)	95.3 (3)	Ag(2)-O(604)-Ag(4)	105.2 (4)
Ag(2)-O(503)-C(511)	96.3 (8)	Ag(2)-O(604)-C(611)	101.2 (7)
Ag(3)-O(503)-C(511)	109.7 (8)	Ag(4)-O(604)-C(611)	138.1 (9)
Ag(2)-O(504)-Ag(4)	93.9 (3)		

Table II (*Continued*)

Angles within Naphthalenedicarboxylic Ligands

O(501)-C(501)-O(502)	125 (1)	O(601)-C(601)-O(602)	122 (1)
O(501)-C(501)-C(501)	116 (1)	O(601)-C(601)-C(602)	120 (1)
O(502)-C(501)-C(502)	119 (1)	O(602)-C(601)-C(602)	118 (1)
O(503)-C(511)-O(504)	122 (1)	O(603)-C(611)-O(604)	127 (1)
O(503)-C(511)-C(512)	118 (1)	O(603)-C(611)-C(612)	115 (1)
O(504)-C(511)-C(512)	120 (1)	O(604)-C(611)-C(612)	117 (1)
C(501)-C(502)-C(503)	112 (1)	C(601)-C(602)-C(603)	113 (1)
C(501)-C(502)-C(512)	124 (1)	C(601)-C(602)-C(612)	123 (1)
C(502)-C(503)-C(504)	123 (1)	C(602)-C(603)-C(604)	124 (1)
C(503)-C(504)-C(505)	122 (1)	C(603)-C(604)-C(605)	121 (1)
C(504)-C(505)-C(506)	121 (2)	C(604)-C(605)-C(606)	119 (1)
C(505)-C(506)-C(507)	121 (2)	C(605)-C(606)-C(607)	119 (1)
C(505)-C(506)-C(512)	121 (1)	C(605)-C(606)-C(612)	122 (1)
C(507)-C(506)-C(512)	117 (1)	C(607)-C(606)-C(612)	119 (1)
C(506)-C(507)-C(508)	121 (1)	C(606)-C(607)-C(608)	121 (1)
C(507)-C(508)-C(509)	121 (1)	C(607)-C(608)-C(609)	121 (2)
C(508)-C(509)-C(510)	120 (1)	C(608)-C(609)-C(610)	119 (1)
C(509)-C(510)-C(511)	118 (1)	C(609)-C(610)-C(611)	117 (1)
C(503)-C(502)-C(512)	123 (1)	C(603)-C(602)-C(612)	124 (1)
C(509)-C(510)-C(512)	120 (1)	C(609)-C(610)-C(612)	120 (1)
C(511)-C(510)-C(512)	122 (1)	C(611)-C(610)-C(612)	122 (1)
C(502)-C(512)-C(506)	115 (1)	C(602)-C(612)-C(606)	115 (1)
C(502)-C(512)-C(510)	125 (1)	C(602)-C(612)-C(610)	126 (1)
C(506)-C(512)-C(510)	120 (1)	C(606)-C(612)-C(610)	119 (1)

[a] Selection from the complete table which is available as supplementary material.

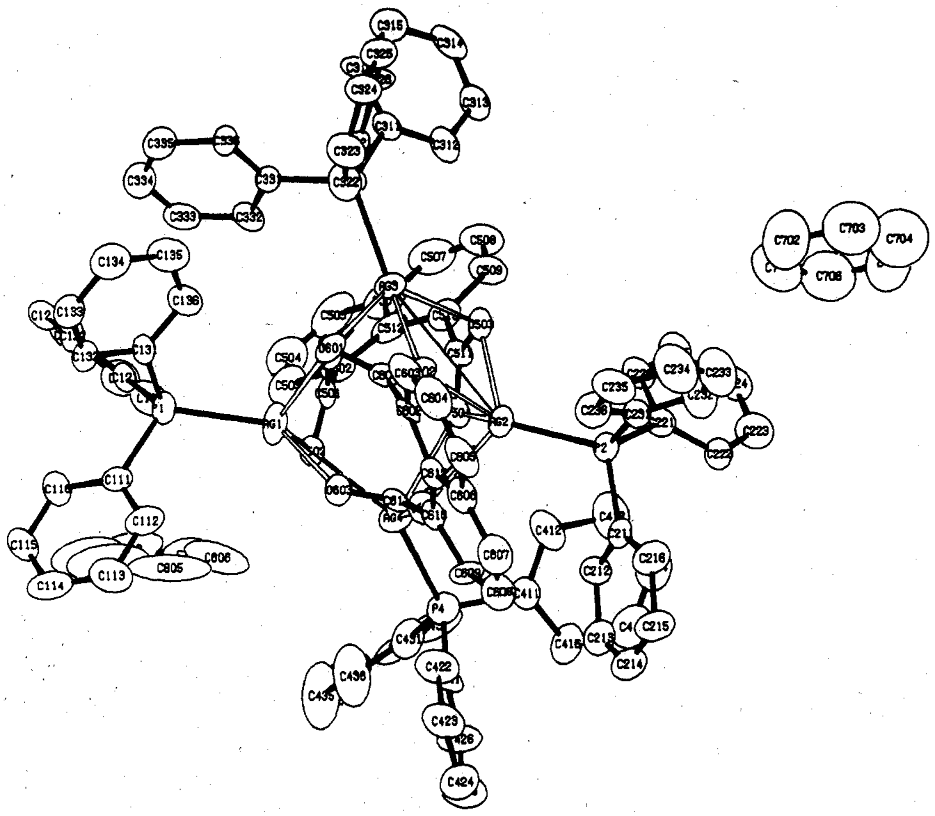

Figure 1. Molecular structure and adopted numbering scheme of $(Ph_3PAg)_4(O_4C_{12}H_6)_2{\cdot}2C_6H_6$ (ORTEP diagram, 40% probability ellipsoids).

Table III. Ag-Ag Distances (Å) in $[(Ph_3PAg)_4(O_4C_{12}H_6)_2]{\cdot}2C_6H_6$

Ag(1)-Ag(2)	4.754 (2)	Ag(2)-Ag(3)	3.672 (2)
Ag(1)-Ag(3)	3.773 (2)	Ag(2)-Ag(4)	3.793 (2)
Ag(1)-Ag(4)	3.961 (2)	Ag(3)-Ag(4)	5.388 (2)

ligand. Both Ag(1) and Ag(2) display the greatest P–Ag–O angle for the shortest Ag–O distance, which is in line with the tendency of Ag(1) to coordinate linearly.[31] Further it is clear that the chelating carboxylato groups have the longer Ag–O distances, which moreover are unequal, thus resulting in an asymmetric chelation. Ag(3) and Ag(4) are both coordinated by three monodentate carboxylato groups. Their O–Ag–O coordination angles vary slightly from 90°, which can be interpreted in terms of coordination of the oxygen atoms to silver via hybrid orbitals at silver having much p character.

The Naphthalenedicarboxylic Ligands. The naphthalene rings in both naphthalenedicarboxylic ligands are distorted. The in-plane deformation, which is illustrated by interatomic distances and bond angles in Figure 4, is a feature normally observed for 1,8-disubstituted naphthalene compounds, e.g., 1,8-diphenylnaphthalene[32] and bis(diseleno)bis(1,8-dimethylnaphthalene).[33] The out-of-plane deformation is rather pronounced as appears from the deviations of the carboxylic

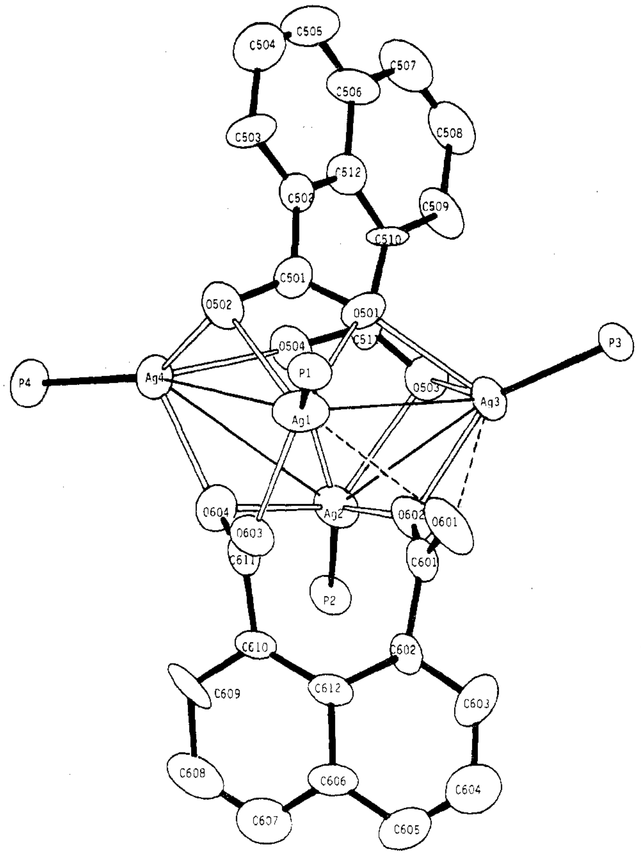

Figure 2. Central part of the molecule $(Ph_3PAg)_4(O_4C_{12}H_6)_2$. The phenyl rings are omitted for clarity. The silver atoms are interconnected in order to indicate their butterfly arrangement; however, no silver–silver interaction is suggested.

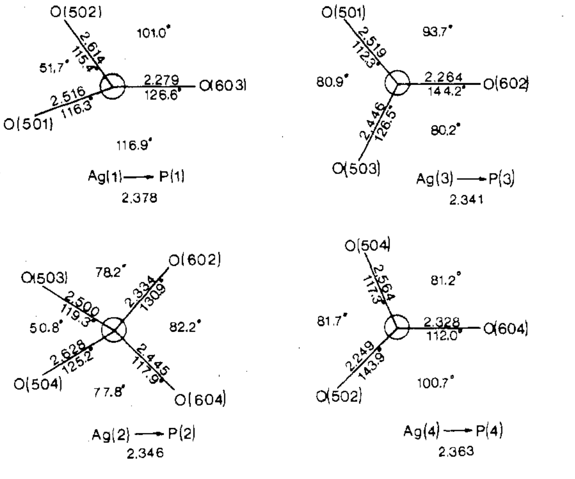

Figure 3. Coordination about the silver atoms projected along the Ag–P bonds. The numbers above, below, and between the Ag–O bars indicate the Ag–O distance (Å), the P–Ag–O angle (deg), and the O–Ag–O angle (deg), respectively (standard deviations are 9, 3, and 3, respectively).

C atoms from the least-squares naphthalene planes: C(501), 0.337 Å; C(511), −0.393 Å; C(601), 0.286 Å; C(611), −0.300 Å. The corresponding deviations for the methyl carbon atoms in 1,8-dimethylnaphthalene are only +0.097 and −0.008 Å.[34]

The carboxylic groups are rotated with respect to the naphthalene plane: C(501)–C(502), 55.7°; C(510)–C(511), 50.6°; C(601)–C(602), 43.9°; C(611)–C(610), 28.5°. The difference in the amount of distortion found in each of the two naphthalenedicarboxylic ligands is reflected in the different mode of coordination. O(601) reveals a shortest Ag–O distance of 2.90 Å, whereas O(603) is coordinated to only one silver atom (2.28 Å). The remaining two oxygen atoms of the same naphthalenedicarboxylic ligand as well as the oxygen atoms of the second naphthalenedicarboxylic ligand coordinate with two silver atoms. Nevertheless, the in-plane deformations of the two naphthalene fragments appear to be similar which indicates that the deformations are intrinsic to the ligand and not caused by the strength of the coordination of the carboxylato groups with the silver atoms.

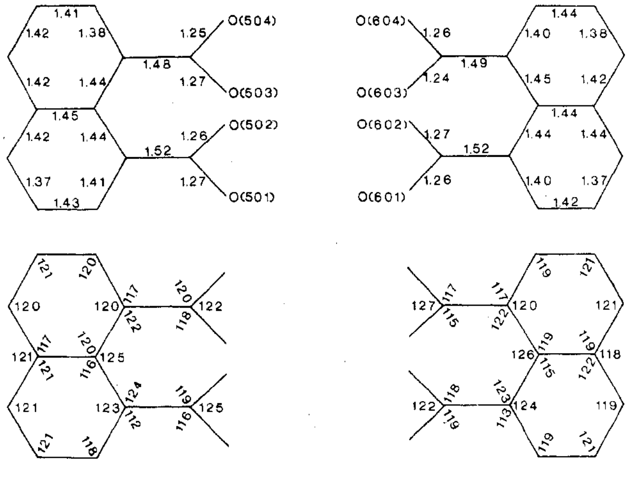

Figure 4. Bond lengths (Å) and bond angles (deg) in the two naphthalenedicarboxylato systems (standard deviations are 2 and 1.5, respectively).

The Ag–Ag distances (3.672–3.961 Å) are much longer than the M–M distances found in the complexes $Ag_2(O_2CCF_3)_2{\cdot}C_6H_6$ (2.851 Å)[35] and $Cu_4(O_2CC_6H_5)_4$ (3.07 (1) Å).[7] In the copper complex, which has two bridging benzoato groups at each side of the central Cu_4 square, the phenyl nuclei are coplanar with the CO_2 groups and are slightly bent away from each other. This striking difference with the structural features of the present complex can be ascribed to the fact that both CO_2 groups are part of the same ligand system. This fact together with the strong silver–phosphine interaction may account for the greater stability of the O_8 core surrounded by four Ag atoms resulting in long Ag–Ag distances as compared with those for a structure consisting of a square of silver atoms, having shorter Ag–Ag distances, bicapped by two naphthalenedicarboxylato ligands.

Structural Features of (Naphthalenedicarboxylato)- and (Acetato)silver Phosphines in Solution. Similar complexes of $Ag_2(O_4C_{12}H_6)$ with the phosphines PPh_3, $P(p\text{-tol})_3$, dppm, and dppe with 1/1 silver-to-phosphorus ratio were prepared. The two bidentate phosphines were chosen because of the difference in preferential coordination mode. dppm normally acts as a bridging ligand,[36] while dppe prefers to act as a chelating ligand.[37] The bidentate phosphine complexes were synthesized in order to investigate their influence on the stability of the tetranuclear molecules. Complexes of AgOAc with dppm and dppe were isolated to compare the behavior of these phosphines with polynuclear silver carboxylates containing monocarboxylic ligands or dicarboxylic ligands containing fixed geometry. The structure of these complexes in the solid state and solution are compared.

$(Ph_3PAg)_4(O_4C_{12}H_6)_2$ and $((p\text{-tol})_3PAg)_4(O_4C_{12}H_6)_2$. The compounds $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ and $((p\text{-tol})_3PAg)_4(O_4C_{12}H_6)_2$, which were prepared by direct reaction of $Ag_2(O_4C_{12}H_6)$ with the phosphines in benzene, show great similarity in their solid-state IR and solution ^{31}P NMR spectra. The presence of different modes of coordination of the carboxylato groups—monodentate, bidentate chelating, and bridging, which has been established by the X-ray structure for $(Ph_3Ag)_4(O_4C_{12}H_6)_2$—can also be deduced partly from the

Table IV. IR Vibrations in the $\nu(CO_2)$ Region (cm^{-1})

complex	frequency
$(Ph_3PAg)_4(O_4C_{12}H_6)_2$	1560, 1401, 1346
$((p\text{-tol})_3PAg)_4(O_4C_{12}H_6)_2$	1565, 1399, 1348
$(dppmAg_2)(O_4C_{12}H_6)$	1570, 1400, 1380, 1328
$(dppeAg_2)(O_4C_{12}H_6)$	1555, 1408, 1348
$(dppmAg_2)(O_2CCH_3)_2$	1550, 1385
$(dppeAg_2)(O_2CCH_3)_2$	1550, 1401

Table V. ^{31}P NMR Results

complex	solvent	t, °C	δ	$J(^{107}Ag-^{31}P)$, Hz
$(Ph_3PAg)_4(O_4C_{12}H_6)_2$	CD_2Cl_2	−25	9.58	650
$((p\text{-tol})_3PAg)_4(O_4C_{12}H_6)_2$	$CDCl_3$	−36	10.44	682
$(dppeAg_2)(O_4C_{12}H_6)$	$CDCl_3$	−36	4.56	230
$(dppmAg_2)(O_2CCH_3)_2$[a]	CD_2Cl_2	−50	3.3	663
$(dppeAg_2)(O_2CCH_3)_2$	CD_2Cl_2	−80	6.5	680[b]

[a] Data used for simulation: $^1J(^{107}Ag-^{31}P) = 663$ Hz, $^1J(^{109}Ag-^{31}P) = 760$ Hz, $^2J(^{31}P-^{31}P) = 175$ Hz. [b] The two doublets due to coupling with ^{107}Ag and ^{109}Ag are still not completely resolved at this temperature.

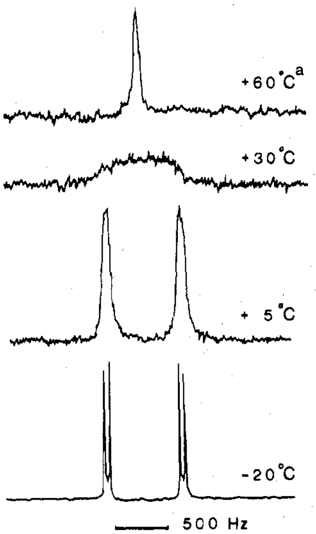

Figure 5. ^{31}P NMR spectrum of $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ in CD_2Cl_2. The spectrum at 60 °C (a) is recorded in $CDCl_3$.

IR spectra (Table IV). Besides a broad band near 1560 cm^{-1} due to $\nu_{asym}(CO_2)$, two bands near 1400 and 1340 cm^{-1} are found which can be assigned to $\nu_{sym}(CO_2)$.[38]

The ^{31}P NMR spectra are temperature dependent, as is shown for $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ in Figure 5. At high temperature, only one singlet is observed, which must be ascribed to a process involving dissociation of the Ag–P bonds. The dissociation strongly depends on the type of solvent used, which is clearly illustrated by the higher coalescence temperature for CD_2Cl_2 (30 °C) as compared with that for $CDCl_3$ (5 °C). Molecular weight data of solutions of $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ in $CHCl_3$ at 26 °C are concentration dependent which likewise points to dissociation.

At low temperature all four phosphines are equivalent while the Ag–P bond does not dissociate on the NMR time scale and this results in a four-line spectrum by coupling of the phosphorus atom with silver. The high value found for the ^1J(Ag–P) coupling in $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ and in $((p\text{-tol})_3PAg)_4(O_4C_{12}H_6)_2$ (Table V) as compared with J(Ag–P) of other silver phosphine compounds, such as 451 Hz for $((p\text{-tol})_3P)_2Ag(O_2CCF_3)$[39] and 394 Hz for $[Ag(PPh_3)_2Ni(S_2C_2(CN)_2)_2]$,[40] is indicative[41] of bonding of the phosphorus atoms via an orbital at silver having much s character which is consistent with the description of the bonding in $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ in the solid state.

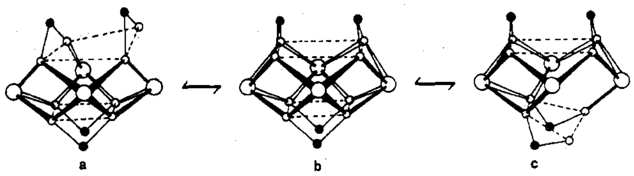

Figure 6. Proposed intramolecular rearrangement for $(Ph_3PAg)_4(O_4C_{12}H_6)_2$ in solution (see text). (Schematic representation of the central part of the molecule consisting of four silver atoms and four carboxylato groups; the dotted lines connect the four oxygen atoms of the same naphthalenedicarboxylato ligand; ◯ = Ag, ○ = O, ● C.)

At low temperature no intermolecular exchange with free phosphine is observed which indicates that another process renders these phospines equivalent. Figure 6a shows a schematical representation of the central part of the structure of $(Ph_3PAg)_4(O_4C_{12}H_6)_2$.

This figure reveals that a process by which the coordination of the oxygen atoms changes with a concomitant movement of the naphthalene nuclei produces an intermediate having a symmetric central Ag_4O_8 core (Figure 6b). Starting from this intermediate, the coordination geometry about each of the silver atoms can be interchanged by bending away one of the oxygen atoms, as is illustrated for one case in Figure 6c. The total process can then be interpreted in terms of a waving of the naphthalene moieties above and below the Ag_4 unit.

$(LAg_2)(O_4C_{12}H_6)$ and $(LAg_2)(O_2CCH_3)_2$ (L = dppm, dppe). For $Ag_2(O_4C_{12}H_6)$ the adducts $(dppmAg_2)(O_4C_{12}H_6)$ and $(dppeAg_2)(O_4C_{12}H_6)$ have been isolated. The IR spectra of these compounds resemble those of the PPh_3 and $P(p\text{-tol})_3$ adducts (Table IV), pointing to a similar structure. However, the ^{31}P NMR spectrum of $(dppeAg_2)(O_4C_{12}H_6)$ shows a remarkably low coupling constant $J(^{107}Ag-^{31}P)$ of 230 Hz, which can not be explained even if silver is supposed to be coordinated by two phosphorus atoms. Furthermore, a structure containing bidentate phosphines by bridging two silver atoms in one molecule should lead to a large deformation of the tetranuclear structure found for $(Ph_3PAg)_4(O_4C_{12}H_6)_2$. In order to obtain more information about the structure of these almost insoluble compounds, the corresponding AgOAc complexes were prepared.

The complexes $\{dppmAg_2(OAc)_2\}$ and $\{dppeAg_2(OAc)_2\}$ were isolated by the direct reaction of AgOAc with the bidentate phosphines in benzene. Molecular weight data of solutions in $CHCl_3$ are in accord with the stoichiometry $LAg_2(OAc)_2$, pointing to a structure in which the bidentate phosphines bridge two silver atoms. This is supported by the ^{31}P NMR spectrum of $\{dppeAg_2(OAc)_2\}$ which displays a $J(^{107}Ag-^{31}P)$ of 680 Hz, which is comparable with $J(^{107}Ag-^{31}P)$ found in $(LAg)_4(O_4C_{12}H_6)_2$, L = PPh_3 and $P(p\text{-tol})_3$ (Table V). The bridging nature of dppm in $dppmAg_2(OAc)_2$ is also reflected by the ^{31}P NMR pattern (Figure 7) which consists of AA′XX′ pattern, resulting from the large ^2J(P–P) of 175 Hz, for the three possible combinations of the two silver isotopes. This pattern was unambiguously established by computer simulation (for data, see Table V).

Recently, Oldham[30] reported the formation of monomeric silver complexes with monocarboxylato ligands and two or three triphenylphosphines. These complexes $L_nAg(O_2CR)$ contain either chelating (n = 2) or monodentate bonded (n = 3) carboxylato ligands. CuOAc also reacts with a large number of phosphines yielding complexes with a Cu:P ratio of 1:2 or 1:3, even in the case of dppm or dppe.[42] For the dimeric complex $\{dppmCu(OAc)\}_2$ a structure with chelating phosphines and bridging carboxylato groups was proposed. However, on the basis of the present results the high value

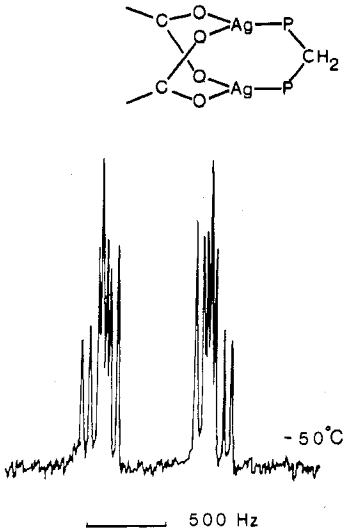

Figure 7. ^{31}P NMR spectrum of $\{dppmAg_2(OAc)_2\}$ in CD_2Cl_2.

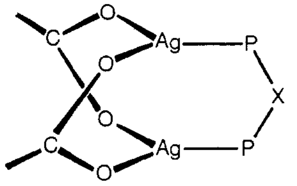

Figure 8. Proposed structure for $\{LAg_2(OAc)_2\}$: X = CH_2, L = dppm; X = C_2H_4, L = dppe.

observed for $\nu_{asym}(CO_2)$ in this complex (1590 cm^{-1}) could better be explained by a structure containing bridging phosphines and monodentate-bonded carboxylato groups. It is then noteworthy that for L = dppm, dppe, and AgOAc only the complexes $\{LAg_2(OAc)_2\}$ with a Ag:P ratio of 1:1 are isolated even under conditions of excess phosphine. On the basis of this different behavior a new structure containing bridging carboxylato groups besides a bridging phosphine is proposed for these complexes (Figure 8). Although a structure containing bidentate carboxylato ligands is supported by the IR data (Table IV), a structure in which the carboxylato groups act as chelating ligands can not be excluded.

It is interesting that reaction of $Ag_2(O_4C_{12}H_6)$ with excess PPh_3 or P(*p*-tol)$_3$ results in the exclusive formation of the complexes with a 1:1 Ag:P ratio. This indicates that, although carboxylato groups are weakly coordinating chelating ligands, phosphines can not successfully compete for coordination sites in $(LAg)_4(O_4C_{12}H_6)_2$ which are occupied by the carboxylic oxygen atoms. This reflects the fact that both carboxylato groups are connected to the same naphthalene skeleton.

The present results show that the use of this type of multidentate ligands having fixed geometry leads to stable polynuclear metal complexes. The scope of this principle is further investigated.[43]

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Registry No. $(C_{12}H_6O_4)_2(Ph_3PAg)_4{\cdot}2C_6H_6$, 69292-09-7; $(C_{12}H_6O_4)_2((p\text{-tol})_3PAg)_4$, 69292-10-0; $(C_{12}H_6O_4)(Ph_2PCH_2CH_2PPh_2)Ag_2$, 69205-06-7; $(C_{12}H_6O_4)(Ph_2PCH_2PPh_2)Ag_2$, 69188-75-6; $(H_3CCO_2)_2Ag_2(Ph_2PCH_2CH_2PPh_2)$, 69155-19-7; $(H_3CCO_2)_2Ag_2(Ph_2PCH_2PPh_2)$, 69155-18-6; $(C_{12}H_6O_4)Ag_2$, 69140-53-0; $(H_3CCO_2)Ag$, 563-63-3.

Supplementary Material Available: A table of observed and calculated structure factors for $(Ph_3PAg)_4(O_4C_{12}H_6)_2{\cdot}2C_6H_6$ and the complete table of interatomic distances and bond angles (64 pages). Ordering information is given on any current masthead page.

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(43) Reaction of $(H_6C_{12}O_4)Ag_2$ with $[RhCl(CO)_2]_2$ yielded $[(H_6C_{12}O_4)\{Rh(CO)_2\}_2]$: ν(CO) 2090, 2080, 2030, and 2010 cm^{-1} and $\nu(CO_2)$ 1540, 1433, and 1352 cm^{-1}, pointing to bidentate coordinated carboxylato groups; the intense bluish black color of the compound indicates a strong metal–metal interaction.[36] Addition of PPh_3 yielded yellow $[(H_6C_{12}O_4)\{Rh(PPh_3)_2CO\}_2]$ in which the carboxylato groups act as monodentate ligands: ν(CO) 1972 cm^{-1}, $\nu(CO_2)$ 1630 and 1312 cm^{-1}, *J*(Rh–P) = 136 Hz (phosphines in trans position).