Oxidation of an *o*-Aminophenol-Derived Schiff-Base Component of a Binucleating Ligand to a Benzoxazole and the Crystal Structures of a Mononuclear Palladium Derivative and a Tetranuclear Pd₂Ag₂ Derivative with an Unusually Short Ag–Ag Distance

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A convenient source of the di-Schiff-base binucleating ligand, L³⁻, derived formally from the condensation of 2 equiv of 2-amino-4,6-di-*tert*-butylphenol with 1 equiv of 2-mercapto-5-methylisophthalaldehyde is provided by the S-protected ligand precursor, III, which with Pd(CH₃CO₂)₂ gave LPd₂(CH₃CO₂) in a one-pot reaction (L³⁻ = C₃₇H₄₇N₂O₂S³⁻). Reaction of triphenylphosphine with LPd₂(CH₃CO₂) in refluxing toluene led to the oxidation of one Schiff base side arm to a benzoxazole, as in complex IV, represented as L_bPd(PPh₃) (in which L_b²⁻ = C₃₇H₄₆N₂O₂S²⁻), whose structure was determined by single-crystal X-ray diffraction. The crystals of C₅₅H₆₁N₂O₂PSPd were rhombohedral, space group R3̄, with *a* = 27.540 (4) Å, α = 117.38°, and Z = 6. The structure was refined to *R* = 0.059 and *R*_w = 0.071 by using 6496 (*I* ≥ 3σ(*I*)) unique reflections. The X-ray study revealed the previously unsuspected benzoxazole residue. L_bPd(PPh₃) was made deliberately by oxidation with lead tetraacetate of (LH)-Pd(PPh₃) (V) (LH²⁻ = C₃₇H₄₈N₂O₂S²⁻), which was obtained by reaction of the ligand precursor, III, with 1 equiv each of Pd(CH₃CO₂)₂ and triphenylphosphine. Reaction of AgClO₄ either with (LH)Pd(PPh₃) (Ag in excess) or with L_bPd(PPh₃) gave [L_bPdAg(PPh₃)]₂(ClO₄)₂, characterized by single-crystal X-ray diffraction: C₁₁₀H₁₂₂Ag₂Cl₂N₄O₁₂P₂Pd₂S₂·~12.5H₂O, monoclinic, space group P2₁/n, *a* = 13.416 (3) Å, *b* = 25.397 (5) Å, *c* = 16.940 (3) Å, β = 96.82 (2)°, Z = 2. The structure was refined to *R* = 0.067 and *R*_w = 0.065 by using 2584 (*I* ≥ 2σ(*I*)) unique reflections. The structure contains centrosymmetric dimeric cations in which monomeric [LPdAg(PPh₃)]⁺ units are linked together by bonds from the sulfur of one to the silver of the other. The Ag–S–Ag angle of 61.9 (1)° is unusually acute and the Ag–Ag distance of 2.779 (3) Å is unusually short.

Introduction

Previous work with dipalladium complexes of binucleating ligands has shown that unusual bridging species can be generated from substrates that provide a good donor to bind to one metal thereby forcing the second metal into close proximity with some other part of the substrate molecule. Thus, for example, the bridge shown in I, was generated from *N*-propyliminazole in a reaction


I
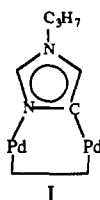
analogous to ortho-metalation.[3,4] The results described in the present paper arose out of attempts to incorporate triphenylphosphine at a dipalladium site in the expectation that the phosphorus would bind to one palladium, forcing the second palladium to interact, possibly in an unusual fashion, with a phenyl ring of the phosphine. These attempts led to the unanticipated oxidation of an *o*-aminophenol-derived Schiff-base side arm of the binucleating ligand to a benzoxazole, which is described below. The synthesis and X-ray crystal structure of a Pd₂Ag₂ derivative of this benzoxazole-containing ligand are also described.

Results and Discussion

The tetra-*tert*-butyl-substituted binucleating ligand represented in the dipalladium complex II was used in the present work in the hope that these substituents would increase the solubilities of the derived complexes in organic solvents. Low solubilities have presented substantial practical problems in related earlier studies. The binucleating ligand component of complex II is represented here as L³⁻ so that II is written LPd₂(Z) (Z being a monoanionic bridging species if the charge on the complex is zero).

II
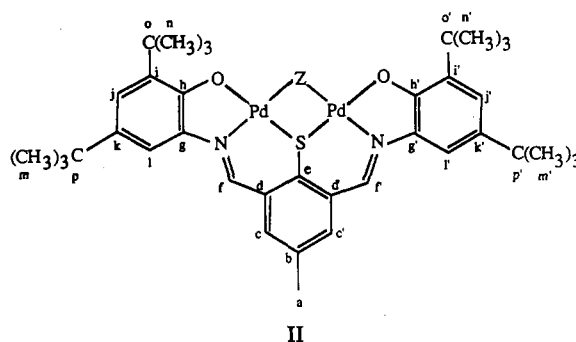
LPd₂(CH₃CO₂) was prepared by reaction of Pd(CH₃CO₂)₂ with the S-protected ligand precursor, III, in which metal-promoted

III
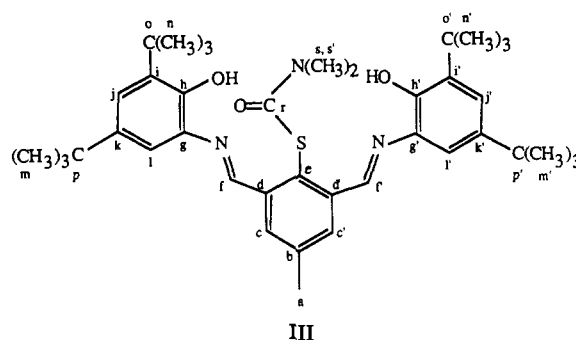
S-deprotection and complex formation occurred in a "one-pot" reaction. In the IR spectrum of the product there was no trace of the ν_co at 1650 cm⁻¹ of the carbamoyl group of III and acetate-derived bands at 1410 and 1550 cm⁻¹(ν_OCO(sym) and -(asym), respectively) were indicative of the three-atom bridging mode, PdOCOPd.[5] The ¹H NMR spectrum (CDCl₃) of LPd₂(CH₃CO₂) showed the acetate protons as a singlet at 1.98 ppm and indicated a symmetrical structure with equivalent ligand side arms; e.g., the two imine protons gave a single peak at 8.25 ppm. It was not

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(3) Robson, R. *Inorg. Chim. Acta* **1982**, *57*, 71.
(4) Hoskins, B. F.; McDonald, I. A. S. *Aust. J. Chem.* **1984**, *37*, 1395.

(5) (a) Louey, M.; Nichols, P. D.; Robson, R. *Inorg. Chim. Acta* **1980**, *47*, 87. (b) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

possible to record a ^{13}C NMR spectrum of $LPd_2(CH_3CO_2)$ because of insufficient solubility in all common NMR solvents, but ^{13}C NMR characterization of the L^{3-} component of a carboxylate-bridged complex was possible with $LPd_2((CH_3)_3CCO_2)$, which was prepared from $LPd_2(CH_3CO_2)$ by reaction with excess pivalic acid in chloroform. $LPd_2(HCO_2)$ was likewise prepared from $LPd_2(CH_3CO_2)$ by reaction with excess formic acid in dioxan. Reaction of $LPd_2(CH_3CO_2)$ with NBu_4I in chloroform and with pyrazole in chloroform afforded $LPd_2(I)$ and $LPd_2(C_3H_3N_2)$ respectively.

The reaction of $LPd_2(CH_3CO_2)$ with triphenylphosphine in refluxing toluene under dinitrogen gave palladium mirrors, and from the reaction filtrate a red crystalline product was obtained whose true nature, namely the benzoxazole IV, was not suspected

IV
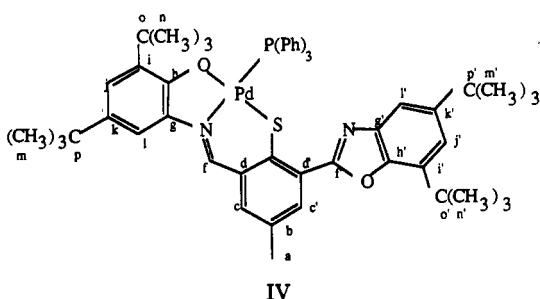
until a single-crystal X-ray diffraction study (below) was completed. A plausible rationalization for the appearance of this product is that the intermediate V with a metal-free Schiff-base

V
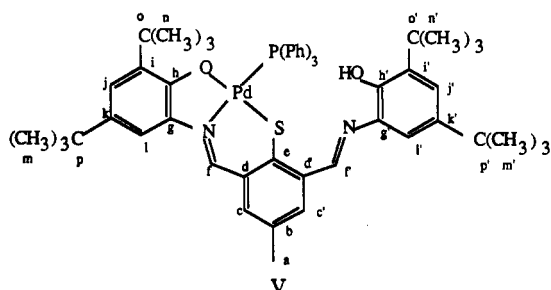
side arm is in equilibrium with the cyclized tautomer VI, which

VI
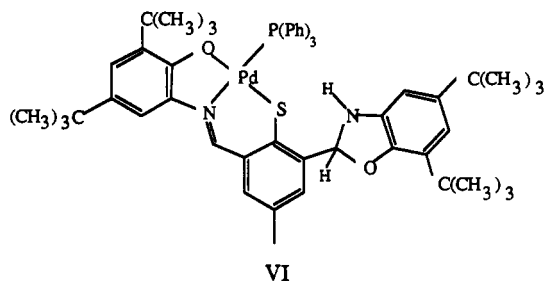
then suffers two-electron dehydrogenative aromatization to give IV. The appearance of metallic palladium in the reaction suggests that Pd^{2+} was responsible for the two-electron oxidation.

We shall refer to the ligand in IV as L_b^{2-} so that IV is represented $L_bPd(PPh_3)$. We were prompted to attempt the deliberate synthesis of L_b^{2-} because it promises the selective binding of two different metal ions giving access to a range of heterobimetallic (as well as homobimetallic) complexes as a consequence of the different donor systems flanking the thiolate bridging center. Moreover, the derived binuclear complexes possess the attractive new feature of providing at one of the metals a potentially exchangeable coordination site cis to the bridging species. Since many processes catalyzed by mononuclear complexes involve the introduction of separate species at cis coordination sites followed by some sort of interaction between the two, complexes of L_b^{2-} may provide new types of binuclear reactivity, stemming from interaction between species at the bimetallic site and at the adjacent coordination site.

Complex V, $(LH)Pd(PPh_3)$, was synthesized by heating the S-protected ligand precursor, III, under reflux in chloroform with 1 equiv each of triphenylphosphine and $Pd(CH_3CO_2)_2$ under dinitrogen; in air, considerable oxidation of the phosphine to phosphine oxide occurred. The IR spectrum of $(LH)Pd(PPh_3)$ showed a phenolic ν_{OH} at 3400 cm^{-1} and strong PPh$_3$-derived bands at 505, 535, 690, and 705 cm^{-1}. In the ^{1}H NMR spectrum the imine proton $H_{f'}$ (see V) appeared as a singlet at 9.21 ppm whereas H_f appeared as a doublet collapsing to a singlet at 9.03 ppm upon phosphorus irradiation ($^4J_{PH}$ = 14.9 Hz). This coupling constant is similar to those seen in other complexes containing an *o*-aminophenol–Schiff-base ligand and a trans phosphine.[6]

Reaction of $(LH)Pd(PPh_3)$ with $Pd(CH_3CO_2)_2$ in chloroform led to displacement of the phosphine by acetate to yield LPd_2-(CH_3CO_2).

Complex IV, $L_bPd(PPh_3)$, was obtained from V, $(LH)Pd(PPh_3)$, by oxidation with lead tetraacetate in benzene solution at room temperature, a procedure that has been used previously to synthesise benzoxazoles.[7] $L_bPd(PPh_3)$ was characterized by elemental analysis, IR and ^{1}H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction. The imine proton, H_f (see IV), appeared in the ^{1}H NMR spectrum as a doublet (9.05 ppm, $^4J_{PH}$ = 15.1 Hz) like the imine trans to phosphine in V.

Reaction of $L_bPd(PPh_3)$ with $Pd(CH_3CO_2)_2$ in chloroform at room temperature yielded $L_bPd_2(\mu\text{-}CH_3CO_2)(CH_3CO_2)$, VII, with

VII
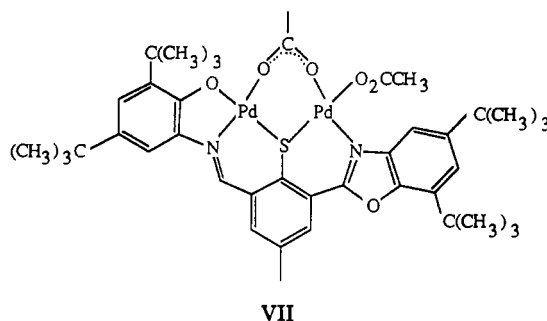
acetate again displacing the phosphine from palladium. The presence of both bridging and terminal acetate was supported by the IR spectrum (bridging acetate, ν(s) = 1420, ν(as) = 1555 cm^{-1}; terminal acetate, ν(as) = 1620 cm^{-1}).[5] This compound was not sufficiently soluble to afford NMR spectra.

Reaction of excess silver perchlorate with $(LH)Pd(PPh_3)$ in benzene at room temperature effected oxidation of the side chain to benzoxazole and coordination of silver to give a material of composition $L_bPdAg(PPh_3)(ClO_4)$ shown subsequently by X-ray crystallography to be dimeric. The same material could also be obtained from $L_bPd(PPh_3)$ with silver perchlorate. The IR spectrum of this compound showed oxazole-derived bands[8] at 1550, 1465, and 1340 cm^{-1}, perchlorate-derived bands at 1100 and 620 cm^{-1} and triphenylphosphine-derived bands at 515, 538, 695, and 715 cm^{-1}. $[L_bPdAg(PPh_3)]_2(ClO_4)_2$ was not sufficiently soluble in any of the common NMR solvents to afford a ^{13}C NMR spectrum but we were able to record a ^{1}H NMR spectrum in $(CD_3)_2SO$ solution that showed the imine proton as a broadened doublet (9.41 ppm, $^4J_{PH}$ = 15.0 Hz).

Crystal and Molecular Structure of $L_bPd(PPh_3)$. Crystal data and details of the crystal structure determination are given in Table I. The unit cell contains six $L_bPd(PPh_3)$ molecules one of which constitutes the asymmetric unit. The molecular geometry and atom-numbering scheme are shown in Figure 1. Atomic coordinates are presented in Table II, and selected interatomic distances and bond angles are given in Table III.

The palladium center is in an essentially square-planar environment consisting of the O(1), N(1), and S(1) donors of L_b^{2-}

(6) Motschi, H.; Nussbaumer, C.; Pregosin, P. S.; Bachechi, F.; Mura, P.; Zambonelli, L. *Helv. Chim. Acta* **1980**, *63*, 2071.

(7) Stephens, F. F.; Bower, J. D. *J. Chem. Soc.* **1949**, 2971; **1950**, 1722.

(8) Boyd, G. V. Oxazoles and their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Potts, K. T., Pergamon: Oxford, England, 1984; Vol. 6, Chapter 4.18.

Table I. Crystallographic Data for $L_bPd(PPh_3)$ and $[L_bPdAg(PPh_3)]_2(ClO_4)_2 \cdot \sim 12.5H_2O$

|	$L_bPd(PPh_3)$	$[L_bPdAg(PPh_3)]_2(ClO_4)_2 \cdot \sim 12.5H_2O$
chem formula	$C_{55}H_{61}N_2O_2PSPd$	$C_{110}H_{122}N_4O_{12}S_2P_2Cl_2Pd_2Ag_2 \cdot 12.5H_2O$
fw	951.5	2542.9
cryst syst	rhombohedral	monoclinic
space group	$R\bar{3}$ (No. 148)	$P2_1/n$ (No. 14)
a, Å	27.540 (4)	13.416 (3)
b, Å		25.397 (3)
c, Å		16.940 (3)
α, deg	117.38 (2)	
β, deg		96.82 (2)
V, Å³	8637	5731
Z	6	2
ρ(calcd), g cm⁻³	1.10	1.47
temp, °C	24 (1)	22 (1)
instrument	Siemens AED diffractometer	Enraf-Nonius CAD-4F diffractometer
radiation (λ, Å)	Cu Kα, nickel-filtered, (λ = 1.5418)	Mo Kα, graphite monochromator, (λ = 0.71069)
μ, cm⁻¹	33.3	7.71
transm factors	0.6203–0.3786	0.9598–0.9040
final R	0.059	0.067
final R_w	0.071	0.065
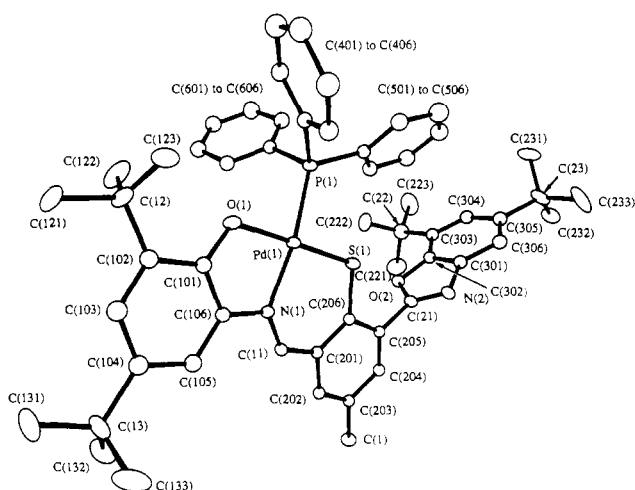
Figure 1. View of the atomic arrangement and atom numbering scheme for $L_bPd(PPh_3)$

together with the phosphine, with only minor deviations from planarity. Metal–donor distances and the bond angles around the metal are unexceptional. The bond angle at the sulfur (Pd-(1)–S(1)–C(206)) is 110.2° with the sulfur displaced 0.103 Å from the plane of the attached 200 aromatic ring (C(201)-C(206)).

The oxazole unit is planar with an average deviation from the plane of 0.005 (10) Å. The dihedral angle between the plane of the 200 aromatic ring and that of the benzoxazole ring is 95.9°, an orientation that presumably minimizes repulsion between the 500 phenyl ring of the phosphine and the benzoxazole.

Crystal and Molecular Structure of [L_bPdAg(PPh_3)]_2-(ClO_4)_2·Solvate. Crystal data and details of the crystal structure determination are given in Table I. The crystal consists of $[L_bPdAg(PPh_3)]_2^{2+}$ cations together with disordered ClO_4^- ions and very disordered solvent molecules. The cation is situated around a crystallographic center of symmetry. An ORTEP diagram, presented in Figure 2, shows the asymmetric unit, $[L_bPdAg-(PPh_3)]^+$, together with its symmetry-related silver atom, Ag(1^I); Figure 2 also indicates the atom-numbering scheme. A view of a selected part of the very congested dimeric cation is shown in Figure 3. Table IV gives atomic coordinates, and Table V, selected interatomic dimensions for $[L_bPdAg(PPh_3)]_2(ClO_4)_2$.

The two $[L_bPdAg(PPh_3)]^+$ units are linked by bonds between the sulfur of one and the silver of the other so that each sulfur atom is bonded to one palladium and to two silver atoms. Each silver atom is bonded less strongly to "its own" sulfur (i.e. the sulphur belonging to the L_b^{2-} ligand, which is bonded to the silver in question via its oxazole nitrogen) than to the other sulfur (S(1)–Ag(1), 2.867 (6) Å; S(1)–Ag(1^I), 2.506 (6) Å). The
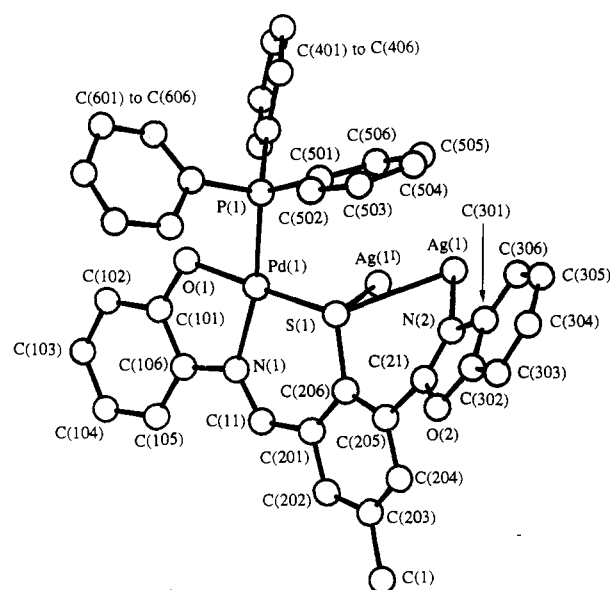
Figure 2. View of the asymmetric unit $[L_bPdAg(PPh_3)]^+$ of $[L_bPdAg-(PPh_3)]_2(ClO_4)_2$·solvate together with its symmetry-related silver atom, Ag(1^I). The *tert*-butyl substituents attached to C(302), C(305), C(102) C(104) have been omitted for clarity.
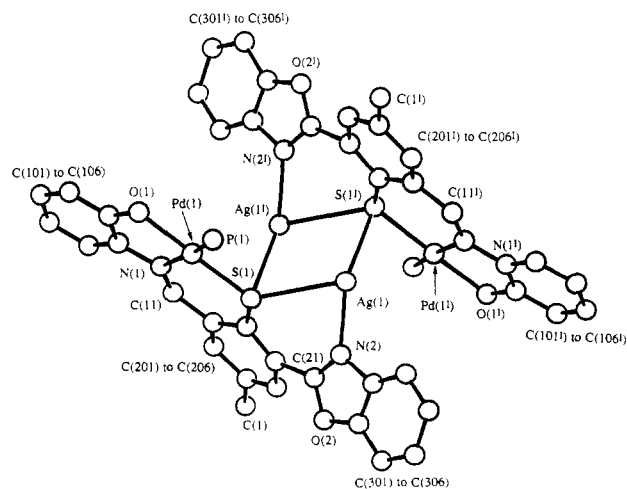
Figure 3. View of the $[L_bPdAg(PPh_3)]_2^{2+}$ cation showing the linking of the two asymmetric units. The phenyl rings of the triphenylphosphines and the *tert*-butyl substituents of L_b^{2-} have been omitted for clarity.

Ag(1)–S(1)–Ag(1^I) angle of 61.9 (1)° is exceptionally acute and the Ag(1)–Ag(1^I) distance of 2.779 (3) Å unusually short, shorter

Table II. Fractional Atomic Coordinates for $L_bPd(PPh_3)$ with Esd Values Given in Parentheses

atom	x	y	z
Pd(1)	0.67870 (4)	0.30379 (4)	0.74488 (4)
S(1)	0.7447 (1)	0.3126 (1)	0.8411 (1)
P(1)	0.5145 (1)	0.1547 (1)	0.6309 (1)
O(1)	0.6206 (4)	0.2948 (4)	0.6559 (4)
O(2)	0.8353 (4)	0.3668 (4)	1.0236 (4)
N(1)	0.8169 (4)	0.4400 (4)	0.8388 (4)
N(2)	0.8374 (5)	0.2910 (5)	0.9459 (5)
C(1)	1.2151 (5)	0.7353 (5)	1.2788 (5)
C(11)	0.9110 (5)	0.5150 (5)	0.9344 (5)
C(21)	0.8672 (5)	0.3659 (5)	0.9973 (5)
C(12)	0.5558 (7)	0.2970 (9)	0.5396 (8)
C(121)	0.5495 (8)	0.319 (1)	0.4954 (9)
C(122)	0.516 (1)	0.306 (1)	0.563 (1)
C(123)	0.4901 (8)	0.1884 (8)	0.4589 (7)
C(13)	0.9482 (8)	0.6378 (8)	0.8354 (8)
C(131)	0.910 (1)	0.637 (1)	0.775 (1)
C(132)	1.0328 (8)	0.7395 (8)	0.9488 (9)
C(133)	1.0003 (9)	0.6269 (9)	0.8334 (9)
C(22)	0.7279 (8)	0.2977 (8)	1.0404 (8)
C(221)	0.844 (1)	0.409 (1)	1.1610 (9)
C(222)	0.693 (1)	0.316 (1)	1.001 (1)
C(223)	0.652 (1)	0.230 (1)	1.018 (1)
C(23)	0.6259 (8)	0.0086 (7)	0.8468 (8)
C(231)	0.5100 (8)	−0.0740 (8)	0.7684 (8)
C(232)	0.6858 (8)	0.0456 (8)	0.9397 (8)
C(233)	0.628 (1)	−0.0394 (9)	0.791 (1)
C(101)	0.6961 (6)	0.3739 (6)	0.6964 (6)
C(102)	0.6702 (6)	0.3803 (6)	0.6435 (6)
C(103)	0.7535 (6)	0.4662 (6)	0.6921 (6)
C(104)	0.8583 (6)	0.5442 (6)	0.7855 (6)
C(105)	0.8795 (6)	0.5338 (6)	0.8330 (6)
C(106)	0.7997 (5)	0.4510 (5)	0.7904 (5)
C(201)	0.9436 (5)	0.5186 (5)	0.9954 (5)
C(202)	1.0510 (5)	0.6130 (5)	1.0975 (5)
C(203)	1.0994 (5)	0.6308 (5)	1.1674 (5)
C(204)	1.0359 (5)	0.5459 (5)	1.1303 (5)
C(205)	0.9303 (5)	0.4520 (5)	1.0311 (5)
C(206)	0.8797 (5)	0.4347 (5)	0.9610 (5)
C(301)	0.7765 (6)	0.2316 (6)	0.9335 (6)
C(302)	0.7775 (6)	0.2793 (6)	0.9820 (6)
C(303)	0.7278 (6)	0.2431 (6)	0.9878 (6)
C(304)	0.6801 (6)	0.1549 (6)	0.9410 (6)
C(305)	0.6795 (7)	0.1054 (7)	0.8932 (7)
C(306)	0.7278 (6)	0.1422 (6)	0.8867 (6)
C(401)	0.4239 (6)	0.0595 (5)	0.4979 (6)
C(402)	0.3267 (6)	0.0007 (6)	0.4222 (6)
C(403)	0.2577 (8)	−0.0753 (7)	0.3190 (8)
C(404)	0.2869 (8)	−0.0910 (7)	0.2942 (8)
C(405)	0.3805 (7)	−0.0354 (7)	0.3651 (7)
C(406)	0.4523 (7)	0.0424 (7)	0.4698 (7)
C(501)	0.4888 (5)	0.0838 (6)	0.6343 (6)
C(502)	0.5290 (6)	0.1266 (7)	0.7190 (7)
C(503)	0.5072 (7)	0.0694 (8)	0.7196 (8)
C(504)	0.4473 (8)	−0.0254 (8)	0.6397 (8)
C(505)	0.4085 (8)	−0.0672 (9)	0.5560 (9)
C(506)	0.4287 (6)	−0.0136 (7)	0.5529 (7)
C(601)	0.4681 (5)	0.1802 (5)	0.6443 (5)
C(602)	0.4017 (7)	0.1274 (5)	0.6294 (7)
C(603)	0.3656 (8)	0.1498 (8)	0.6370 (8)
C(604)	0.3975 (7)	0.2225 (7)	0.6617 (7)
C(605)	0.4631 (7)	0.2751 (7)	0.6773 (7)
C(606)	0.5002 (6)	0.2549 (6)	0.6703 (6)

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $L_bPd(PPh_3)$ with Esd Values Given in Parentheses

(a) Distances

Pd(1)–P(1)	2.274 (2)	Pd(1)–S(1)	2.227 (2)
Pd(1)–O(1)	2.023 (5)	Pd(1)–N(1)	2.034 (5)
P(1)–C(401)	1.812 (7)	S(1)–C(206)	1.741 (7)
P(1)–C(501)	1.807 (7)	P(1)–C(601)	1.811 (7)
O(2)–C(21)	1.374 (7)	N(2)–C(21)	1.274 (8)
O(2)–C(302)	1.381 (8)	N(2)–C(301)	1.430 (8)
C(11)–N(1)	1.308 (8)	N(1)–C(106)	1.419 (8)
O(1)–C(101)	1.336 (8)		

(b) Angles

O(1)–Pd(1)–P(1)	89.8 (1)	P(1)–Pd(1)–S(1)	91.22 (7)
S(1)–Pd(1)–N(1)	96.9 (2)	N(1)–Pd(1)–O(1)	82.3 (2)
Pd(1)–S(1)–C(206)	110.2 (2)	C(11)–N(1)–C(106)	121.1 (5)
C(106)–N(1)–Pd(1)	110.4 (4)	Pd(1)–N(1)–C(11)	128.2 (4)
C(101)–O(1)–Pd(1)	111.5 (4)	N(1)–C(11)–C(201)	129.3 (6)
C(401)–P(1)–Pd(1)	110.8 (2)	C(501)–P(1)–Pd(1)	120.2 (2)
C(601)–P(1)–Pd(1)	110.1 (2)	C(21)–N(2)–C(301)	103.2 (6)
C(21)–O(2)–C(302)	103.3 (5)	O(2)–C(21)–N(2)	116.2 (6)
O(2)–C(302)–C(301)	108.3 (6)	N(2)–C(301)–C(302)	109.0 (6)

or not bonding interactions are possible between d^{10} metal centers has been a matter of some dispute;[13] Schmidbauer, however, has recently presented convincing evidence for definite $Au^I \cdots Au^I$ bonding interactions,[14] and the very short $Ag \cdots Ag$ separation reported here may well reflect a similar attractive interaction.

The $Pd(1)$–$S(1)$–$Ag(1^I)$ angle of 75.6 (2)° is larger than the $Ag(1)$–$S(1)$–$Ag(1^I)$ angle above, but is nevertheless relatively acute. The $Pd(1)$–$Ag(1^I)$ distance is 2.912 (2) Å. We have been unable to find in the literature any examples of Pd,Ag species for comparison but some Pt,Ag systems have been reported with Pt–Ag distances in the range 2.787–3.146 Å.[15] Whether the present $Pd(1)$–$Ag(1^I)$ separation arises from some bonding interaction or not is a question we are unable to answer, but the remainder of the Pd coordination environment (discussed below) appears negligibly disturbed by the proximity of the Ag.

Some interaction between the silver and one of the phenyl rings of the phosphine unit is implied by the displacement of Ag(1) 0.475 Å from the plane of its three bonded atoms, S(1), S(1^I), and N(2), toward the 500 phenyl ring of the phosphine. The distances from the silver atom to the closest atoms of this phenyl ring are 2.98 (2) Å to C(505), 3.02 Å to H(505), 3.10 (2) Å to C(506), and 3.25 Å to H(506). The perpendicular to the plane of the 500 ring passing through silver intersects the plane at a point outside the C_6 ring and closer to the C(505)–H bond than to the C(505)–C(506) bond. In other words the silver may be interacting as much with the electron pair of the C(505)–H bond as with the π electrons of the ring. It is unfortunate that $[L_bPdAg(PPh_3)]_2(ClO_4)_2$ is so insoluble that a ^{13}C NMR spectrum was unobtainable and a ^1H NMR spectrum barely obtainable, but there was no

even than the Ag–Ag distance in metallic silver.[9] The only shorter Ag–Ag distances of which we are aware are 2.67 Å in $[Ag(C_6H_5NNNC_6H_5)]_2$[10] and 2.72 Å in $[Ag(EtOC_6H_4NNNC_6H_4OEt)]_2$.[11] Generally, Ag–Ag distances in silver–thiolate cluster compounds are in the range 2.9–3.5 Å.[12] Whether

(9) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. III, p 278.

(10) Hartmann, E.; Strahle, J. *Z. Naturforsch.* **1986**, *41B*, 4.

(11) Hartmann, E.; Strahle, J. *Z. Naturforsch.* **1988**, *43B*, 525.

(12) (a) Bircher, P. J.; Verchoor, G. C. *J. Chem. Soc., Chem. Commun.* **1981**, 322. (b) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *Inorg. Chem.* **1984**, *23*, 2276. (c) Dance, I. G.; Fitzpatrick, L. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 3785. (d) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L.; Craig, D. *J. Chem. Soc., Chem. Commun.* **1984**, 17. (e) Dance, I. G.; Fitzpatrick, L. J.; Craig, D. C.; Scudder, M. L. *Inorg. Chem.* **1989**, *28*, 1853. (f) Cusick, J.; Scudder, M. L.; Craig, D. C.; Dance, I. G. *Polyhedron* **1989**, *8*, 1139. (g) Henkel, G.; Betz, P.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 145. (h) Block, E.; Gernon, M.; Kang, H.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1342. (i) Schuerman, J. A.; Fronczec, F. R.; Selbin, J. *Inorg. Chim. Acta* **1989**, *160*, 43.

(13) (a) Merz, K. M.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120. (b) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074. (c) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187.

(14) (a) Rosch, N.; Gorling, A.; Ellis, D. E.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1357. (b) Schmidbaur, H.; Graf, W.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417. (c) Schmidbaur, H.; Reber, G.; Schier, A.; Wagner, F. E.; Muller, G. *Inorg. Chim. Acta* **1988**, *147*, 143.

(15) (a) Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomas, M. *Inorg. Chem.* **1985**, *24*, 4651. (b) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1987**, *26*, 3482. (c) Douglas, G.; Jennings, M. C.; Manojlovic-Muir, L.; Puddephatt, R. J. *Inorg. Chem.* **1988**, *27*, 4516.

Table IV. Fractional Atomic Coordinates for [L$_b$PdAg(PPh$_3$)]$_2$(ClO$_4$)$_2$·~12.5H$_2$O with Esd Values Given in Parentheses

atom	x	y	z	atom	x	y	z
Pd(1)	−0.1017 (1)	0.0623 (1)	−0.1841 (1)	C(206)	−0.088 (1)	0.1182 (7)	−0.006 (1)
Ag(1)	0.0882 (2)	0.0101 (1)	0.0494 (1)	C(301)	0.216 (2)	0.1039 (8)	0.137 (1)
S(1)	−0.0167 (4)	0.0800 (2)	−0.0647 (3)	C(302)	0.209 (2)	0.1556 (9)	0.155 (1)
P(1)	0.0395 (4)	0.0307 (2)	−0.2305 (3)	C(303)	0.287 (2)	0.1802 (9)	0.201 (1)
O(1)	−0.176 (1)	0.0462 (5)	−0.2901 (7)	C(304)	0.378 (2)	0.1537 (9)	0.216 (1)
N(1)	−0.232 (1)	0.0967 (6)	−0.1637 (8)	C(305)	0.389 (2)	0.0988 (8)	0.192 (1)
O(2)	0.112 (1)	0.1722 (6)	0.1333 (8)	C(306)	0.304 (2)	0.0715 (2)	0.154 (1)
N(2)	0.122 (1)	0.0886 (6)	0.0944 (8)	C(401)	0.036 (2)	−0.0354 (8)	−0.269 (1)
C(1)	−0.252 (2)	0.2105 (8)	0.153 (1)	C(402)	−0.055 (2)	−0.0605 (8)	−0.281 (1)
C(11)	−0.256 (1)	0.1224 (7)	−0.100 (1)	C(403)	−0.061 (2)	−0.1125 (8)	0.314 (1)
C(12)	−0.292 (2)	0.038 (1)	−0.444 (1)	C(404)	0.020 (2)	−0.1361 (9)	−0.333 (1)
C(121)	−0.276 (2)	−0.020 (1)	−0.427 (1)	C(405)	0.115 (2)	−0.1128 (9)	−0.321 (1)
C(122)	−0.363 (2)	0.043 (1)	−0.520 (1)	C(406)	0.123 (2)	−0.0623 (9)	−0.286 (1)
C(123)	−0.191 (2)	0.062 (1)	−0.459 (1)	C(501)	0.150 (2)	0.0334 (7)	−0.162 (1)
C(13)	−0.567 (2)	0.1350 (9)	−0.325 (1)	C(502)	0.213 (2)	0.0758 (7)	−0.154 (1)
C(131)	−0.593 (2)	0.166 (1)	−0.253 (2)	C(503)	0.291 (2)	0.0805 (9)	−0.097 (1)
C(132)	−0.642 (2)	0.092 (1)	−0.342 (2)	C(504)	0.316 (2)	0.0376 (9)	−0.043 (1)
C(133)	−0.576 (2)	0.174 (1)	−0.395 (1)	C(505)	0.254 (1)	−0.0082 (8)	−0.050 (1)
C(21)	0.067 (2)	0.1302 (8)	0.095 (1)	C(506)	0.174 (1)	−0.0091 (8)	−0.111 (1)
C(22)	−0.279 (2)	−0.2389 (9)	−0.228 (2)	C(601)	0.059 (1)	0.0722 (7)	−0.314 (1)
C(221)	−0.255 (2)	−0.2732 (9)	−0.151 (2)	C(602)	0.073 (1)	0.0542 (8)	−0.387 (1)
C(222)	−0.196 (2)	−0.2449 (9)	−0.282 (1)	C(603)	0.085 (2)	0.089 (1)	−0.451 (1)
C(223)	−0.374 (2)	−0.260 (1)	−0.274 (2)	C(604)	0.070 (2)	0.1416 (9)	−0.0438 (1)
C(23)	0.483 (2)	0.071 (1)	0.207 (2)	C(605)	0.053 (2)	0.1634 (8)	−0.369 (1)
C(231)	0.488 (2)	0.016 (1)	0.177 (1)	C(606)	0.043 (2)	0.1267 (7)	−0.306 (1)
C(232)	0.527 (3)	0.073 (1)	0.288 (2)	Cl	−0.0241 (5)	0.2900 (3)	0.4732 (5)
C(233)	0.562 (2)	0.097 (1)	0.166 (2)	O(11)	0.0094 (2)	0.3387 (8)	0.450 (1)
C(101)	−0.270 (2)	0.0682 (8)	−0.300 (1)	O(12)^a	0.016 (2)	0.2803 (9)	−0.446 (5)
C(102)	−0.330 (1)	0.0660 (9)	−0.372 (1)	O(13)^a	0.052 (3)	0.254 (2)	0.442 (2)
C(103)	−0.423 (2)	0.0875 (7)	−0.378 (1)	O(14)^a	−0.125 (3)	0.304 (1)	0.489 (2)
C(104)	−0.460 (1)	0.1134 (7)	−0.313 (1)	O(15)^a	−0.091 (3)	0.260 (1)	0.426 (2)
C(105)	−0.400 (1)	0.1151 (7)	−0.241 (1)	O1S^b	−0.168 (1)	−0.2353 (7)	0.1839 (9)
C(106)	−0.302 (1)	0.0951 (7)	−0.235 (1)	O2S	−0.172 (2)	−0.3137 (9)	0.066 (1)
C(201)	−0.190 (1)	0.1328 (7)	−0.026 (1)	O3S^c	−0.185 (2)	−0.247 (1)	0.076 (2)
C(202)	−0.240 (2)	0.1623 (7)	0.027 (1)	O4S^c	−0.098 (2)	−0.298 (1)	0.038 (2)
C(203)	−0.194 (2)	0.1794 (8)	0.100 (1)	O5S	−0.117 (1)	−0.1922 (6)	0.0696 (9)
C(204)	−0.093 (2)	0.1676 (7)	0.115 (1)	O6S	−0.067 (2)	−0.2241 (8)	0.046 (1)
C(205)	0.041 (2)	0.1395 (7)	0.066 (1)	O7S^c	−0.177 (2)	−0.2726 (9)	0.170 (1)

^{a} Parameters of O(12), O(13), O(14) and O(15) were refined with a common fixed isotropic thermal parameter of 0.150; the site occupation factors were allowed to vary and at convergence their values were 0.933 (8), 0.600 (8), 0.645 (8), and 0.638 (8), respectively. ^{b} O1S, O2S, etc. denote atoms of solvent molecules. ^{c} These atoms were refined with a fixed site occupation factor of 0.75.

Table V. Selected Interatomic Distances (Å) and Angles (deg) for [L$_b$PdAg(PPh$_3$)]$_2$(ClO$_4$)$_2$·~12.5H$_2$O with Esd Values Given in Parentheses

(a) Distances

Pd(1)–S(1)	2.246 (5)	Pd(1)–P(1)	2.281 (6)
Pd(1)–O(1)	1.99 (1)	Pd(1)–N(1)	2.02 (1)
S(1)–Ag(1)	2.867 (6)	S(1)–Ag(1^I)^a	2.506 (6)
Ag(1)–Ag(1^I)	2.779 (3)	Pd(1)–Ag(1^I)	2.919 (3)
Ag(1)–Pd(1)	4.637 (3)	Ag(1)–N(2)	2.16 (2)
S(1)–C(206)	1.75 (2)	P(1)–C(401)	1.80 (2)
P(1)–C(501)	1.77 (2)	P(1)–C(601)	1.80 (2)
O(2)–C(21)	1.36 (3)	N(2)–C(21)	1.29 (3)
N(1)–C(11)	1.33 (2)	N(1)–C(106)	1.43 (2)
O(1)–C(101)	1.36 (2)		

(b) Angles

P(1)–Pd(1)–S(1)	91.5 (2)	O(1)–Pd(1)–N(1)	83.7 (5)
P(1)–Pd(1)–O(1)	88.1 (3)	N(1)–Pd(1)–S(1)	96.7 (4)
S(1)–Ag(1)–S(1^I)	118.1 (2)	S(1)^I–Ag(1)–N(2)	150.7 (4)
S(1)–Ag(1)–N(2)	74.5 (4)	Ag(1)–S(1)–Ag(1^I)	61.9 (1)
C(206)–S(1)–Pd(1)	111.5 (6)	Pd(1)–S(1)–Ag(1^I)	75.6 (2)
Pd(1)–P(1)–C(401)	117.9 (8)	Pd(1)–P(1)–C(501)	115.4 (7)
Pd(1)–P(1)–C(601)	105.3 (6)	Pd(1)–S(1)–Ag(1)	129.7 (2)
Ag(1^I)–S(1)–C(206)	101.5 (7)	Ag(1)–S(1)–C(206)	102.7 (6)

^{a} I: (−x, −y, −z).

evidence in the latter for an agostic interaction in the form of any unusual chemical shift.

The ligand arrangement and palladium coordination environment show no unusual features. The angles at the palladium atom are almost identical with the analogous angles in L$_b$Pd(PPh$_3$) (see Tables III and IV), the largest discrepancy being less than 2°.

Coordination of the silver center brings the benzoxazole ring more into coplanarity with the 200 aromatic ring than was evident in L$_b$Pd(PPh$_3$), the dihedral angles being 138.9° in the Pd,Ag case and 95.9° in the other. The chelating system consisting of the 100 and 200 rings and their interconnecting imine unit is only slightly distorted from coplanarity, the dihedral angle between the 100 and 200 rings being 11.2° and the imine C(11) and N(1) centers being displaced 0.131 and 0.195 Å from the 200 ring plane.

Experimental Section

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

S-Protected Ligand Precursor III, C$_{40}$H$_{55}$N$_3$O$_3$S. The synthesis of III has been described previously[16] when it was used directly, without characterization, for the preparation of metal complexes. NMR spectral characterization is provided here. ^{1}H NMR (ppm, CDCl$_3$, for labeling see structure III): 1.34 (s, 18 H, Hmm′), 1.46 (s, 18 H, Hnn′), 2.52 (s, 3 H, Ha), 3.23 (d, 6 H, Hss′), 7.21 (q, 4 H, Hjj′ll′, J$_{lj}$ = 2.20 Hz), 7.63 (s, 2 H, phenolic OH), 8.22 (s, 2 H, Hcc′), 9.26 (s, 2 H, Hff′). ^{13}C NMR (ppm, CDCl$_3$, assignment assisted by DEPT, labeling shown in structure III): 21.3 (Ca); 29.5, 31.6 (Cmm′nn′); 34.6, 34.9 (Coo′pp′); 37.2 (Css′); 110.6, 123.6 (Cjj′ll′); 128.6 (Ce); 131.1 (Ccc′); 135.4, 139.7 (Cii′kk′dd′); 140.5 (Cb); 141.4 (Cgg′); 148.9 (Chh′); 154.8 (Cff′); 164.7 (Cr).

LPd$_2$(CH$_3$CO$_2$). The S-protected ligand precursor, III (0.21 g, 0.3 mmol), in chloroform (2 mL) was added to a solution of Pd(CH$_3$CO$_2$)$_2$ (0.16 g, 0.73 mmol) in chloroform (3 mL). The dark brown solution was heated under reflux for 2 h. The volume of the solution was reduced to

(16) Iliopoulos, P.; Murray, K. S.; Robson, R.; Wilson, J. C.; Williams, G. A. *J. Chem. Soc. Dalton Trans.* **1987**, 1585.

1 mL by boiling at atmospheric pressure. On cooling, the solution deposited fine brown needles of LPd$_2$(CH$_3$CO$_2$), which were collected, washed with petroleum ether, and dried in vacuo at 80 °C. Yield: 31%. ^{1}H NMR (ppm, CDCl$_3$, labeling of L^{3-} as in structure II): 1.33 (s, 18 H, Hnn'), 1.52 (s, 18 H, Hmm'), 1.98 (s, 3 H, CH$_3$CO$_2$), 2.17 (s, 3 H, Ha), 7.26 (s, 4 H, Hjj'll'), 7.53 (s, 2 H, Hcc'), 8.25 (s, 2 H, Hff'). Anal. Calcd for C$_{49}$H$_{50}$N$_2$O$_4$Pd$_2$S·0.3CHCl$_3$: C, 53.0; H, 5.7; N, 3.1. Found: C, 52.9; H, 5.7; N, 3.1. (Chloroform of solvation, evident in the ^{1}H NMR in DMSO-d_6 could not be completely removed in vacuo at 80 °C.)

LPd$_2$((CH$_3$)$_3$CCO$_2$). A solution of LPd$_2$(CH$_3$CO$_2$) (0.062 g, 0.074 mmol) and pivalic acid (0.26 g, 2.56 mmol) in chloroform (10 mL) was heated under reflux for 1 h. The volume of the solution was reduced to 1 mL by boiling at atmospheric pressure and boiling methanol (5 mL) was added. The dark purple crystalline solid which separated was collected, washed with methanol, and dried in vacuo at 110 °C. Yield: 94%. ^{1}H NMR (ppm, CDCl$_3$, labeling of L^{3-} as in structure II): 1.27 (s, 9 H, (CH$_3$)$_3$CCO$_2$); 1.31 (s, 18 H, Hnn'); 1.49 (s, 18 H, Hmm'); 2.47 (s, 3 H, Ha); 7.22, 7.24 ("d", 4 H, Hjj'll'); 7.64 (s, 2 H, Hcc'); 8.24 (s, 2 H, Hff'). ^{13}C NMR (ppm, CDCl$_3$, labeling of L^{3-} as in structure II): 20.5 (Ca); 28.3 (CH$_3$ of pivalate); 29.4 (Cnn'); 31.7 (Cmm'); 34.3 (Coo'); 35.4 (Cpp'); 41.6 (quaternary C of pivalate); 109.6, 127.1 (Cjj'll'); 122.9 (Ce); 133.3 (Cdd'); 136.4 (Cb); 137.3, 140.7 (Cii'kk'); 141.3 (Cgg'); 141.9 (Ccc'); 147.9 (Cff'); 165.1 (Chh'); 186.7 (carboxylate of pivalate).

LPd$_2$(HCO$_2$). Formic acid (0.5 mL) was added to a solution of LPd$_2$(CH$_3$CO$_2$) (0.053 g, 0.062 mmol) in dioxan (2 mL), and the resulting solution was heated under reflux for 1 h during which time very dark crystalline LPd$_2$(HCO$_2$) separated. After the mixture had cooled to room temperature, the solid was collected, washed with methanol, and dried in vacuo at 80 °C. Yield: 82%. LPd$_2$(HCO$_2$) could be recrystallized from chloroform/methanol. ^{1}H NMR (ppm, CDCl$_3$, labeling of L^{3-} as in structure II): 1.32 (s, 18 H, Hnn'), 1.54 (s, 18 H, Hmm'), 2.01 (s, 3 H, Ha), 6.62 (s, 1 H, formate), 7.21 (4 H, Hjj'll'), 7.48 (s, 2 H, Hcc'), 8.17 (s, 2 H, Hff').

LPd$_2$I. Tetrabutylammonium iodide (0.095 g, 0.26 mmol) in chloroform (1 mL) was added to a solution of LPd$_2$(CH$_3$CO$_2$) in boiling chloroform (20 mL), and the resulting solution was heated under reflux for 2 h. The volume of chloroform was reduced to ca. 2 mL by boiling down at atmospheric pressure, and boiling methanol (4 mL) was added. After the solution had been allowed to cool and stand, the LPd$_2$I crystals that had separated were collected, washed with methanol, and dried in vacuo at 110 °C. Yield: 48%. ^{1}H NMR (ppm, CDCl$_3$, labeling as in structure II): 1.32 (s, 18 H, Hnn'), 1.40 (s, 18 H, Hmm'), 2.43 (s, 3 H, Ha), 7.23 (4 H, Hjj'll'), 7.56 (s, 2 H, Hcc'), 7.96 (s, 2 H, Hff'). ^{13}C NMR (ppm, CDCl$_3$, labeling as in structure II, assignments assisted by DEPT): 21.0 (Ca); 29.2 (Cnn'); 31.5 (Cmm'); 34.2 (Coo'); 35.3 (Cpp'); 109.2, 127.4 (Cjj'll'); 121.9 (Ce); 134.3, 136.5 (Cii'kk'); 137.4 (Cb); 139.7 (Cdd'); 139.8 (Ccc'); 141.1 (Cgg'); 145.5 (Cff'). Anal. Calcd for C$_{37}$H$_{47}$IN$_2$O$_2$Pd$_2$S: C, 48.1; H, 5.1, N, 3.0; I, 13.7. Found: C, 48.4; H, 5.2; N, 2.8, I, 13.3.

LPd$_2$(C$_3$H$_3$N$_2$). A solution of Pd(CH$_3$CO$_2$)$_2$ (0.15 g, 0.67 mmol) in boiling chloroform (10 mL) was added to a mixture of the S-protected ligand precursor III (0.046 g, 0.07 mmol) and pyrazole (0.046 g, 0.68 mmol) in chloroform (2 mL). The resulting solution was heated under reflux for 1 h. The volume of the solution was reduced to ca. 3 mL by boiling at atmospheric pressure, and boiling methanol (3 mL) was added. The crystalline LPd$_2$(C$_3$H$_3$N$_2$), which separated after the mixture had been allowed to cool and stand, was collected, washed with methanol, and dried in vacuo at 110 °C. Yield: 53%. ^{1}H NMR (ppm, CDCl$_3$, labeling as in structure II): 1.33 (s, 18 H, Hnn'), 1.53 (s, 18 H, Hmm'), 2.30 (s, 3 H, Ha), 6.18 (t, 1 H, pyrazole b H), 7.27 (4 H, Hjj'll'), 7.80 (d, 2 H, pyrazole a H), 7.57 (s, 2 H, Hcc'), 8.28 (s, 2 H, Hff'). ^{13}C NMR (ppm, CDCl$_3$, labeling as in structure II): 20.2 (Ca); 29.2 (Coo'); 31.7 (Cpp'); 34.3 (Cnn'); 35.0 (Cmm'); 104.4 (pyrazole b C); 108.8, 126.4 (Cjj'll'); 124.4 (Ce); 129.2 (Cb); 132.8 (Cdd'); 136.9, 139.1 (Cii'kk'); 139.3 (a C's of pyrazole); 140.1 (Ccc'); 141.4 (Cgg'); 150.7 (Cff'); 163.3 (Chh').

(LH)Pd(PPh$_3$). A solution containing the S-protected ligand precursor III (0.30 g, 0.45 mmol), Pd(CH$_3$CO$_2$)$_2$ (0.11 g, 0.5 mmol), and triphenylphosphine (0.12 g, 0.47 mmol) in chloroform (15 mL) was heated under reflux 0.5 h in an atmosphere of dinitrogen. The chloroform solution was then boiled down in the air to ca. 2 mL and boiling methanol (10 mL) was added. The orange (LH)Pd(PPh$_3$), which crystallized after the mixture had been allowed to cool and stand, was collected, washed with methanol, and dried in vacuo at 80°C. Yield: 0.39 g, 87%. ^{1}H NMR (ppm, CDCl$_3$, labeling as in structure V): 1.08 (s, 9 H, Hn), 1.35 (s, 9 H, Hn'), 1.38 (s, 9 H, Hm), 1.46 (s, 9 H, Hm'), 2.44 (s, 3 H, Ha), 6.9–7.9 (complex, PPh$_3$ plus aromatics of LH^{2-}): 9.03 (d, 1 H, Hf, $^4J_{PH}$ 14.9 Hz), 9.21 (s, 1 H, Hf'). ^{13}C NMR (ppm, CDCl$_3$, complex, assignment of aromatic C's of LH^{2-} not attempted, labeling as in structure V) 20.4 (Ca); 29.3, 29.5, 31.8 (Cnn'mm'); 34.4, 35.0, 35.1 (Coo'pp'); 148.5, 148.8 (Cff'); 128.3 (d, meta C of PPh$_3$, $^3J_{PC}$ = 11.0

Hz); 131.1 (d, para C of PPh$_3$, $^4J_{PC}$ = 2.4 Hz); 135.0 (d, ortho C of PPh$_3$, $^3J_{PC}$ = 11.0 Hz).

L$_b$Pd(PPh$_3$). A solution in benzene (10 mL) of (LH)Pd(PPh$_3$) (0.085 g, 0.09 mmol) and Pb(CH$_3$CO$_2$)$_4$ (0.065 g, 0.15 mmol) at room temperature gradually deposited Pb(CH$_3$CO$_2$)$_2$. After 3 h the Pb(CH$_3$CO$_2$)$_2$ was filtered off and the volume of the filtrate was reduced to ca. 2 mL by boiling at atmospheric pressure. Boiling methanol was added, and the crude L$_b$Pd(PPh$_3$), which separated on standing, was collected and purified by flash chromatography (Keiselgel 60, column length 15 cm, diameter 2.5 cm, eluant chloroform). The eluant containing the major band was concentrated, and addition of methanol yielded crystalline L$_b$Pd(PPh$_3$), which was collected, washed with methanol, and dried in vacuo at 80 °C. Yield: 0.025 g, 29%. ^{1}H NMR (ppm, CDCl$_3$, labeling as in structure IV): 1.03 (s, 9 H, Hn), 1.38 (s, 9 H, Hn'), 1.39 (s, 9 H, Hm), 1.49 (s, 9 H, Hm'), 2.43 (s, 3 H, Ha), 7–8 (complex, PPh$_3$ plus aromatics of L$_b$$^{2-}$), 9.05 (d, 1 H, Hf, $^4J_{PH}$ = 14.6 Hz). ^{13}C NMR (ppm, CDCl$_3$, very complex, assignment of C's of L$_b$$^{2-}$ not attempted, labeling as in structure IV): 20.3 (Ca); 29.3, 30.0, 31.8, 32.0 (Cmm'nn'); 34.4, 35.0 (Coo'pp'); 148.3 (Cf); 163.3 (Cf'); 128.0 (d, meta C of PPh$_3$, $^3J_{PC}$ = 11.0 Hz); 130.6 (d, para C of PPh$_3$, $^4J_{PC}$ < 1 Hz); 137.2 (d, ortho C of PPh$_3$, $^2J_{PC}$ = 12.2 Hz). Anal. Calcd for C$_{55}$H$_{61}$N$_2$O$_2$PPdS: C, 69.4; H, 6.5; N, 2.9; P, 3.3; Pd, 11.2. Found: C, 69.4; H, 6.4; N, 2.9, P, 3.3; Pd, 11.3.

L$_b$Pd$_2$(μ-CH$_3$CO$_2$)(CH$_3$CO$_2$) (VII). A solution containing L$_b$Pd(PPh$_3$) (0.030 g, 0.03 mmol) and Pd(CH$_3$CO$_2$)$_2$ (0.022 g, 0.1 mmol) in chloroform (4 mL) turned deep purple on being heated briefly to the boiling point (10 min). After being allowed to cool and stand, the solution deposited crystalline L$_b$Pd$_2$(μ-CH$_3$CO$_2$)(CH$_3$CO$_2$), which was collected, washed with methanol, and dried in vacuo at 80 °C. Yield: 0.015 g, 52%. Anal. Calcd. for C$_{41}$H$_{52}$N$_2$O$_6$Pd$_2$S: C, 53.9; H, 5.7; N, 3.0. Found: C, 53.1; H, 5.8; N, 3.0.

[L$_b$PdAg(PPh$_3$)]$_2$(ClO$_4$)$_2$·Solvate. A solution of L$_b$Pd(PPh$_3$) (0.033 g, 0.035 mmol) and AgClO$_4$ (0.10 g, 0.48 mmol) in benzene (10 mL) was allowed to stand at room temperature. After 20 h a small amount of dark material that had separated was removed by filtration, and the filtrate on further standing for several days deposited crystalline solvated [L$_b$PdAg(PPh$_3$)]$_2$(ClO$_4$)$_2$. Due to the risk of explosion with perchlorate complexes, this product was prepared only in very small amounts and drying under vacuum was conducted only at room temperature. Analytical data support the presence of ca. eight H$_2$O's per dimeric formula unit, and although the crystal structure analysis indicated considerable interstitial solvent, this was so disordered that its nature was not determined. Anal. Calcd for C$_{55}$H$_{61}$AgClN$_2$O$_6$PPdS·4H$_2$O: C, 53.7; H, 5.7; N, 2.2. Found: C, 53.5; H, 5.9; N, 2.2. ^{1}H NMR (ppm, (CD$_3$)$_2$SO, labeling of L$_b$$^{2-}$ as in structure IV) 0.94 (s, 9 H, Hn), 1.40 (s, 9 H, Hn'), 1.41 (s, 9 H, Hm), 1.48 (s, 9 H, Hm'), 7–8 (complex, PPh$_3$ plus aromatics of L$_b$$^{2-}$), 9.41 (d, 1 H, Hf, $^4J_{PH}$ = 15.0 Hz). Ha was not observed and is presumed obscured by dmso-derived bands.

Physical Measurements and Microanalysis. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX 90 and JEOL JNM GX 400 spectrometers. Infrared spectra were recorded as KBr disks on a JASCO A302 spectrophotometer. Microanalysis were performed by Analytisch Laboratorien, Engelskirchen, Germany, the University of Queensland Microanalytical Service, St. Lucia, Queensland, Australia, and the University of Otago Microanalytical Service, Otago, New Zealand.

X-ray Crystallography. Crystal structure analyses using single crystal X-ray diffraction methods were performed on L$_b$Pd(PPh$_3$) and [L$_b$PdAg(PPh$_3$)]$_2$(ClO$_4$)$_2$·solvate. A summary of the crystal data for each compound is given in Table I. The intensity data were corrected for Lorentz, polarization and absorption effects; absorption corrections[17a,18,19a] were numerically evaluated by Gaussian integration to a precision of 0.5%; no allowance was necessary for extinction. Crystallographic calculations were performed by using the SHELX-76[19a] and SHELXS-86[19b] systems. Parameters for the scattering curves of atomic Pd and Ag, together with those for anomalous dispersion corrections, were taken from ref 17b,c whereas for the remaining atoms the values incorporated in the SHELX-76 system were used. An analysis of variance at convergence of refinement for each analysis showed no special features. Crystallographic diagrams were obtained by using the ORTEP program.[20]

(17) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV: (a) p 55; (b) p 100; (c) p 149.

(18) Cromer, D. T.; Lieberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(19) (a) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976. (b) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; p 175.

Supplementary Material Available: Details of the structural determination and Table S-I, listing full crystal data and details of data collections and refinements for both $L_bPd(PPh_3)$ and $[L_bPdAg(PPh_3)]_2(ClO_4)_2$, Tables S-II–S-V, listing hydrogen atom parameters, thermal parameters, equations of least-squares planes, and intermolecular contacts for $L_bPd(PPh_3)$, and Tables S-VI–S-IX, listing the same data for $\{L_bPdAg(PPh_3)\}_2(ClO_4)_2$·solvate (15 pages); Tables S-X and S-XI, listing structure factors for the two compounds (82 pages). Ordering information is given on any current masthead page.

(20) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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Phosphole Complexes of Silver(I). Investigations of Structure and Bonding by X-ray Crystallography, Infrared Spectroscopy, and CP/MAS and Solution 31P NMR Spectroscopy

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A series of complexes of 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP), of the type $[L_nAgX]_m$ ($n = 1$, $m = 4$, L = DMPP; $n = 2$, $m = 2$, L = DMPP, DBP; $n = 3$, $m = 1$, L = DBP; X = Cl, Br, I), have been prepared and characterized. The structure of $[(DBP)_2AgCl]_2$ has been determined by X-ray crystallography. It crystallizes in the space group $P\bar{1}$ with $a = 10.831$ (3) Å, $b = 11.683$ (3) Å, $c = 11.243$ (3) Å, $\alpha = 82.73$ (2)°, $\beta = 89.39$ (2)°, $\gamma = 78.01$ (2)°, and $Z = 1$. The structure was refined by least-squares methods with $R_F = 0.066$ for 2273 unique reflections with $I/\sigma(I) \geq 3.0$. The complex crystallizes as a dimer with a structure similar to that which has previously been observed for 2:1 complexes of PPh_3 with silver(I) halides. In this structure both of the silver atoms are tetracoordinated through bonds to the P atoms of two phosphole ligands and two μ_2-chlorine atoms, which bridge the two silver atoms. The dimer lies on a crystallographic inversion center. The bond lengths in the $P_2Ag_2Cl_2$ core are Ag–P = 2.504 (3), 2.525 (4), Ag–Cl = 2.643 (3), 2.634 (4), and Ag---Ag = 3.750 Å, and the bond angles are Ag–Cl–Ag = 90.5 (1), Cl–Ag–Cl = 89.4 (1), P–Ag–Cl = 108.5 (1), 122.4 (1), 121.5 (1), 102.6 (1), and P–Ag–P = 111.5 (1)°. The Ag_2Cl_2 unit in this complex is thus almost perfectly square, with a difference of less than 0.01 Å between the symmetrically inequivalent Ag–Cl bond lengths. This contrasts with the structure of the corresponding PPh_3 complex, $[(PPh_3)_2AgCl]_2$, where the Ag–Cl bond lengths differ by nearly 0.15 Å. The structures of the other members of the phosphole/AgX series were deduced from their far IR and cross-polarization magic-angle-spinning (CP/MAS) 31P NMR spectra. Thus, the 1:1 complexes ($n = 1$), which exist only for L = DMPP, are shown to have the tetrameric cubane structure. The 2:1 complexes all have the halogen-bridged dimeric structures, $[L_2AgX]_2$, which was proved for the L = DBP, X = Cl case by X-ray diffraction. Their far-IR spectra appear to be very sensitive to distortion of the Ag_2X_2 core. The 3:1 complexes, which exist only for L = DBP, have mononuclear $[L_3AgX]$ structures. The CP/MAS 31P NMR spectra show splitting due to $^1J(Ag–P)$ coupling, which progressively decreases in magnitude from the 1:1 complexes (450–580 Hz) to the 3:1 complexes (ca. 250 Hz). A further splitting of about 100 Hz was observed for some of the 2:1 and 3:1 complexes, and this is assigned to $^2J(P–P)$ coupling between crystallographically inequivalent phosphorus atoms that are bound to a common silver atom in the complex. The ionic 4:1 complexes $[L_4Ag]BF_4$ (L = DMPP, DBP) were also prepared and characterized by CP/MAS 31P NMR spectroscopy. The Ag–P bond length r may be estimated with reasonable accuracy from $^1J(Ag–P)$ via the empirical relation $1/(r/\text{Å})^3 = (3.707 \times 10^{-5})J/\text{Hz} + 4.788 \times 10^{-2}$. The solution 31P NMR spectrum of $[LAgCl]_4$ (L = DMPP) in CH_2Cl_2 at -80 °C shows a signal due to $[L_4Ag]^+$, as well as that due to the parent $[LAgCl]_4$. Likewise, $[L_2AgX]_2$ complexes (L = DMPP; X = Cl, Br) show signals due to $[LAgCl]_4$, $[L_3AgCl]$, and $[L_4Ag]^+$. Solutions of $[L_3AgX]$ (L = DBP; X = Cl, Br, I) show signals due to $[L_4Ag]^+$ and uncoordinated L, as well as to the parent $[L_3AgX]$. Thus, although the binuclear complexes $[L_2AgX]_2$ are the prevalent ones in the solid state, they do not exist in solution in detectable amounts. The nonexistence of $[LAgX]_4$ (L = DBP) and $[L_3AgX]$ (L = DMPP) in the solid state is consistent with the absence or, in the latter case, high lability of these species in solution.

Introduction

Tertiary phosphine complexes of silver(I) of the type $[L_nAgX]$ (L = tertiary phosphine; $n = 1$–4; X = coordinating or noncoordinating anion) were first prepared in 1937 by Mann, Wells, and Purdie.[2] Their general method of preparation involves the reaction of stoichiometric amounts of the phosphine ligand with the appropriate silver(I) salt. These complexes display a diversity of structural types, and several reviews on this topic have been published.[3–6] The established structural chemistry of the $[L_nAgX]$

complexes is quite similar to that of the copper(I) analogues, although fewer X-ray crystallographic studies have appeared in the case of silver(I). The similarities and differences between the silver(I) and copper(I) cases are well illustrated by the complexes with L = triphenylphosphine, Ph_3P. Thus, for $n = 1$, tetramers $[L_nAgX]_4$ with both the "cubane" and "step" structures have been characterized,[7–9] and these have close parallels in the corresponding

(1) (a) University of Nevada. (b) University of Warwick. (c) University of Auckland. (d) Colorado State University. (e) JEOL.
(2) Mann, F. G.; Wells, A. F.; Purdie, D. *J. Chem. Soc.* **1937,** 1828.
(3) (a) Booth, G. *Adv. Inorg. Chem. Radiochem.* **1964,** *6,* 1. (b) Booth, G. *In Organic Phosphorus Compounds*; Vol. 1, Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, pp 433–545.

(4) (a) McAuliffe, C. A. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979. (b) McAuliffe, C. A. *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; Halstead: New York, 1973.
(5) Smith, W. E. *Coord. Chem. Rev.* **1981,** *35,* 253; **1982,** *45,* 307; **1985,** *67,* 297.
(6) Lancashire, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Vol. 5, p 775.
(7) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976,** *15,* 2467.
(8) Teo, B.-K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976,** 185.
(9) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976,** *15,* 2474.