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Article

Silver Coordination Chemistry of a New Versatile “Janus”-type N_2,O_2-Bichelating Donor, Formation of an Unprecedented Supramolecular Network of Binuclear Silver Building Blocks Containing a Five-Coordinate β-Diketonate, and Isolation of Unexpected Silver–Tin–Silver Heterotrimetallic Complexes from Silver Metathesis Reactions

Augusto Cingolani,[†] Effendy,[‡,§] Fabio Marchetti,[*,†] Claudio Pettinari,[†] Riccardo Pettinari,[†] Brian W. Skelton,[‡] and Allan H. White[‡]

Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, via S. Agostino 1, 62032 Camerino, Italy, Department of Chemistry, The University of Western Australia, Crawley, Western Australia 6009, Australia, and Jurusan Pendidikan Kimia, Universitas Negeri Malang, Jalan Surabaya 6, Malang 65145, Indonesia

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Synthetic, spectroscopic, and single-crystal X-ray studies are reported for several complexes of silver(I) with the N_2,O_2-bichelating Q^{py} ligand (HQ^{py} = 1-(2-pyridyl)-3-methyl-4-trifluoroacetylpyrazol-5-one). Direct interaction between HQ^{py} and $AgNO_3$ in methanol, in the presence of $NaOCH_3$, affords derivative $Ag(Q^{py})$, showing a polynuclear structure composed of dinuclear building blocks with two different Ag environments and two Q^{py} donors differently connected. By adding neutral ligands such as PR_3 (R = Ph, Cy, C_6H_4-*o*-CH_3, C_6H_4-*p*-F, Bu^i) to $Ag(Q^{py})$, dinuclear $Ag(Q^{py})(PR_3)$ derivatives have been isolated, containing bridging N_2,O-exotridentate Q^{py} donors spanning a pair of $AgPR_3$ moieties. Reaction of $Ag(Q^{py})(PPh_3)$ with excess PPh_3 produces the mononuclear $Ag(Q^{py})(PPh_3)_2$ containing N_2-chelate Q^{py}. $Ag(Q^{py})$ interacts with 1,2-bis(diphenylphosphino)ethane (dppe) yielding the derivative $Ag(Q^{py})$(dppe), having a polynuclear structure in the solid state which is seemingly disrupted in solution, with the formation of two new species, a mononuclear neutral compound and a dinuclear ionic one. By the interaction of $Ag(Q^{py})$ with nitrogen donors L (L = imidazole (imH), 1-methylimidazole (Meim), 1-methyl-2-mercaptoimidazole (Hmimt), 1,10-phenanthroline (phen)), mononuclear species $Ag(Q^{py})(L)$ have been obtained, where Q^{py} is coordinated to silver in N_2-chelating mode. $Ag(Q^{py})(PPh_3)_2$ reacts with $SnRCl_3$ (R = Ph, Bu^n) affording heterotrimetallic $[\{(Ph_3P)_2AgCl\}_2SnRCl_3]$ derivatives.

Introduction

Multimetallic arrays, controlled by predesigned multidentate ligands, have recently received increased attention.[1–3] The self-assembly of polymers and nanostructures through the use of polydentate ligands can allow the synthesis of supramolecular metal-organic structures with new functionalities applicable in several fields, e.g. as potential luminescent or catalytic materials.[4–10] Examples in the literature of

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[*] Corresponding author. E-mail: fabio.marchetti@unicam.it. Phone: 0039 0737 402217. Fax: 0039 0737 637345.

[†] Università degli Studi di Camerino.

[‡] The University of Western Australia.

[§] Universitas Negeri Malang.

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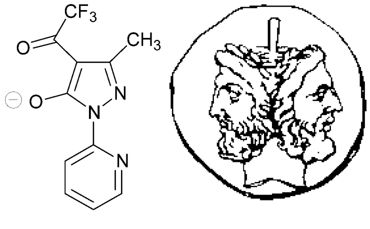
10.1021/ic0497376 CCC: $27.50

polydentate donors are mainly neutral[11] or dianionic homoditopic ligands,[12−14] consisting of two equivalent binding sites for two metal ions, so as to synthesize homodinuclear compounds. However, they preclude straightforward preparation of heterodinuclear complexes, whereas heteroditopic ligands, which offer two different binding sites for different metal ions, permit a far simpler synthesis of heterodinuclear species.[15]

We are currently interested in the synthesis of heterodi- and heteropoly-nuclear metal compounds, and have recently reported heteropolymetallic Fe−Pt−M (M = Zn, Cd, and Hg) compounds based on pyrazolate bridging ligands[16] and heterobimetallic Rh−Sn compounds with polydentate pyrazolones.[17] To our knowledge, no structurally defined bis-chelating mixed N_2-neutral, O_2-monoanionic ligands have been reported till now.

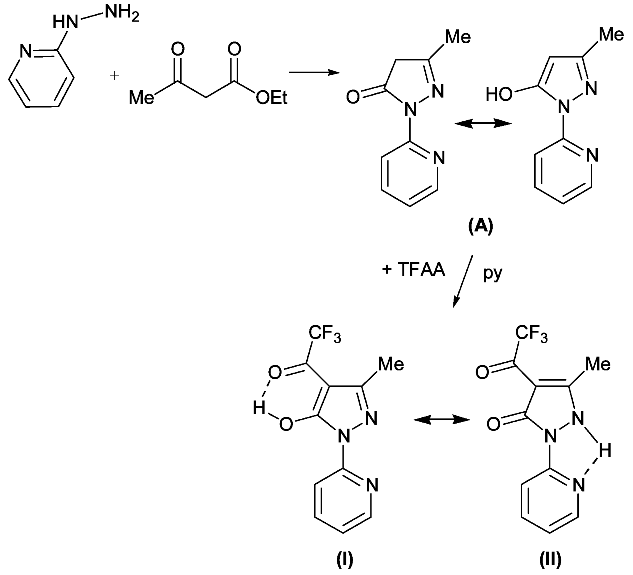
4-Acyl-5-pyrazolones are an exotic variation of classical *β*-diketonates.[18] We are currently developing 4-acyl-5-pyrazolonates with novel functionalities and testing their coordinative ability toward several metal acceptors,[19−24] with a strategy based on systematic substitution of the peripheral groups in order to tune their steric and electronic features.[25−29]



(Q^{py})$^-$ **Janus**

Figure 1. Ligand (Q^{py})$^-$.

Scheme 1



Here we report the synthesis of a new 4-acyl-5-pyrazolone, namely HQ^{py} with a pyridine ring bonded to the pyrazole (Figure 1) which possesses two completely different potential chelating faces, oppositely directed, cf. Janus, the Roman God of doorways, entrances, gateways, thresholds, and beginnings.

While the N_2-chelating moiety is similar to those of common *N*,*N*′-aromatic bidentate ligands, the O_2-chelating moiety may be considered analogous to that of acetylacetone and should act both in neutral and anionic form. The coordination chemistry of classical 4-acyl-5-pyrazolones toward silver(I) has been previously explored, and Ag(I) was shown to be able to bind not only to the oxygen atoms of 4-acyl-5-pyrazolonates but also to the nitrogen of the pyrazole, affording mononuclear, dinuclear, and polynuclear derivatives, where the different nuclearity may be tuned by appropriate choice of ancillary N-, S-, or P-donors.[30,31]

Results and Discussion

Synthesis of the Ligand HQ^{py}. HQ^{py} has been prepared in two steps: (a) reaction between 1-(2-pyridyl)-hydrazine and ethyl acetoacetate, affords 1-(2-pyridyl)-3-methyl-5-pyrazolone (A); (b) reaction of A with trifluoroacetic anhydride (TFAA) in pyridine, produces the HQ^{py} ligand (Scheme 1).

The proligand HQ^{py} is very soluble in acetone, acetonitrile, THF, DMSO, alcohols, and chlorinated solvents. The IR

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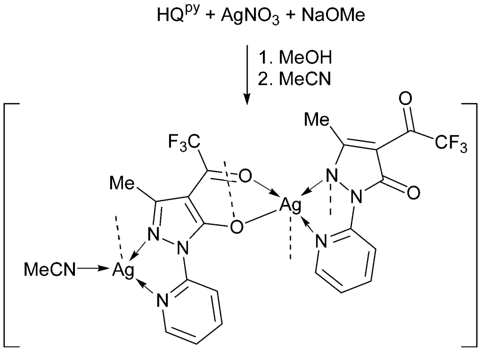
Scheme 2



1

band at 3138 cm^{-1} is indicative of the presence of an intramolecular (N−H···N) hydrogen bonding (tautomeric form (II)), whereas at 1652 and 1620 cm^{-1} strong absorptions have been detected, due to chain carbonyl and heterocyclic carbonyl stretching modes, respectively.

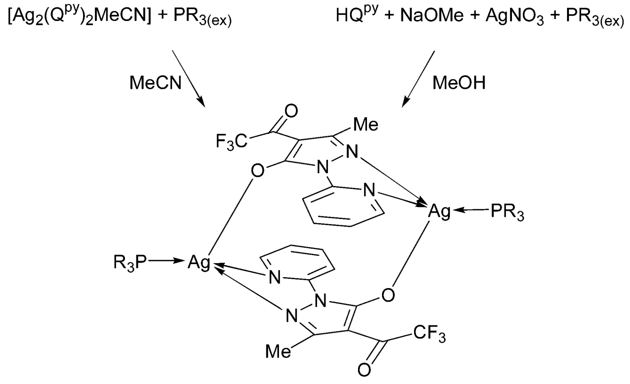
Synthesis of Silver Complexes and Characterization. The interaction between $AgNO_3$ and HQ^{py} in methanol in the presence of a base such as NaOMe afforded the derivative **1**, soluble only in DMSO and acetonitrile (Scheme 2), from which it was recrystallized.

Derivative **1** is polynuclear in the solid state, with two different silver environments and two different Q^{py} ligands (see crystallographic discussion below). The IR spectrum of **1** shows two bands at 2312 and 2278 cm^{-1}, typical of silver-bonded MeCN,[32] with several overlapped bands between 1615 and 1660 cm^{-1}, arising from several (C═O) vibration modes.[33] In acetonitrile solution, the polymeric structure disappears, with only one set of proton and carbon resonances being observed in the ^1H, ^{19}F, and ^{13}C NMR spectra. Moreover, it is partially dissociated into $Ag(MeCN)_n^+$ and $(Q^{py})^-$, as indicated by its conductance value Λ_M of 39.2 ohm^{-1} cm^2 mol^{-1} in acetonitrile.

The interaction of **1** with PR_3 donors (R = Ph, C_6H_4-*o*-CH_3, C_6H_4-*p*-F, Cy, Bu^i) in acetonitrile has afforded derivatives **2**−**6** of stoichiometry $Ag/Q^{py}/PR_3$ 1:1:1, independently of the amount of phosphine employed. Compounds **2**−**6** can also be obtained by the direct interaction of $AgNO_3$, HQ^{py}, and PR_3 in methanol in the presence of NaOMe (Scheme 3).

Derivatives **2**−**6** are all dinuclear species in the solid state (see crystallographic discussion below). The ν(C═O) absorptions in the IR spectra of **2**−**6** are found essentially unchanged with respect to those in free, neutral HQ^{py}, in accordance with the coordination of Q^{py} primarily through the N atoms of the pyrazole and pyridine rings. In the far IR region, several new bands are present, some of which arise from phosphine modes.[34,35] Derivatives **2**−**6** are very soluble in chlorinated solvents, in which they are nonelectrolytes. The ^1H, ^{19}F, and ^{13}C NMR spectra of **2**−**6** show one set of resonances, as expected. Low temperature ^{31}P NMR spectra show a double doublet with $^1J_{P-Ag}$ in the range 620−750 Hz, typical of compounds containing one phosphine bound to a silver with increased s character in its hybridization, analogously to previously reported dinuclear $[Ag_2(Q)_2(PR_3)_2]$.[30,31,36] Differences in steric and electronic properties of the phosphines employed do not greatly impact on the stoichiometry and structure of derivatives **2**−**6**.

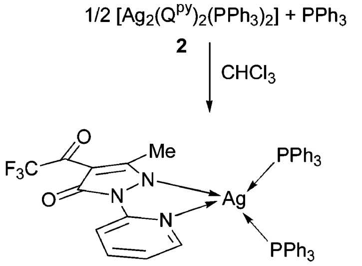
Scheme 3



2 - 6

(**2**, R = Ph; **3**, R = C_6H_4-*o*-CH_3; **4**, R = C_6H_4-*p*-F; **5**, R = Cy; **6**, R = Bu^i)

Scheme 4



7

The interaction of **2** with excess PPh_3 in chloroform yields the mononuclear derivative $[Ag(Q^{py})(PPh_3)_2]$, **7** (Scheme 4).

The elemental composition is similar to that of analogous $[Ag(Q)(PR_3)_2]$ (R = Ph, Cy) as reported in previous papers.[30,31] However, the solid state structure differs significantly, as the pyrazolone coordinates to silver through both the N atoms (see crystallographic discussion below). Accordingly, the IR carbonyl band is found at 1669 cm^{-1}, at higher frequency with respect to those of derivatives **2**−**6**, in which one O atom is involved in bonding with silver. The ^{31}P NMR spectrum recorded at 218 K always exhibits a pair of doublets, with $^1J_{P-Ag}$ values of 437 and 390 Hz, typical of compounds containing two phosphines bound to silver.[36−38]

Attempts to obtain derivative **7** by direct interaction between $AgNO_3$, HQ^{py}, NaOMe, and PPh_3 failed, even if a

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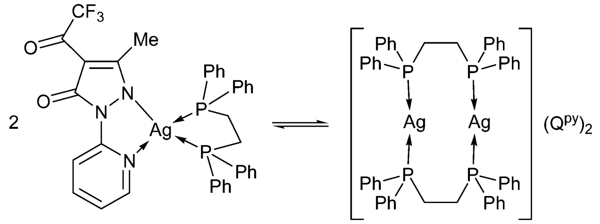
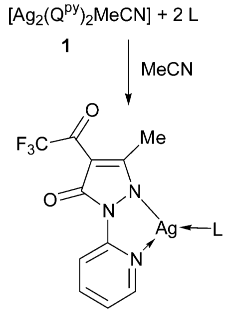
Scheme 5



Scheme 6



9 - 11

(**9**, L = Meim; **10**, L = imH; **11**, L = Hmimt)

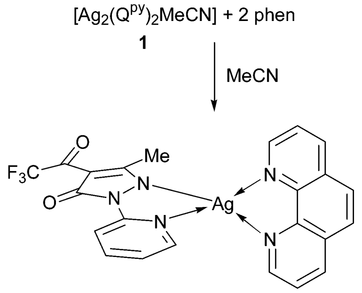
large excess of phosphine with prolonged warming was employed. The interaction of derivative **2** with excess tricyclohexylphosphine, carried out with the intention of obtaining a mixed phosphine silver compound, gave only derivative **5** by a complete substitution of PPh_3 by PCy_3.

The reaction between derivative **1** and dppe in acetonitrile afforded compound **8** $[Ag(Q^{py})(dppe)]$. It is only slightly soluble in DMSO, acetonitrile, acetone, and chlorinated solvents, where at least two different species have been identified. In fact, the NMR spectra in chlorinated solvents show a unique set of resonances at room temperature (rt) which split into two sets at low temperature. In particular, the ^{31}P NMR at 223 K shows two different signals. The pair of doublets at −4.8 ppm, with $^1J_{P-Ag}$ values of 366 and 317 Hz, is assignable to a species with a AgP_2N_2 core. Whereas the broad doublet centered at 6.7 ppm is assigned to a dinuclear ionic species such as $[Ag_2(dppe)_2](Q^{py})_2$, $^1J_{P-Ag} =$ 410 Hz is consistent with two-coordinate silver bonded to phosphorus, as in other dinuclear species containing almost linear P−Ag−P moieties.[39] Moreover, the existence in solution of an equilibrium between an ionic species such as $[Ag_2(dppe)_2](Q^{py})_2$ and a neutral one such as $[Ag(Q^{py})(dppe)]$ (Scheme 5) is further confirmed by the conductance Λ_M value in dichloromethane.

We have also explored the reactivity of derivative **1** toward N- and S-donor ligands. The interaction of **1** with 1-methylimidazole (Meim), imidazole (imH), and 1-methyl-2-mercaptoimidazole (Hmimt) in acetonitrile afforded derivatives **9**−**11**, respectively (Scheme 6).

While derivative **9** is very soluble in most organic solvents, derivative **10** is sparingly soluble in chlorinated solvents and acetonitrile, and **11** is only soluble in DMSO, consistent with a polynuclear form for the latter. The broad bands above 3100 cm^{-1} in the IR spectra of **10** and **11** indicate the presence of an extensive hydrogen-bonding network involving the N−H of imH and Hmimt donors, which could be the instrument of polymerization. The IR spectrum of derivative **9**, which exhibits an AgN_3 central core (see crystallographic discussion below), shows a strong ν(C═O) band at 1673 cm^{-1}. Similarly, the ν(C═O) modes in the IR spectra of **10** and **11** fall at very high frequencies, presumably due to uncoordinated carbonyl groups. The unique set of resonances in the proton spectra of **10** and **11** indicates the presence of a fast metal/proton exchange in solution at room temperature.

Scheme 7



12

The interaction of derivative **1** with phen in acetonitrile afforded $[Ag(Q^{py})(phen)]$ **12**, presumably a mononuclear derivative containing an AgN_4 central core (Scheme 7); in fact, its IR and NMR data agree well with the previous data of derivatives **9** and **10** containing Q^{py} bonded only through N atoms. However, the presence of two sets of resonances in its ^1H, ^{19}F, and ^{13}C NMR spectra and conductance Λ_M values suggest partial dissociation of the $(Q^{py})^-$ ligand in solution.

Further, from the reaction between derivative **2** and phen in chloroform in equivalent amounts, both derivatives **7** and **12** have been obtained, being separately recovered from the reaction solution due to their lower solubility (eq 1):

$$\underset{\mathbf{2}}{[Ag_2(Q^{py})_2(PPh_3)_2]} + \text{phen} \xrightarrow[\text{CHCl}_3]{} \underset{\mathbf{7}}{[Ag(Q^{py})(PPh_3)_2]} + \underset{\mathbf{12}}{[Ag(Q^{py})(phen)]}$$

Synthesis of Heterometallic Silver−Tin Complexes. To test the usefulness of (Q^{py}) as heterobitopic ligand, we have studied the interaction of **1** and **7** with organotin acceptors. Tin possesses no spectroscopically silent isotopes, being mainly ^{117}Sn and ^{119}Sn, which can be used as a “spin spy” in the study of the solution properties of their derivatives.[40]

From the reaction of **1**, which exists in acetonitrile as solvated $\{(MeCN)Ag(Q^{py})\}$ units, with the O_2-chelating moiety of Q^{py} probably uncoordinated, and $SnPh_2Cl_2$ in acetonitrile, AgCl immediately precipitated, and a new derivative identified as $(Q^{py})_2SnPh_2$[41] was recovered from solution. Thus, only silver metathesis has taken place.

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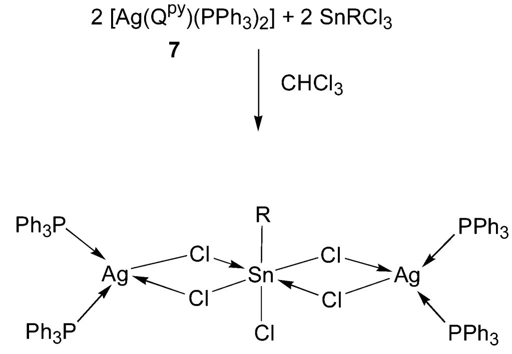
Scheme 8



13, R = Ph; **14**, R = Bu^i

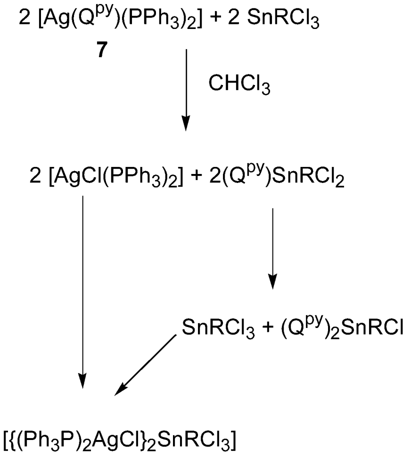
Derivative **7**, having only the N_2-chelating moiety involved in bonding with silver leaving the O_2-chelating moiety free, seemed the best candidate for the synthesis of new mixed metal complexes, useful also because of the presence of the phosphine−silver moiety, investigable by ^{31}P NMR. From interaction of **7** and $SnRCl_3$ in chloroform, we have unexpectedly obtained the heterotrimetallic $[\{(Ph_3P)_2AgCl\}_2SnRCl_3]$, **13** (R = Ph) and **14** (R = Bu^n) (Scheme 8).

The derivatives **13** and **14** are low melting compounds, very soluble in most organic solvents, partially dissociated in dichloromethane. The far-IR spectra of **13** and **14** show the typical bands due to phosphines between 520 and 400 cm^{-1} and very strong and broad bands between 320 and 290 cm^{-1}, due to Sn−Cl. Moreover, in the spectrum of **13** two new bands at 265 and 228 cm^{-1} have been tentatively assigned to Sn−Ph; in the spectrum of **14** a strong band at 587 cm^{-1} has been assigned to Sn−Bu^n, following previous reports.[25−28] The ^{119}Sn NMR spectra of **13** and **14** exhibit resonances at −495 and −441 ppm, respectively, both typical of six-coordinated tin. In the low temperature ^{31}P NMR of **13** and **14**, a resonance with $^1J_{P-Ag}$ of ca. 430 Hz is assignable to the undissociated trimetallic species, whereas the broad doublet at 7.3 ppm ($^1J_{P-Ag}$ of 618 Hz) for **13**, and that at 5.6 ppm ($^1J_{P-Ag}$ of 228 Hz) for **14**, have been respectively assigned to $\{AgCl(PPh_3)\}$ and $[Ag(PPh_3)_4]^+$ fragments, in accordance with the conductance values in chlorinated solvents, indicating the lability of adducts **13** and **14**. ESI-MS spectra of derivatives **13** and **14** recorded in acetonitrile show peaks assignable to $[Ag(PPh_3)_2]^+$ and $[Ag_2(PPh_3)_2Cl]^+$.

As well as the formation of derivatives **13** and **14**, successive pink precipitates identified as $(Q^{py})_2SnRCl$ (R = Ph, Bu^n) have also been obtained.[42] A further third type of colorless crystals has been identified crystallographically as $AgCl/PPh_3$ (1:2).[43]

Silver salt metathesis is the most widely used method of introducing weakly coordinating anions to a metal ion.[44−46] It requires a metal halide and a silver derivative of a weakly coordinating ligand as starting materials. It is known from the literature that in some instances the metathesis completely fails or proceeds very slowly, especially when large, weakly coordinating anions are used in the reaction and, on rare occasions, these mixtures produce long-lived, isolable intermediates.[47] In our case, the metal halide is $RSnCl_3$, and the silver derivative is $(PPh_3)_2Ag(Q^{py})$ where $(Q^{py})^-$ is the weakly coordinating ligand. It is probable that derivatives **13** and **14** and $(Q^{py})_2SnRCl$ are the final products of the silver metathesis with $[AgCl(PPh_3)_2]$ the isolable intermediate (Scheme 9).

Scheme 9



13, R = Ph; **14**, R = Bu^i

Crystal Structures. Crystal/refinement data are available in Table 1. The structurally characterized species comprise an interesting sequence of adducts of AgQ^{py}. In no case is the structure that of the naked AgQ^{py} array, but rather, a solvate in which the solvent invasively interacts with the substrate, or adducts, successively, with one or two molecules of triphenylphosphine.

The simplest of these adducts, **1**, $Ag(Q^{py})$, solvated with half a mole of acetonitrile, in many ways is the most

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(41) $(Q^{py})_2SnPh_2$: The compound is soluble in DMSO and chlorinated solvents. Mp: 260−263 °C. Anal. Calcd for $C_{34}H_{24}F_6N_6O_4Sn$: C, 50.21; H, 2.97; N, 10.33. Found: C, 49.98; H, 3.05; N, 10.03%. Λ_M in dichloromethane: 0.6 ohm^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3117w $\nu(C_{arom}-H)$; 1662vs, 1607s $\nu(C{=}O)$; 446vs, 434s, 347s $\nu(Sn-O)$; 267s, 230m $\nu(Sn-Ph)$. ^1H NMR ($CDCl_3$, 298 K): δ 2.33s (6H, C3−CH_3); 7.05−7.55m br, 7.70d br, 7.98td br, 8.04d, 8.48m br (18H, $N_1-C_6H_4N$ and Sn−C_6H_5).^{119}Sn NMR ($CDCl_3$, 298 K): δ −547.3.

(42) $(Q^{py})_2SnPhCl$: The compound is soluble in DMSO and chlorinated solvents. Mp: 220−223 °C. Anal. Calcd for $C_{28}H_{19}ClF_6N_6O_4Sn$: C, 43.58; H, 2.48; N, 10.89. Found: C, 43.12; H, 2.55; N, 10.66%. Λ_M in dichloromethane: 0.8 ohm^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3120w $\nu(C_{arom}-H)$, 1669vs, 1609s $\nu(C{=}O)$; 450vs, 432s, 352s $\nu(Sn-O)$; 290vs br $\nu(Sn-Cl)$; 270s, 243m $\nu(Sn-Ph)$. ^1H NMR ($CDCl_3$, 298 K): δ 2.38s br (6H, C3−CH_3); 7.00−7.50m br, 7.84d br, 8.10d br, 8.36d br, 8.90m br (13H, $N_1-C_6H_4N$ and Sn−C_6H_5).^{119}Sn NMR ($CDCl_3$, 298 K): δ −556.3. $(Q^{py})_2SnBu^nCl$: The compound is soluble in DMSO and chlorinated solvents. Mp: 206−208 °C. Anal. Calcd for $C_{26}H_{33}ClF_6N_6O_4Sn$: C, 41.55; H, 3.08; N, 11.18. Found: C, 41.78; H, 3.16; N, 11.45%. Λ_M in dichloromethane: 0.5 ohm^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3124w $\nu(C_{arom}-H)$, 1674vs, 1612s $\nu(C{=}O)$; 579m $\nu(Sn-Bu^n)$; 454m, 426s, 374m, 346s $\nu(Sn-O)$; 294vs br $\nu(Sn-Cl)$. ^1H NMR ($CDCl_3$, 298 K): δ 0.85m br, 1.38m br, 1.65m br, 1.99m br (9H, Sn−C_4H_9); 2.40s br (6H, C3−CH_3); 7.47m br, 8.18t br, 8.38d br, 8.89d br (8H, $N_1-C_6H_4N$). ^{119}Sn NMR ($CDCl_3$, 298 K): δ −512.4.

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(46) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133−139.

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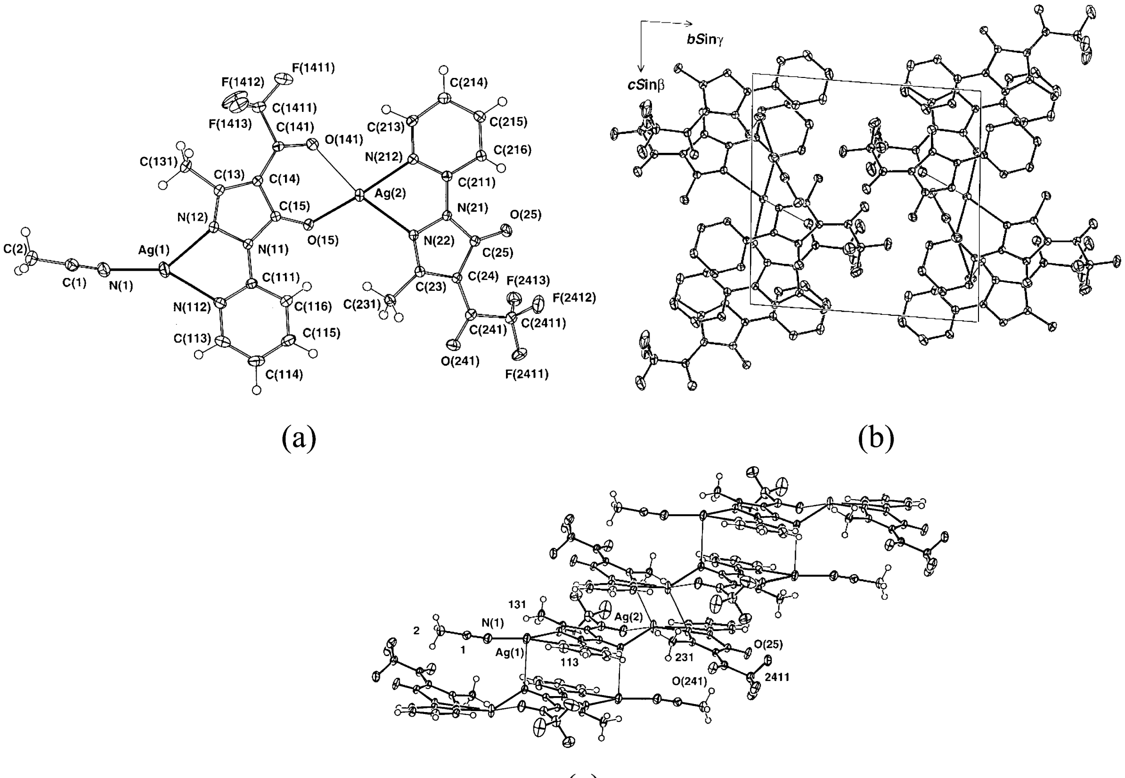
Table 1. Crystal Refinement Data

	1	**2**	**7**	**9**·CHCl$_3$	**14**
formula	$C_{24}H_{17}Ag_2F_6N_7O_4$	$C_{58}H_{44}Ag_2F_6N_6O_4P_2$	$C_{47}H_{37}AgF_3N_3O_2P_2$	$C_{16}H_{14}AgCl_3F_3N_5O_2$	$C_{76}H_{69}Ag_2Cl_5P_4Sn$
M_r/Da	797.2	1280.7	902.6	579.5	1618.0
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	10.3534(7)	8.2987(6)	10.763(2)	7.970(3)	10.2625(8)
b/Å	11.5317(7)	10.7641(7)	10.977(2)	10.929(4)	12.958(1)
c/Å	11.7707(7)	14.910(1)	35.225(2)	13.388(4)	14.482(1)
α/deg	81.425(2)	95.551(2)		104.359(7)	67.144(3)
β/deg	71.291(2)	97.688(2)	97.179(2)	106.418(7)	81.879(2)
γ/deg	74.634(2)	92.473(2)		103.726(7)	74.320(2)
V/Å^3	1280	1312	4129	1022	1707
D_c/g cm^{-3}	2.06_8	1.62_1	1.45_2	1.88_2	1.57_4
Z	2	1	4	2	1
μ(Mo)/mm^{-1}	1.62	0.88	0.62	1.43	1.26
cryst size/mm^3	0.55 × 0.45 × 0.40	0.34 × 0.14 × 0.05	0.34 × 0.24 × 0.16	0.18 × 0.13 × 0.08	0.39 × 0.28 × 0.57
$T_{min/max}$	0.81	0.83	0.93	0.54	0.83
$2\theta_{max}$/deg	75	75	58	65	75
N_t	17914	26877	39134	6183	33994
N (R_{int})	11915 (0.020)	13562 (0.028)	10210 (0.021)	5834 (0.025)	17429 (0.024)
N_o	9461	9892	9281	4496	13099
R	0.036	0.033	0.032	0.070	0.037
R_w	0.046	0.030	0.057	0.094	0.047
$(x, y, z, U_{iso})_H$	refined	refined	constrained	constrained	constrained



(a) (b)

(c)

Figure 2. (a) Single binuclear aggregate of **1**, projected normal to its plane. (b) Unit cell contents projected down the *a*-axis. (c) Extended stack, viewed (approximately) down the *b*-axis.

complex. The results of the determination are consistent in terms of stoichiometry and connectivity with the formulation 2AgQ^{py}·MeCN; that formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure (Figure 2).

Each of the two independent silver atoms is *N*,*N*-chelated by a Q^{py} ligand. The remaining void in the coordination sphere about Ag(1) is filled by the coordination of a solvating acetonitrile molecule: Ag−N(acetonitrile) distances are considerably shorter than the pair of essentially equivalent distances to the chelating nitrogen atoms of the ligand, with the N(acetonitrile)−Ag−*N*,*N′*(chelate) angles not too dissimilar (Table 2), comprising an array reminiscent of (MeCN)Ag(5,5′-me$_2$bpy) in which Ag−N(CMe) is 2.102(9) Å and Ag−*N*,*N′*(bidentate) is 2.292(3), 2.221(3) Å.[48] The void about Ag(2) is filled by the back end of ligand 1, incipiently chelating by virtue of CO(14) being oriented “endo” to O(15)

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Table 2. Selected Geometries for **1**[a]

atoms	param	atoms	param
	Distances (Å)		
Ag(1)−N(12)	2.294(2)	Ag(2)−N(22)	2.390(2)
Ag(1)−N(112)	2.300(2)	Ag(2)−N(212)	2.312(1)
Ag(1)−N(1)	2.131(2)	Ag(1)−O(15)	2.273(1)
Ag(1)···O(15^i)[b]	2.798(2)	Ag(2)···O(141)	2.570(2)
Ag(2)···N(22^{ii})	2.663(2)		
	Angles (deg)		
N(12)−Ag(1)−N(112)	71.36(6)	N(22)−Ag(2)−N(212)	70.88(6)
N(1)−Ag(1)−N(12)	139.39(7)	O(15)−Ag(2)−N(22)	112.66(5)
N(1)−Ag(1)−N(112)	149.25(7)	O(15)−Ag(2)−N(212)	145.99(7)
Ag(1)−N(1)−C(1)	169.2(2)	O(141)−Ag(2)−N(22)	162.41(6)
Ag(2)−O(15)−C(15)	120.8(1)	O(141)−Ag(2)−N(212)	95.84(6)
Ag(2)−O(141)−C(141)	121.7(2)	O(141)−Ag(2)−O(15)	71.74(5)
Ag(2^{ii})−N(22)−Ag(2)	69.46(4)	N(22^{ii})−Ag(2)−N(22)	110.54(6)
Ag(2^{ii})−N(22)−N(21)	123.1(1)	N(22^{ii})−Ag(2)−N(212)	117.13(6)
Ag(2^{ii})−N(22)−C(23)	108.8(1)	N(22^{ii})−Ag(2)−O(15)	93.92(5)
		N(22^{ii})−Ag(2)−O(141)	85.55(6)

[a] In this table, where two silver/ligand combinations comprise the asymmetric unit, the first digit in the atom numbering denotes the "molecule". [b] Transformations of the asymmetric unit: i, $1 - x$, $\bar{y}$, $\bar{z}$; ii, $1 - x$, $\bar{y}$, $1-z$.

to enable this interaction (the only ligand in the present study defined in this conformation, all others being "exo"). The interaction is unsymmetrical: that with O(15) is much stronger than that with O(141), with O(15)−Ag(2)−N(212) quasilinear. This development of quasi-two-coordinate stereochemistry is accompanied by a lengthening of Ag(2)−N(22), cf. the other Ag−N(Q^{py}) distances in this structure. The totality of the array is quasiplanar, perturbed by interaction between successive inversion-related molecules stacked up the *a*-axis. These interactions are of two types, involving, respectively, inversion related pairs of the two different silver atoms. Ag(1) interacts with inversion related O(15) at 2.798(2) Å; the coordination environment remains exactly planar (angle sum: $360._0$°), Ag(1) deviating from the heterocycle ring planes by 0.377(3) Å (C_3N_2) and 0.210(3) Å (C_5N). Inversion related N(22) interacts more strongly with Ag(2), at 2.663(2) Å; Ag(2) deviates appreciably from coplanarity with the heterocycle plane of the *N*,*N′*-chelate (by 0.971(2) Å, cf. 0.168(3) Å (C_5N)), and even further from the heterocycle plane of ligand 1 (1.276(2) Å), the relative orientation of the pair of inversion-related moieties 2 being such that Ag(2)···Ag(2) is very close at 2.8875(3) Å. The interplanar dihedral angle between the two heterocycle components of ligand 2 is appreciable: 23.53(6)°. The incipiently chelate interaction of ligand 1 with Ag(2) is reflected in slight differences in the C−O distances (Table 5), which may also be impacted by the difference in orientation, exo cf. endo, of the carbonyl groups, with substantial concomitant differences in the exocyclic angles at C(n4) and, also, C(n3).

Compound **9**, in principle, may be regarded as a similar array, with the methyl-imidazole ligand supplanting the acetonitrile in the Ag(1)-type environment of **1** (Figure 3).

Here, Ag−N(2, 12) values of the chelate are 2.280(6) and 2.289(6) Å, with the bite angle 71.9(2)°; Ag−N(101) (Meim) is 2.127(6) Å, which is very similar to the Ag−N (acetonitrile) distance, with a greater asymmetry in N(101)−Ag−N(2, 12) (135.5(2), 152.0(2)°). The angle sum about the silver is $359._3$°, and the C_3N_2/C_5N interplanar dihedral angle is 5.9(3)°, with δAg = 0.04(1) Å (both). Ag−N(101)−C(102, 105) values are 129.8(4)°, 124.3(5)°, with the C_3N_2 (im) ring essentially parallel to the Q^{py} (C_3N) planes (dihedrals 13.4(3)°, 7.8(3)°). The molecules again stack up a (short) crystallographic axis; the shortest intermolecular nonhydrogen contact to the silver here is to inversion related N(1), 3.137(6) Å, but interestingly, there is a short Ag···Ag distance (Ag···Ag ($1 - x$, $1 - y$, $1 - z$) 3.068(1) Å). Formation of a Janus-type chelate, as in **1**, here, is precluded/supplanted by a close interaction of O(5) with the hydrogen of the chloroform solvent (O(5)···H 2.2 Å (est)), so that the asymmetric unit of the structure is a [(Meim)(AgQ^{py})($HCCl_3$)] aggregate.

The structure of **2** (Figure 4, Table 3) may be considered as a development of **1** (component 1) and **9** in that the void previously occupied by solvent/unidentate N-donor is now occupied by a phosphine ligand. The asymmetric unit of the structure is (Ph_3P)Ag(Q^{py}); it lies close to a second inversion related moiety, with a Ag···O(5) interaction shorter than that of **1**.

Table 3. Selected Geometries for **2**

Atoms	param	atoms	param
	Distances (Å)		
Ag−N(2)	2.222(1)	Ag−P(1)	2.3429(4)
Ag−N(12)	2.393(1)	Ag−O(5^i)[a]	2.689(1)
	Angles (deg)		
P(1)−Ag−N(2)	149.37(3)	N(2)−Ag−N(12)	69.82(4)
P(1)−Ag−N(12)	139.13(3)	N(2)−Ag−O(5^i)	93.25(4)
P(1)−Ag−O(5^i)	100.15(2)	N(12)−Ag−O(5^i)	81.69(4)
		Agi−O(5)−C(5)	119.8(1)

[a] Transformation of the asymmetric unit: i, $\bar{x}$, $1 - y$, $1 - z$.

Table 4. Selected Geometries for **7** and **14**

(a) **7** ([$(Ph_3P)_2AgQ^{py}$])[a]

atoms	param	atoms	param
	Distances (Å)		
Ag−P(1)	2.4585(7)	Ag−N(2)	2.400(2)
Ag−P(2)	2.4494(7)	Ag−N(12)	2.349(1)
	Angles (deg)		
P(1)−Ag−P(2)	119.36(2)	N(2)−Ag−N(12)	68.59(6)
P(1)−Ag−N(2)	116.48(5)	P(2)−Ag−N(2)	111.02(5)
P(1)−Ag−N(12)	114.89(5)	P(2)−Ag−N(12)	116.12(5)

(b) **14** ([$(Ph_3P)_2AgCl_2Sn(Cl)(Bu^n)Cl_2Ag(PPh_3)_2$])[b]

atoms	param	atoms	param
	Distances (Å)		
Ag−P(1)	2.4692(6)	Ag−Cl(1)	2.8026(5)
Ag−P(2)	2.4668(6)	Ag−Cl(2)	2.6475(5)
	Angles (deg)		
P(1)−Ag−P(2)	123.96(2)	Cl(1)−Ag−Cl(2)	79.63(2)
P(1)−Ag−Cl(1)	108.13(2)	P(2)−Ag−Cl(1)	100.02(2)
P(1)−Ag−Cl(2)	111.10(2)	P(2)−Ag−Cl(2)	121.16(2)

[a] Torsions Ag−P(*m*)−C(*m*n1)−C(ortho) = −49.5(2)°, −34.3(2)°, −36.1(2)° (*m* = 1); 27.2(2)°, 26.5(2)°, 39.5(2)° (*m* = 2) (cf. the ligand in **2**: 66.1(1)°, 37.4(1)°, 32.3(1)°). [b] Sn−Cl(1,2,3) = 2.5175(6), 2.5781(4), 2.3579(11) Å; Sn−C(1) = 2.182(4) Å; and Sn···Ag = 3.9148(2) Å. Sn−Cl(1,2)−Ag = 94.60(2)°, 97.02(2)°; Cl(1)−Sn−Cl(2) = 86.50(2)°; C(1)−Sn−Cl(1,2) = 85.9(1)°, 90.39(8)°; Cl(3)−Sn−Cl(1,2) = 89.91(3)°, 88.98(2)°; and C(1)−Sn−Cl(3) = 4.4(1)°.

Table 5. Selected Q^{py} Ligand Non-Hydrogen Geometries

compd/(ligand)/CO*:^{a}	**1**/1/endo	**1**/2/exo	**2**/exo	**7**/exo	**9**/exo
			Distances (Å)		
N(1)−N(2)	1.389(2)	1.401(2)	1.398(2)	1.397(3)	1.407(8)
N(1)−C(5)	1.393(2)	1.420(2)	1.408(2)	1.420(3)	1.403(9)
N(1)−C(11)	1.406(2)	1.402(2)	1.403(2)	1.400(3)	1.407(7)
N(2)−C(3)	1.318(2)	1.322(2)	1.312(2)	1.310(3)	1.308(7)
C(3)−C(4)	1.435(2)	1.423(2)	1.426(2)	1.429(3)	1.422(10)
C(4)−C(5)	1.433(2)	1.441(3)	1.441(2)	1.448(3)	1.447(8)
C(4)−C(41)	1.426(2)	1.428(3)	1.429(2)	1.417(3)	1.415(8)
C(41)−O(41)	1.237(2)	1.226(2)	1.224(2)	1.235(3)	1.242(7)
C(5)−O(5)	1.254(2)	1.233(2)	1.235(2)	1.224(3)	1.238(9)
C(11)−N(12)	1.335(2)	1.341(2)	1.338(2)	1.336(3)	1.336(9)
			Angles (deg)		
C(11)−N(1)−N(2)	119.6(1)	120.2(1)	118.2(1)	119.0(2)	118.7(6)
C(11)−N(1)−C(5)	129.1(1)	126.6(1)	129.9(1)	128.5(2)	129.4(6)
N(2)−N(1)−C(5)	111.0(1)	111.5(1)	111.8(1)	112.4(2)	111.7(4)
N(1)−N(2)−C(3)	107.3(1)	106.2(1)	106.4(1)	105.9(2)	106.1(6)
Ag−N(2)−N(1)	113.0(1)	112.0(1)	115.63(8)	116.4(1)	114.5(3)
Ag−N(2)−C(3)	138.5(1)	134.6(1)	133.62(9)	137.5(2)	139.4(5)
N(2)−C(3)−C(4)	110.9(2)	112.3(1)	111.9(1)	112.6(2)	112.5(5)
C(31)−C(3)−N(2)	116.8(2)	119.8(1)	118.7(1)	119.8(2)	119.1(6)
C(31)−C(3)−C(4)	132.2(2)	127.9(2)	129.4(1)	127.5(2)	128.4(5)
C(3)−C(4)−C(5)	105.4(1)	106.2(1)	106.1(1)	106.1(3)	105.9(5)
C(3)−C(4)−C(41)	134.5(2)	124.0(2)	124.6(1)	124.7(2)	126.1(6)
C(5)−C(4)−C(41)	120.0(1)	129.8(1)	129.3(1)	128.8(2)	128.0(7)
C(4)−C(41)−O(41)	124.9(2)	125.2(2)	125.3(1)	125.4(2)	124.9(7)
C(4)−C(41)−C(411)	121.0(2)	119.3(2)	119.1(1)	119.5(2)	120.3(5)
O(41)−C(41)−C(411)	114.1(2)	115.5(2)	115.6(1)	115.0(2)	114.9(6)
N(1)−C(5)−C(4)	105.2(1)	103.8(1)	103.6(1)	102.9(2)	103.8(6)
N(1)−C(5)−O(5)	122.6(2)	123.7(2)	123.7(1)	124.0(2)	123.7(5)
C(4)−C(5)−O(5)	132.1(2)	132.5(2)	132.6(1)	133.1(2)	132.4(6)
N(1)−C(11)−N(12)	116.0(2)	116.0(1)	115.6(1)	116.5(2)	116.5(6)
N(1)−C(11)−C(16)	120.9(2)	120.9(2)	121.5(1)	120.7(2)	120.6(6)
N(12)−(11)−C(16)	123.1(2)	123.1(2)	122.9(1)	122.8(2)	122.9(5)
C(11)−N(12)−C(13)	117.9(2)	118.0(2)	117.7(1)	117.8(2)	117.9(6)
Ag−N(12)−C(11)	117.2(1)	118.8(1)	114.37(9)	117.7(2)	118.2(4)
Ag−N(12)−C(13)	124.8(1)	123.1(1)	127.0(1)	123.2(2)	123.9(5)
			Interplanar Dihedral Angles (deg)		
C_3N_2/C_5N	10.58(7)	23.53(6)	7.64(6)	6.89(8)	5.9(3)
C_3N_2/C.CO.C(4)	1.18(5)	0.69(11)	10.79(7)	8.4(1)	2.6(3)
δAg $(C_3N_2)^{+\,b}$	0.377(3)	0.971(2)	0.692(3)	0.146(4)	0.04(1)
δAg $(C_5N)^{+}$	0.210(3)	0.168(3)	0.448(3)	0.496(4)	0.04(1)

[a] Asterisk designates the location of the C(4) carbonyl as "exo" or "endo" (see text). [b] $^{+}\delta$ (Å) values are the chelated silver atom deviations from the plane specified.

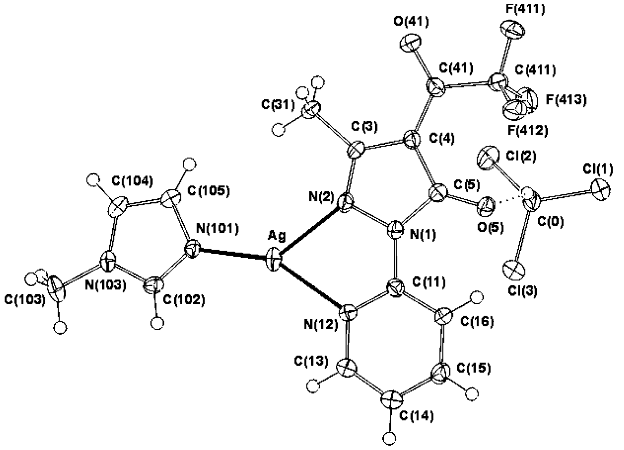

Figure 3. Single molecule of **9**, with the associated chloroform.

Although similar dinuclear R_3P/Ag/Q derivatives have been previously reported,[30,31] here Q^{py} is acting as a bridging N_2O-exotridentate donor while other Q species were found to coordinate in a bridging NO_2-exotridentate fashion. Extension of the array by a Janus-type interaction as observed in **1**, however, is precluded by the bulk of the inversion-related phosphine ligand, with concomitant exo orientation of the carbonyl group. The silver environment is slightly perturbed from planarity (angle sum: $358._3$°); despite the close similarity of the angles about the silver to those of **1**, the *N*,*N′*-chelate distances are now quite unsymmetrical, suggesting some greater predisposition toward a two-coordinate environment concomitant with the replacement of the unidentate-N donor by the phosphine.

The structure of **7** (Table 4) is a 1:2 AgQ^{py}/PPh_3 adduct of the familiar $[(Ph_3P)_2AgQ]$ type;[30,31] in this case also Q^{py} binds to silver through the N_2-chelating moiety (Figure 5).

The results of the structural study of **14** (Table 4) show it to be a trinuclear heterometallic adduct of $[(Ph_3P)_2AgCl]/Bu^nSnCl_3$ (2:1) stoichiometry, or, alternatively, an array of the notional combination $([Ag(PPh_3)_2]^+)_2[Bu^nSnCl_5]^{2-}$, resulting in a neutral molecular array wherein a six-coordinate quasioctahedral tin(IV) atom is, as modeled in space group $P\bar{1}$, disposed on a crystallographic inversion center. This entails disorder between the *n*-butyl donor and the chloride *trans* to it, both terminal axial donors in the coordination sphere (Figure 6). A further alternative view is that of $[(Ph_3P)_2Ag(\mu\text{-Cl})_2Ag(PPh_3)_2]$ expanded by insertion of Bu^nSnCl_3. The four equatorial sites of the tin are occupied by bridging chloride species, bridging pairwise as bidentate ligands to silver atoms to either side, so that the array overall is $[\{(Ph_3P)_2Ag(\mu\text{-Cl})_2\}_2SnClBu^n]$. The pair of $[(Ph_3P)_2Ag(\mu\text{-Cl})_2]$ components is inversion related. Sn−Cl(terminal) is appreciably shorter than Sn−Cl(bridging). Despite the considerable difference in bidentate donors at the silver in this compound (cf., e.g., **7**), the Ag−P distance is, as usual, resistant to change despite an appreciable enlargement in the P−Ag−P angle. The disorder in the terminal/axial donors about the tin is accompanied by disorder in the nearby phenyl substituents of the phosphine ligands, seemingly concerted, there being untenable contacts between the butyl hydrogen atoms and the hydrogens of the primed phenyl ring components of the disorder.

The present compound provides a further interesting member of the quite limited set of arrays of the form $\{(Ph_3P)_2M(\mu\text{-X})_2\}_2M'(X/R)_2$, M = univalent coinage metal (=Ag; there do not seem to be any structurally authenticated examples as yet for Cu(I) or Au(I)), X = halide (=Cl only, so far), and M′ = an octahedral tetravalent metal [accompanied by (2×)(X/R)], trans in the coordination sphere (as in $[\{(Ph_3P)_2Ag(\mu\text{-Cl})_2\}_2OsCl_2]$[49]), or tetrahedral divalent metal (as in $[\{(Ph_3P)_2Ag(\mu\text{-Cl})_2\}_2Co]$[50]). Despite the very substantial difference in M−(μ-Cl) distances and one of the axial substituents, the osmium complex, remarkably, is isomorphous with the present. Os−(μ-Cl) values are 2.356(2), 2.334(2) Å; Os−Cl (axial) is more akin to the present, 2.315(3) Å. P−Ag−P is further enlarged here to 128.49(9)° with Ag−P 2.452(3), 2.455(3) Å and Ag−Cl 2.678(2), 2.807-

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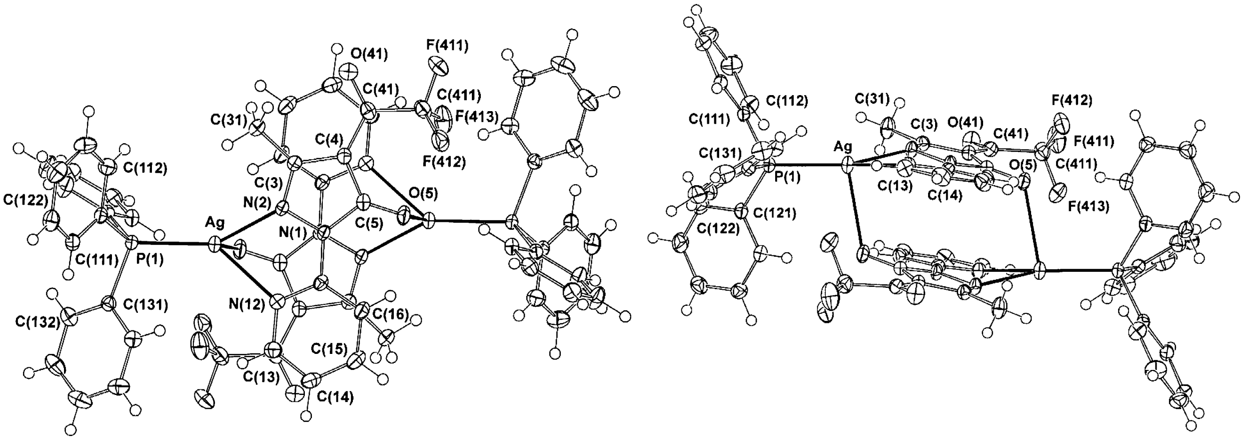
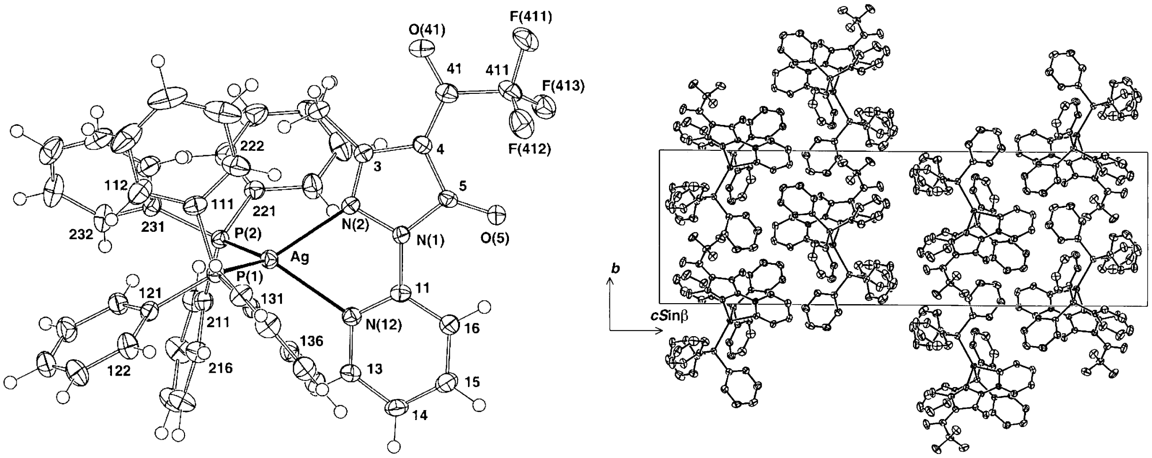


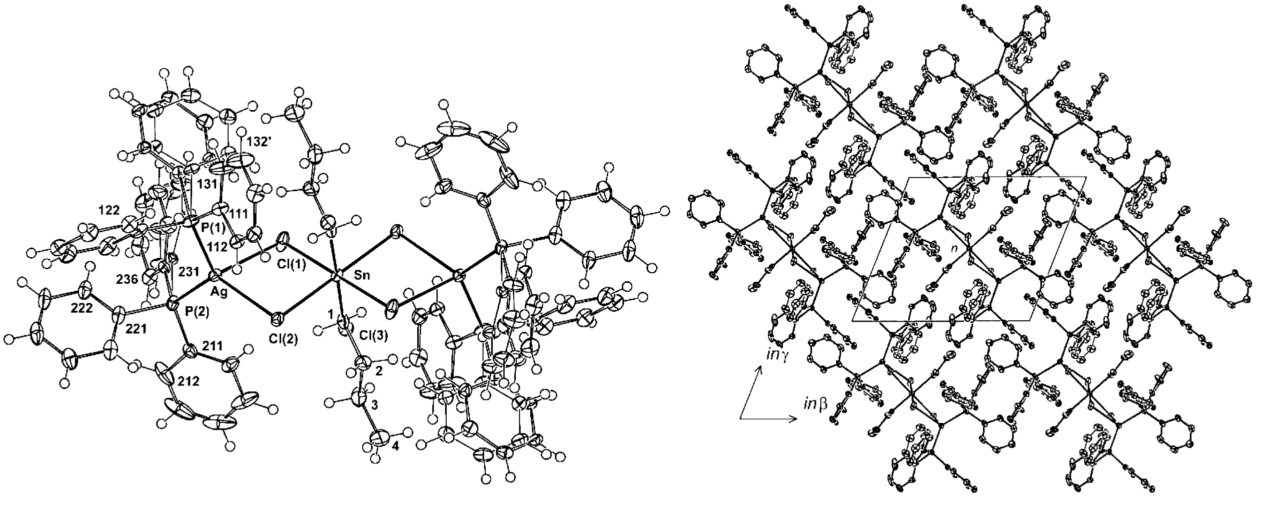
(a) (b)

Figure 4. Single dimer of **2** projected: (a) normal to the ligand plane (down the *a*-axis), and (b) through the dimer (approximately down the *b*-axis).



(a) (b)

Figure 5. (a) Projection of a molecule of **7** normal to the ligand plane. (b) Unit cell contents projected down the *a*-axis.



(a) (b)

Figure 6. (a) Single aggregate of trinuclear **14**. The tin atom is disposed on a crystallographic inversion center entailing disorder between the chloro and *n*-butyl ligands. (b) Unit cell contents projected down the *a*-axis.

(3) Å similar to the present; in the cobalt adduct, Ag−Cl values are 2.687(6)−2.776(6) Å, and Ag−P values are 2.419(10)−2.465(7) Å, with P−Ag−P 128.4(2)°, 126.7(3)°.

The lattice array of the present complex is interesting with inversion-related planar arrays dominating the packing (Figure 6).

Conclusion

The new potentially O_2,N_2-tetradentate Janus-type ligand Q^{py} interacts with silver(I) nitrate affording $[Ag_2(Q^{py})_2(MeCN)]$, polynuclear in the solid state and containing terminal N_2-chelating Q^{py} and bridging N_2,O_2-bichelating Q^{py}. This compound is a useful starting material for the synthesis of several silver complexes containing additional ancillary ligands. Q^{py} prefers to bind silver through its N_2-face, in accordance with the softness of the silver, whereas oxygen donors do not participate in bonding to silver when its coordination sphere is completed by P- and N-donor atoms from phosphines and azoles. In the reaction between $[Ag(Q^{py})(PPh_3)_2]$ and $SnRCl_3$, exchange of Q^{py} ligand from silver to tin has been found, with formation of $(Q^{py})_2SnRCl$ and the heterotrimetallic $[\{(Ph_3P)_2AgCl\}_2SnRCl_3]$ derivatives. The latter are stable in the solid state but labile in solution where they partially dissociate affording several neutral and ionic species.

Further developments of this research will be directed to the synthesis of different mixed metal derivatives, with studies in this field currently ongoing in our laboratory.

Experimental Section

General Remarks. Solvents were used as supplied or distilled using standard methods. All chemicals were purchased from Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried in a vacuum to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in house with Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to 100 cm^{-1} using a Perkin-Elmer system 2000 FT-IR instrument. ^{1}H, ^{13}C, ^{31}P, and ^{19}F, NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C, 121.4 MHz for ^{31}P, and 282.3 MHz for ^{19}F). Proton and carbon chemical shifts are reported in ppm versus Me_4Si while phosphorus chemical shifts are reported in ppm versus 85% H_3PO_4 and fluoro chemical shifts are reported versus $CFCl_3$. The electrical conductances of the dichloromethane solutions were measured with a Crison CDTM 522 conductometer at room temperature. The positive and negative electrospray mass spectra were obtained with a series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade chloroform. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.[51] Peaks containing silver(I) ions are identified as the center of an isotopic cluster.

Syntheses. 1-(2-Pyridyl)-3-methyl-4-trifluoroacetylpyrazol-5-one (HQ^{py}). 2-Hydrazinopyridine (4.49 g, 0.041 mol) was added to ethyl acetoacetate (5.36 g, 0.041 mol) in a 100 mL flask. A solution of KOH (0.10 g, 1.78×10^{-3} mol) in MeOH (10 mL) was subsequently added. The mixture was heated at reflux and stirred for 1 h, the solvent removed on a rotary evaporator and the brown oily product washed with MeCN (20 mL). After filtration, the red-brown powder was dried in vacuo to constant weight and shown to be 1-(2-pyridyl)-3-methylpyrazol-5-one. Yield 74%. The compound is soluble in acetone, DMSO, alcohols, and chlorinated solvents, in which it exists mainly in the enolic form, as shown by its proton NMR spectrum. Mp: 99−101 °C. Anal. Calcd for $C_9H_9N_3O$ (fw = 175.19): C, 61.70; H, 5.18; N, 23.99. Found: C, 61.52; H, 5.10; N, 23.72%. IR (Nujol, cm^{-1}): 1625s $\nu(C{=}O)$; 624s, 572m, 514m, 411m, 363m, 335s, 295m, 232w. ^{1}H NMR ($CDCl_3$, 298 K): δ 2.25s (3H, C3−CH_3); 5.42s (1H, C4H); 7.12dt, 7.82d, 7.86dt, 8.24d (4H, N1−C_5H_4N); 12.8sbr (1H, C5−OH).

The donor HQ^{py} was then synthesized by using trifluoroacetic anhydride in pyridine, following a procedure similar to that reported by Okafor for the synthesis of 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one.[52] Yield 74%. The compound is soluble in acetone, acetonitrile, THF, DMSO, alcohols, and chlorinated solvents. Mp: 209−210 °C. Anal. Calcd for $C_{11}H_8N_3O_2F_3$ (fw = 271.20): C, 48.72; H, 2.97; N, 15.49. Found: C, 48.57; H, 3.08; N, 15.40%. IR (Nujol, cm^{-1}): 3138m $\nu(N{-}H\cdots N)$, 3097w $\nu(C_{arom}{-}H)$, 1652s, 1620vs $\nu(C{=}O)$; 673vs, 636m, 621m, 608s, 572s, 522w, 515s, 475m, 427s, 403w, 382s, 309vs, 289w, 278s, 239m, 223m, 208w. ^{1}H NMR ($CDCl_3$, 298 K): δ 2.50s (3H, C3−CH_3); 7.31dt, 8.00d, 8.05dt, 8.27d (4H, N1−C_5H_4N). ^{13}C NMR ($CDCl_3$, 298 K): δ 16.2 (s, C3-CH_3), 99.4 (s, C4), 113.4, 120.7, 142.1, 142.6, 156.0 (s, C_{arom} del Q^{py}), 147.8 (s, C3), 162.1 (s, C5), CF_3 and CO not observed.

$[Ag_2(Q^{py})_2(MeCN)]$ (1). A methanol solution (30 mL) of the ligand HQ^{py} (0.271 g, 1.0 mmol) and NaOMe (0.054 g, 1.9 mmol) was added to a water solution (5 mL) of silver nitrate (0.170 g, 1.0 mmol). A brown precipitate immediately resulted, which was filtered off, washed with Et_2O (10 mL), dried in vacuo to constant weight, and shown to be compound **1**. Yield 66%. It is soluble in DMSO and acetonitrile. Mp: 276−278 °C. Anal. Calcd for $C_{24}H_{17}Ag_2F_6N_7O_4$: C, 36.07; H, 2.10; N, 12.27. Found: C, 35.79; H, 1.75; N, 11.02%. Λ_M in acetonitrile: 39.2 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3064w $\nu(C_{arom}{-}H)$, 2312w, 2278m $\nu(C{\equiv}N_{MeCN})$, 1654vs, 1648vs, 1642s, 1627s, 1618vs $\nu(C{=}O)$. ^{1}H NMR (CD_3CN): δ 2.38s (3H, C3−CH_3); 7.10dd, 7.84dd, 8.22d, 8.75d, (4H, N1−C_5H_4N). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ 18.7s (C3−CH_3), 99.6s (C4), 117.8q ($^{1}J_{(F-C)}$: 285.6 Hz, CF_3), 114.0s, 120.0s, 140.3s, 148.9s, 155.7s (C_{arom} of Q^{py}), 151.3s (C3), 164.7s (C5), 172.9s (CO). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −77.4s (CF_3) (T = 293 K).

$[Ag_2(Q^{py})_2(PPh_3)_2]$ (2). PPh_3 (0.524 g, 2.0 mmol) was added to an acetonitrile solution (20 mL) of $[Ag_2(Q^{py})_2(MeCN)]$ (**1**) (0.797 g, 1.0 mmol). A colorless precipitate slowly formed. After 1 h, the mixture was filtered off and the precipitate washed with Et_2O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **2**. It is soluble in chlorinated solvents and DMSO and only slightly soluble in acetone and acetonitrile. Yield 66%. Mp: 279−281 °C. Anal. Calcd for $C_{58}H_{44}Ag_2F_6N_6O_4P_2$: C, 54.40; H, 3.46; N, 6.56. Found: C, 54.45; H, 3.66; N, 6.33%. Λ_M in dichloromethane: 0.8 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3067w $\nu(C_{arom}{-}H)$, 1705m, 1656vs, 1632vsbr $\nu(C{=}O)$, 503s, 493vs ν(y-mode of PPh_3), 443w, 435w, 425w ν(t-mode of PPh_3). ^{1}H NMR ($CDCl_3$): δ 2.48s (3H, C3−CH_3), 7.40−7.60m, (15H, H_{arom} PPh_3), 7.82q, 8.09d, 9.05d, (4H, N1−C_5H_4N). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 19.3s (C3-CH_3), 100.1s (C4), 117.8q ($^{1}J_{(F-C)}$: 287.7 Hz, CF_3), 114.4s, 119.1s, 140.1s, 147.6s, 156.9s (C_{arom} of Q^{py}), 129.7d ($^{3}J_{(P-C)}$: 10.9 Hz, m-C of PPh_3), 130.5d ($^{1}J_{(P-C)}$: 40.0 Hz, C-P of PPh_3), 131.7d ($^{4}J_{(P-C)}$: 1.8 Hz, p-C of PPh_3), 133.9d ($^{2}J_{(P-C)}$: 16.4 Hz, o-C of PPh_3), 150.5s (C3), 164.2s (C5), 173.7q ($^{2}J_{(F-C)}$: 37.8 Hz, CO). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 18.5dbr, (T = 293 K); 18.6 2d [$^{1}J(^{31}P{-}^{109}Ag)$ = 740.2 Hz, $^{1}J(^{31}P{-}^{107}Ag)$ = 647.8 Hz) (T = 218 K). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −76.2s (CF_3) (T = 293 K).

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(51) Senko, M. W. National High Magnetic Field Laboratory.

(52) Okafor, E. C. *Talanta* **1982**, *29*, 275−278.

Derivative **2** can be also prepared as follows: an aqueous solution/suspension (20 mL) of $AgNO_3$ (0.170 g, 1.0 mmol) and PPh_3 (0.262 g, 1.0 mmol) was added to a methanol solution (20 mL) of HQ^{py} (0.271 g, 1 mmol) and of NaOMe (0.054 g, 1.0 mmol). A colorless precipitate immediately formed. After 1 h, the mixture was filtered off and the precipitate washed with methanol (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **2**.

[$Ag_2(Q^{py})_2\{P(C_6H_4\text{-}o\text{-}CH_3)_3\}_2$] (3). Derivative **3** was prepared the same way **2** was prepared. It is soluble in DMSO, acetone, and chlorinated solvents. Yield 57%. Mp: 270−272 °C. Anal. Calcd for $C_{32}H_{28}AgF_3N_3O_2P$: C, 56.3; H, 4.14; N, 6.16. Found: C, 56.42; H, 4.67; N, 6.00%. Λ_M in dichloromethane: 0.7 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3070w $\nu(C_{arom}-H)$, 1652s, 1609vs, $\nu(C=O)$, 462s $\nu(P(C_6H_4\text{-}o\text{-}CH_3)_3)$. ^1H NMR ($CDCl_3$): δ 2.20s (3H, C3−CH_3), 6.96m, 7.27m, 7.39m (12H, H_{arom} of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 2.57s (9H, $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 7.47m, 7.79m, 9.02d (4H, N1−C_5H_4N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.5s (C3-CH_3), 117.7q ($^1J_{(F-C)}$: 288.5 Hz, CF_3), 114.3s, 119.0s, 140.0s, 146.8s, 156.9s (C_{arom} of Q^{py}), 133.3d ($^3J_{(P-C)}$: 7.0 Hz, *m-C* of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 127.5d ($^3J_{(P-C)}$: 7.0 Hz, *m-C* of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 126.6d ($^1J_{(P-C)}$: 39.0 Hz, *C*−P of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 131.7d ($^4J_{(P-C)}$: 1.5 Hz, *p-C*$P(C_6H_4\text{-}o\text{-}CH_3)_3$), 142.1d ($^2J_{(P-C)}$: 15.6 Hz, *o-C* of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 132.2d ($^2J_{(P-C)}$: 7.6 Hz, *o-C* of $P(C_6H_4\text{-}o\text{-}CH_3)_3$), 99.9s (*C*4), 150.5s (*C*3), 164.0s (*C*5), 173.4q ($^2J_{(F-C)}$: 36.6 Hz, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −15.6 2d (T = 293 K); −18.1 2d [$^1J(^{31}P-^{109}Ag)$ = 727.5 Hz, $^1J(^{31}P-^{107}Ag)$ = 632.3 Hz] (T = 218 K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −76.1s (CF_3) (T = 293 K).

[$Ag_2(Q^{py})_2\{P(C_6H_4\text{-}p\text{-}F)_3\}_2$] (4). Derivative **4** was prepared using the same method as that used for **2**. It is soluble in acetone, DMSO, acetonitrile, and chlorinated solvents. Yield 65%. Mp: 252−255 °C. Anal. Calcd for $C_{29}H_{19}AgF_6N_3O_2P$: C, 50.17; H, 2.76; N, 6.05. Found: C, 50.45; H, 2.95; N, 6.33%. Λ_M in dichloromethane: 0.9 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3068w $\nu(C_{arom}-H)$, 1700w, 1658s, 1631vs $\nu(C=O)$; 532vs $\nu(P(C_6H_4\text{-}p\text{-}F)_3)$. ^1H NMR ($CDCl_3$): δ 2.39s (3 H, C3−CH_3); 7.43m, 7.21t (12 H, H_{arom} of $P(C_6H_4\text{-}p\text{-}F)_3$) 8.95dd, 7.98dd, 7.78dd, 7.01t (4H, N1−C_5H_4N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2s (C3−CH_3), 99.9s (*C*4), 117.6q ($^1J_{(F-C)}$: 289.0 Hz, CF_3), 114.0s, 119.1s, 140.1s, 139.7s, 147.7s, 156.2s (C_{arom} of Q^{py}), 117.3dd ($^3J_{(P-C)}$: 12.15 Hz, $^2J_{(F-C)}$: 21.3 Hz *m-C* of $P(C_6H_4\text{-}p\text{-}F)_3$), 126.3d ($^1J_{(P-C)}$: 41.2 Hz, *C*-P of $P(C_6H_4\text{-}p\text{-}F)_3$), 164.9dd ($^4J_{(P-C)}$: 1.8 Hz, $^1J_{(F-C)}$: 253.1 Hz, *p-C* of $P(C_6H_4\text{-}p\text{-}F)_3$), 135.9dd ($^2J_{(P-C)}$: 18.8 Hz, $^3J_{(F-C)}$: 8.5 Hz, *o-C* of $P(C_6H_4\text{-}p\text{-}F)_3$), 150.2s (*C*3), 164.1s (*C*5), 173.1q ($^2J_{(F-C)}$: 35.2 Hz, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.69dbr (T = 293 K); 14.82 2d [$^1J(^{31}P-^{109}Ag)$ = 744.5 Hz, $^1J(^{31}P-^{107}Ag)$ = 646.3 Hz) (T = 218 K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −76.1s (CF_3), −106.9s ($P(C_6H_4\text{-}p\text{-}F)_3$) ($T$ = 293 K).

[$Ag_2(Q^{py})_2(PCy_3)_2$] (5). Derivative **5** was prepared using the same method as that used for **2**. It is soluble in acetone, DMSO, and chlorinated solvents. Yield 58%. Mp: 251−252 °C. Anal. Calcd for $C_{29}H_{40}AgF_3N_3O_2P$: C, 52.09; H, 6.12; N, 6.38%. Found: C, 51.86; H, 6.01; N, 6.98. Λ_M in dichloromethane: 0.8 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3062w $\nu(C_{arom}-H)$, 1686w, 1656s, 1615vs $\nu(C=O)$; 513s $\nu(PCy_3)$. ^1H NMR ($CDCl_3$): δ 2.54s (3H, C3−CH_3); 1.86t, 1.35m, (26H, Cy_3P); 7.06t, 7.80t, 8.14d, 9.01d (4H, N1−C_5H_4N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2s (C3−CH_3), 114.4s, 119.1s, 139.9s, 147.1s, 156.6s (C_{arom} of Q^{py}), 32.1dd ($^1J_{(P-C)}$: 51.0 Hz, α-*C* of PCy_3), 27.3d ($^2J_{(P-C)}$: 27.1 Hz, β-*C* of PCy_3), 31.7d ($^3J_{(P-C)}$: 6.7 Hz, γ-*C* of Cy_3P), 26.1s (δ-*C* of Cy_3P), 99.8s (*C*4), 150.6s (*C*3), 164.0s (*C*5), 173.8q ($^2J_{(F-C)}$: 16.5 Hz, *C*O); 117.8q ($^1J_{(F-C)}$: 288 Hz, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.5 2d [$^1J(^{31}P-^{109}Ag)$ = 715.3 Hz, $^1J(^{31}P-^{107}Ag)$ = 619.4 Hz) (T = 293 K); 44.2 2d [$^1J(^{31}P-^{109}Ag)$ = 717.7 Hz; $^1J(^{31}P-^{107}Ag)$ = 621.9 Hz], (T = 218 K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −75.7s (CF_3) (T = 293 K).

[$Ag_2(Q^{py})_2(PBu^i{}_3)_2$] (6). Derivative **6** was prepared the same way **2** was. It is soluble in acetone, DMSO, and chlorinated solvents. Yield 58%. Mp: 187−189 °C. Anal. Calcd for $C_{23}H_{43}AgF_3N_3O_2P$: C, 46.87; H, 7.35; N, 7.13. Found: C, 46.65; H, 7.29; N, 7.25%. Λ_M in dichloromethane: 0.7 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3070w $\nu(C_{arom}-H)$, 1682w, 1662vs, 1640vs $\nu(C=O)$; 517s $\nu(PCy_3)$. ^1H NMR ($CDCl_3$): δ 2.51s (3H, C3−CH_3); 1.13m, 1.68m, 1.90m (27H, PCy_3), 7.04t, 7.79t, 8.10d, 9.03d (4H, N1−C_5H_4N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.1s (C3-CH_3), 99.8s (*C*4), 117.8q ($^1J_{(F-C)}$: 565 Hz, CF_3), 114.3s, 119.0s, 139.9s, 147.1s, 156.6s (C_{arom} of Q^{py}), 37.7d ($^1J_{(P-C)}$: 20.9 Hz, α-*C* of $PBu^i{}_3$), 27.2d ($^2J_{(P-C)}$: 4.5 Hz, β-*C* of $PBu^i{}_3$), 24.7d ($^3J_{(P-C)}$: 9.0 Hz, γ-*C* of $PBu^i{}_3$), 150.5s (*C*3), 164.0s (*C*5), 173.2q ($^2J_{(F-C)}$: 55.2 Hz, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −11.5 2d [$^1J(^{31}P-^{109}Ag)$ = 729.8 Hz, $^1J(^{31}P-^{107}Ag)$ = 632.2 Hz] (T = 293 K); −12.7 2d [$^1J(^{31}P-^{109}Ag)$ = 731.1 Hz; $^1J(^{31}P-^{107}Ag)$ = 633.5 Hz] (T = 218 K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −76.1s (CF_3) (T = 293 K).

[$Ag(Q^{py})(PPh_3)_2$] (7). PPh_3 (0.262 g, 1.0 mmol) was added to a chloroform solution (20 mL) of [$Ag_2(Q^{py})_2(PPh_3)_2$] (**2**) (0.640 g, 0.5 mmol). The clear solution was stirred at room temperature overnight. Then petroleum ether 40-60 was added (10 mL) and a pale pink precipitate afforded, which was filtered off, washed with Et_2O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **7**. It is soluble in chlorinated solvents, DMSO, acetone, and acetonitrile. Yield 74%. Mp: 207−208 °C. Anal. Calcd for $C_{47}H_{37}AgF_3N_3O_2P_2$: C, 62.40; H, 4.35; N, 4.64. Found: C, 62.06; H, 4.16; N, 4.82%. Λ_M in dichloromethane: 0.8 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3065w $\nu(C_{arom}-H)$, 1693m, 1669vs, 1625vs, $\nu(C=O)$; 509s, 502vs, 494s ν(*y*-mode of PPh_3), 440m, 430w, 420w ν(*t*-mode of PPh_3). ^1H NMR ($CDCl_3$): δ 2.16s (3H, C3−CH_3), 7.20−7.45m (30H, H_{arom} of PPh_3), 6.81dd, 7.65dd, 7.74dbr, 8.96dbr (4H, N1−C_5H_4N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.7s (C3-CH_3), 100.0s (*C*4), 118.0q ($^1J_{(F-C)}$: 292.5 Hz, CF_3), 114.4s, 118.9s, 139.1s, 147.2s, 155.9s (C_{arom} of Q^{py}), 129.2d ($^3J_{(P-C)}$: 9.7 Hz, *m-C* of PPh_3), 130.5d ($^4J_{P-C}$: 1.2 Hz, *p-C* of PPh_3), 132.6d ($^1J_{(P-C)}$: 24.9 Hz, *C*−P of PPh_3), 133.7d ($^2J_{(P-C)}$: 16.4 Hz, *o-C* of PPh_3), 151.1s (*C*3), 165.0s (*C*5), *C*O not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.6s (T = 293 K), 9.6 2d [$^1J(^{31}P-^{109}Ag)$ = 436.9 Hz, $^1J(^{31}P-^{107}Ag)$ = 390.1 Hz] (T = 218 K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −75.9s (T = 293 K).

[$Ag(Q^{py})(dppe)$] (8). Derivative **8** was prepared the same was **2** was. It is soluble in DMSO but only sparingly soluble in acetone, acetonitrile, and chlorinated solvents. Yield 62%. Mp: 294−296 °C. Λ_M (CH_2Cl_2, 10^{-3} M): 2.3 ohm^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{37}H_{31}AgF_3N_3O_2P_2$: C, 57.23; H, 4.02; N, 5.41. Found: C, 57.93; H, 4.56; N, 5.83%. Λ_M in dichloromethane: 4.5 ohm^{-1} cm^2 mol^{-1}. Λ_M in acetonitrile: 47.3 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3064w $\nu(C_{arom}-H)$, 1694m, 1672s, 1624vs $\nu(C=O)$. ^1H NMR ($CDCl_3$): δ 2.21s br (3H, C3−CH_3); 2.46s br (4H, dppe), 7.30−7.50m (20H, H_{arom} dppe), 6.95t br, 7.78t br, 7.95d br, 9.06d br (4H, N1−C_5H_4N) (T = 298 K). ^1H NMR ($CDCl_3$): δ 1.68s, 1.79s (3H, C3−CH_3); 2.21m, 2.50s (4H, dppe), 7.05−7.50m (20H, H_{arom} dppe), 6.85t, 7.62m, 7.76t, 7.83t, 8.15d, 8.96d, 9.09d (4H, N1−C_5H_4N) (T = 223 K). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2s (C3−CH_3), 24.7br ($Ph_2PCH_2CH_2PPh_2$), 99.8s (*C*4), 117.9q ($^1J_{(F-C)}$: 288.4 Hz, CF_3), 114.5s, 119.0s, 147.4s, 150.9s, 155.8s (C_{arom} of Q^{py}), 129.6sbr, 131.2sbr, 132.0sbr, 132.7sbr (C_{arom} of dppe), 139.5s (*C*3), 164.7s (*C*5), 173.8q ($^2J_{(F-C)}$: 34.8 Hz, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.96mbr, (T = 293 K); 6.7dbr [$^1J(^{31}P-^{109/107}Ag)$ = 410 Hz], −4.8 2d [$^1J(^{31}P-^{109}Ag)$ = 366 Hz; $^1J(^{31}P-^{107}Ag)$ = 317 Hz] (T =

218 K). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −75.9s (CF_3) (T = 293 K). ^{19}F{^{1}H} NMR (CDCl$_3$): δ - -75.7s, −75.8s (CF_3) (T = 223 K).

[Ag(Q^{py})(Meim)] (9). 1-Methylimidazole (Meim) (0.164 g, 2.0 mmol) was added to an acetonitrile solution (20 mL) of [Ag$_2$(Q^{py})$_2$(MeCN)] (**1**) (0.797 g, 1.0 mmol). The clear yellow solution was stirred at reflux overnight, during which time a red color developed. The volume of the solvent was subsequently reduced to 10 mL and Et$_2$O added (20 mL). A red precipitate formed, which was filtered off, washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.11 Torr) to constant weight, and shown to be derivative **9**. It is soluble in DMSO, acetone, acetonitrile, and chlorinated solvents. Yield 20%. Mp: 156−158 °C. Anal. Calcd for $C_{15}H_{13}AgF_3N_5O_2$: C, 39.15; H, 2.85; N, 15.22. Found: C, 38.62; H, 2.92; N, 15.03%. Λ_M in dichloromethane: 0.9 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3117m ν(C$_{arom}$−H), 1702w, 1673s, 612vs ν(C═O). ^{1}H NMR (CDCl$_3$): δ 2.44s (3H, C3−CH_3), 3.73s (3H, CH_3 of Meim), 8.12d, 7.07s (3H, H2, H4, and H5 of Meim), 6.98t, 7.71m, 8.88d (4H, N1−C$_5H_4$N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 19.4s (C3−CH$_3$), 29.9s, 31.1s (N−CH$_3$ of Meim), 99.4s (C4), 116.8q ($^{1}J_{(F-C)}$: 288.6 Hz, CF$_3$), 114.2s, 118.9s, 147.5s, 149.7s, 154.5s (C_{arom} of Q^{py}), 118.6s, 121.1s, 130.1s (C_{arom} of Meim), 139.4s (C3), 162.8s (C5), 169.5q ($^{2}J_{(F-C)}$: 34.2 Hz, CO). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −75.9s (CF_3) (T = 293 K).

[Ag(Q^{py})(imH)] (10). Imidazole (imH) (0.136 g, 2.0 mmol) was added to an acetonitrile solution (20 mL) of [Ag$_2$(Q^{py})$_2$(MeCN)] (**1**) (0.797 g, 1.0 mmol). A colorless precipitate immediately formed. After 1 h, the mixture was filtered off and the precipitate washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **10**. It is soluble in DMSO and sparingly soluble in chlorinated solvents. Yield 56%. Mp: 257−259 °C. Anal. Calcd for $C_{14}H_{11}AgF_3N_5O_2$: C, 37.69; H, 2.49; N, 15.70. Found: C, 37.76; H, 2.01; N, 15.54%. Λ_M in dichloromethane: 0.9 ohm^{-1} cm^2 mol^{-1}. Λ_M in acetonitrile: 22.1 ohm^{-1} cm^2 mol^{-1}. Λ_M in DMSO: 10.3 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3157sbr ν(N−H$_{imH}$), 3065w ν(C$_{arom}$−H), 1714w, 1664vs, 1634vs ν(C═O). ^{1}H NMR (CDCl$_3$): δ 2.49s (3H, C3−CH_3); 7.19m, 7.99s (3H, H2, H4, and H5 of imH) 8.67d, 8.33d, 7.93t (4H, N1−C$_5H_4$N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.1s (C3−CH$_3$), 98.2s (C4), 117.4q ($^{1}J_{(F-C)}$: 289.1 Hz, CF$_3$), 112.5s, 119.2s, 147.9s, 149.4s, 154.0s (C_{arom} of Q^{py}), 116.6s, 121.8s, 153.5s (C_{imH}), 139.7s (C3), 163.0s (C5), 170.7q ($^{2}J_{(F-C)}$: 34.2 Hz, CO). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −73.5s (CF_3) (T = 293 K).

[Ag(Q^{py})(Hmimt)] (11). 1-Methyl-2-mercaptoimidazole (Hmimt) (0.228 g, 2.0 mmol) was added to an acetonitrile solution (20 mL) of [Ag$_2$(Q^{py})$_2$(CH$_3$CN)] (**1**) (0.797 g, 1.0 mmol). A yellow precipitate slowly formed. After 10 h, the mixture was filtered off and the precipitate washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **11**. It is soluble only in DMSO. Yield 68%. Mp: 247−248 °C. Anal. Calcd for $C_{15}H_{13}AgF_3N_5O_2S$: C, 36.60; H, 2.66; N, 14.23; S, 6.51. Found: C, 36.43; H, 2.38; N, 14.23; S, 6.16%. Λ_M in DMSO: 6.2 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3189m, 3143m ν(N−H of Hmimt), 3065mbr ν(C$_{arom}$−H), 1708vs, 1693vs ν(C═O). ^{1}H NMR (DMSO-d_6): δ 2.28s (3H, C3−CH_3), 3.61s (3H, N−CH_3), 7.37s, 7.23s (2H, H4 and H5 of Hmimt), 7.20m, 7.80t, 8.22m, 8.62d (4H, N1−C$_5H_4$N). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 18.1s (C3−CH$_3$), 34.4s (N−CH$_3$ of Hmimt), 98.2s (C4), 117.4q ($^{1}J_{(F-C)}$: 277.4 Hz, CF$_3$), 112.5s, 119.3s, 139.7s, 147.9s, 154.0s (C_{arom} of Q^{py}), 116.5s, 121.8s, 153.6s (C_{arom} of Hmimt), 149.4s (C3), 162.9s (C5), 170.7q ($^{2}J_{(F-C)}$: 34.1 Hz, CO-CF$_3$). ^{19}F{^{1}H} NMR (DMSO-d_6): δ −73.5s (CF_3) (T = 293 K).

[Ag(Q^{py})(phen)] (12). 1,10-Phenanthroline (phen) (0.360 g, 2.0 mmol) was added to an acetonitrile solution (20 mL) of [Ag$_2$(Q^{py})$_2$(CH$_3$CN)] (**1**) (0.797 g, 1.0 mmol). A pink precipitate slowly formed. After 10 h, the mixture was filtered off and the precipitate washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **12**. It is soluble in DMSO and sufficiently soluble in acetonitrile and chlorinated solvents. Yield 54%. Mp: 269−272 °C. Anal. Calcd for $C_{23}H_{15}AgF_3N_5O_2$: C, 49.48; H, 2.71; N, 12.54. Found: C, 50.82; H, 2.85; N, 10.26%. Λ_M in dichloromethane: 4.4 ohm^{-1} cm^2 mol^{-1}. Λ_M in acetonitrile: 47.3 ohm^{-1} cm^2 mol^{-1}. Λ_M in DMSO: 16.0 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3086w ν(C$_{arom}$−H), 1700m, 1667s, 1614vs, ν(C═O). ^{1}H NMR (CDCl$_3$): δ 2.41s, 2.45s (3H, C3−CH_3), 7.49m, 7.86m, 7.91s, 7.97s, 9.02d, 9.07d (8H, H_{arom} phen), 6.96t, 7.00t, 8.10m, 8.52d, 8.56d, 9.09d (4H, N1−C$_5H_4$N). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.6s, 19.2s (C3-CH$_3$), 99.9s (C4), 117.8q ($^{1}J_{(F-C)}$: 287.9 Hz, CF$_3$), 114.4s, 119.0s, 143.4s, 150.6s, 157.1s (C_{arom} of Q^{py}), 124.7s, 127.4s, 129.5s, 129.6s, 129.8s, 130.1s, 131.0s, 131.6s, 131.7s, 133.7s, 134.0s, 138.0s, 147.4s, 151.1s (C_{phen}), 139.7s, 140.2s (C3), 164.3s, 166.4s (C5), 173.0q ($^{2}J_{(F-C)}$: 32.8 Hz, CO). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −76.0s, −75.2 (CF_3) (T = 293 K).

Derivative **12** can be also prepared as follows: 1,10-Phenanthroline (phen) (0.180 g, 1.0 mmol) was added to a chloroform solution (20 mL) of [Ag$_2$(Q^{py})$_2$(PPh$_3$)$_2$] (**2**) (0.640 g, 0.5 mmol). The clear solution was stirred at room temperature for 2 h, and then light petroleum was added (10 mL) and a pink precipitate afforded, which was filtered off, washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **12**. From the filtrate a second product was recovered, which was shown to be derivative [Ag(Q^{py})(PPh$_3$)$_2$], **7**.

[{(PPh$_3$)$_2$AgCl}$_2$SnPhCl$_3$] (13). SnPhCl$_3$ (0.302 g, 1.0 mmol) was added to a chloroform solution (40 mL) of [Ag(Q^{py})(PPh$_3$)$_2$] (**2**) (0.902 g, 1.0 mmol). The clear solution was stirred at room temperature overnight, and then solvent was removed to half volume and Et$_2$O (20 mL) added. A colorless precipitate was afforded, which was filtered off, washed with Et$_2$O (10 mL), dried under reduced pressure (20 °C, 0.1 Torr) to constant weight, and shown to be derivative **13**. It is soluble in chlorinated solvents, DMSO, acetone and acetonitrile. Yield 35%. Mp: 123−125 °C. Anal. Calcd for $C_{78}H_{65}Ag_2Cl_5P_4Sn$: C, 57.20; H, 4.00. Found: C, 57.66; H, 4.12%. Λ_M in dichloromethane: 15.1 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3052w ν(C$_{arom}$−H), 514vs, 504vs, 489s ν(y-mode of PPh$_3$), 427m br ν(t-mode of PPh$_3$), 291vs br ν(Sn−Cl), 264m, 228m ν(Sn−Ph). ^{1}H NMR (CDCl$_3$): δ 7.20−7.45m, 7.55−7.60m (65H, H_{arom} of PPh$_3$ and of SnPh). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 7.3s (T = 293 K), 8.1d br [^{1}J(^{31}P−$^{107/109}$Ag) = 421.5 Hz), 4.7br (T = 218 K). ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −494.9 (T = 293 K). ^{119}Sn{^{1}H} NMR (CD$_3$CN): δ −502.5 (T = 293 K). ESI-MS (CHCl$_3$) (+): m/z (%) = 632.45 (100) [Ag(PPh$_3$)$_2$]$^+$, 775.77 (40) [Ag$_2$(PPh$_3$)$_2$Cl]$^+$.

[{(PPh$_3$)$_2$AgCl}$_2$SnBu^{n}Cl$_3$] (14). Derivative **14** was prepared the same way **13** was. It is soluble in chlorinated solvents, DMSO, acetone, and acetonitrile. Yield 39%. Mp: 106−108 °C. Anal. Calcd for $C_{84}H_{70}Ag_2Cl_4P_4Sn$: C, 56.42; H, 4.30. Found: C, 56.76; H, 4.26%. Λ_M in dichloromethane: 14.2 ohm^{-1} cm^2 mol^{-1}. IR (Nujol) data: 3048w ν(C$_{arom}$−H), 515vs, 501vs, 490s ν(y-mode of PPh$_3$), 427m br ν(t-mode of PPh$_3$), 288vs br, 273vs ν(Sn−Cl), 587m ν(Sn−Bu^n). ^{1}H NMR (CDCl$_3$): δ 0.87t, 1.37m, 1.80m, 2.08m (9H, H of SnBu^n), 7.15−7.25m, 7.35−7.45m (60H, H_{arom} of PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 9.6s (T = 293 K), 11.6 2d [^{1}J(^{31}P−^{109}Ag) = 468.7 Hz, ^{1}J(^{31}P−^{107}Ag) = 406.4 Hz), 10.5 2d [^{1}J(^{31}P−^{109}Ag) = 362.5 Hz, ^{1}J(^{31}P−^{107}Ag) = 317.9 Hz], 5.6d br [^{1}J(^{31}P−$^{107/109}$Ag) = 228.3 Hz], 5.9br (T = 218 K). ^{119}Sn{^{1}H} NMR

($CDCl_3$): δ −441.0 ($T = 293$ K). ESI-MS ($CHCl_3$) (+): m/z (%) = 632.45 (100) $[Ag(PPh_3)_2]^+$, 775.77 (10) $[Ag_2(PPh_3)_2Cl]^+$.

Crystal Structure Determination. Crystals suitable for the X-ray work were obtained from chloroform solution, except for crystals of derivative **1**, which were obtained from acetonitrile solution. Full spheres of low-temperature CCD diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding $N_{t(otal)}$ reflections, which merged to N unique (R_{int} cited) after empirical/multiscan absorption correction (proprietary software). N_o with $F > 4\sigma(F)$ were considered "observed" and used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms (x, y, z, $U_{iso})_H$ refined or constrained at estimates as stated. Conventional residuals R, R_w on $|F|$ are cited at convergence (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[53] Pertinent results are given below and in the tables and figures, the latter showing 20% probability amplitude displacement envelopes for the non-hydrogen atoms, with hydrogen atoms having arbitrary radii of 0.1 Å; full CIF depositions (excluding structure factor amplitudes) are available as Supporting Information.

For **6**, only small crystals were available. A determination was undertaken on the available data yielding a model in which the ligands were modeled as slightly displaced pairs of components about a nondisordered silver atom on a general position in space group $P2_1/n$ ($a = 10.792(2)$ Å, $b = 15.348(8)$ Å, $c = 16.045(3)$ Å, $\beta = 105.061(4)°$, $V = 2566$ Å^3). Attempted refinement in a lower symmetry was unfruitful, as were checks for overlooked superlattice reflections. As the model was very similar to that of **2**, it offers little new information and is not recorded.

In **14**, as modeled in space group $P\bar{1}$, the tin atom lies on a crystallographic inversion center, entailing disorder between the terminal chlorine and butyl donors, seemingly concerted with further disorder in two of the six phenyl groups (13n, 23n), with the fragments modeled with site occupancies of 0.5. Attempted refinement in space group $P1$ was unfruitful, and no superlattice was observed.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **7**, **9**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(53) *The Xtal 3.7. System*; Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds.; University of Western Australia: Crawley, Australia, 2001.