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Silver(I) Pyrazolates. Synthesis and X-ray and ^{31}P-NMR Characterization of Triphenylphosphine Complexes and Their Reactivity toward Heterocumulenes

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Silver(I) pyrazolate was reacted with triphenylphosphine, leading to the dinuclear $[Ag_2(pz)_2(PPh_3)_2]$ and $[Ag_2(pz)_2(PPh_3)_3]$ complexes (Hpz = pyrazole), which were extensively characterized by ^{31}P-NMR methods and single-crystal X-ray analyses. Crystals of $[Ag_2(pz)_2(PPh_3)_2]$ are triclinic, space group $P\bar{1}$, with $a = 9.567(2)$ Å, $b = 11.440(2)$ Å, $c = 10.073(2)$ Å, $\alpha = 93.59(2)°$, $\beta = 64.01(2)°$, $\gamma = 107.24(2)°$, $Z = 1$, and $D_{calc} = 1.539$ g·cm^{-3}; final $R = 0.028$ for 2532 independent reflections having $F > 4\sigma(F)$. They contain centrosymmetric dimers with trigonally coordinated silver atoms, which are 3.870(1) Å apart. Crystals of $[Ag_2(pz)_2(PPh_3)_3]$ are triclinic, space group $P\bar{1}$, with $a = 9.752(2)$ Å, $b = 14.163(2)$ Å, $c = 20.450(2)$ Å, $\alpha = 101.84(1)°$, $\beta = 99.83(2)°$, $\gamma = 100.68(2)°$, $Z = 2$, and $D_{calc} = 1.424$ g·cm^{-3}; final $R = 0.025$ for 7075 independent reflections having $F > 4\sigma(F)$. Each molecule contains two inequivalent silver ions, bearing one and two phosphines, respectively, and a Ag(μ-pz)$_2$Ag ring with a rare twisted conformation. Both complexes readily react with heterocumulenes such as CS_2, COS, CO_2, and RNCO, affording new derivatives, the nature of which is dependent on the experimental conditions. Single-crystal X-ray analysis of $[Ag(pz\text{-}CS_2)(PPh_3)_2]$ has shown the unexpected S,S coordination of the pyrazolecarbodithioate fragment. Its crystals are triclinic, space group $P\bar{1}$, with $a = 10.329(4)$ Å, $b = 13.082(2)$ Å, $c = 14.284(3)$ Å, $\alpha = 86.71(2)°$, $\beta = 75.14(2)°$, $\gamma = 74.79(2)°$, $Z = 2$, and $D_{calc} = 1.431$ g·cm^{-3}; final $R = 0.028$ for 5179 independent reflections having $F > 4\sigma(F)$.

Introduction

We have been actively working in the field of metal pyrazolates and have extensively reported on Cu(I) and Cu(II) species, demonstrating the structural versatility caused by the pyrazolate ligands and the catalytic activity of some of its derivatives.[3] As early as 1889, Büchner reported the synthesis of the insoluble "silver salt" $[Ag(pz)]_n$ (Hpz = pyrazole).[4] Since then, this derivative has always been claimed to be polymeric, but its molecular structure has never been clearly identified. As a part of a systematic study of the chemistry of group 11 metal pyrazolates, we recently reported the *ab-initio* crystal structure determination from powder diffraction data of, among others, $[Ag(pz)]_n$, confirming its polymeric nature.[5]

Despite the fact that $[Ag(pz)]_n$ was first synthesized over a century ago, its chemical reactivity has never been fully explored, probably because of its poor solubility. In this paper, we report the synthesis of the dinuclear $[Ag(pz)(PPh_3)]_2$ and $[Ag_2(pz)_2(PPh_3)_3]$ species derived from reaction of $[Ag(pz)]_n$ with triphenylphosphine, their structural characterization, and their reactivity with heterocumulenes. The full structural characterization of the monomeric derivative $[Ag(pz\text{-}CS_2)(PPh_3)_2]$, obtained by reacting $[Ag_2(pz)_2(PPh_3)_3]$ with CS_2, is also reported.

Results and Discussion

The reaction of $[Ag(pz)]_n$ with PPh_3 in dichloromethane leads to the isolation of two distinct products depending on the PPh_3:Ag ratio employed. The dimeric complex $[Ag(pz)(PPh_3)]_2$, **1**, is isolated in the presence of a PPh_3:Ag ratio of 1.5:1. When the reaction is carried out with excess triphenylphosphine (PPh_3:Ag > 5:1), the reaction product is the dinuclear species $[Ag_2(pz)_2(PPh_3)_3]$, **2**.

In both cases it has proved essential, in order to isolate analytically pure products, to operate in the presence of a slight excess of PPh_3 with respect to the stoichiometric amount required; in fact, only an excess of PPh_3 ensures complete depolymerization of the starting $[Ag(pz)]_n$ phase and, on the other hand, represses dissociation of the coordinated phosphine.

Complex **2** can also be obtained by reaction of **1** with PPh_3, suggesting the intermediacy of **1** in the formation of **2**. Moreover, as revealed by ^{31}P-NMR spectroscopy (see later), complex **1** is generated when **2** is dissolved in CH_2Cl_2, and as expected, when **2** is suspended in diethyl ether, an easy dissociation of one triphenylphosphine ligand takes place, restoring $[Ag(pz)(PPh_3)]_2$, **1**:

$$(2/n)[Ag(pz)]_n \xrightarrow{2PPh_3} [Ag(pz)(PPh_3)]_2 \underset{-PPh_3}{\overset{PPh_3}{\rightleftharpoons}} [Ag_2(pz)_2(PPh_3)_3] \quad (1)$$

Complexes **1** and **2** exhibit, in the 4000−900 cm^{-1} region, similar IR spectra. This similarity is attributable to the (roughly)

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** and **2**[a]

Complex **1**			
Ag···Ag′	3.870(1)	Ag−N2′	2.213(3)
Ag−N1	2.204(3)	Ag−P	2.376(1)
N1−Ag−N2'	110.68(10)	N2′−Ag−P	124.04(8)
N1−Ag−P	125.24(8)		
Complex **2**			
Ag1···Ag2	3.706(1)	Ag1−P2	2.484(1)
Ag1−N1	2.295(2)	Ag2−N2	2.235(2)
Ag1−N3	2.323(2)	Ag2−N4	2.176(2)
Ag1−P1	2.461(1)	Ag2−P3	2.370(1)
N1−Ag1−N3	100.67(8)	N3−Ag1−P1	99.38(5)
N1−Ag1−P1	112.03(6)	N3−Ag1−P2	111.70(6)
N1−Ag1−P2	108.98(6)	P1−Ag1−P2	121.73(3)
N2−Ag2−N4	110.39(8)	N4−Ag2−P3	132.24(6)
N2−Ag2−P3	117.28(6)		

[a] Primed atoms are generated by the $-x$, $-1 - y$, $1 - z$ symmetry operation.

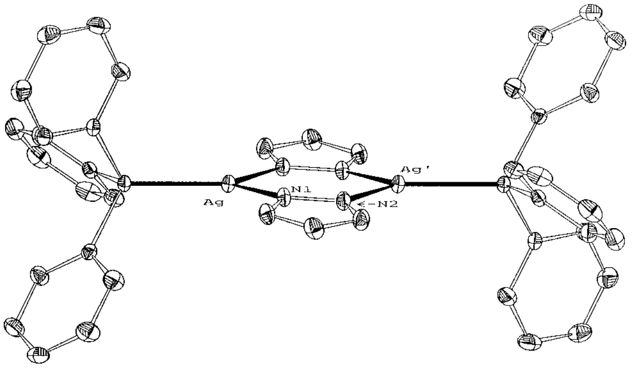

Figure 1. ORTEP drawing of the $[Ag_2(pz)_2(PPh_3)_2]$ molecule, **1**, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

similar coordination modes of the pyrazolate ligands in the two species. Differences are evident in the 900−600 region of the spectra, where the absorptions of the phenyl rings of the PPh_3 ligands appear. In this region, complex **1** shows two bands at 748 and 694 cm^{-1}. In contrast, complex **2** shows a more complex pattern, with three bands at 764, 735, and 691 cm^{-1}, revealing the presence of (at least) two inequivalent PPh_3 ligands, which were confirmed by single-crystal X-ray structural analyses.

Crystal and Molecular Structures of 1 and 2. Crystals of **1** and **2** contain discrete molecules, packed by normal van der Waals interactions. Relevant bond distances and angles are collected in Table 1.

Molecules of **1** and **2** are based on a central $Ag(\mu\text{-pz})_2Ag$ core (Ag···Ag 3.870(1) and 3.706(1) Å, for **1** and **2**, respectively), surrounded by two and three phosphines, respectively (see Figures 1 and 2). Therefore, while in **1** the crystallographically unique silver atom is trigonally coordinated, in **2** Ag(2) is tri-coordinated and Ag(1), bearing two phosphines, has a pseudotetrahedral geometry. Consistently, the Ag−P bond distances show shorter (2.376(1) Å in **1** and 2.370(1) Å in **2**) and longer (2.461(1) and 2.484(1) Å in **2**) interactions, in agreement with the different coordination geometries about the metal atoms, for trigonal and tetrahedral silver atoms, respectively. Surprisingly, a search in the Cambridge Structural Database revealed that the Ag−P bond distances for tri- and tetracoordinated silver atoms are almost equal [mean Ag−P values: 2.433 Å (33 cases) and 2.454 Å (109 cases), respectively], possibly reflecting the wide variety of ligands and lacking, therefore, internal consistency.

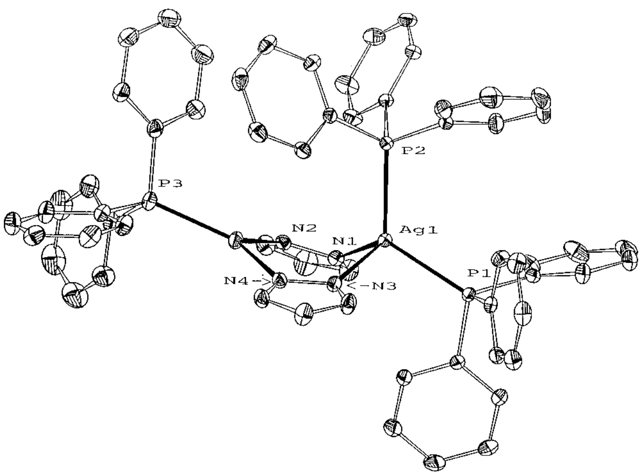

Figure 2. ORTEP drawing of the $[Ag_2(pz)_2(PPh_3)_3]$ molecule, **2**, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The influence of different coordinations around a silver atom on the Ag-N distances is also visible ([N,P]Ag−N ca. 2.20 Å and [N,P,P]Ag−N ca. 2.30 Å); moreover, the central ring conformation is markedly different: **1** (which possesses crystallographically imposed inversion symmetry) contains a planar six-membered metallacycle (maximum deviation 0.033(2) Å), while in **2** a flattened chair is observed, with the presence of a rare case of a "twisted" Ag−N−N−Ag conformation, where the two silver atoms lie on opposite sides of one pyrazolate ligand (Ag1−N1−N2−Ag2 −31.6(2)°). Such an unfavorable twist is rare but is present, for example, in the $[Cu(dppz)(RNC)]_2$[6] (Hdppz = 3,5-diphenylpyrazole) and $[(Cp)_2Ti(pz)]_2$[7] (Cp = η^5-cyclopentadienyl) dimers, where the [M−N−N−M−N−N−] rings possess a chair conformation. This geometry, which is unexpected on the basis of the structural model put forward in ref 8 for dimeric Cu(I) pyrazolates, has been attributed to the steric demand of the bulky ligands on the metals, which is probably the source of the observed distortion also in **2**. Accordingly, we failed to isolate the hypothetical $[(PPh_3)_2Ag(\mu\text{-pz})_2Ag(PPh_3)_2]$ species even by operating in the presence of a large excess of triphenylphosphine; instead, formation of monomeric silver complexes was observed.

$^{31}P\{^1H\}$-NMR Spectra. It is well-known that the solution and solid state structures of transition-metal complexes are not necessarily the same. This is particularly true for substitutionally labile complexes such as $(PR_3)_nAgX$, where it is possible for several species to exist in solution through fast ligand-exchange equilibria.[9,10]

In order to establish the real nature of complexes **1** and **2** also in solution, we decided to carry out a ^{31}P-NMR study on these complexes. Due to (^{107}Ag, ^{109}Ag)−P coupling, the solution ^{31}P-NMR spectra for silver(I) phosphine complexes are typically characterized by a diagnostic pair of doublets for each phosphorus environment. The high kinetic lability of monodentate phosphines generally leads to a rapid ligand exchange on the NMR time scale and necessitates low temperatures for resolution of the silver−phosphorus coupling.[11]

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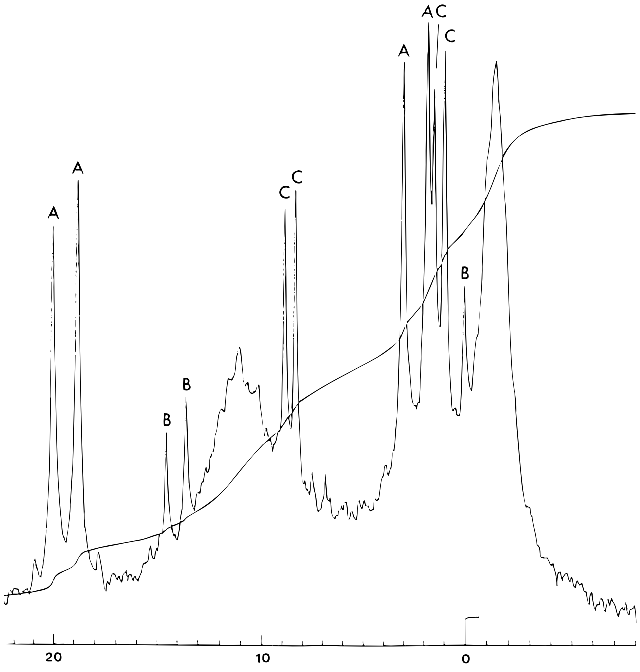

Figure 3. $^{31}P\{^1H\}$-NMR of complex **2** ($CD_2Cl_2/CDCl_3$, 158 K).

(a) $[Ag(pz)(PPh_3)]_2$, 1. The $^{31}P\{^1H\}$-NMR spectrum of **1** at room temperature shows a single sharp signal at 9.87 ppm. When the temperature is lowered, the signal broadens, and at 223 K, it begins to split into two broad resonances. A further lowering of the temperature causes the resolution of the signals into two sharp doublets centered at 10.96 ppm, and the splitting due to the coupling to the silver centers can be accurately measured, giving $^1J(^{107}Ag-^{31}P) = 513$ Hz and $^1J(^{109}Ag-^{31}P) = 592$ Hz (Figure S1 in the Supporting Information). The measured coupling constants are higher than those reported in the literature for sp^2-hybridized silver(I) complexes of the L_2Ag-X (L = monodentate arylphosphine) type[11] but are comparable with those reported for similar pyrazolate complexes containing a silver(I) center in a trigonal planar geometry, *i.e.* $[\eta^5\text{-Cp*Ir(pz)}(\mu\text{-pz})_2Ag(PPh_3)]$ ($^1J(^{107}Ag-^{31}P) = 565$ Hz),[12] $[\eta^5\text{-Cp*Ir(pz)}_3\{Ag(PPh_3)\}_2]^+$ ($^1J(^{107}Ag-^{31}P) = 573$ Hz)[12] and $[\eta^5\text{-Cp*(PPh}_3)Ir(pz)_2Ag(PPh_3)]^+$ ($^1J(^{107}Ag-^{31}P) = 590$ Hz).[13] Therefore, the spectral data indicate that, at 173 K, only one type of PPh_3 ligand is present, bound to a sp^2 -hybridized silver center and that complex **1** maintains its dimeric structure also when in solution.

(b) $[Ag_2(pz)_2(PPh_3)_3]$, 2. The solution behavior of **2** is much more complex. From the $^{31}P\{^1H\}$-NMR spectrum of a solution of **2** in CH_2Cl_2 at room temperature, only one sharp signal, centered at 6.13 ppm, is observed, suggesting a fluxional process equalizing all PPh_3 ligands. When the temperature is lowered, the signal broadens and splits: At −90 °C the spectrum contains two sharp doublets and three broad resonances. At −115 °C eleven sharp and two broad peaks can be observed.

As a matter of fact, at this limiting temperature, at least five different PPh_3 environments exist: for four of them, the coupling constant $^1J(Ag-P)$ can be accurately measured (the assignment of each set of signals is based on their relative intensities and on the calculation of the $^1J(^{109}Ag-P)/^1J(^{107}Ag-P)$ ratio, which should approach the theoretical value of $\gamma(^{109}Ag)/\gamma(^{107}Ag) = 1.15$). Figure 3 shows the ^{31}P-NMR spectrum of **2** recorded at −115 °C ($CD_2Cl_2/CDCl_3$, 2:1 mixture).

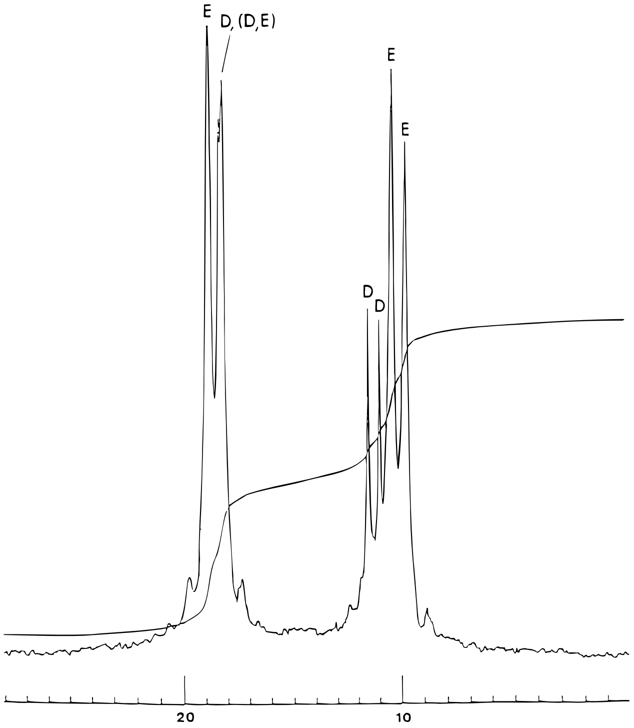

Figure 4. $^{31}P\{^1H\}$-NMR of complex **2** obtained in the presence of free PPh_3 (CD_2Cl_2, 173 K).

The set of signals labeled with A is the same as in the limiting spectrum of **1** and is therefore attributable to the $[Ag(pz)(PPh_3)]_2$ species, generated from **2** by dissociation of one PPh_3 ligand. This agrees with our observations that, when complex **2** is suspended in diethyl ether at room temperature, dissociation of one triphenylphosphine rapidly occurs, affording complex **1** in an analytically pure form.

The set of signals labeled with C, centered at 4.85 ppm, shows a $^1J(^{107}Ag-P)$ of 223 Hz. Coupling constants of this order are found in ionic species of the type $[AgL_4]X$ (L = arylphosphines; X = Cl^-, Br^-, PF_6^-, NO_3^-, CF_3COO^-). The value of *J* for this class of compounds is practically independent of the nature of the (uncoordinated) counteranion.[11] On the basis of these considerations, the observed coupling constants and chemical shifts for **2** suggest the presence, in solution, of the ionic species $[Ag(PPh_3)_4]^+(pz)^-$ containing a pyrazolate anion in a noncoordinating fashion. As further support of the above interpretation, we observed that, when the ^{31}P-NMR spectrum of **2** is registered in acetone-d_6 (instead of CD_2Cl_2), the spectrum dramatically simplifies. In this solvent, at 183 K only two well-resolved sets of signals are detected. The first one presents a $^1J(^{107}Ag-P)$ of 223 Hz and is assignable to the ionic $[Ag(PPh_3)_4](pz)$ species, whose formation is favored by the presence of a solvent of higher dielectric constant. The second set of signals presents coupling constant values ($^1J(^{107}Ag-P = 253$ Hz, $^1J(^{109}Ag-P) = 292$ Hz) agreeing with a silver(I) center in a tetrahedral arrangement of the L_3AgX (sp^3-hybridized) type.[11,14] These peaks can therefore be associated with the $[Ag(PPh_3)_3(pz)]$ species, containing a monodentate pyrazolate group. Similar behavior is observed when the ^{31}P-NMR spectrum of **2** is recorded in CD_2Cl_2 in the presence of free PPh_3 (Figure 4). In fact, also in this case, only two sets of signals were detected (in addition to that due to free phosphine itself at −7.8 ppm)

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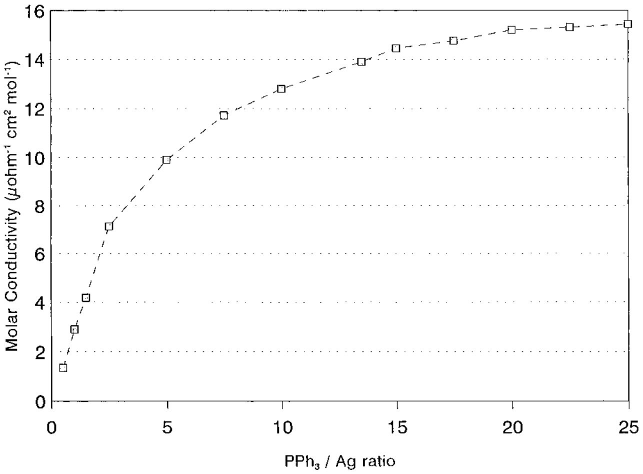


Figure 5. Molar conductivity vs the Ag:PPh_3 ratio for complex **2** (CH_2Cl_2).

and are assigned to the $[Ag(PPh_3)_4](pz)$ (set D, Figure 4) and $[Ag(PPh_3)_3(pz)]$ (set E, Figure 4) species, their relative ratio depending on the amount of PPh_3 added.

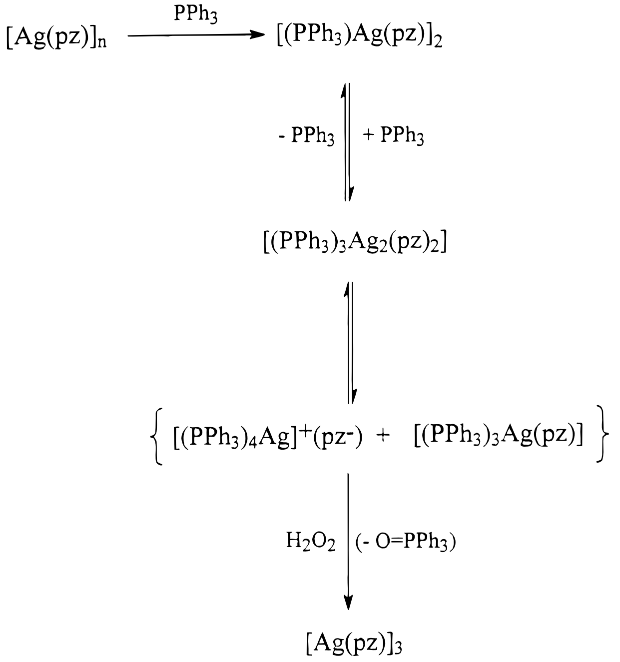
Moreover, conductance measurements carried out on CH_2Cl_2 solutions of **2** in the presence of free PPh_3 shows a clear dependence of Λ_{mol} on the amount of added PPh_3 in the range PPh_3:Ag = 1−20. For PPh_3:Ag ratios higher than 20, the molar conductivity of the solution remains practically constant, indicating complete conversion of the silver(I) existing in solution to the ionic $[Ag(PPh_3)_4](pz)$ species (Figure 5).

Returning to the discussion of the ^{31}P-NMR spectrum of **2**, the remaining set of clear signals labeled with B, centered at 7.24 ppm, presents a $^1J(^{107}Ag-P)$ of 409 Hz ($^1J(^{109}Ag-P = 472$ Hz)). This value can tentatively be attributed to the PPh_3 ligands bound to a tetracoordinated silver(I) center such as $X_2Ag(PPh_3)_2$. *i.e.* to the tetrahedral silver center of the undissociated dinuclear species $[Ag_2(pz)_2(PPh_3)_3]$, **2**. The related set of signals corresponding to the trigonal silver(I) center probably coincides with those of **1** (set A, Figure 3).

The solution behavior of complex **2** in CH_2Cl_2 is obviously quite complicated, and some aspects are still obscure. Moreover, the presence of unresolved sets of signals causes a lack of precious spectral information. The above results show that complex **2** dissociates, upon dissolution, forming a variety of complexes of very different stoichiometries. This behavior is not surprising, as it has previously been reported for dimeric silver(I) complexes containing 1-phenyl-3,4-dimethylphosphole (DMPP) or 1-phenyldibenzophosphole (DBP).[9] In these cases halide derivatives such as $[(DBP)_2AgX]_2$ or $[(DMPP)_2AgCl]_2$ were shown to dissociate to give ionic species such as $[Ag(DMPP)_4]X$ and $[Ag(DBP)_4]X$ and mononuclear covalent derivatives, *i.e.* $[Ag(DMPP)_3X]$ or $[Ag(DBP)_3X]$.[9]

Several attempts to isolate $[Ag(PPh_3)_4](pz)$ or $[Ag(PPh_3)_3(pz)]$ from solutions of **2** in the presence of excess PPh_3 failed, $[Ag_2(pz)_2(PPh_3)_3]$ being always restored in pure form. It thus appears that steric considerations result in the formation of the dinuclear species in the solid state. The fact that steric effects play a determining role on the nature of the solid state species is confirmed by the observation that, when $[Ag(pz)]_n$ is reacted with a bulky phosphine such as $P(Cy)_3$, a unique product, the dimeric $[Ag(pz)(PCy_3)]_2$ species, **3**, was isolated, also in the presence of a large excess of ligand, with no evidence for the formation of the more crowded dinuclear $[Ag_2(pz)_2(PCy_3)_3]$ species.

Scheme 1



It is worth mentioning here that, when coordinated PPh_3 is removed from complexes **1** and **2** by using H_2O_2, selective formation of a new silver−pyrazolate phase, different from the starting polymeric $[Ag(pz)]_n$ was observed.

$$3[Ag(pz)(PPh_3)]_2 \xrightarrow{H_2O_2} 2[Ag(pz)]_3 + 6O{=}PPh_3 \quad (2)$$

$$3[Ag_2(pz)_2(PPh_3)_3] \xrightarrow{H_2O_2} 2[Ag(pz)]_3 + 9O{=}PPh_3 \quad (3)$$

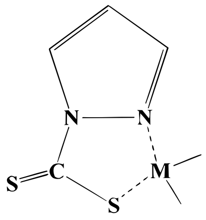
The full structural characterization of the $[Ag(pz)]_3$ phase has been already reported.[5]

Despite the substantial structural differences, the reactivity of $[Ag(pz)]_3$ toward PPh_3 parallels that of the polymeric phase $[Ag(pz)]_n$. Evidently, the first step of the reaction with PPh_3, in both cases, is the formation of mononuclear species such as $[Ag(PPh_3)_x(pz)]$, which, depending on the experimental conditions, later evolve to the final products. Scheme 1 summarizes the solution behavior of **2**.

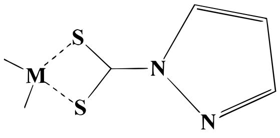
Reactions with Heterocumulenes. Complexes **1** and **2** readily react with heterocumulenes such as CS_2, COS, CO_2, and RNCO (R = cyclohexyl and *p*-tolyl) giving rise to new derivatives, the nature of which is dependent on the experimental conditions.

(a) Reaction with Carbon Disulfide. Carbon disulfide reacts with complexes **1** and **2** in a variety of solvents in the presence of PPh_3, affording a pale-pink product, formulated on the basis of elemental analysis as $[Ag(PPh_3)_2(pz\text{-}CS_2)]$, **4**, containing a pyrazolecarbodithioate anion derived from the formal nucleophilic addition of the pyrazolate anion to the carbon atom of the CS_2 molecule.

The pyrazolecarbodithioate anion can, in principle, coordinate to a metal center in a (chelating) N,S or S,S fashion. The



N,S



S,S

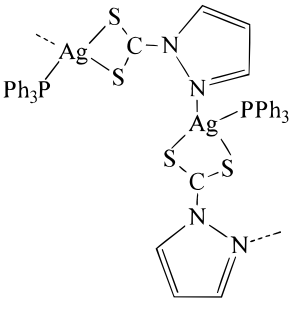
synthesis of a series of metal(II) pyrazolecarbodithioates (Mn, Fe, Co, Ni, Cu, Zn) was reported by Trofimenko,[15] who suggested that the coordination properties of the polydentate pzCS_2^- ligand produce MN_2S_2 instead of MS_4 coordination environments. In the case of copper(II) centers, the N_2S_2 coordination was confirmed in 1978 by Bereman *et al.*[16] on the basis of spectroscopic evidence. Recently, we reported the crystal structure of the product derived by reacting CS_2 with [Cu(dmpz)(RNC)]$_2$ (Hdmpz = 3,5-dimethylpyrazole, RNC = cyclohexyl isocyanide), showing the N,S coordination mode also for a rather soft metal center like copper(I).[17]

The IR spectrum of **4** does not show any band assignable to the C=S stretching (in the 1300−1350 cm^{-1} region) expected for a N,S coordination mode. Instead, strong absorptions are present in the 1150−1250 cm^{-1} region, which we attribute to $\nu(CS_2^-)$ vibration modes,[18] indicating a S,S coordination of the pyrazolecarbodithioate ligand. However, overlap with other ligand modes precluded an unambiguous assignment. The S,S coordination mode has been confirmed by an X-ray crystal structure analysis.

When complex **4** is dissolved in CH_2Cl_2, a rapid dissociation of PPh_3 takes place, affording an insoluble orange compound analyzing as [Ag(PPh_3)(pz-CS_2)], **5**. Formation of the latter species takes place also upon suspending **4** in diethyl ether. The dissociation is reversible, and complex **4** is easily restored by treating **5** in diethyl ether with PPh_3:

$$[(PPh_3)_2Ag(pz\text{-}CS_2)] \rightleftharpoons \mathbf{5} + PPh_3$$

Complex **5** can also be obtained by reacting [Ag(pz)(PPh_3)]$_2$, **1**, or [(Ag_2(pz)$_2$(PPh_3)$_3$], **2**, with CS_2 in the absence of PPh_3. The IR spectrum of complex **5** is similar to that of the parent [(PPh_3)$_2$Ag(pz-CS_2)] species, suggesting that the S,S coordination mode is maintained also after the dissociation of a PPh_3 molecule. The formulation of **5** as a monomeric species conflicts with its marked insolubility in common, noncoordinating solvents. Most probably, **5** possesses a more complex structure, oligomeric or maybe polymeric, where the pyrazolecarbodithioate group behaves as a tridentate ligand, in a S,S,N fashion, with two sulfur atoms chelating to a silver(I) center and the free nitrogen atom of the pyrazole group bridging a second metal, giving rise to a sequence of tetracoordinated silver(I) centers.



Interestingly, complex **5** reacts with 1,2-bis(diphenylphosphino)ethane (dppe) giving a derivative formulated as [(dppe)-Ag(pz-CS_2)], **4a**. Complex **4a**, which is pink, has been verified to be stable in solution due the chelating effect of dppe. The analogies between **4** and **4a** (IR spectra and color) seem to indicate the S,S coordination mode of the pyrazolecarbodithioate group also in the latter species.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**

Ag−P1	2.474(1)	Ag−S1	2.630(1)
Ag−P2	2.441(1)	Ag−S2	2.710(1)
C1−S1	1.672(3)	N1−N2	1.362(4)
C1−S2	1.678(3)	N1−C2	1.360(4)
C1−N1	1.414(3)		
P1−Ag−P2	123.96(3)	P2−Ag−S1	124.73(3)
P1−Ag−S1	108.96(3)	P2−Ag−S2	109.57(3)
P1−Ag−P2	104.53(3)	S1−Ag−S2	67.20(3)
N1−C1−S1	118.8(2)	S1−C1−S2	124.9(2)
N1−C1−S2	117.3(2)		

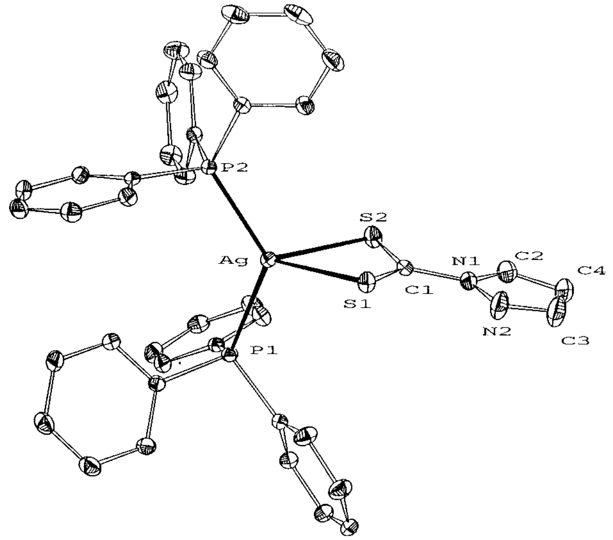


Figure 6. ORTEP drawing of the [Ag_2(pz-CS_2)(PPh_3)$_2$] molecule, **4**, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

When complex **4** is suspended in refluxing acetone, complete abstraction of the phosphine ligands occurs, leaving a (highly insoluble) brown residue, analyzing as [Ag(pz-CS_2)], **6**. It is worthy of note that, in contrast to complex **5**, [Ag(pz-CS_2)], in the presence of excess triphenylphosphine, does not restore the parent compound **4**, thus suggesting a different coordination mode of the pyrazolecarbodithioate ligand. Studies are in progress to assess its complete crystal structure by *ab-initio* powder diffraction techniques.

(b) Crystal and Molecular Structure of 4. Crystals of **4** contain discrete molecules, packed by normal van der Waals interactions. Relevant bond distances and angles are collected in Table 2. Compound **4**, which is monomeric and contains a pseudotetrahedral silver atom (Ag−P1 2.441(1) Å and Ag−P2 2.474(1) Å; P1−Ag−P2 123.96(3)°), bears a chelating R−CS_2 ligand, bonded through the two sulfur atoms (Ag−S1 2.630(1) Å and Ag−S2 2.710(1) Å; see Figure 6). The molecule, which has no imposed crystallographic symmetry, shows, however, an idealized mirror plane passing through the silver and phosphorus atoms, bisecting the CS_2 and pyrazolato ring (once disordered C and N atoms for the azaaromatic moiety are assumed; see Experimental Section).

Interestingly, this compound shows the first structurally characterized S,S coordination of a pyrazolecarbodithioate (bearing a nucleophilic N atom), contrasting with previous observations and the structural hypothesis put forward by Trofimenko back in 1968.[15] Although no evidence for a N,S coordinated moiety, leading to a rather stable five-membered

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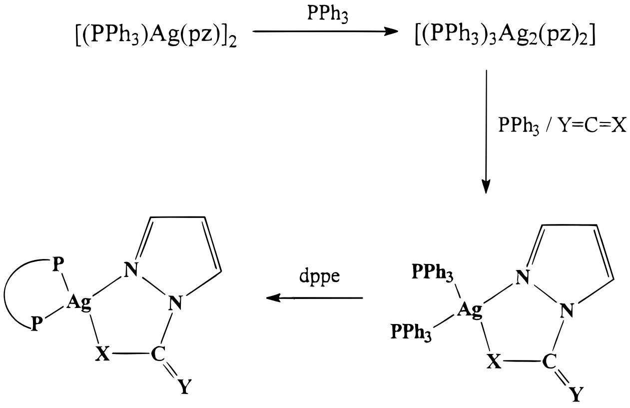
ring similar to those found for [Cu(dmpz-CS_2)$(RNC)_2$][17] and [Pd(dmpz-COS)$_2$][19] was found, and in spite of the soft character of the Ag(I) ion (favoring the S, rather than the N, coordination), we could expect possible interconversion of **4** into [Ag(pz-CS_2-*N,S*)$(PPh_3)_2$] if suitable conditions are found. This would agree with our recent observation of the coexistence, in the solid state, of the two coordination modes for the [Pd(dmpz-CS_2)]$_2$ complex,[20] showing that both linkage isomers can exist, despite their different steric interactions and bonding patterns.

(c) Reactions with COS, CO_2, and Isocyanates. When COS is bubbled at room temperature through a solution of complex **1** or **2** containing free PPh_3, a rapid color change of the solution, from colorless to pale yellow and finally to deep brown, takes place. The (brown) solid isolated after workup of the solution shows an IR absorption at 1619 cm^{-1}, indicating that a reaction has occurred. However, it has been verified that under these experimental conditions, extraction of sulfur from COS easily takes place and that the final product is always contaminated by variable amounts of Ag_2S. Indeed, it has been shown that the weakening of the C=S bond of COS upon coordination to a metal, due to $d\pi-\pi^*$ back-donation, is sufficient to promote elimination of sulfur, if a suitable sulfur acceptor is present.[21,22]

When the reaction is carried out at −80 °C in the absence of solvent, it is possible to isolate a white product, **7**, showing a strong IR band at 1612 cm^{-1}. This species is quite stable at low temperatures, also under vacuum, but when the temperature is raised above −10 °C, rapid sulfur extraction once again takes place even in the solid state. A full characterization of this derivative was hampered by its low stability; nevertheless, if complex **1** or **2** is reacted with COS at −80 °C in the presence of dppe, a rather stable (also at room temperature) derivative, **7a**, is isolated. The IR spectrum of the latter shows a strong IR band at 1621 cm^{-1}, attributable to the ν(C=O) of the pyrazolecarbothioate anion, pz-COS$^-$, derived from nucleophilic addition of the pyrazolate group to the COS molecule. According to the elemental analysis, complex **7a** was formulated as [Ag(dppe)(pz-COS)]. On the basis of the IR spectrum of **7a**, and taking into account the scarce affinity of the soft silver(I) centers for hard oxygen-donor ligands, we assign to the ligand pyrazolecarbothioate a N,S coordination mode, analogous to that of the known [Cu(dmpz-COS)$(RNC)_2$][23] (1670 cm^{-1}) and [Pd(dmpz-COS)$_2$][19] (1658 cm^{-1}) derivatives.

If a PPh_3-containing diethyl ether suspension of complex **1** or **2** is saturated with CO_2, the formation of a white product, showing a strong IR absorption at 1740 cm^{-1}, occurs. On the basis of the IR spectrum and in analogy to the reaction with COS previously described, the new species is formulated as [Ag(pz-CO_2)$(PPh_3)_2$], **8**. Complex **8** shows a very fast loss of CO_2 if suspended or dissolved in any solvent, and even in the solid state it rapidly extrudes carbon dioxide, giving the starting [$Ag_2(pz)_2(PPh_3)_3$] complex and free PPh_3. If **8** is reacted with dppe (under a CO_2 atmosphere), a product formulated as [Ag(pz-CO_2)(dppe)], **8a**, is obtained. Complex **8a** exhibits a strong IR band centered at 1713 cm^{-1}. However, although **8a** is apparently more stable than complex **8**, also in this case any further characterization is hampered by the easy loss of carbon dioxide.

Scheme 2



The extreme lability of CO_2 in the pyrazolecarboxylate derivatives, *i.e.* the reversibility of the insertion process, can be ascribed to the low stability of Ag−O bonds, which is easily avoided in the COS or RNCO derivatives. Thus, the extremely soft nature of the silver center seems to play again a determinant role.[24]

In contrast, the reactions of complexes **1** and **2** with RNCO give well-characterized derivatives of the general formula [Ag(pz-N(CO)R)$(PPh_3)_2$] (R = cyclohexyl, **9**; R = *p*-tolyl, **10**):

$$[Ag_2(pz)_2(PPh_3)_3] + 2RNCO \xrightarrow{PPh_3} 2[Ag(pz\text{-}N(CO)R)(PPh_3)_2] \qquad (4)$$

Complexes **9** and **10** exhibit in their IR spectra strong absorptions at 1653 and 1667 cm^{-1}, respectively, attributable to the ν(CO) mode of the pz-N(CO)R ligand coordinated in a N,N fashion. These values compare well with those previously reported for the copper(I) [Cu(dmpz-N(CO)R)$(RNC)_2$] (1670 cm^{-1}) derivative[23] and for the copper(II) species containing the chelating dmpz-N(CO)H$^-$ ligand, derived by nucleophilic attack of 3,5-dimethylpyrazole on NCO$^-$ (about 1690 cm^{-1}).[25]

Complexes **9** and **10** are quite stable, also in solution, but the two PPh_3 ligands can be easily displaced by dppe, giving the substituted derivatives [Ag(pz-N(CO)R)(dppe)] (R = cyclohexyl, **9a**; R = *p*-tolyl, **10a**) showing ν(C=O) shifts to 1637 and 1649 cm^{-1} respectively.

Reactions of complexes **1** and **2** with COS, CO_2, and RNCO (R = cyclohexyl or *p*-tolyl) give a series of products which have similar structures (as inferred on the basis of IR spectra) but present different stabilities, depending on the nature of the heterocumulene employed. The common reaction pathway can be exemplified by Scheme 2. In all cases, the presence of free PPh_3 in the reaction medium was proved to be necessary to obtain high yields (>90%) of analytically pure products.

Probably, in order to favor the reactions between complex **1** or **2** and heterocumulenes, the (incipient) opening of the Ag(μ-pz)$_2$Ag bridge is necessary. The presence of free PPh_3 transforms **1** into **2** and then promotes the formation of monomeric species, such as [$(PPh_3)_3$Ag(pz)] and [$(PPh_3)_4$Ag]-

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(19) Masciocchi, N.; Moret, M.; Sironi, A.; Ardizzoia, G. A.; Cenini, S.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1955.

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(24) However, the formation of a labile Ag(I)−{CO_2} species, *i.e.* [L_2Ag(pz)(CO_2)], cannot be ruled out. For comparison, [Ni$(PCy_3)_2(CO_2)$], which contains a side-on CO_2 bound to the nickel atom, has been reported to exhibit a $\nu(CO_2)$ at 1740 cm^{-1}, exactly at the same frequency evidenced by complex **8**. See: Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 637.

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(pz) (detected by ^{31}P-NMR spectra), where nucleophilic attack of uncoordinated nitrogen atoms on the heterocumulenes can occur.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen to avoid moisture. All chemicals (Aldrich Chemical Co.) were used as supplied except 1,2-bis(diphenylphosphino)ethane (dppe), which was recrystallized from methanol. Solvents were purified and dried by standard methods. [Ag(pz)]$_n$ was prepared according to the Büchner method.[4] Infrared spectra were recorded on a Bio-Rad FTIR 7 instrument, ^{31}P-NMR spectra were acquired on a Varian XL-200 spectrometer operating at 81 MHz, and conductivity measurements were performed on an Orion Research Type 101-A instrument. Elemental analyses were carried out at the microanalytical laboratory of this university.

[Ag(pz)(PPh$_3$)]$_2$, 1. To a suspension of [Ag(pz)]$_n$ (2.78 g, 15.9 mmol) in CH_2Cl_2 (40 mL) was added solid PPh_3 (6.20 g, 23.7 mmol). The suspension was stirred overnight and then filtered, and the white solid was washed with diethyl ether (50 mL) and dried under vacuum (82% yield). Anal. Calcd for $C_{21}H_{18}AgN_2P$: C, 57.66; H, 4.12; N, 6.41. Found: C, 57,42; H, 4.35; N, 6.35. Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **1**.

[Ag$_2$(pz)$_2$(PPh$_3$)$_3$], 2. To a suspension of [Ag(pz)]$_n$ (2.74 g, 15.7 mmol) in 150 mL of CH_2Cl_2 was added PPh_3 (20.4 g, 78.5 mmol) with stirring. In a few minutes, [Ag(pz)]$_n$ dissolved, giving a clear solution. The solution was stirred for an additional 1 h and then evaporated to dryness. The oily residue was treated with diethyl ether, giving a white solid, which was filtered off, washed with diethyl ether, and dried under vacuum (92% yield). Anal. Calcd for $C_{60}H_{51}Ag_2N_4P_3$: C, 63.38; H, 4.49; N, 4.93. Found: C, 63.56; H, 4.28; N, 5.01. Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **2** containing PPh_3.

[Ag(pz)(PCy$_3$)]$_2$, 3. The preparation of **3** was similar to that of complex **1** (87% yield). Employing a large PCy_3:Ag molar ratio, we isolated only the 1:1 adduct. Anal. Calcd for $C_{21}H_{36}AgPN_2$: C, 55.39; H, 7.91; N, 6.15. Found: C, 55.43; H, 7.84; N, 6.21. ^{31}P-NMR (223 K, CD_2Cl_2): two doublets centered at 37.9 ppm; $^1J(^{107}Ag-P) = 583$ Hz, $^1J(^{109}Ag-P) = 672$ Hz.

[Ag(pz-CS$_2$)(PPh$_3$)$_2$], 4. To a solution of complex **1** or **2** (about 100 mg) in CH_2Cl_2 (6 mL) containing PPh_3 (1:2 Ag:PPh_3 ratio) was added CS_2 (0.5 mL). The solution rapidly turned red. After 30 min, the volume was reduced to *ca.* 1 mL, and diethyl ether (10 mL) was added. The pink precipitate was filtered off, washed with diethyl ether (2 mL), and dried under vacuum (78% yield). The reaction can also be carried out in pure CS_2 or in diethyl ether, complex **4** being always recovered in an analytically pure form. Anal. Calcd for $C_{40}H_{33}AgN_2P_2S_2$: C, 61.94; H, 4.26; N, 3.61. Found: C, 62.01; H, 4.20; N, 3.53. Crystals suitable for X-ray analysis were obtained by slow evaporation of a CS_2 solution of **4**.

[Ag(pz-CS$_2$)(dppe)], 4a. Complex **4** was suspended in acetone, and solid dppe (Ag:dppe molar ratio of 1:1.2) was added. The solution was stirred for 2 h, and then the pink solid was filtered off, washed with acetone, and dried under vacuum (84% yield). Anal. Calcd for $C_{30}H_{27}AgN_2P_2S_2$: C, 55.47; H, 4.16; N, 4.31. Found: C, 55.51; H, 4.27; N, 4.42.

[Ag(pz-CS$_2$)(PPh$_3$)], 5. Complex **5** was simply obtained by suspending **4** in diethyl ether. The initially pink suspension became orange within a few minutes. After 2 h of stirring, the orange solid was filtered off, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{22}H_{18}AgN_2P_2S_2$: C, 51.46; H, 3.51; N, 5.46. Found: C, 51.59; H, 3.47; N, 5.48.

[Ag(pz-CS$_2$)]$_n$, 6. Complex **4** or **5** was suspended in acetone, and the suspension was stirred at 50 °C for 2 h, affording a brown solid, which was recovered by filtration, washed with acetone and diethyl ether, and dried under vacuum. Anal. Calcd for $C_4H_3AgN_2S_2$: C, 19.12; H, 1.19; N, 11.16. Found: C, 19.17; H, 1.18; N, 11.08.

[Ag(pz-COS)(PPh$_3$)$_2$], 7. At −78 °C, 3 mL of COS was condensed onto 300 mg (0.26 mmol) of complex **2** and 140 mg of PPh_3 (0.53 mmol). The suspension was stirred for 2 h at −78 °C, and then COS was removed under vacuum. A 20 mL portion of diethyl ether (maintained at −78 °C) was then added, and the suspension was stirred for an additional $^1/_2$ h. The diethyl ether (containing excess PPh_3) was carefully decanted, and the procedure was repeated twice. Finally, the white residue was vacuum-pumped to remove residual Et_2O. Complex **7** shows a strong IR absorption at 1612 cm^{-1}, and is quite stable at −78 °C, but rapidly turns brown when the temperature is raised above −10 °C, thus preventing any further characterization.

[Ag(pz-COS)(dppe), 7a. When the aforementioned procedure was carried out in the presence of dppe (in place of PPh_3), after workup of the residue (employing acetone instead of diethyl ether) it was possible to isolate complex **7a**, which was sufficiently stable to allow an analytical characterization. Anal. Calcd for $C_{30}H_{27}AgN_2P_2OS$: C, 56.87; H, 4.27; N, 4.42. Found: C, 56.90; H, 3.95; N, 4.44.

[Ag(pz-CO$_2$)(PPh$_3$)$_2$], 8. CO_2 was bubbled through a suspension of **2** (250 mg, 0.22 mmol) in diethyl ether containing PPh_3 (120 mg, 0.46 mmol). The suspension was stirred for 2 h in a CO_2 atmosphere, and then the solid was isolated by filtration (under CO_2) and dried in a flow of carbon dioxide. The extreme lability of the functionalized CO_2 molecule in complex **8** hampered any further characterization of the species.

[Ag(pz-CO$_2$)(dppe)], 8a. This derivative was obtained by reacting **2** with CO_2 in the presence of dppe in acetone under the experimental conditions used for **8**. Also in this case, the rapid loss of CO_2 from complex **8a** prevented characterization.

[Ag(pz-N(CO)R)(PPh$_3$)$_2$] (R = Cyclohexyl, 9; R = *p*-Tolyl, 10). To a diethyl ether suspension (10 mL) of **2** (250 mg, 0.22 mmol) were added under stirring 120 mg of PPh_3 (0.46 mmol) and the appropriate isocyanate (200 μL). After 30 min, the white solid was filtered off, washed with diethyl ether, and dried under vacuum (yields >90%). Anal. Calcd for $C_{46}H_{44}AgN_3P_2O$ (**9**): C, 66.99; H, 5.34; N, 3.40. Found: C, 66.95; H, 5.30; N, 3.42. Calcd for $C_{47}H_{40}AgN_3P_2O$ (**10**): C, 67.79; H, 4.81; N, 5.05. Found: C, 67.81; H, 4.79; N, 5.10.

[Ag(pz-N(CO)R)(dppe)] (R = Cyclohexyl, 9a; R = *p*-Tolyl, 10a). Complex **9** or **10** was dissolved in the minimum amount of dichloromethane, and solid dppe (Ag:dppe molar ratio of 1:1.2) was added. The solution was stirred for 2 h and then concentrated to a small volume. The white solid that formed was isolated by filtration, washed with acetone, and dried under vacuum. Anal. Calcd for $C_{36}H_{38}AgN_3P_2O$ (**9a**): C, 61.89; H, 5.44; N, 6.02. Found: C, 61.93; H, 5.43; N, 6.05. Calcd for $C_{37}H_{34}AgN_3P_2O$ (**10a**): C, 62.89; H, 4.82; N, 5.95. Found: C, 62.67; H, 4.68; N, 5.88.

Crystallography. Crystal data and experimental conditions are summarized in Table 3. A least-squares fit of 25 randomly oriented intense reflections in the 10−14° (θ) range provided the unit cell parameters. Intensities were collected, at room temperature, on a four-circle automated CAD4 diffractometer, using graphite-monochromatized Mo Kα radiation ($\lambda = 0.701\ 73$ Å) and a variable scan range with a 25% extension at each end for background evaluation. Three standard reflections, measured at regular intervals, showed stability of the crystals over the data collection period. All data were corrected for Lorentz and polarization effects. An empirical absorption correction,[26] based on ψ scans of three reflections having χ near 90°, was applied (ψ 0−360°, every 10°).

The structures were solved by direct methods (SIR 92[27]) and difference Fourier methods and refined by full-matrix least-squares procedures using the SHELX 93 suite of programs,[28] locally adapted on a Silicon Graphics Indigo computer running IRIX 4.01. Scattering factors, corrected for the real and imaginary anomalous dispersion terms, were taken from the internal library of SHELX 93. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Phenyl rings were treated as rigid bodies, with C−C bond distances of 1.390 Å and internal angles of 120°; the contribution of the hydrogen atoms to the scattering factors was included in the last stages of the refinement, setting the H atoms in ideal positions with isotropic thermal parameters

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Table 3. Crystal Data and Data Collection Parameters for Compounds **1**, **2**, and **4**

	1	**2**	**4**
formula	$C_{42}H_{36}Ag_2N_4P_2$	$C_{60}H_{51}Ag_2N_4P_3$	$C_{40}H_{33}AgN_2P_2S_2$
fw	874.42	1136.70	775.61
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.567(2)	9.752(2)	10.329(4)
b, Å	11.440(2)	14.163(2)	13.082(2)
c, Å	10.073(2)	20.450(2)	14.284(3)
α, deg	93.59(2)	101.84(1)	86.71(2)
β, deg	64.01(2)	99.83(2)	75.14(2)
γ, deg	107.24(2)	100.68(2)	74.79(2)
V, Å^3	943.5(3)	2651.8(7)	1800.1(8)
Z	1	2	2
D_{calc} g·cm^{-3}	1.539	1.424	1.431
μ, mm^{-1}	1.16	0.87	0.80
T, °C	22	22	22
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.710\,73$ Å		
crystal size, μm	60 × 60 × 80	70 × 120 × 200	30 × 200 × 250
min transm factor	0.92	0.81	0.64
R,[a] R_w[b]	0.028, 0.065	0.025, 0.064	0.028, 0.070

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

riding on those of the carbon atoms to which they are attached. For complex **4**, the X-ray data did not allow discrimination among the two possible orientations of the pyrazolato ring; therefore, we arbitrarily attributed the N and C labels to the atoms adjacent to the *ipso* nitrogen atom, bearing in mind that, as evidenced also from the molecular features (see Results and Discussion), they are probably disordered over the two sites. The peaks in the final difference Fourier maps were randomly located. Final fractional atomic coordinates and bond distances and angles are supplied as Supporting Information.

Conclusions

The synthesis, the structural properties, and the reactivity toward heterocumulenes of the dinuclear triphenylphosphine/pyrazolate derivatives of silver(I) $[Ag(pz)(PPh_3)]_2$ and $[Ag_2(pz)_2(PPh_3)_3]$ have been described. The lability of the triphenylphosphine ligands, evidenced, in solution, by the presence of several (complex) equilibria processes, suggests that a rich chemistry involving substitution (and insertion) at the silver metals might be accessible. In principle, fine tuning of such properties could be achieved by varying the electronic, and steric, properties of the phosphine ligands, as well as by employing suitably substituted pyrazoles. Studies are in progress to verify these hypotheses.

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Supporting Information Available: The ^{31}P-NMR spectrum of complex **1** (CD_2Cl_2, 173 K) (1 page). X-ray crystallographic files, in CIF format, for compounds **1**, **2**, and **4** are available on the Internet only. Ordering and access information is given on any current masthead page.

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