Inorg. Chem. **2002**, *41*, 1151–1161

Inorganic Chemistry

Article

First Structurally Characterized Silver(I) Derivatives with Nonfluorinated *β*-Diketones

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, FMIPA Universitas Negeri Malang, Jalan Surabaya 6, Malang 65145, Indonesia

Received August 30, 2001

Synthetic, spectroscopic, and single-crystal X-ray structural studies of diverse complexes of silver(I) acylpyrazolonate salts $AgQ^{R'}$ (QH = 1-phenyl-3-methyl-4-R′(C=O)-pyrazol-5-one; Q^1, R = Ph; Q^2, R′ = CF_3; Q^3, R′ = Me) with neutral ligands L = unidentate PR_3 (R = Ph, *o*-tolyl, cyclohexyl) and Hmimt (1-methyl-2-mercaptoimidazole) and bidentate dppe ($Ph_2P(CH_2)_2PPh_2$) and trimen (*N*,*N*,*N*′-trimethylethylenediamine) define the donor capability of the anionic $Q^{R'}$ ligand in a variety of roles. In the free ligand Q^3H (which crystallizes in the monoclinic space group *C2/c* (no. 15), *Z* = 8, unit cell parameters *a* = 17.981(6) Å, *b* = 5.0641(4) Å, *c* = 24.271(6) Å, and β = 99.67(2)°), the acidic OH group hydrogen-bonds intramolecularly to the adjacent pyrazolone oxygen, i.e., the two oxygen atoms are *cis*, true of the other $Q^{R'}$ species structurally characterized here in their anionic complexed forms, in which they chelate the silver in the usual β-diketonate manner, but not of the free anion, found in the array $[Ag(Ph_3P)(Hmimt)_2](Q^1)$ (triclinic space group $P\bar{1}$ (no. 2), *Z* = 2, unit cell parameters *a* = 11.553(1) Å, *b* = 11.943(1) Å, *c* = 15.479(2) Å, α = 74.829(2)°, β = 76.094(2)°, and γ = 78.185(2)°), or $[Ag(trimen)Q^1]$ (monoclinic space group $P2_1/c$ (no. 14), *Z* = 4, unit cell parameters *a* = 7.982(1) Å, *b* = 12.299(2) Å, *c* = 21.507(3) Å, and β = 95.119(3)°), which forms an infinite one-dimensional polymer string, Q^1 linking successive silver(I) atoms by coordination by way of the unsubstituted nitrogen and the pyrazolonate oxygen. In all $[Ag(R_3P)_2(chelate\text{-}Q^1)]$ (R = Ph, Cy) complexes, $P_2Ag(O,O')$ arrays are found (R = Ph, monoclinic space group *C2/c* (no. 15), *Z* = 8, unit cell parameters *a* = 16.193(8) Å, *b* = 13.859(7) Å, *c* = 39.306(7) Å, and β = 100.02(3)°; R = Cy, triclinic space group $P\bar{1}$ (no. 2), *Z* = 2, unit cell parameters *a* = 10.4655(9) Å, *b* = 12.079(1) Å, *c* = 22.804(2) Å, α = 104.872(2)°, β = 95.180(2)°, and γ = 104.144(2)°), also true of $[Ag(Ph_3P)_2(O,O'\text{-}Q^2)]$ (triclinic space group $P\bar{1}$ (no. 2), *Z* = 2, unit cell parameters *a* = 10.672(2) Å, *b* = 10.710(2) Å, *c* = 18.713(3) Å, α = 87.573(2)°, β = 80.972(2)°, and γ = 81.734(2)°), whereas $[Ag(o\text{-}tol_3P)Q^1]$ (monoclinic space group $P2_1/c$ (no. 14), *Z* = 2 dimers, unit cell parameters *a* = 11.8221(6) Å, *b* = 13.2601(6) Å, *c* = 20.5141(10) Å, and β = 91.758(1)°) exists as a dinuclear species containing two AgO_2NP units where the acylpyrazolonate is coordinated in a bridging *O*,*O*′-Q-*N* fashion. Silver atoms are four-coordinate in all except the Hmimt complex.

Introduction

β-Diketonate complexes of coinage metal ions have proved to be useful for several applications: in classical metal–organic chemical vapor deposition (MOCVD),[1] in supercritical fluid transport (SFT) CVD[2] of thin metal films as contacts in microelectronic devices or as components in high-temperature superconducting materials, and also as coordination polymer species in inorganic crystal engineering.[3] Recent papers have described the synthesis and structural characterization of Ag(I) derivatives with β-diketonates and several Lewis base donors,[4] presenting low or very low stability in

---

* To whom correspondence should be addressed. E-mail: fabio.marchetti@unicam.it. Fax: +39 0737/637345.

[†] Università degli Studi di Camerino.

[‡] The University of Western Australia.

[§] FMIPA Universitas Negeri Malang.

(1) (a) *The Chemistry of Metal CVD*; Kodas, T. T., Hampden, Smith, M. J., Eds.; VCH Publishers: New York, 1994. (b) Hampden-Smith, M. J.; Kodas, T. T. *Polyhedron* **1995**, *14*, 699–732.

(2) Hansen, B. N.; Brooks, M. H.; Barkley, R. M.; Sievers, R. E. *Chem. Mater.* **1992**, *4*, 749–752 and references therein.

10.1021/ic0109391 CCC: $22.00

air and solution, being easily hydrolyzed and decomposed by contact with moisture. Among them, several silver(I) derivatives containing alkenes[4a,e,h] or alkynes[4g] and only a few with phosphines,[4b−d] amines,[4j] or sulfur donors[4e,f,l] have been prepared, with no systematic study of the structural variations induced by phosphines with different steric hindrances yet reported. Moreover, the structural features of Ag(I) derivatives with bidentate amines are poorly defined.[4j] Building on our experience in the coordination chemistry of several metals with the acylpyrazolone class of β-diketones (QH),[5] particularly with copper,[6] tin,[7] zinc, and cadmium,[8] we extend our investigation to encompass the field of silver(I), for a variety of reasons. First, presumably due to the presence of the pyrazole ring fused to one carbonyl group in acylpyrazolones, their metal derivatives are generally more stable relative to analogous acetylacetonates.[6−9] Second, the Ag(I) β-diketonates hitherto reported and structurally characterized have always contained fluorinated β-diketones (hfac, tfac, or fod).[4] Third, the acylpyrazolones possess a potentially donating nitrogen atom in the pz ring, which has been shown to be involved in extensive H-bonding networks influencing the supramolecular structure of several metal acylpyrazolonates,[6−8,10] and also their coordination to "soft" metal atoms.[11] In this work we describe the synthesis and spectroscopic and structural characterization of a number of silver(I) derivatives containing a variety of acylpyrazolones (Figure 1), with coligating unidentate phosphines such as Ph_3P, Cy_3P, and *o*-tol_3P in diverse ligand/metal ratios, with the bidentate bis(diphenylphosphino)ethane (dppe), or with the S-donor 1-methyl-2-mercaptoimidazole (Hmimt) and the N_2-donor *N*,*N*,*N*′-trimethylethylenediamine (trimen). We show here that Ag(I) can form air-stable derivatives with nonfluorinated β-diketones, and that the combination of acylpyrazolones with bidentate amines allows the formation of one-dimensional polymeric species.

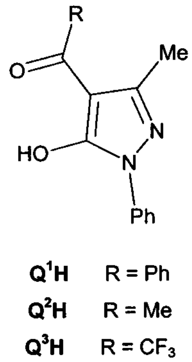


Figure 1. Proligands QH used in this work.

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 a Fisons Instruments 1108 CHNS/O elemental analyzer. Molecular weight determinations were performed in chloroform solution (*m* = mol/kg of solvent) at 313 K with a Knauer membrane osmometer. 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 parts per million vs Me_4Si, while phosphorus chemical shifts are reported in parts per million vs 85% H_3PO_4

---

(3) (a) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W,-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327−2329. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895−1898. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562−4569. (d) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gardner, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030−2040. (e) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960−2968. (f) Blake, A. J.; Champness, N. R.; Crew, M.; Parson, S. *New J. Chem.* **1999**, *23*, 13−15.

(4) (a) Bailey, A.; Corbitt, T. S.; Hampden-Smith, M. J.; Duesler E. N.; Kodas, T. T. *Polyhedron* **1993**, *12*, 1785−1792. (b) Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Chem. Mater.* **1993**, *5*, 765−766. (c) Lin, W.; Warren, T. H.; Nuzzo R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11644−11645. (d) Yuan, Z.; Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1994**, *72*, 1605−1609. (e) Xu, C.; Corbitt, T. S.; Hampden-Smith, M. J.; Kodas T. T.; Duesler, E. N. *J. Chem. Soc., Dalton Trans.* **1994**, 2841−2849. (f) Xu, C.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N.; Rheingold A. L.; Yap, G. *Inorg. Chem.* **1995**, *34*, 4767−4773. (g) Chi, K.-M.; Lin, C.-T.; Peng S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 2660−2663. (h) Doppelt, P.; Baum T. H.; Ricard, L. *Inorg. Chem.* **1996**, *35*, 1286−1291. (i) Chi, K.-M.; Chen, K.-H.; Lin H.-C.; Lin, K.-J. *Polyhedron* **1997**, *16*, 2147−2154. (j) Darr, J. A.; Poliakoff, M., Li, W.-S.; Blake, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2869−2674. (k) Darr, J. A.; Poliakoff, M.; Blake, A. J.; Li, W.-S. *Inorg. Chem.* **1998**, 5491−5496. (l) Blake, A. J.; Champness, N. R.; Howdle, S. M.; Webb, P. B. *Inorg. Chem.* **2000**, *39*, 1035−1038.

(5) These molecules were first synthesised at the turn of the last century: Stoltz, F. *J. Prakt. Chem.* **1897**, *55*, 145−148. The first work on the use of acylpyrazolones as chelating agents was by Jensen: Jensen, B. S. *Acta Chem. Scand.* **1959**, *13*, 1890−1896.

(6) (a) Marchetti, F.; Pettinari, C.; Cingolani, A.; Leonesi, D.; Camalli M.; Pifferi, A. *Polyhedron* **1996**, *15*, 3835−3849. (b) Drozdov, A.; Troyanov, S. I.; Fedorchenko, O.; Battiston, G.; Pettinari, C.; Marchetti F.; Cingolani, A. Proceedings of the Twelfth European Conference on CVD, vol II. *J. Phys. IV* **1999**, *9*, 929−934. (c) Marchetti, F.; Pettinari, C.; Pettinari, R.; Cingolani, A.; Camalli M.; Spagna, R. *Inorg. Chim. Acta* **2000**, *299*, 65−79. (d) Marchetti, F.; Pettinari, C.; Cingolani, A.; Leonesi, D.; Drozdov A.; Troyanov, S. I. *J. Chem. Soc., Dalton Trans.* **1998**, 3325−3333. (e) Pettinari, C.; Marchetti, F.; Santini, C.; Pettinari, R.; Drozdov, A.; Troyanov, S. I. *Inorg. Chim. Acta* **2001**, *315*, 88−95.

(7) (a) Pettinari, C.; Marchetti, F.; Cingolani, A.; Leonesi, D.; Mundorff, E.; Rossi M.; Caruso, F. *J. Organomet. Chem.* **1998**, *557*, 187−201. (b) Caruso, F.; Rossi, M.; Marchetti F.; Pettinari, C. *Organometallics* **1999**, *18*, 2398−2400. (c) Caruso, F.; Leonesi, D.; Marchetti, F.; Rivarola, E.; Rossi, M.; Tomov, V.; Pettinari, C. *J. Organomet. Chem.* **1996**, *519*, 29−44. (d) Marchetti, F.; Pettinari, C.; Cingolani, A.; Gioia Lobbia, G.; Cassetta, A.; Barba, L. *J. Organomet. Chem.* **1996**, *517*, 141−154. (e) Marchetti, F.; Pettinari, C.; Cingolani, A.; Brocanelli, L.; Rossi, M.; Caruso, F. *J. Organomet. Chem.* **1999**, *580*, 344−353. (f) Pettinari, C.; Marchetti, F.; Gregori, A.; Cingolani, A.; Tanski, J.; Rossi, M.; Caruso, F. *Inorg. Chim. Acta* **1997**, *257*, 37−48. (g) Pettinari, C.; Marchetti, F.; Cingolani, A.; Lorenzotti, A.; Mundorff, E.; Rossi, M.; Caruso, F. *Inorg. Chim. Acta* **1997**, *262*, 33−46. (h) Pettinari, C.; Marchetti, F.; Cingolani, A.; Marciante, C.; Spagna R.; Colapietro, M. *Polyhedron* **1994**, *13*, 939−950.

(8) (a) Pettinari, C.; Marchetti, F.; Cingolani, A.; Pettinari, R.; Troyanov S. I.; Drozdov, A. *J. Chem. Soc., Dalton Trans.* **2000**, 831−836. (b) Marchetti, F.; Pettinari, C.; Pettinari, R.; Arriva, D.; Troyanov S. I.; Drozdov, A. *Inorg. Chim. Acta* **2000**, *307*, 97−105. (c) Marchetti, F. *Main Group Met. Chem.* **2001**, *24*, 257−266.

(9) (a) Mahon, M. F.; Molloy, K. C.; Omotowa, B. A.; Mesubi, M. A. *J. Organomet. Chem.* **1996**, *525*, 239−246. (b) Mahon, M. F.; Molloy, K. C.; Omotowa, B. A.; Mesubi, M. A. *J. Organomet. Chem.* **1998**, *560*, 95−101.

(10) Pettinari, C.; Marchetti, F.; Cingolani, A.; Leonesi, D.; Troyanov, S. I.; Drozdov, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1555−1562.

(11) Uzoukwu, B. A.; Adiukwu, P. U.; Al-Juaid, S. S.; Hitchcock, P. B.; Smith, J. D. *Inorg. Chim. Acta* **1996**, *250*, 173−176.

and fluoro chemical shifts vs $CFCl_3$. The electrical conductances of the dichloromethane solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The proligands Q^1H, Q^2H, and Q^3H were synthesized according to the procedure described by Jensen.[5]

Synthesis of Complexes. $[Ag(Q^1)(Ph_3P)_2]$ (1). Silver nitrate (170 mg, 1 mmol) was added to a methanol solution (30 mL) of triphenylphosphine (524 mg, 2.0 mmol). After a few minutes a colorless precipitate was obtained. The mixture was then added to a methanol solution (20 mL) of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (278 mg, 1 mmol) and sodium methoxide (54 mg, 1 mmol). A yellow precipitate slowly formed. The mixture was set aside and stirred at room temperature for 1 h and then filtered. The precipitate was washed with methanol (10 mol) and dried under reduced pressure to constant weight. Yield: 87%. Mp: 168−169 °C. Anal. Calcd for $C_{53}H_{43}AgN_2O_2P_2$: C, 69.97; H, 4.76; N, 3.08. Found: C, 69.63; H, 4.65; N, 3.09. FW: 910. MW ($CHCl_3$): 895 ($c = 0.9 \times 10^{-2}$ m); 902 ($c = 1.1 \times 10^{-2}$ m). IR (Nujol) data: 1615vs, ν(C═O); 523m, 512vs, 493s, ν(P─Ph); 380m, 337m, ν(Ag─O). ^1H NMR ($CDCl_3$): δ 1.88s (3 H, $C^{3-}CH_3$); 7.10t, 7.20−7.50m, 7.65−7.75m, 7.95d (40 H, aromatics of Q and Ph_3P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.9 (s, C3−CH_3), 120.5, 124.4, 127.6, 128.1, 128.6, 142.0, 149.6 (s, C_{arom} of Q^1), 128.9 (d, $^3J_{P-C} = 9.7$ Hz, *m-C* of Ph_3P), 130.5 (s, *p-C* of Ph_3P), 131.5 (d, $^1J_{P-C} = 32.2$ Hz, *C*−P of Ph_3P), 133.9 (d, $^2J_{P-C} = 16.3$ Hz, *o-C* of Ph_3P), 104.8 (s, *C*4) 139.4 (s, *C*3) 165.5 (s, *C*5), 192.0 (s, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.7s br ($T = 293$ K); 9.7dd [$^1J(^{31}P-^{109}Ag) = 468$ Hz; $^1J(^{31}P-^{107}Ag) = 405$ Hz], 8.4dd [$^1J(^{31}P-^{109}Ag) = 500$ Hz; $^1J(^{31}P-^{107}Ag) = 433$ Hz] ($T = 218$ K).

$[Ag(Q^1)(Cy_3P)_2]$ (2). Compound **2** has been synthesized similarly to **1**. Yield: 55%. Mp: 147−149 °C dec. Anal. Calcd for $C_{53}H_{79}AgN_2O_2P_2$: C, 67.29; H, 8.42; N, 2.96. Found: C, 67.14; H, 8.54; N, 2.68. IR (Nujol) data: 1622vs, ν(C═O); 509s, ν(P─Cy); 360m, ν(Ag─O). ^1H NMR ($CDCl_3$): δ 1.15−1.45m, 1.64−2.00m (66 H, P−C_6H_{11}); 1.95s (3 H, $C^{3-}CH_3$); 7.10t, 7.26−7.30m, 7.40−7.45m, 7.55−7.62m, 8.03d (10 H, aromatics of Q). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.0 (s, C3−CH_3), 26.1, 27.4, 30.6, 32.1 (s br, $(C_6H_{11})_3P$), 119.4, 123.4, 127.7, 127.8, 128.3, 129.5, 142.3, 150.1 (s, C_{arom} of Q^1), 103.7 (s, *C*4) 140.0 (s, *C*3) 164.5 (s, *C*5), 190.3 (s, *C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.5s br ($T = 293$ K); 28.0dd [$^1J(^{31}P-^{109}Ag) = 482$ Hz; $^1J(^{31}P-^{107}Ag) = 419$ Hz] ($T = 218$ K). In dilute solution also a resonance at 11.8, due to free Cy_3P, and double doublet at 43.4 [$^1J(^{31}P-^{109}Ag) = 776$ Hz; $^1J(^{31}P-^{107}Ag) = 675$ Hz] slowly appeared at 218 K.

$[Ag(Q^1)(o\text{-}tol_3P)_2]$ (3). Compound **3** has been synthesized similarly to **1**. Yield 75%. Mp: 140−142 °C dec. Anal. Calcd for $C_{59}H_{55}AgN_2O_2P_2$: C, 71.30; H, 5.58; N, 2.82. Found: C, 71.14; H, 5.44; N, 2.97. IR (Nujol) data: 1632vs, ν(C═O); 462s, 438m, ν(P─*o*-tol); 386w, ν(Ag─O). ^1H NMR ($CDCl_3$): δ 1.74s (3 H, $C^{3-}CH_3$); 2.39s (18 H, *o*-CH_3); 6.86t, 7.15t, 7.26−7.35m, 8.00d (34 H, aromatics of Q and *o*-tol_3P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.6 (s, C3−CH_3), 21.7, 22.0 (s, *o*-CH_3), 120.7, 125.3, 127.7, 128.3, 128.8, 129.4, 129.8, 130.7, 140.5, 140.2 (s, C_{arom} of Q^1), 126.6 (d, $^3J_{P-C} = 4.8$ Hz, *m*-*C*H of *o*-tol_3P) 130.2 (s, *p*-*C*H of *o*-tol_3P) 131.3 (d, $^3J_{P-C} = 5.5$ Hz, *m*-*C*H of *o*-tol_3P) 133.3 (d, $^2J_{P-C} = 5.5$ Hz, *o*-*C*H of *o*-tol_3P) 142.8 (d, $^2J_{P-C} = 18.6$ Hz, *o*-*C*−CH_3 of *o*-tol_3P), 102.2 (s, *C*4), 138.6 (s, *C*3), 176.9 (s, *C*5 and/or *C*O), C−P of *o*-tol_3P not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.1s br ($T = 293$ K); −16.4dd [$^1J(^{31}P-^{109}Ag) = 482$ Hz; $^1J(^{31}P-^{107}Ag) = 418$ Hz], −20.4dd [$^1J(^{31}P-^{109}Ag) = 816$ Hz; $^1J(^{31}P-^{107}Ag) = 707$ Hz], −29.0s ($T = 203$ K).

$[Ag(Q^2)(Ph_3P)_2]$ (4). Compound **4** was obtained similarly to **1**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.5br ($T = 293$ K); 10.5dd [$^1J(^{31}P-^{109}Ag) = 480$ Hz; $^1J(^{31}P-^{107}Ag) = 415$ Hz], −8.8dd [$^1J(^{31}P-^{109}Ag) = 514$ Hz; $^1J(^{31}P-^{107}Ag) = 446$ Hz] ($T = 218$ K). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −72.1br ($T = 293$ K); −71.6s, −75.5s ($T = 218$ K).

$[Ag(Q^2)(Cy_3P)_2]$ (5). Compound **5** was obtained similarly to **1**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.2br ($T = 293$ K); 31.6dd [$^1J(^{31}P-^{109}Ag) = 501$ Hz; $^1J(^{31}P-^{107}Ag) = 439$ Hz] ($T = 218$ K). In dilute solution also a resonance at 11.8, due to free Cy_3P, and a double doublet at 43.5 [$^1J(^{31}P-^{109}Ag) = 708$ Hz; $^1J(^{31}P-^{107}Ag) = 613$ Hz] appeared at 218 K. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −72.8br ($T = 293$ K); −70.9s, −75.3s ($T = 218$ K).

$[Ag(Q^3)(Ph_3P)_2]$ (6). Compound **6** was obtained similarly to **1**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.0s br ($T = 293$ K); 9.7dd [$^1J(^{31}P-^{109}Ag) = 469$ Hz; $^1J(^{31}P-^{107}Ag) = 406$ Hz] ($T = 218$ K).

$[Ag(Q^3)(Cy_3P)_2]$ (7). Compound **7** was obtained similarly to **1**.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.3br ($T = 293$ K); 28.5dd [$^1J(^{31}P-^{109}Ag) = 488$ Hz; $^1J(^{31}P-^{107}Ag) = 421$ Hz] ($T = 218$ K). In dilute solution also a resonance at 11.8, due to free Cy_3P, and a double doublet at 43.4 [$^1J(^{31}P-^{109}Ag) = 707$ Hz; $^1J(^{31}P-^{107}Ag) = 613$ Hz] slowly appeared at 218 K.

$[Ag(Q^1)(Ph_3P)]_2$ (8). Compound **8** has been synthesized similarly to **1**, but using only 1 mmol of triphenylphosphine. FW: 647. MW ($CHCl_3$): 664 ($c = 0.9 \times 10^{-2}$ m); 777 ($c = 1.1 \times 10^{-2}$ m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.5s br ($T = 293$ K); 16.3dd [$^1J(^{31}P-^{109}Ag) = 802$ Hz; $^1J(^{31}P-^{107}Ag) = 696$ Hz] ($T = 218$ K).

$[Ag(Q^1)(Cy_3P)]_2$ (9). Compound **9** has been synthesized similarly to **8**. FW: 665. MW ($CHCl_3$): 721 ($c = 0.9 \times 10^{-2}$ m); 803 ($c = 1.1 \times 10^{-2}$ m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.6dd [$^1J(^{31}P-^{109}Ag) = 777$ Hz; $^1J(^{31}P-^{107}Ag) = 674$ Hz] ($T = 293$ K).

$[Ag(Q^1)(o\text{-}tol_3P)]_2$ (10). Compound **10** has been synthesized similarly to **8**. Yield: 83%. Mp: 235−237 °C. Anal. Calcd for $C_{38}H_{34}AgN_2O_2P$: C, 66.19; H, 4.97; N, 4.06. Found: C, 65.95; H, 5.07; N, 4.11. FW: 689. MW ($CHCl_3$): 1056 ($c = 0.9 \times 10^{-2}$ m); 1170 ($c = 1.1 \times 10^{-2}$ m). IR (Nujol) data: 1632vs, ν(C═O); 462s, 438m, ν(P─*o*-tol); 343m, ν(Ag─O). ^1H NMR ($CDCl_3$): δ 1.78s (3 H, $C^{3-}CH_3$); 2.54s (9 H, *o*-CH_3); 6.82t, 7.15t, 7.30−7.48m, 7.95d (22 H, aromatics of Q and *o*-tol_3P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.0 (s, C3−CH_3), 22.3 (s, *o*-CH_3), 22.5 (s, *o*-CH_3), 120.2, 124.1, 127.4, 128.1, 128.5, 129.6, 139.6, 142.2 (s, C_{arom} of Q^1), 126.8 (d, $^3J_{P-C} = 7.3$ Hz, *m*-*C*H of *o*-tol_3P) 131.0 (d, $^4J_{P-C} = 1.2$ Hz, *p*-*C*H of *o*-tol_3P) 131.9 (d, $^3J_{P-C} = 7.3$ Hz, *m*-*C*H of *o*-tol_3P) 133.0 (d, $^2J_{P-C} = 6.1$ Hz, *o*-*C*H of *o*-tol_3P) 142.7 (d, $^2J_{P-C} = 15.7$ Hz, *o*-*C*−CH_3 of *o*-tol_3P), 166.3 (s, *C*5), 192.1 (s, *C*O), *C*−P of *o*-tol_3P not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −17.1d br ($T = 293$ K); −20.4dd [$^1J(^{31}P-^{109}Ag) = 817$ Hz; $^1J(^{31}P-^{107}Ag) = 709$ Hz] ($T = 193$ K).

$[Ag(Hmimt)_2(Ph_3P)](Q^1)$ (11). Compound **1** (909 mg, 1 mmol) was dissolved in hot diethyl ether (50 mL), and 1-methylimidazoline-2-thione (Hmimt) was then added (218 mg, 2 mmol). A yellow precipitate slowly formed. The mixture was set aside and stirred at room temperature for 1 h and then filtered. The precipitate was washed with diethyl ether (10 mol) and dried under reduced pressure to constant weight. Yield: 75%. Mp: 108−110 °C. FW: 876.8. MW ($CHCl_3$): 845 ($c = 0.9 \times 10^{-2}$ m); 868 ($c = 1.2 \times 10^{-2}$ m). Anal. Calcd for $C_{43}H_{37}AgN_6O_2PS_2$: C, 58.97; H, 4.60; N, 9.60. Found: C, 58.64; H, 4.52; N, 9.78. IR (Nujol) data: 2300−3200br, ν(N─H···O); 1620vs, ν(C═O); 517s, 512s, 503vs, ν(P─Ph). ^1H NMR ($CDCl_3$): δ 1.84s (3 H, $C^{3-}CH_3$); 3.53s, (6 H, N−CH_3, of Hmimt); 5.40br (2 H, N−*H* of Hmimt); 6.50d, (4 H, aromatics of Hmimt); 7.10t, 7.25−7.35m, 7.42d, 7.98d, (25 H, aromatics of Q and Ph_3P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.7 (s, C3−CH_3), 34.2 (s, N−CH_3 of Hmimt), 120.4, 123.8, 127.7, 128.1, 142.2, 150.0 (s, C_{arom} of Q^1), 116.2, 119.1, 129.7 (s, C_{arom} of Hmimt), 128.7 (d,

$^3J_{P-C} = 9.6$ Hz, *m-C* of Ph$_3$P), 129.9 (s, *p-C* of Ph$_3$P), 132.8 (d, $^1J_{P-C} = 24.0$ Hz, *C*-P of Ph$_3$P), 133.8 (d, $^2J_{P-C} = 16.5$ Hz, *o-C* of Ph$_3$P), 100.3 (s, *C*4), 139.6 (s, *C*3), 177.3 (s, *C*5 and/or *C*O). ^{31}P NMR (CDCl$_3$): δ 6.1s br ($T = 293$ K); 6.8dd [$^1J(^{31}\text{P}-^{109}\text{Ag}) = 523$ Hz; $^1J(^{31}\text{P}-^{107}\text{Ag}) = 494$ Hz] ($T = 218$ K).

[Ag(dppe)$_2$](Q^1) (12). Compound **1** (909 mg, 1 mmol) was dissolved in hot diethyl ether (50 mL), and bis(diphenylphosphino)ethane (dppe) was then added (796 mg, 2 mmol). The clear solution was set aside and stirred at room temperature for 4 h, and then solvent was removed and chloroform added (20 mL). The mixture was filtered, to remove NaNO$_3$, and *n*-hexane added (40 mL). A yellow precipitate immediately formed, which was filtered off, washed with methanol (10 mol), and dried under reduced pressure to constant weight. Yield: 66%. Mp: 94−95 °C. FW: 1182. MW (CHCl$_3$): 540 ($c = 0.9 \times 10^{-2}$ m); 588 ($c = 1.2 \times 10^{-2}$ m). Anal. Calcd for $C_{69}H_{61}AgN_2O_2P_4$: C, 70.11; H, 5.20; N, 2.37. Found: C, 69.88; H, 512; N, 2.32. Molar conductance Λ_M in dichloromethane solution: 32.5 Ω^{-1} cm^2 mol^{-1}. IR (Nujol) data: 1632vs, ν(C═O); 509s, ν(P−Ph). ^{1}H NMR (CDCl$_3$): δ 2.30s (3 H, C^{3-}C*H*$_3$); 2.40−2.45m (4 H, P−C*H*$_2$C*H*$_2$P of dppe); 7.18−7.32m, 7.36−7.40m, 8.05d (50 H, aromatics of Q^1 and dppe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.1 (s, C3−*C*H$_3$), 25.6 (s br, P−*C*H$_2$CH$_{2-}$P of dppe), 119.6, 122.4, 124.8, 126.3, 127.3, 128.1, 128.3, 128.7, 135.9, 140.3.1 (s, C_{arom} of Q^2), 129.2 (s, *m-C* of Ph−P) 130.6 (s, *p-C* of Ph−P) 132.1 (br, *C*-P of Ph−P) 132.5 (s, *o-C* of Ph−P), resonances of *C*3, *C*4, *C*5, and *C*O were not observed. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 5.6d br ($T = 293$ K); 5.6dd [$^1J(^{31}\text{P}-^{109}\text{Ag}) = 265$ Hz; $^1J(^{31}\text{P}-^{107}\text{Ag}) = 230$ Hz] ($T = 218$ K).

Derivative **12** could also be synthesized by the following alternative method.

Silver nitrate (170 mg, 1 mmol) was added to a methanol solution (30 mL) of dppe (796 mg, 2.0 mmol). Then the mixture was added to a methanol solution (20 mL) of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (278 mg, 1 mmol) and sodium methoxide (54 mg, 1 mmol). The clear solution was set aside and stirred at room temperature for 4 h, and then solvent was removed and chloroform added (20 mL). The mixture was filtered, to remove NaNO$_3$, and *n*-hexane added (40 mL). A yellow precipitate immediately formed, which was filtered off, washed with methanol (10 mol), and dried under reduced pressure to constant weight.

[Ag(dppe)$_2$](Q^2) (13). Compound **13** has been synthesized similarly to **12**.^{31}P{^{1}H} NMR (CDCl$_3$): δ 5.7d br ($T = 293$ K); 5.7dd [$^1J(^{31}\text{P}-^{109}\text{Ag}) = 264$ Hz; $^1J(^{31}\text{P}-^{107}\text{Ag}) = 231$ Hz] ($T = 218$ K). ^{19}F{^{1}H} NMR (CDCl$_3$): δ 75.2 ($T = 293$ K).

[Ag(Q^1)dppe)] (14). Silver nitrate (170 mg, 1 mmol) was added to a methanol solution (30 mL) of dppe (398 mg, 1.0 mmol). The mixture was then added to a methanol solution (20 mL) of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (278 mg, 1 mmol) and sodium methoxide (54 mg, 1 mmol). A brown precipitate immediately formed. The mixture was set aside and stirred at room temperature for 1 h, then filtered, washed with methanol (10 mol), and dried under reduced pressure to constant weight. Derivative **14** is insoluble in all solvents, except DMSO. Yield: 85%. Mp: 190−191 °C. Anal. Calcd for $C_{43}H_{237}AgN_2O_2P_2$: C, 65.91; H, 4.76; N, 3.57. Found: C, 65.72; H, 4.70; N, 3.65. Molar conductance Λ_M in DMSO solution: 12.4 Ω^{-1} cm^2 mol^{-1}. IR (Nujol) data: 1613vs, ν(C═O); 511s, ν(P−Ph). ^{1}H NMR (DMSO-*d*$_6$): δ 2.22s (3 H, C^{3-}C*H*$_3$); 2.55s (4 H, P−C*H*$_2$C*H*$_{2-}$P); 7.22−7.55m, 7.58−7.75m (30 H, aromatics of Q).

[Ag(Q^1)(trimen)] (15). Silver nitrate (170 mg, 1 mmol) was added to a methanol solution (30 mL) of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (278 mg, 1 mmol) and sodium methoxide (54 mg, 1 mmol), and trime then added (102 mg, 1 mmol). A dark green precipitate immediately formed. The mixture was set aside and stirred at room temperature for 1 h, and then it was filtered. The precipitate was washed with diethyl ether (10 mol) and dried under reduced pressure to constant weight. It was shown to be soluble in DMSO and chlorinated solvents. Yield: 65%. Mp: 151−152 °C dec. Anal. Calcd for $C_{22}H_{27}AgN_4O_2$: C, 54.22; H, 5.58; N, 11.50. Found: C, 54.02; H, 5.70; N, 11.65. IR (Nujol) data: 1612vs, ν(C═O); 335m, ν(Ag−O); 284m, ν(Ag−N). ^{1}H NMR (CDCl$_3$): δ 2.11s (6 H, N(C*H*$_3$)$_2$); 2.15s (3 H, N′∠C*H*$_3$ of trime); 2.26s (3 H, C^{3-}C*H*$_3$); 2.20−2.24m, 2.42−2.45m (4 H, N−C*H*$_2$C*H*$_{2-}$N′ of trime); 7.15t, 7.22−7.40m, 7.58d, 7.75−7.80m (10 H, aromatics of Q).^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.4 (s, C3−*C*H$_3$), 38.6 (s, N−*C*H$_3$), 49.3 (s, N(*C*H$_3$)$_2$), 49.4, 58.8 (s, N(*C*H$_2$)$_2$N), 123.0, 125.5, 127.4, 128.8, 129.0, 130.2, 141.3, 154.2 (s, C_{arom} of Q^1), 103.4 (s, *C*4), 139.5 (s, *C*3), 163.9 (s, *C*5), 190.3 (s, *C*O).

[Ag(Q^2)(trimen)] (16). Compound **16** has been synthesized similarly to **15**. It was shown to be soluble in DMSO and chlorinated solvents. ^{1}H NMR (CDCl$_3$): δ 2.10s (6 H, N(C*H*$_3$)$_{2\text{ trime}}$); 2.23s (3 H, N′∠C*H*$_{3\text{ trime}}$); 2.34q (3 H, C^{3-}C*H*$_3$); 2.28−2.34m, 2.58−2.66m (4 H, N−C*H*$_2$C*H*$_{2-}$N′$_{\text{trime}}$); 2.94br (1 H, N′∠*H*$_{\text{trime}}$); 7.15t, 7.26t, 7.54d, (5 H, N−C$_6$*H*$_5$). ^{19}F{^{1}H} NMR (CDCl$_3$): δ 76.0br (293 K).

All other analytical and spectroscopic data of derivatives **4**−**9**, **13**, and **16** are available as Supporting Information.

X-ray Crystallographic Studies. Crystals suitable for structural analysis of Q^{3}H, **1**, **2**, **4**, **10**, **11**, and **15** were grown from chloroform at 4 °C. They were all pale yellow, except **15**, which was light green. Full spheres of CCD area detector diffractometer data were measured (Bruker AXS instrument; ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T as specified; $2\theta_{\max}$ as specified), yielding N_{total} reflections, merging to N unique reflections (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered "observed" and used in the full-matrix least-squares refinement, refining anisotropic thermal parameter forms for the non-hydrogen atoms $(x, y, z, U_{\text{iso}})_H$ treatment as indicated. [Exception: For **1** and Q^{3}H hemispheres of data were measured using an Enraf-Nonius CAD-4 sequential/single counter instrument ($2\theta/\theta$ scan mode)]. Conventional residuals R $(\sum\Delta/\sum|F_o|)$ and R_w $([\sum(\omega\Delta^2/\sum(\omega F_o{}^2)^2)]^{1/2})$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted at convergence. Pertinent results are given in the tables and figures, full details being deposited. In the figures displacement ellipsoid amplitudes are 20% (room temperature) and 50% (low temperature) for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Further individual variations are as follows:

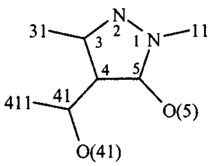
(**1**) A difference map residue was assigned as a water molecule oxygen, fully populated after trial refinement, hydrogens not located. A Gaussian absorption correction was applied.

(**15**) Diamine ring methylene groups were modeled as disordered, concerted, over two sets of sites, occupancies 0.66(1) and complement.

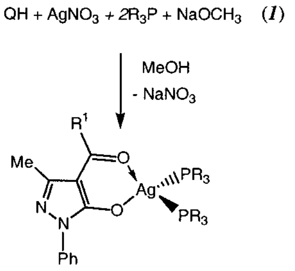
(**2**) Difference map residues were modeled in terms of acetone of solvation, site occupancy set at unity after trial refinement.

(Q^{3}H) No absorption correction was applied.

Atoms numberings of the Q ligand cores are based on the following scheme:

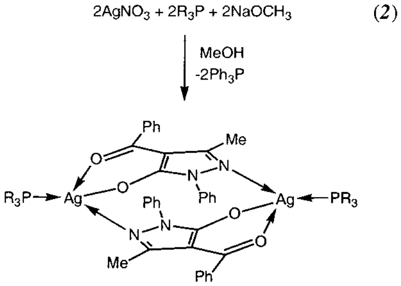


Scheme 1



1	$R^1 = R = Ph$
2	$R^1 = Ph, R = Cy$
3	$R^1 = Ph$, R = *o*-tol
4	$R^1 = CF_3, R = Ph$
5	$R^1 = CF_3, R = Cy$
6	$R^1 = Me, R = Ph$
7	$R^1 = Me, R = Cy$

Scheme 2



8	R = Ph
9	R = Cy
10	R = *o*-tol

Results and Discussion

From the interaction of 1 equiv of $AgNO_3$ with 1 equiv of the proligands QH in methanol, in the presence of 1 equiv of $NaOCH_3$ and 2 equiv of R_3P ligands, we have synthesized the derivatives **1**−**7** (Scheme 1).

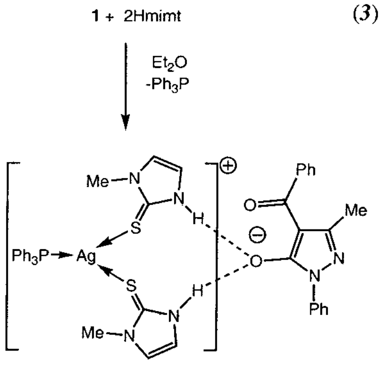
They are very soluble in DMSO, acetone, diethyl ether, aromatic hydrocarbons, and chlorinated solvents, in which they are nonelectrolytes.

On the other hand, with equimolar amounts of all reactants, the derivatives **8**−**10** have been obtained (Scheme 2).

They are soluble in DMSO, acetone, and chlorinated solvents, in which they are nonelectrolytes. They exist in the solid state as dinuclear species (see the structural discussion below), but in solution vaporimetric molecular weight determinations suggest they are almost completely dissociated into the mononuclear fragments.

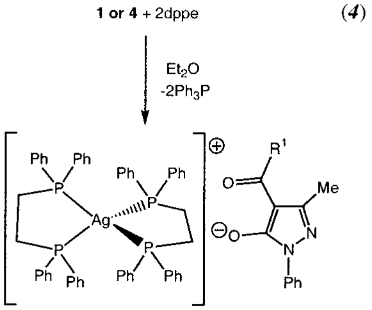
The reaction of derivative **1** with 2 equiv of the unidentate S-donor ligand Hmimt in hot diethyl ether affords the derivative **11** (Scheme 3).

Scheme 3



11

Scheme 4



12	$R^1 = Ph$
13	$R^1 = CF_3$

Derivative **11** is very soluble in most organic solvents and a is non-electrolyte in acetone and dichloromethane. This may be due to an ion-pairing effect, resulting from H-bonding between the hydrogen of the coordinated Hmimt and the acylpyrazolonate oxygen, as found in the solid state (see the infrared and structural discussion below).

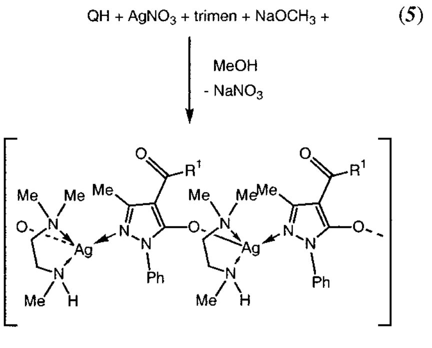
By interaction of derivatives **1** and **4** with excess dppe in hot diethyl ether, the derivatives **12** and **13**, respectively, have been obtained (Scheme 4).

These are 1:1 electrolytes in dichloromethane, vaporimetric molecular weight determinations being consistent with an ionic structure. These derivatives can also be synthesized by direct interaction of 1 equiv of $AgNO_3$ with 1 equiv of the proligands QH in methanol, in the presence of 1 equiv of $NaOCH_3$ and 2 equiv of dppe. An excess of the bidentate chelating dppe always displaces the acylpyrazolone from the coordination sphere of silver. If the reaction is carried out using equivalent amounts of $AgNO_3$, Q^1H, $NaOCH_3$, and dppe in methanol, the 1:1:1 derivative **14** is obtained, which is insoluble in all common solvents except DMSO, presumably polymeric.

These results led us to investigate the behavior of a bidentate amine, exemplified by trimen, which, like dppe, can form five-membered chelate rings, but possesses two nitrogen atoms which are harder donors than phosphorus. The trimen donor has been previously used to form the derivative [Ag(hfac)(trimen)],[4j] but its solid-state structure has not been investigated.

The attempted displacement of Q^- or Ph_3P from the silver environment in **1** or **4** by a large excess of trimen in Et_2O was unsuccessful, whereas, from the direct interaction with

Scheme 5



15 R^1 = Ph

16 R^1 = CF_3

equimolar amounts of the reactants in methanol, derivatives **15** and **16** were obtained (Scheme 5).

They are soluble in DMSO but only slightly soluble in acetone and chlorinated solvents, where they are nonelectrolytes. They exist in the solid state as polymers (see the structural discussion below).

Spectroscopic Characterization. The infrared spectra of derivatives **1**−**12** show the presence of the deprotonated Q ligand: the strong broad band around 3000 cm^{-1} arising from intramolecular OH···O bonding disappears after coordination. By contrast, the strong absorption ascribed to the C═O stretching seems almost unaffected, only a slight shift to lower frequencies being observed, as previously found in the spectra of analogous copper(I) acylpyrazolonates.[6] In derivative **11** a broad absorption between 2300 and 3200 cm^{-1} is indicative of H-bonding between the H atom of Hmimt and the Q^1 donor oxygen, as found in the crystal structure (see below). By comparison with the spectrum of the free acylpyrazolone in the far-infrared region, we have tentatively assigned a number of absorptions to ν(Ag−O), ν(Ag−N), and ν(Ag−S) modes.[12]

The ^{1}H NMR spectra of **1**−**16** show resonances and integration in agreement with the formulas proposed. The resonances are broad, especially in the spectra of derivatives **1**−**7**, suggesting fluxionality in solution.

The ^{13}C NMR spectra of derivatives **1**−**10** exhibit one set of carbon resonances. In all R_3P-containing compounds the presence of further doublets due to C−P coupling assists in the assignment of signals arising from the C atoms of the phosphine ligand.[13]

^{1}H and ^{13}C NMR spectra of derivatives **15** and **16**, which contain the trimen donor, appear consistent with dissociation of the polymeric chain and coordination of the N_2-donor to the {Ag(Q)} fragment, providing no further insight into the solution structures.

The room temperature ^{31}P NMR spectra of derivatives **1**−**13** generally exhibit broad single resonances which, on cooling of the samples at 218 or even to 193 K, generally split into one or two double doublets, from which it is possible to determine the $^1J(^{109}Ag-^{31}P)$ and $^1J(^{107}Ag-^{31}P)$ coupling constants. This indicates that **1**−**13** undergo exchange at room temperature, leading to partial loss of Ag−P coupling information. For previous silver phosphine β-diketones, the mechanism proposed was a reversible dissociation of the anionic β-diketonate ligand in solution.[4d] The ^{19}F NMR spectra of the derivatives **4** and **5**, which contain the fluorinated Q^2, further support this hypothesis: the broad signal detected at room temperature splits into one signal due to anionic Q^2 at −75 ppm and another one, at higher field, due to the complex $[Ag(Q^2)(R_3P)_2]$. The absence of conductivity in dichloromethane is presumably a consequence of ion-pairing effects.

Scheme 6

$$\mathbf{3} \rightleftharpoons Ag(Q)(o\text{-}tol_3P) + o\text{-}tol_3P \quad (6)$$

For $[Ag(Q)(R_3P)_2]$-type complexes the chemical shift $\Delta\delta(^{31}P\{^1H\})$ $(=\delta_{complex} - \delta_{phosphine})$ values lie in the range 13−20 ppm, independent of the nature of the acylpyrazolonate donor. The ^1J(Ag−P) coupling constants, which are determined mainly by the bond orbital overlap between Ag and P on the basis of the Fermi contact term,[14] can be related to the number of coordinated phosphines and covalent vs ionic character of Ag−P bonds.[15] In the present complexes the $^1J(^{107}Ag-^{31}P)$ values range from 230 to 709 Hz and the $^1J(^{109}Ag-^{31}P)$ values from 264 to 817 Hz.

In the case of derivatives **1** and **4**, the broad absorptions detected at room temperature split into two pairs of double doublets on lowering of the temperature, in accordance with the presence of two different Ag−P bonds (see the structural discussion of **1** and **4** below).

Derivative **3**, containing the bulky *o*-tol_3P ligand, partially dissociates in $CDCl_3$ solution (Scheme 6), the resonances of both $Ag(Q^1)(o\text{-}tol_3P)_2$ and $Ag(Q^1)(o\text{-}tol_3P)$ species, together with the signal due to the free phosphine at −29.0 ppm, being observed in the ^{31}P NMR spectra. The formation of derivative **10** from concentrated chloroform solution of **3** gives further support to the possibility of dissociation.

In the cyclohexylphosphine derivatives **2**, **5**, and **7**, dissociation occurs in dilute solution several hours after dissolution of the samples: the signal of free Cy_3P and an

---

(12) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Nakamoto, K., Ed.; Wiley-Interscience: New York, 1986.

(13) Pettinari, C.; Marchetti, F.; Polimante, R.; Cingolani, A.; Portalone, G.; Colapietro, M. *Inorg. Chim. Acta* **1996**, *249*, 215−229.

(14) Pople, J. A. Santry, D. P. *Mol. Phys.* **1964**, *8*, 1−18.

(15) (a) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114−4115. (b) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386-6391. (c) van der Ploeg, A. F. M. J.; van Koten, G.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1052−1060. (d) van der Ploeg, A. F. M. J.; van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225−239. (e) Barrow, M.; Bürgi, H.-B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356−2362. (f) Socol, S. M.; Verdake, R. A. *Inorg. Chem.* **1984**, *23*, 3487−3493. (g) Socol, S. M.; Jacobson, R. A. Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88−94. (h) Barron, P. F.; Dyason, J. C. Healy, P. C.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1965−1970. (i) Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1987**, *127*, 209−213. (i) Dean, P. A: W. Vittal, J. J.; Srivastava, R. S. *Can. J. Chem.* **1987**, *65*, 2628−2633. (j) Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1988**, *144*, 205−211. (k) Obendorf, D.; Probst, M.; Peringer, P.; Falk, A.; Muller, N. *J. Chem. Soc., Dalton Trans.* **1988**, 1709−1711. (l) Bowmaker, G. A.; Effendy; Harvey, P. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2459−2466.

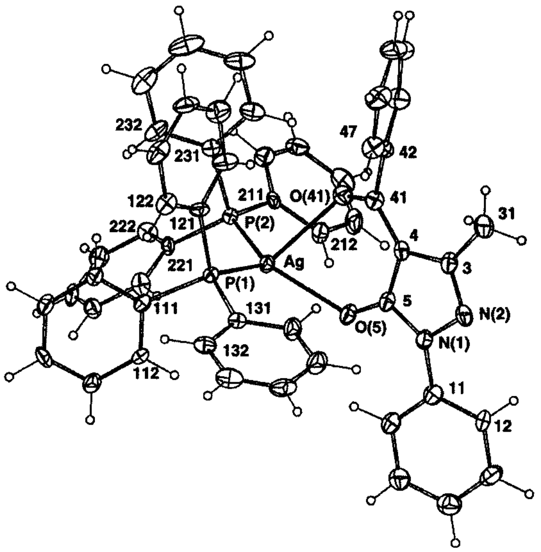


Figure 2. Molecular projection of **1**.

additional double doublet, with the J(Ag−P) corresponding to a Ag(Q)(Cy_3P) species, slowly appear.

In the low-temperature ^{31}P NMR spectra of the derivatives **8**−**10**, containing only one R_3P, one double doublet was detected, $^1J(^{109}Ag-^{31}P)$ and $^1J(^{107}Ag-^{31}P)$ being 802 and 696 Hz for **8**, 777 and 674 Hz for **9**, and 817 and 709 Hz for **10**, respectively. These high ^1J(Ag−P) values may be rationalized in terms of formation of a mononuclear Ag(Q^1)(R_3P) fragment, containing an sp-hybridized silver,[15f] arising from the dissociation of the dinuclear species, as indicated by molecular weight values in chloroform.

The derivative **11** shows one double doublet at low temperature; $^1J(^{109}Ag-^{31}P)$ and $^1J(^{107}Ag-^{31}P)$ are larger (523 and 494 Hz, respectively) than those found for **1**−**7** and consistent with the presence of only one phosphine on a tricoordinate silver atom.

The ionic derivatives **12** and **13** present identical low-temperature ^{31}P spectra, with $^1J(^{109}Ag-^{31}P)$ and $^1J(^{107}Ag-^{31}P)$ having the values 265 and 230 Hz, respectively, typical of compounds with a AgP_4 central core.[15,16]

Structural Discussion. The results of the single-crystal X-ray structure determinations are consistent with the stoichiometries and connectivities implied in the above formulas; in each case, one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. All contain Q moieties in various forms; the methyl-substituted ligand, crystallizing nicely as Q^3H, provides an example of a parent undeprotonated ligand form (drawing given in the Supporting Information); in derivatives **1** (Figure 2), **2** (Figure 3), and **4** (Figure 4), the Q^1 and Q^2 ligands are found as simple chelates, in **10** (Figure 5) and **15** (Figure 6), they are found with *O*-Q^1-*N* and *O,O′*-Q^1-*N* bridges, respectively, and finally, in the derivative **11** (Figure 7), the anionic ligand Q^1 is totally displaced from the coordination environment of the metal by other ligands, and provides an example of an anionic form. Many of the determinations are nicely precise, as a consequence of the availability of full spheres of extensive data at low temperature, permitting a usefully comparative array of ligand geometries, as presented in Table 1; we comment on them further after consideration of the individual structures.

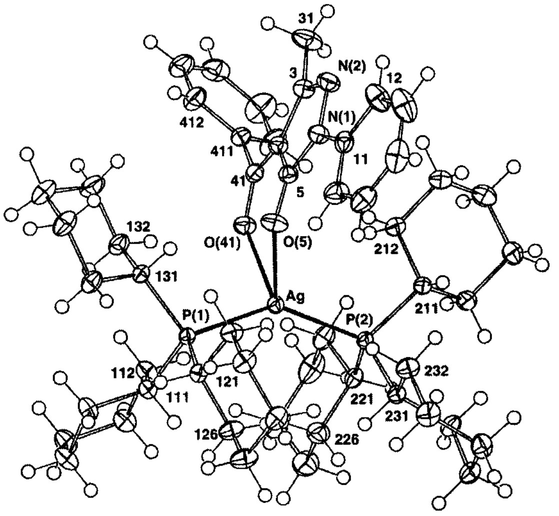


Figure 3. Molecular projection of **2**.

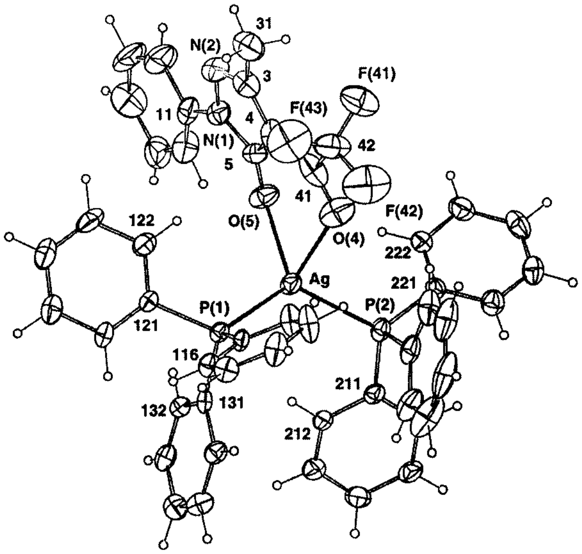


Figure 4. Molecular projection of **4**.

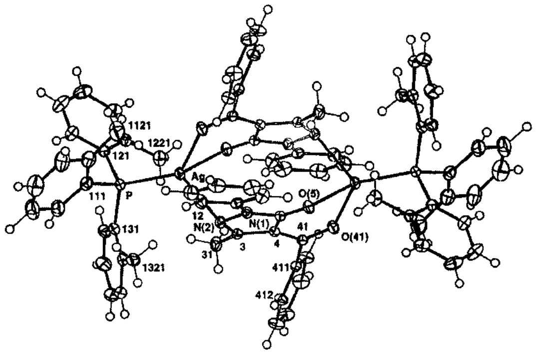


Figure 5. Molecular projection of **10**.

Crystal Structure of Q^3H. A representative structure of a QH ligand, in its neutral *O*-protonated acid form, is

---

(16) (a) Di Bernardo, P.; Dolcetti, G.; Portauova, R.; Tolazzi, M.; Tomat, G.; Zanonato P. *Inorg. Chem.* **1990**, *29*, 2859−2862. (b) Harker, C. S. W., Tiekink, E. R. T. *J. Coord. Chem.* **1990**, *21*, 287−293.

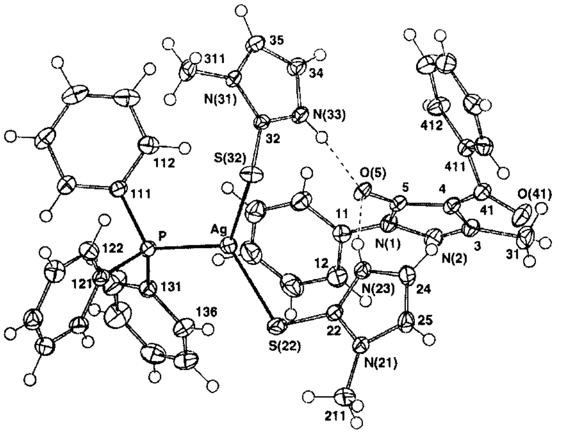


Figure 6. Projection of the ion pair of **11**.

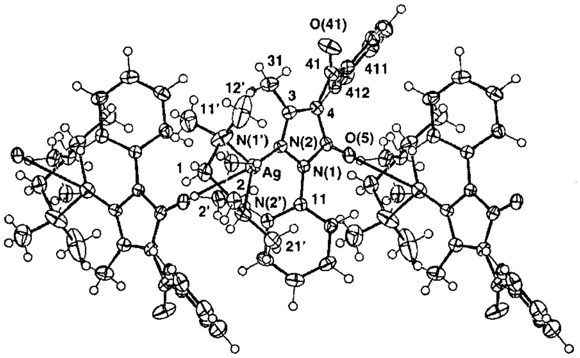


Figure 7. Section of the polymer of **15**.

Table 1. Comparative Geometries of Ligands Q in Various Forms[a]

ligand/mode	HQ^3 Q^3/acid	**11** Q^1/anion	**10** Q^1/*O,O′*-chelated bridge	**15** Q^1/O,N-bridging	**2** Q^1/simple chelate
Distances (Å)					
N(1)−C(11)	1.427(2)	1.410(3)	1.417(2)	1.416(4)	1.410(2)
N(1)−N(2)	1.395(3)	1.391(1)	1.404(2)	1.399(4)	1.402(2)
N(2)−C(3)	1.312(2)	1.322(2)	1.326(2)	1.321(4)	1.312(3)
C(3)−C(31)	1.493(3)	1.495(2)	1.494(2)	1.482(5)	1.492(3)
C(3)−C(4)	1.424(2)	1.422(3)	1.422(2)	1.409(4)	1.439(2)
C(4)−C(5)	1.392(2)	1.415(2)	1.435(2)	1.436(5)	1.435(2)
C(5)−N(1)	1.345(2)	1.385(1)	1.390(2)	1.406(5)	1.387(2)
C(5)−O(5)	1.316(2)	1.282(1)	1.254(2)	1.250(4)	1.250(2)
C(4)−C(41)	1.428(2)	1.449(2)	1.432(2)	1.452(5)	1.429(2)
C(41)−O(41)	1.247(2)	1.240(2)	1.248(2)	1.231(4)	1.249(2)
C(41)−C(411)	1.487(3)	1.499(2)	1.493(2)	1.504(5)	1.500(2)
O(41)···O(5)	2.587(2)		2.972(2)		2.992(2)
Angles (deg)					
C(11)−N(1)−N(2)	119.0(1)	118.96(9)	119.1(1)	119.6(2)	118.9(1)
C(11)−N(1)−C(5)	130.9(1)	128.62(9)	129.3(1)	128.7(3)	128.6(1)
N(2)−N(1)−C(5)	110.1(1)	112.20(9)	111.4(1)	111.6(2)	112.1(1)
N(1)−N(2)−C(3)	106.1(1)	105.0(1)	106.1(1)	105.8(2)	105.7(1)
N(2)−C(3)−C(4)	111.5(1)	112.3(1)	111.6(1)	112.3(3)	112.3(1)
N(2)−C(3)−C(31)	119.4(2)	120.1(1)	118.8(1)	119.0(3)	117.9(2)
C(31)−C(3)−C(4)	129.1(2)	127.5(1)	129.4(1)	128.6(3)	129.7(2)
C(3)−C(4)−C(5)	104.0(1)	105.4(1)	105.9(1)	106.3(3)	104.9(1)
C(3)−C(4)−C(41)	135.6(1)	125.9(1)	130.1(1)	123.9(3)	130.2(2)
C(5)−C(4)−C(41)	120.4(1)	128.6(1)	123.9(1)	129.8(3)	124.3(1)
C(4)−C(41)−O(41)	118.7(2)	121.7(1)	123.4(1)	121.0(3)	124.4(2)
C(4)−C(41)−C(411)	121.3(2)	119.9(1)	119.9(1)	121.7(3)	119.1(1)
O(41)−C(41)−C(411)	120.0(2)	118.4(1)	116.7(1)	117.2(3)	116.5(2)
N(1)−C(5)−C(4)	108.4(1)	105.10(9)	104.8(1)	103.9(3)	104.9(1)
N(1)−C(5)−O(5)	124.8(1)	122.9(1)	124.1(1)	123.6(3)	123.4(2)
C(4)−C(5)−O(5)	126.9(1)	131.6(1)	131.1(1)	132.5(3)	131.6(2)
Interplanar Dihedral Angles (deg)					
$C_6(1)/N_2-C_3$	5.33(1)	32.92(6)	6.96(5)	31.2(1)	6.29(7)
$C(4(n))_3-O(4)/N_2-C_3$	2.71(8)	32.61(6)	21.69(5)	24.9(1)	12.83(6)
$C(4(n))_3-O(4)/C_6(41)$		25.87(6)	50.27(6)	29.9(1)	70.94(8)

[a] Examples are given of the parent acid, as HQ^3, the anion, as found in **11** as Q^1, the coordinated ligand, in two bridging modes as in **10** and **15**, and a simple chelate, as most precisely exemplified in **2**. The determination of HQ^3 was at ca. 300 K, the remainder at ca. 153 K.

provided by Q^{3}H, the molecules packing in herringbone fashion in projection down *a* (Figure deposited as part of the supporting information), seemingly little affected by any intermolecular interactions potentially arising out of hydrogen bonds between the acidic OH groups peripheral to the central ring and basic entities of the neighbors.[17] Rather, the acidic hydrogen atom bonds intramolecularly to the adjacent ketonic oxygen atom of the acetyl group to which it lies *cis*, poised for chelating, which, in this case, pertains to the hydrogen, seemingly unsymmetrically disposed (H(5)···O(5,41) = 1.16(3), 1.51(3) Å). The non-hydrogen skeleton of the whole molecule is quasi-planar (Table 1). Its geometry is generally in agreement with those of other 4-acyl-5-pyrazolones from previously reported crystal structures.[17]

Crystal Structure of 1, 2, and 4. The metal atom environments in complexes **1** (Figure 2) and **4** (Figure 4) closely resemble each other, silver being in a distorted tetrahedral array, with P−Ag−P angles of 120.9(1)° and 121.4(1)°, respectively, and two sets of Ag−O (**1**, 2.349(7) and 2.498(6) Å; **4**, 2.354(8) and 2.42(1) Å) and Ag−P (**1**, 2.475(3) and 2.465(3) Å; **4**, 2.457(3) and 2.462(3) Å) bond distances. They differ radically from the environment of **2** (Figure 3), where the disposition of the P−Ag−P array is more nearly linear (142.12(1)°), with concomitantly shorter Ag−P distances (2.4342(6) and 2.3992(5) Å). The O−Ag−O bite angles are 73.0(2)° in **1**, 75.91(5)° in **2**, and 73.6(4)° in **4**. In the analogous crystal structure of [Ag(hfac)(Me$_3$P)$_2$],[4c] despite the use of the seemingly less hindered phosphine Me$_3$P, the distortion is higher, P−Ag−P being 159.4(2)° and the O−Ag−O bite angle 70.3(7)°, with appreciably longer Ag−O (2.45(2) and 2.64(2) Å) but shorter Ag−P (2.335(9) and 2.417(9) Å) distances, in accordance with the higher electron-donating power of Me$_3$P with respect to Ph$_3$P, and the diminished basicity of hfac (which contains two electron-withdrawing CF$_3$ groups) with respect to Q^1 or Q^2. The Cy$_3$P ligand conformations of **2** are of a familiar type[18] (Table 2), while those of the PPh$_3$ ligands throughout **1** and **4** are quite similar.[6a,c] In all three complexes, the silver atom lies well out of the essentially planar C$_3$O$_2$ array: (δ Ag(Å), χ^2 plane) 0.824(2), 5 × 10^3 (**2**); 1.26(1), 173 (**1**); 1.07(2), 10 (**4**). In **1**, the crystal packing is of interest, the molecules packing in layers normal to *c**, with difference map residues modeled as water molecules located on *2*-axes in between, i.e., a "hemihydrate".

---

(17) (a) O'Connell, M. J.; Ramsay, C. G.; Steel, P. J. *Aust. J. Chem.* **1985**, *38*, 401−409. (b) Uzoukwu, A. B.; Al-Juaid, S. S.; Hitchcock, P. B.; Smith, J. D. *Polyhedron* **1993**, *12*, 2719−2724. (c) Akama, Y.; Shiro, M.; Ueda, T.; Kajitani, M. *Acta Crystallogr.* **1995**, *C51*, 1310−1314. (d) Guard, J. A. M.; Steel, P. J. *Aust. J. Chem.* **1994**, *47*, 1453−1459. (e) Holzer, W.; Mereiter, K.; Plagens, B. *Heterocycles* **1999**, *50*, 799−818.

(18) Bowmaker, G. A.; Brown, C. L.; Hart, R. D.; Healy, P. C.; Rickard, C. E. F.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 881−890.

Table 2. R_3P Phosphine Ligand Conformation Descriptors: Torsion Angles (deg)[a]

compd/ligand	$n = 1$	$n = 2$	$n = 3$
1/1	62.7(10)	−3.8(10)	24.2(9)
1/2	24.6(9)	13.1(1)	66.8(9)
2/1	−43.6(1)	56.8(1)	67.3(1)
	−174.0(1)	−65.1(1)	−163.4(1)
2/2	−26.2(2)	56.2(1)	−59.1(1)
	−153.1(1)	−65.8(1)	173.5(1)
4/1	−0.4(1)	−25.1(10)	−66.5(11)
4/2	−14.6(10)	−23.3(11)	−69.1(15)
10	36.4(2)	42.9(1)	61.2(1)
11	20.1(1)	63.9(1)	23.9(1)

[a] Values are given for rings $n = 1-3$, for the angles Ag−P−C(*n*1)−C(2/6) (whichever acute; both values for compound **2** (R = cy)).

Table 3. Selected Geometries: Mononuclear $AgQ^R:PR_3$ (1:2)

Q^R/PR_3 (compd)	Q^1/PPh_3 (**1**)	Q^1/PCy_3 (**2**)	Q^2/PPh_3 (**4**)
	Distances (Å)		
Ag−P(1)	2.475(3)	2.4342(6)	2.457(3)
Ag−P(2)	2.465(3)	2.3992(5)	2.462(3)
Ag−O(41)	2.498(6)	2.473(1)	2.42(1)
Ag−O(5)	2.349(7)	2.391(1)	2.354(8)
	Angles (degrees)		
P(1)−Ag−P(2)	120.9(1)	142.12(1)	121.4(1)
P(1)−Ag−O(41)	114.3(2)	103.63(3)	110.8(3)
P(1)−Ag−O(5)	114.0(2)	88.13(4)	114.9(3)
P(2)−Ag−O(41)	92.1(2)	107.12(3)	91.5(2)
P(2)−Ag−O(5)	124.3(2)	120.34(4)	123.4(2)
O(41)−Ag−O(5)	73.0(2)	75.91(5)	73.6(4)

Crystal Structure of 10. The other phosphine ligand complex of 1:1 R_3P:AgQ stoichiometry, devoid of other (potential) coligands, is complex **10** (Figure 5). Despite this, the coordination number of the silver is 4, achieved by virtue of the complex being a centrosymmetric dimer, by way of the Q^1 ligands bridging pairs of silver atoms through an *O,O′*-chelate array at one end and the unsubstituted pz ring nitrogen at the other:

$$\left[(o\text{-tol}_3\text{P})\text{Ag}\left\{\begin{matrix} O,O'\text{-Q}^1\text{-}N \\ N\text{-Q}^1\text{-}O,O' \end{matrix}\right\}\text{Ag}(\text{P}o\text{-tol}_3)\right]$$

Ag−P,O(41′,5′),N(2) being 2.3715(5), 2.325(1), 2.368(1), and 2.450(1) Å, with P−Ag−O(41′,5′),N(2) all enlarged well above the tetrahedral norm, 127.85(3)°, 128.98(3)°, and 121.75(3)°, N(2)−Ag−O(41′,5′) being 98.87(4) and 88.17(4) Å, and the O(41′)−Ag−O(5′) "bite" angle being 78.58(4)°, accommodating any crowding as a consequence of the large phosphine ligand "cone angle". Previously the acylpyrazolonate ligands have been found to show a similar η^3-coordinating behavior only with lead.[11] The non-hydrogen skeleton of the ligand here is *quasi*-planar, except for the pendant ring 41, the two centrosymmetrically related bridging planes obligate parallel; the two silver atoms deviate considerably from the bridging OC_3N_2CO planes by 1.149(2) and 2.102(1) Å (coordinated by O,O and N, respectively). The molecules pack in layers normal to *c*.

Crystal Structure of 11. The ionic compound **11**, of the form $[Ag(Hmimt)_2(Ph_3P)]^+(Q^1)^-$, is of interest from a number of aspects. It is the only complex of the present array in which the silver atom lies in a mononuclear tricoordinate environment (Figure 6), here AgS_2P, with three unidentate ligands, seemingly, further, the only structurally defined complex of this type at all, Ag−P = 2.4387(4) Å, Ag−S = 2.4866(5), 2.5003(4) Å, the latter two comparable with Ag−S distances in $[Ag(hfac)(SEt_2)]$ (2.47(9) Å)[4g] and in $[Ag(hfac)(C_4H_8OS)_2]$ (2.468(2) and 2.473(2) Å),[4e] with P−Ag−S = 118.25(1)°, 122.50(1)° and S−Ag−S = 116.13(1)°, sum $356._9$°, quasi-planar. This is despite the availability of other ligands, most notably the anion, with which it cocrystallizes, and, presumably, it is of inferior donor capacity compared to the phosphorus and sulfur donors, capable of filling a fourth coordination site, either as unidentate or chelate. For the AgS_2P array, χ^2(plane) is 4.3×10^4, with deviations δAg,P,S,S = 0.190(1), −0.066(1), −0.061(1), and −0.063(1) Å, a slight but significant pyramidal distortion; Ag−S−C are 109.46(5)° and 105.66(4)°, the Hmimt C_3N_2S ligand planes having dihedral angles of 42.97(4)° and 81.28(5)° to the coordination plane. Trisubstituted phosphine conformational descriptors, given for all complexes in Table 2, show the present PPh_3 ligand to have the common quasi-3 symmetry in this compound. Although not coordinated, the anion nevertheless interacts strongly with the cation, the totality perhaps best viewed as a neutral ion pair, the deprotonated oxygen pendant from the ring hydrogen-bonded strongly to both imidazole ring N hydrogens, presumably influencing the overall cation conformation, O(5)⋯H,N(23);H,N(33) = 1.84(3), 2.696(2); 1.83(2), 2.658(2) Å (Figure 6). The non-hydrogen system of the anion is rather more distorted from planarity than in the acid ligand Q^3H, with, interestingly, the carbonyl group now disposed quasi-*trans* to the pendant ring oxygen, as is also the case in **15** (see below).

Crystal Structure of 15. Yet another coordination mode for anionic Q-type ligands is found in the 1:1 adduct formed with "trimen", derivative **15** (Figure 7), the complex again containing four-coordinate silver(I), with two coordination sites occupied by the *N,N′*-bidentate trimen. The other two coordination sites are filled by a pair of Q^1 donor atoms, this time from successive ligands which bridge successive silver atoms into a one-dimensional polymer, the donor atoms being the unsubstituted pyrazole nitrogen and the (deprotonated) O(5), any potential chelation in concert with O(41) being obviated by the disposition of the latter in a *trans* orientation, as in **10**, the ligand approximately planar. The two Ag−N(diamine) distances differ quite markedly, Ag−N(1′) (carrying Me_2) = 2.421(3) Å and Ag−N(2′) (monomethylated) = 2.258(3) Å. Ag−N(2) (Q^1) is 2.155(2) Å and Ag−O(5) 2.969(2) Å; i.e., the coordination of the Q^1 ligand here is dominated by Ag−N rather than Ag−O interactions. Indeed, the sum of the N−Ag−N angles (N(2)−Ag−N(1′,2′) = 134.3(1)°, 146.6(1)°; N(1′)−Ag−N(2′) (the diamine "bite" angle) = 78.2(1)°) is $359._1$°, although the Ag−N(2) distance is similarly short or linearly opposed and the array should presumably be best considered as a trigonal planar AgN_3 (≡$(N_2)AgN$) array. O(5)−Ag−N(2,1′,2′) are 112.44(8)°, 87.19(9)°, and 69.85(9)°, as appropriate to an approach of the oxygen of the next Q^1 ligand quasi-normal to the AgN_3 plane.

Table 4. Crystal/Refinement Data

	HQ^3	**1**	**2**	**4**	**10**	**11**	**15**
	HQ^3	$[Ag(Q^1)(P h_3P)_2]\cdot{}^1/_2H2O$	$[Ag(Q^1)(C y_3P)_2]\cdot Me_2CO$	$[Ag(Q^2)(P h_3P)_2]$	$[Ag(Q^1)(o\text{-t ol}_3P)]_2$	$[\{Ag(Ph_3 P)\text{-}(Hmimt)_2\}Q^1]$	$[Ag(Q^1)(tr imen)](\vert)$
empirical formula	$C_{12}H_{12}N_2 O_2$	$C_{53}H_{44}Ag N_2O_{2.5}P_2$	$C_{56}H_{85}Ag N_2O_3P_2$	$C_{48}H_{38}Ag F_3N_2O_2P_2$	$C_{76}H_{68}Ag_2 N_4O_4P_2$	$C_{43}H_{40}Ag N_6O_2PS_2$	$C_{22}H_{27}Ag N_4O_2$
M_r	216.2	918.8	1004.1	901.7	1379.1	875.8	487.4
T (K)	ca. 295	ca. 295	ca. 153	ca. 298	ca. 153	ca. 153	ca. 153
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (Å)	17.981(6)	16.193(8)	10.4655(9)	10.672(2)	11.8221(6)	11.553(1)	7.982(1)
b (Å)	5.0641(4)	13.859(7)	12.079(1)	10.710(2)	13.2601(6)	11.943(1)	12.299(2)
c (Å)	24.271(6)	39.306(7)	22.804(2)	18.713(3)	20.5141(10)	15.479(2)	21.507(3)
α (deg)			104.872(2)	87.573(2)		74.829(2)	
β (deg)	99.67(2)	100.02(3)	95.180(2)	80.972(2)	91.758(1)	76.094(2)	95.119(3)
δ (deg)			104.144(2)	81.734(2)		78.185(2)	
V (Å^3)	2179	8686	2665	2090	3214	1978	2103
Z	8	8	2	2	2 dimers	2	4
D_c (g cm^{-3})	1.318	1.405	1.251	1.432	1.425	1.470	1.539
μ (cm^{-1})	0.9	5.8	4.8	6.1	7.1	7.0	9.8
specimen (mm)	0.90 × 0.60 × 0.40	0.25 × 0.38 × 0.12	0.35 × 0.25 × 0.20	0.22 × 0.05 × 0.04	0.3 × 0.12 × 0.12	0.4 × 0.35 × 0.30	0.15 × 0.13 × 0.11
'T' min, max	n/a	0.87, 0.95	0.72, 0.80	0.45, 0.60	0.75, 0.86	0.73, 0.85	0.72, 0.86
2θ max (deg)	50	50	75	50	75	75	75
N_{total}	5894	13300	52246	17927	65629	37475	43851
N (R_{int})	1900 (0.026)	7357 (0.12)	26492 (0.027)	7481 (0.041)	16774 (0.040)	19223 (0.022)	11051 (0.10)
N_o	1610	2895	20455	2950	11517	15850	4722
R^a	0.042	0.054	0.041	0.068	0.035	0.031	0.047
$R_w{}^b$	0.057	0.062	0.046	0.063	0.038	0.039	0.044
$\vert\Delta\rho$ max (e Å^{-3})$\vert$	0.16(1)	0.59(2)	1.45(7)	0.85(3)	1.43(9)	1.14(4)	1.7(1)
$(x, y, z, U_{iso})_H$	refined	constrained	refined^c	constrained	refined	refined	constrained

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

Considering those ligand geometries offering adequate precision in overview (Table 1), the most pronounced differences are to be found in association with the protonated parent, Q^3H, compared to the remainder, such differences as are found appearing more attributable to the presence of the hydrogen rather than the substitution of the phenyl (as found in the remainder) by the methyl. Compared with the simple and more complex (*cis*) chelate systems of **2** and **10**, the O$\cdots$O distance is diminished, presumably because of the hydrogen bond and the small effective size of the hydrogen compared to silver. Other distances are remarkably similar except about O(5), consistent with incorporation of the bond to the latter into the conjugated system as a consequence of deprotonation. The most substantial angular changes are found in the vicinity also, within the "chelate" ring, as a consequence of change in the "chelated" entity. Passage from the simple chelate mode found in **2** to the chelate/bridging mode of **10** introduces no further nontrivial change into the bonding parameters of the ligand.

Even more profound changes are found in the angular geometries in the vicinity of C(4) on passing to the anionic ligand type, in which the oxygen atoms lie *trans*, these being relatively little further affected by passing to the bridging mode of **15**, except with respect to the C(5)−O(5) distance, where further contraction occurs.

Several crystal structures of silver derivatives have been previously reported containing bridging β-diketonates, as in diene−silver $[Ag_2(hfac)_2(cod)_2]$,[4a] $[Ag_2(hfac)_2(dmcod)_2]$,[4h] $[\{Ag(hfac)\}_2(nbd)]_2$,[4e] $[Ag(hfac)]_4(SEt_2)$,[4f] and $[Ag(hfac)]_2$-(7-Bu^{t}O-nbd),[4i] in alkyne−silver $[\{Ag(hfac)\}_2(Pr^nC{\equiv}CPr^n)]_2$,[4g] in polyether−silver $[Ag_2(hfac)_2(diglyme)_2]$ and $[Ag_2(hfac)(O_2CCF_3)(diglyme)_2]$,[4k] in polythioether−silver $[Ag_2(hfac)_2([9]aneS_3)_2]$ and $[Ag_2(hfac)_2([14]aneS_3)_2]$,[4l] and in diphosphine−silver $[Ag_2(hfac)_2(dmpm)_2]$.[4d] However, derivative **15** is the first structurally characterized with an acylpyrazolonate acting as bridging O,N-donor.

Conclusion

We have synthesized and characterized 16 novel silver(I) derivatives of acylpyrazolonates. Some derivatives are ionic, and some are neutral mononuclear, dinuclear, or polynuclear in the solid state, depending on the nature and quantity of the ancillary donor employed.

Derivatives $[Ag(Q)(R_3P)_2]$, containing two phosphines bonded to silver, are mononuclear with a distorted tetrahedral geometry, with distortions essentially dependent on the cone angle of R_3P. Derivatives containing only one phosphine, $[Ag(Q)(R_3P)]_2$, are dinuclear species, with a bridging Q ligand acting as O_2N-tridentate donor, in contrast with species such as $[Ag(hfac)(Me_3P)]$ that have been found to be mononuclear.[4c] The $[Ag(Q)(R_3P)_2]$ complexes containing two sterically hindered R_3P groups undergo partial dissociation, and the $[Ag(Q)(R_3P)]_2$ complexes dissociate in solution into the $Ag(Q)(R_3P)$ fragments. The acylpyrazolonates can be displaced from the inner silver coordination sphere in $[Ag(Q)(R_3P)_2]$ compounds by excess dppe or Hmimt, affording 1:1 ionic species with $[AgP_4]$ and $[AgS_2P]$ cores, respectively. The insoluble [Ag(Q)(dppe)] species is likely polymeric, as also derivatives of formula [Ag(Q)(trimen)], where the N_2-donor behaves as chelating, with the acylpyrazolonate donor bridging two Ag atoms, through one oxygen and one nitrogen atom. In conclusion the N_2-donor trimen can be used to build up linear silver(I) coordination polymers, with acylpyrazolonates as blocking anions, able to restrict polymer dimensionality.

The air and moisture stability of silver acylpyrazolonato derivatives here reported, in contrast to analogue silver fluorinated acetylacetonates, may be realized by the unique property of the ligands Q, where the fused peripheral pyrazolyl backbone plays an important role, not only in the bonding formation through the N2 atom, but likely also in protecting the metal environment, whereas, on the basis of the results reported, substitution in the acyl fragment of Ph with Me or CF_3 does not seem to deeply influence the stability of silver compounds.

Acknowledgment. Thanks are due to the University of Camerino (Italy) and Carima Foundation for financial support.

Supporting Information Available: Complete analytical and spectroscopic data for derivatives **5**, **6**, **7**, and **13**, X-ray crystallographic files, in CIF format, for the structure determinations of Q^3H, **1**, **2**, **4**, **10**, **11**, and **15**, and a drawing for the crystal structure of Q^3H. This material is available free of charge via the Internet at the http://pubs.acs.org.

IC0109391