environment. The semicoordination affects somewhat the energies of d orbitals, displacing, in particular, the d_{z^2} orbital to higher energies. As the ability of the counterion to coordinate becomes stronger, that is, as the size becomes smaller, d_{z^2} and $d_{x^2-y^2}$ orbitals approach each other in energy. Hence, an increase of a z^2-type contribution in the magnetic orbital, which could promote an increase in antiferromagnetic exchange interaction, would be expected. From the above argument, the stronger $|J|$ value exhibited by the ClO_4 complex (II) compared to the PF_6 one (III) could be in agreement with the smaller size of the former counterion, if a negative sign of J (antiferromagnetic coupling) is assumed.

Finally, the different temperature dependence of $|J|$ observed in Figure 7 could be suggestive of different signs of the values of J. In fact, preliminary EPR results on similar systems containing the BF_4^- counterion agree with a minimum in the plot of $|J|$ vs T.[39] This observation may be indicative of a reversal in the sign of J.[40] Further investigations on these and similar systems are still required in order to conclude about the sign of the exchange and are in progress.

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Registry No. I, 111435-04-2; II, 111554-23-5; III, 111435-03-1; IV, 111433-86-4.

Supplementary Material Available: Tables SI–SVI, listing atomic coordinates, thermal parameters, hydrogen positions, bond distances and angles, and mean least-squares planes for I and III, and Table SIX, listing experimental and calculated magnetic susceptibility data for IV (15 pages); Tables SVII and SVIII, listing calculated and observed structure factors for I and III (33 pages). Ordering information is given on any current masthead page.

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(39) Folgado, J. V. Ph.D. Thesis, University of Valencia, Valencia, Spain, 1987.

(40) Reibenspies, J. H.; Anderson, O. P.; Eaton, S. S.; More, K. M.; Eaton, G. R. *Inorg. Chem.* **1987**, *26*, 132.

Contribution from the Department of Chemistry and Laboratory for Molecular
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Syntheses and X-ray Structures of Group 11 Pyrazole and Pyrazolate Complexes. X-ray Crystal Structures of Bis(3,5-diphenylpyrazole)copper(II) Dibromide, Tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)trisilver(I)-2-Tetrahydrofuran, Tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)trigold(I), and Hexakis(μ-3,5-diphenylpyrazolato-*N*,*N'*)hexagold(I)

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The reaction of anhydrous $CuBr_2$ with 3,5-diphenylpyrazole in a 1:2 ratio in THF yields bis(3,5-diphenylpyrazole)dibromocopper(II). The reaction of $AgNO_3$ in THF with sodium 3,5-diphenylpyrazolate gives tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)trisilver(I). The reaction of $Au(S(CH_2)_4)Cl$ with 1 molar equiv of sodium 3,5-diphenylpyrazolate in THF yields tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)trigold(I). Hexakis(μ-3,5-diphenylpyrazolato-*N*,*N'*)hexagold(I) was obtained from a reaction of $Au(PPh_3)Cl$, AgO_2CPh, and sodium 3,5-diphenylpyrazolate in THF. The monomer, both trimers, and the hexamer have been characterized by X-ray crystallography. The copper monomer, bis(3,5-diphenylpyrazole)dibromocopper(II), crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with cell dimensions of a = 14.644 (3) Å, b = 11.679 (2) Å, c = 16.640 (3) Å, β = 108.82 (2)°, V = 2693.6 (8) Å^3, and Z = 4. The four-coordinate Cu(II) center has a geometry best described as being between tetrahedral and square planar. The silver trimer, $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3\cdot 2THF$,[§] crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with cell dimensions of a = 14.066 (6) Å, b = 14.987 (3) Å, c = 23.306 (6) Å, β = 106.88 (3)°, V = 4701 (3) Å^3, and Z = 4. The three silver centers are bridged by three 3,5-diphenylpyrazolate units. The Ag···Ag distances are significantly different (3.305 (2), 3.362 (2), and 3.486 (2) Å). The nine-membered Ag_3N_6 ring is not planar. The gold trimer, $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$, crystallizes in the trigonal space group $R\bar{3}c$ (No. 167) with cell dimensions (on hexagonal axes) of a = 16.091 (3) Å, c = 25.726 (4) Å, V = 5770 (2) Å^3, and Z = 6. The gold centers form an equilateral triangle with nonbonding Au···Au distances of 3.368 (1) Å, bridged by pyrazolate ligands, giving a rigorously planar nine-membered inorganic ring with Au–N–N as the repeat unit. The hexamer, $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$, crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with cell dimensions of a = 16.048 (3) Å, b = 17.850 (3) Å, c = 29.663 (5) Å, β = 92.47 (1)°, V = 8489 (2) Å^3, and Z = 4. This complex contains an 18-membered inorganic ring in the shape of a two-bladed propeller. The geometry of the six gold centers is best described as an edge-sharing bitetrahedron. The intramolecular Au···Au distances range from 3.085 (2) to 6.010 (1) Å.

The chemistry of pyrazole and pyrazolate metal complexes is quite extensive.[1] Monomeric pyrazole and pyrazolate coordination complexes are well-known;[2] dimeric species often contain two bridging pyrazolate ligands and have shown a plethora[3] of fascinating reactions. The pyrazolate ligand is known to form an A-frame-like bridge with rhodium dppm, dam, and dapm dimers.[4] Polymeric metal complexes containing a single pyrazolate bridge

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[†] Synthesis.

[‡] Crystallography.

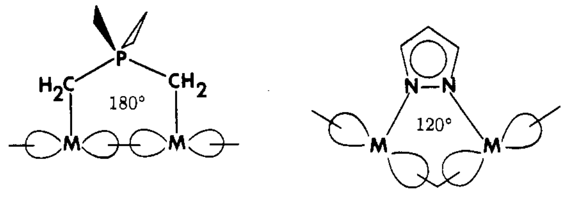
[§] Abbreviations used: pz = pyrazolate anion; 3,5-Ph_2pz = 3,5-diphenylpyrazolate anion; 3,5-Me_2pz = 3,5-dimethylpyrazolate anion; 3,5-Ph_2pzH = 3,5-diphenylpyrazole; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dam = bis(diphenylarsino)methane; dapm = (diphenylarsino)(diphenylphosphino)methane; THF = tetrahydrofuran; THT = tetrahydrothiophene; pz(11) identifies a μ-3,5-diphenylpyrazolate ring (metal coordinated) by using the crystallographic numbering scheme of the carbon in the 4-position of that ring.

(1) (a) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115–210.

(2) (a) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peadin, J. *Inorg. Chem.* **1979**, *18*, 3369. (b) Coletta, F.; Eltore, R.; Gambaro, A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 314. (c) Rettig, S. J.; Singbeil, D. L.; Storr, A.; Trotter, J. *Can. J. Chem.* **1978**, *56*, 2099.

(3) (a) Atwood, J. L.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1984**, *23*, 4050. (b) Bushnell, G. W.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 282. (c) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* **1983**, *2*, 1447. (d) Powell, J.; Kuksis, A.; Nyburg, S. C.; Ng, W. W. *Inorg. Chim. Acta* **1982**, *64*, L211. (e) Usón, R.; Oro, L. A.; Ciriano, M. A.; Carmona, D.; Tiripicchio, A.; Camellini, M. T. *J. Organomet. Chem.* **1982**, *224*, 69.

Chart I



Ylide Bridge

Pyrazolate Bridge

ligand have also been reported.[5] The synthesis of polymeric $[Ag(pz)]_n$ compounds has been reported[6] as well as the use of a $[Ag(pz)]_n$ electrode[7] for the determination of stability constants of other metal pyrazolates. The synthesis of an "at least trimeric" complex of the type $[Ag(pz)]_n$ has also been reported.[8]

If one imposes the constraint of a two-coordinate linear geometry on the coordinated metal center, then unusual pyrazolate products are obtained. Such is the case for gold(I) pyrazolate complexes. Despite the fact that some of these complexes were first synthesized over 10 years ago[9] little structural information is available.[10] A $[SO_4Cu(\mu\text{-pz})_2Pt(dppe)]$ complex has been reported;[11] however, its structure has not been crystallographically determined, nor has its chemistry been thoroughly examined. Similarly, dinuclear complexes, $X_2M(\mu\text{-pz})_2PtL_2$ (M = Zn, Cd, Hg; X = halide), as well as trinuclear ones, $M'[(\mu\text{-pz})_2PtL_2]_2$ (M' = Zn, Ni), have been reported but not thoroughly investigated.[12] It is expected that heterometallic complexes containing bridging pyrazolate ligands will structurally resemble the $[LXIr(\mu\text{-pz})]_2$ complex, for which activation of small molecules has been observed at the Ir_2-bridging site.[3] Compound **1**, $Cu(3,5\text{-}Ph_2pzH)_2Br_2$, can be thought of as a starting material for the stepwise synthesis of di- and trinuclear heterometallic complexes.[13] These considerations and our interest[14] in heterovalent group 11 complexes have led us to undertake a more complete study of the structural nature of group 11 pyrazolate complexes.

Our group has a longstanding interest in "nonclassical"[15] Au^{II} and heterovalent[14] dimeric gold systems. Four-coordinate Au^{II} complexes containing a gold–gold bond may be formed by oxidation of bimetallic Au^I systems. The Au^I precursors to many such systems have intramolecular Au···Au distances of ~3.00 Å. The orientation of the linear two-coordinate Au^I centers is roughly parallel. They can be described as axially constrained metal centers. This allows for good orbital overlap in the Au^{II} product due to the distance (flexible ylide bridge) and relative geometry of the σ bonds of the Au^{II} centers. Heterovalent Au^I/Au^{III} binuclear complexes also have been characterized.[16] Gold(III), the common[17] higher oxidation state, generally is four-coordinate square planar, with five-coordinate square-pyramidal structures also known.[18]

Many of the properties that govern the formation of hetero- versus homovalent products in multinuclear complexes are yet unresolved. In exploring this fundamental question we have turned our attention to the gold pyrazolate trimer system as it contains *two* attributes not found in the now well-explored[19] gold ylide dimer system. The metal centers of these trimeric complexes are kept apart at distances that are significantly longer[10] than in dimers and are bridged by the more rigid pyrazolate ligands. Perhaps more important is the relative geometry of the metal orbitals directed toward other metal atoms in the pyrazolate trimers. The Au–Au bonding directions on different metal centers are approximately 60° away from the N–Au–N axis. Orbitals perpendicular to the N–Au–N axes form a 120° angle with respect to each other in contrast to the collinear d–d orbitals, which produce Au–Au bond formation in many dinuclear systems (Chart I). Consistent with this is the report[20] of the oxidation of the similar $[Au(\mu\text{-}3,5\text{-}Me_2pz)]_3$ at only one Au^I center by 1 equiv of I_2. The Mössbauer spectrum[21] of the oxidized product shows the presence of Au^I and Au^{III} in 2:1 ratio, in agreement with the proposed mixed-valence formulation. Finally, the gold–gold interactions in the phosphorus ylide dimer are restricted to only direct interactions between the two metal centers since the ylide bridge is saturated. With the conjugated pyrazolate bridge π interactions can easily contribute to transfer of charge.[22]

During exploratory studies of the chemistry of group 11 metal pyrazolates as materials for the synthesis and study of potentially heterovalent polynuclear complexes, the gold pyrazolate trimer $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ has been synthesized. Only one other gold pyrazolate trimer[10] and no silver pyrazolate trimers have been structurally characterized. In this paper we report the complete X-ray crystallographic characterization of a gold pyrazolate trimer, the first gold pyrazolate hexamer, a silver pyrazolate trimer, and a copper pyrazole monomer.

Experimental Section

Materials. All solvents were distilled and dried by standard methods[23] and were stored over molecular sieves. All reactions were carried out under an atmosphere of argon (water and oxygen free) by standard Schlenk techniques. The synthesis of (tetrahydrothiophene)gold(I) chloride (Au(THT)Cl) is given elsewhere.[24] The 3,5-diphenylpyrazole ($3,5\text{-}Ph_2pzH$) was purchased from Fluka and deprotonated with NaH in THF. Carbon and hydrogen analyses were done by Galbraith Laboratories, Knoxville, TN.

$Cu(3,5\text{-}Ph_2pzH)_2Br_2$ (1). To 250 mg (1.12 mmol) of anhydrous $CuBr_2$ (MCB Inc.) in 20 mL of dry THF was added 500 mg (2.26 mmol) of ($3,5\text{-}Ph_2pzH$). The dark purple solution was stirred for 2 h, and THF was removed in vacuo, leaving a sticky dark solid behind. The residue was triturated with diethyl ether (2 × 20 mL), leaving 592 mg, 80% yield, of a free-flowing dark purple powder. Dark purple crystals suitable for X-ray diffraction were obtained via slow evaporation of a CH_2Cl_2 solution of the product, mp 153–155 °C. Anal. Calcd for $C_{30}H_{22}Br_2CuN_4$: C,

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[4] (a) Janke, C. J.; Tortorelli, L. J.; Burn, J. L. E.; Tucker, C. A.; Woods, C. *Inorg. Chem.* **1986**, *25*, 4597. (b) Oro, L. A.; Carmona, D.; Perez, P. L.; Esteban, M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1985**, 973.

[5] (a) Buchner, E. *Chem. Ber.* **1889**, *22*, 2165. (b) Reimlinger, H.; Noels, A.; Jabot, J.; V-Overstraeten, A. *Chem. Ber.* **1970**, *103*, 1942.

[6] Vos, J. G.; Groeneveld, W. L. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 137.

[7] Blais, M. J.; Berthon, G. *Can. J. Chem.* **1977**, *55*, 199.

[8] Okkersen, H.; Groeneveld, W. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 945.

[9] Bonati, F.; Minghetti, G.; Banditelli, G. *J. Chem. Soc., Chem. Commun.* **1974**, 88.

[10] (a) Bovio, B.; Bonati, F.; Banditelli, G. *Inorg. Chim. Acta* **1984**, *87*, 25. (b) The hexameric gold pyrazolate complex has recently been characterized: Raptis, R. G.; Murray, H. H., III; Fackler, J. P., Jr. *J. Chem. Soc., Chem. Commun.* **1987**, 737.

[11] Cariati, F.; Micera, G.; Scozzafava, A.; Minghetti, G.; Banditelli, G. *Inorg. Chem.* **1982**, *21*, 3843.

[12] Minghetti, G.; Banditelli, G.; Bonati, F. *Chem. Ind.* (*London*) **1977**, 123.

[13] Murray, H. H.; Briggs, D. A.; Fackler, J. P., Jr.; Garzón, G.; Porter, L. C.; Raptis, R. G. *Organometallics* **1987**, *6*, 1992.

[14] (a) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801. (b) Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics*, **1985**, *4*, 1891.

[15] (a) Fackler, J. P., Jr.; Basil, J. D. *Organometallics*, **1982**, *1*, 871. (b) Fackler, J. P., Jr.; Basil, J. D. In *Inorganic Chemistry Towards the 21st Century*; Chisholm, M. H., Ed. Advances in Chemistry 201; American Chemical Society: Washington, DC, 1983.

[16] Raptis, R. G.; Fackler, J. P., Jr., unpublished results.

[17] (a) Puddephatt, R. J. In *The Chemistry of Gold*; Clark, R. J. H., Ed.; Monograph 16, Topics in Inorganic and General Chemistry; Elsevier: Amsterdam, 1978. (b) Schmidbaur, H. In *Gmelin Handbuch der Anorganischen Chemie*; Slawisch, A., Ed.; Springer-Verlag: Berlin, 1980; Organogold Compounds.

[18] Robinson, W. T.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 726.

[19] (a) Murray, H. H.; Fackler, J. P., Jr.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1278. (b) Murray, H. H.; Fackler, J. P., Jr.; Mazany, A. M.; Porter, L. C.; Shain, J.; Falvello, L. R. *Inorg.* Chim. *Acta* **1986**, *114*, 171. (c) Murray, H. H.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **1985**, *115*, 207.

[20] Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658.

[21] Katada, M.; Sato, K.; Uchida, Y.; Iijima, S.; Sano, H.; Wei, H. H.; Sakai, H.; Maeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 945.

[22] (a) Schenk, T. G.; Milne, C. R. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2338. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2522.

[23] Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

[24] Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* in press; personal communication.

Table I. Crystallographic Data for **1–4**

	complex **1**	complex **2**	complex **3**	complex **4**
formula	$C_{30}H_{24}Br_2CuN_4$	$C_{53}H_{49}Ag_3N_6O_2$	$C_{45}H_{33}Au_3N_6$	$C_{90}H_{66}Au_6N_{12}$
fw	663.90	1125.63	1248.42	2497.40
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$R\bar{3}c$ (No. 167)	$P2_1/n$ (No. 14)
syst absences	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$hh0l$, $l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2$
a, Å	14.644 (3)	14.066 (6)	16.091 (3)	16.048 (3)
b, Å	11.679 (2)	14.987 (3)		17.850 (3)
c, Å	16.640 (3)	23.306 (6)	25.726 (4)	29.663 (5)
α, deg				
β, deg	108.82 (2)	106.88 (3)		92.47 (1)
γ, deg				
V, Å^3	2693.6 (8)	4701 (3)	5770 (2)	8489 (2)
Z	4	4	6	4
d_{calcd}, g/cm^3	1.65	2.04	2.15	1.95
cryst size, mm	0.5 × 0.3 × 0.1	0.3 × 0.25 × 0.3	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.4
$F(000)$, e	1323.7	2175.7	3490.8	5091.7
μ(Mo Kα), cm^{-1}	37.8	12.42	114.3	155.2
radiation	monochromated in Mo Kα (λ = 0.71069 Å) incident beam			
orientation reflcns: no.; range (2θ), deg	18; $25 < 2\theta < 36$	20; $30 < 2\theta < 35$	23; $24 < 2\theta < 41$	25; $30 < 2\theta < 35$
temp, °C	22	22	22	22
scan method	ω	ω	ω	ω
data collcn range (2θ), deg	$0 < 2\theta < 45$	$0 < 2\theta < 45$	$0 < 2\theta < 45$	$0 < 2\theta < 45$
tot. no. of reflcns measd	4027	6927	979	12385
tot. no. of reflcns with $F_o^2 > 3\sigma(F_o^2)$	1951	3056	653	6052
check reflcns	3 every 97	3 every 97	3 every 97	3 every 97
no. of params refined	166	244	69	469
trans factors: max, min	0.974, 0.436	1.0, 0.97 (normalized)	0.408, 0.245	0.016, 0.005
R^a	0.057	0.060	0.036	0.078
$R_w{}^b$	0.058	0.060	0.035	0.083
goodness-of-fit indicator^c	1.524	5.849	1.200	1.677
largest shift/esd, final cycle	0.016	0.027	0.036	0.016
largest peak, e/Å^3	1.6	1.18	1.3	2.20
g	0.0007	d	0.0005	0.0026

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$. [d] Unit weight.

53.27; H, 3.64. Found: C, 53.81; H, 3.64.

[Ag(μ-3,5-Ph$_2$pz)]$_3$ (2). To 250 mg (1.03 mmol) of Na(3,5-Ph$_2$pz) in 15 mL of dry THF at 25 °C was added 175 mg (1.03 mmol) of $AgNO_3$. After 6 days of vigorous stirring (ambient light), a brown precipitate formed. A small amount of the THF was removed from the reaction flask and filtered. Crystals of **2** suitable for X-ray structural investigation were obtained by slowly allowing diethyl ether to diffuse into the THF solution; after 3 days at ambient temperature clear, water-white crystals formed. Subsequent crystallographic investigation revealed this product to be the silver trimer with two molecules of THF in the lattice per trimer molecule. The clear crystals turned opaque white (aparent loss of solvent) upon exposure to the atmosphere. Anal. Calcd for $C_{45}H_{33}Ag_3N_6$: C, 55.07; H, 3.39. Found: C, 54.81; H, 3.32.

[Au(μ-3,5-Ph$_2$pz)]$_3$ (3). To 151 mg (0.62 mmol) of Na(3,5-Ph$_2$pz) in 10 mL of dry THF at 25 °C was added 200 mg (0.62 mmol) of Au(THT)Cl; the mixture was stirred for 18 h and then reduced to about one-fourth of the original volume. A hexane wash (2 × 20 mL) was used to completely precipitate the trimer and remove the THF and THT. Water-white single crystals, mp 333–335 °C, suitable for X-ray diffraction study were obtained via vapor diffusion of diethyl ether into a CH_2Cl_2 solution of the trimer in a closed system. Complex **3** is soluble in CH_2Cl_2, THF, $CDCl_3$, and CH_3CN.

[Au(μ-3,5-Ph$_2$pz)]$_6$ (4). ClAuPPh$_3$ (20 mg, 0.040 mmol) was dissolved in 20 mL of THF. To this solution were added AgO$_2$CPh (6 mg, 0.026 mmol) and Na(3,5-Ph$_2$pz) (14.7 mg, 0.061 mmol). The turbid solution was stirred at ambient temperature for 18 h. The reaction was filtered, and the solvent was removed in vacuo. The resulting white solid was dissolved in ~10 mL of methylene chloride. Diethyl ether vapor was allowed to slowly diffuse into the methylene chloride solution. Colorless crystals, mp 310–314 °C (color change at ~270 °C), were obtained by this procedure.

Crystallographic Procedures

The single-crystal X-ray analyses of Cu(3,5-Ph$_2$pzH)$_2$Br$_2$, [Ag(μ-3,5-Ph$_2$pz)]$_3$, [Au(μ-3,5-Ph$_2$pz)]$_3$, and [Au(μ-3,5-Ph$_2$pz)]$_6$ (**1–4**) were performed by procedures (Nicolet R3m/E diffractometer, SHELXTL software) that have been described in detail elsewhere.[14,19]

The initial unit cell dimensions were determined by using orientation reflections obtained from photographic data. Accurate unit cell dimensions were calculated from the setting angles of 20–25 high-angle reflections. The Laue group of **3** was identified by axial photographs. Intensity data for this complex were collected in $+h,+k,+l$ with $-h + k + l = 3n$ index restriction. Intensity data for **1** were collected in the $-h,+k,\pm l$ quadrant. Data for **2** and **4** were collected in the $+h,+k,\pm l$ quadrant. No symmetry-equivalent reflections were collected.

Data collection and structure solution information are summarized in Table I. The intensity data for complexes **1–4** were corrected for standard decay, Lorentz, and polarization effects. The intensity data for **1**, **3**, and **4** were corrected for absorption effects by using an empirical estimation based on azimuthal scans of medium-intensity refelctions. Due to the extent of decomposition and low μ value for **2**, no empirical absorption was applied to the data. Initial positional parameters for the Cu atom of **1** were obtained from a sharpened Patterson map. Initial positional parameters for the metal centers of **2–4** were obtained from the SHELXTL direct-methods program. All other atomic coordinates, including hydrogen atoms in **3** (final refinement used calculated hydrogen atom positions), were obtained from cycles of Fourier synthesis, least-squares refinement, and difference Fourier maps.

In **1**, all non-hydrogen atoms were refined anisotropically, except for the carbon atoms of the phenyl rings, which were refined as rigid hexagons with C–C distances of 1.395 Å and C–C–C angles of 120°. Hydrogen atom positions were calculated. The final refinement of **1** contained a peak of 1.6 e Å^{-3} 1.64 Å from C(2). The least-squares refinement converged uneventfully, giving $R = 0.057$ and $R_w = 0.058$, using 1951 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ for 166 parameters.

For complex **2**, all atoms other than the carbons of the six phenyl rings and hydrogen atoms were refined anisotropically; the phenyl rings were refined as rigid groups with C–C–C angles of 120° and C–C distances of 1.395 Å. Two molecules of THF are in the asymmetric unit. As decay (ca. 40% as measured from standard reflections) in the intensity data was observed, the site occupancy factor of the THF molecule was initially refined then fixed at 0.75 for the remainder of the refinement, and the thermal parameters were refined. A weighting scheme employing unit weights was used. The refinement converged to $R = 0.060$ and $R_w = 0.060$ uneventfully with the largest peak of electron density (1.18 e Å^{-3}) near one of the THF molecules.

Nine of the ten non-hydrogen atoms of **3** were refined anisotropically; the hydrogen atoms of the phenyl ring used in the refinement are in idealized positions. Unit weights were used in the final refinement. A final difference Fourier map for **3** contained a peak with electron density of about 1.3 e Å^{-3} approximately 1.1 Å from the gold center and of no chemical significance. The final refinement converged giving $R = 0.036$

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Cu(3,5-Ph$_2$pzH)$_2$Br$_2$ (**1**)

	x	*y*	*z*	*U*, Å^2
Cu	2751 (1)	10 862 (1)	5487 (1)	35 (1)^a
Br(1)	3536 (1)	10 013 (1)	4601 (1)	63 (1)^a
Br(2)	1469 (1)	9 517 (1)	5201 (1)	57 (1)^a
N(1)	3297 (7)	12 403 (7)	5369 (5)	35 (4)^a
N(2)	4222 (7)	12 494 (8)	5402 (5)	36 (4)^a
N(3)	2643 (7)	11 259 (8)	6639 (6)	39 (4)^a
N(4)	1733 (7)	11 269 (8)	6700 (6)	40 (4)^a
C(1)	3024 (8)	13 430 (9)	5601 (7)	34 (5)^a
C(2)	3815 (9)	14 212 (11)	5789 (7)	40 (5)^a
C(3)	4565 (8)	13 558 (10)	5657 (7)	35 (5)^a
C(4)	3203 (8)	11 860 (10)	7318 (7)	35 (5)^a
C(5)	2667 (8)	12 267 (10)	7802 (7)	37 (5)^a
C(6)	1727 (9)	11 878 (9)	7401 (7)	34 (5)^a
C(11)	1845 (5)	14 333 (6)	6186 (4)	49 (3)
C(12)	908	14 449	6215	60 (4)
C(13)	153	13 843	5645	55 (4)
C(14)	335	13 121	5047	54 (4)
C(15)	1272	13 004	5018	47 (4)
C(16)	2027	13 610	5587	35 (3)
C(31)	5935 (5)	14 902 (6)	6218 (5)	48 (3)
C(32)	6901	15 193	6375	61 (4)
C(33)	7498	14 482	6091	57 (4)
C(34)	7129	13 480	5649	61 (4)
C(35)	6163	13 189	5492	51 (4)
C(36)	5566	13 900	5777	34 (3)
C(41)	4804 (5)	11 257 (5)	7203 (5)	46 (3)
C(42)	5776	11 483	7331	53 (4)
C(43)	6186	12 507	7713	58 (4)
C(44	5624	13 304	7966	59 (4)
C(45)	4651	13 078	7838	42 (3)
C(46)	4241	12 054	7456	32 (3)
C(61)	827 (4)	12 855 (7)	8234 (5)	50 (4)
C(62)	−37	13 173	8356	56 (4)
C(63)	−910	12 733	7828	56 (4)
C(64)	−919	11 975	7177	52 (4)
C(65)	−55	11 657	7055	55 (4)
C(66)	818	12 097	7584	41 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

and $R_w = 0.035$, using 653 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ for 69 parameters.

For complex **4**, all gold, nitrogen, and carbon atoms except those of the phenyl groups were refined anisotropically. The phenyl groups were treated as rigid groups with ideal geometries, and hydrogen atoms were placed in calculated positions (C–H = 0.96 Å). Refinement of 469 parameters using 6052 reflections with $|F_o|^2 > 3\sigma(|F_o|)$ and employing a weighting scheme with $g = 0.0026$ converged to $R = 0.078$ and $R_w = 0.083$, leaving the largest peak of electron density (2.20 e Å^{-3}) at 0.43 Å from Au(3).

Tables of observed and calculated structure factors with their esd's, listings of atomic positional and anisotropic thermal parameters, and complete lists of bond lengths and angles for all four complexes discussed have been deposited as supplementary material.

Structural Description

To the best of our knowledge there is only one report[10] of the crystal structure of a gold(I) pyrazolate complex, tris[μ-3,5-bis(trifluoromethyl)pyrazolato-*N,N'*]trigold(I). The authors stated that this structure was not determined accurately due to decomposition, resulting in the formation of small gold particles. This paucity of structural data regarding group 11 pyrazolate trimers and our interest in heterovalent complexes led us to characterize and determine the X-ray crystal structures of bis(3,5-diphenylpyrazole)copper(II) dibromide (**1**), tris(μ-3,5-diphenylpyrazolato-*N,N'*)trisilver(I) (**2**), tris(μ-3,5-diphenylpyrazolato-*N,N'*)trigold(I) (**3**), and hexakis(μ-3,5-diphenylpyrazolato-*N,N'*)hexagold(I) (**4**).

Positional and isotropic equivalent thermal parameters for the copper monomer, silver and gold trimers, and gold hexamer are given in Tables II–V, respectively. Tables VI–IX contain lists of significant interatomic distances and angles for **1**–**4**, respectively. Drawings of complexes **1**–**4**, with the crystallographic numbering scheme, are given in Figures 1–4, respectively. Figure 5a is a diagram of the Au$_6$ core of **4**, and Figure 5b is a view of the Au$_6$N$_{12}$ twisted 18-atom-ring backbone of the hexamer.

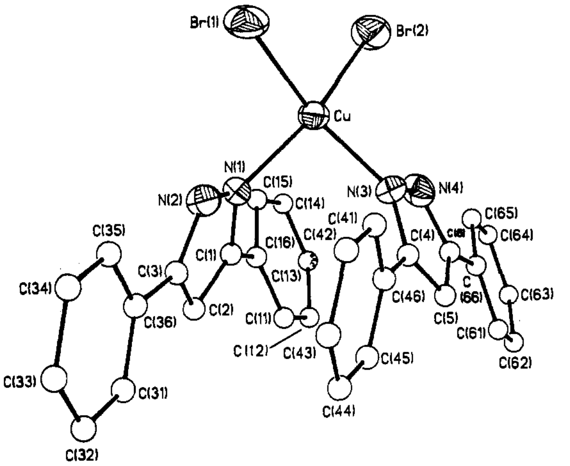

Figure 1. A drawing of Cu(3,5-Ph$_2$pzH)$_2$Br$_2$ (**1**) in perspective with the crystallographic numbering scheme. The carbon atoms have been given arbitrary radii for clarity. Thermal ellipsoids are drawn at the 50% probability level.

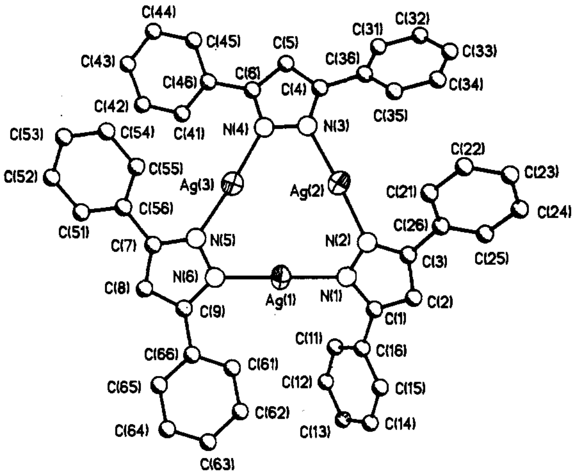

Figure 2. A drawing of [Ag(μ-3,5-Ph$_2$pz)]$_3$ (**2**). The carbon (shaded circles) and nitrogen atoms have been given arbitrary radii for clarity. Thermal ellipsoids are drawn at the 50% probability level. The two molecules of THF that cocrystallized with **2** are not shown.

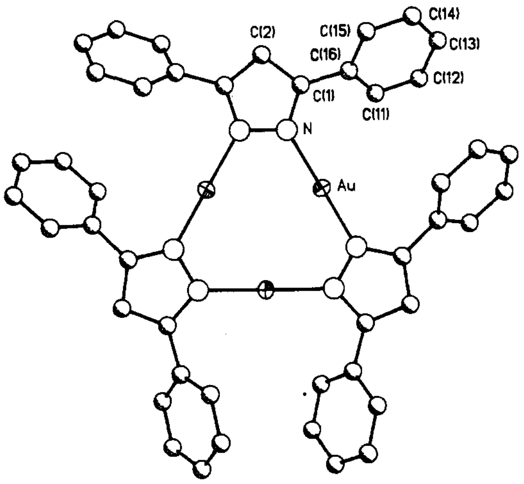

Figure 3. A drawing of [Au(μ-3,5-Ph$_2$pz)]$_3$ (**3**) in perspective with the crystallographic numbering scheme. The carbon (shaded circles) and nitrogen atoms have been given arbitrary radii for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Cu(3,5-Ph$_2$pzH)$_2$Br$_2$ (1). The asymmetric unit consists of the discrete monomeric copper molecule shown in Figure 1. None of the atoms lie on special positions even though this molecule

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3 \cdot 2THF$ (**2**)

	x	*y*	*z*	*U*, Å^2
Ag(1)	1768 (1)	10984 (1)	142 (1)	56 (1)^a
Ag(2)	3148 (1)	11266 (1)	−869 (1)	59 (1)^a
Ag(3)	3022 (1)	9303 (1)	−198 (1)	58 (1)^a
N(1)	1925 (9)	12228 (8)	−224 (6)	54 (6)^a
N(2)	2139 (10)	12224 (8)	−766 (7)	58 (6)^a
N(3)	4113 (10)	10247 (9)	−947 (6)	56 (6)^a
N(4)	4115 (10)	9468 (8)	−626 (5)	52 (6)^a
N(5)	1940 (9)	9033 (7)	223 (5)	48 (5)^a
N(6)	1505 (9)	9718 (8)	436 (5)	46 (5)^a
C(1)	1517 (12)	13029 (10)	−157 (8)	58 (7)^a
C(2)	1429 (13)	13533 (11)	−670 (9)	68 (8)^a
C(3)	1844 (12)	13015 (10)	−1037 (8)	55 (7)^a
C(4)	4905 (12)	10210 (10)	−1151 (7)	52 (7)^a
C(5)	5457 (12)	9424 (11)	−977 (7)	55 (7)^a
C(6)	4914 (12)	8980 (11)	−649 (7)	54 (7)^a
C(7)	1583 (14)	8257 (11)	391 (8)	68 (8)^a
C(8)	895 (13)	8438 (12)	690 (7)	58 (8)^a
C(9)	867 (11)	9370 (11)	725 (7)	52 (7)^a
C(11)	1809 (7)	12938 (7)	951 (6)	75 (5)
C(12)	1568	13185	1468	88 (6)
C(13)	761	13748	1427	87 (6)
C(14)	195	14064	868	91 (6)
C(15)	436	13817	351	78 (6)
C(16)	1243	13254	393	64 (5)
C(21)	1821 (10)	12564 (7)	−2080 (6)	84 (6)
C(22)	1810	12805	−2660	123 (9)
C(23)	1880	13702	−2803	99 (7)
C(24)	1961	14357	−2366	123 (9)
C(25)	1971	14116	−1786	109 (8)
C(26)	1902	13219	−1643	69 (5)
C(31)	6117 (7)	11106 (7)	−1515 (5)	71 (5)
C(32)	6338	11803	−1849	93 (7)
C(33)	5577	12343	−2196	94 (7)
C(34)	4595	12183	−2209	96 (7)
C(35)	4374	11483	−1875	69 (5)
C(36)	5135	10943	−1528	58 (5)
C(41)	4842 (8)	7887 (7)	161 (5)	65 (5)
C(42)	5056	7049	427	74 (6)
C(43)	5545	6413	180	84 (6)
C(44)	5819	6616	−333	99 (7)
C(45)	5604	7454	−599	71 (5)
C(46)	5115	8090	−353	52 (4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ (**3**)

	x	*y*	*z*	*U*, Å^2
Au	8792 (1)	0	2500	27 (1)^a
N	9506 (7)	1418 (7)	2504 (4)	27 (5)^a
C(1)	9203 (9)	2070 (10)	2505 (4)	29 (6)^a
C(2)	10000	3015 (11)	2500	29 (4)^a
C(11)	7569 (6)	1158 (6)	2901 (3)	44 (7)^a
C(12)	6621	955	2930	62 (10)^a
C(13)	6289	1395	2587	62 (10)^a
C(14)	6906	2039	2214	60 (9)^a
C(15)	7854	2242	2185	41 (7)^a
C(16)	8186	1801	2528	32 (6)^a

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

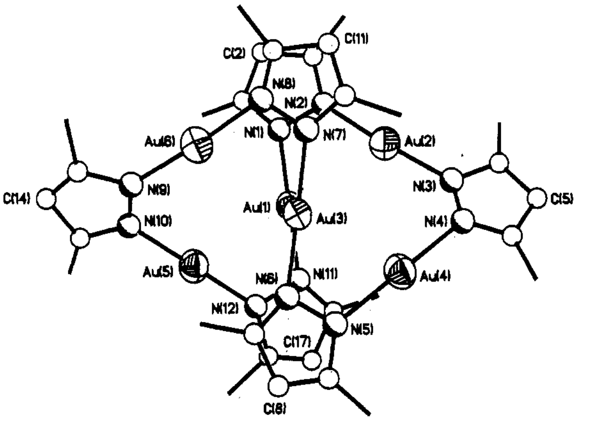

Figure 4. A drawing of $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ (**4**) in perspective with the crystallographic numbering scheme less the 12 phenyl rings. The carbon (shaded circles) and nitrogen atoms have been given arbitrary radii for clarity. Thermal ellipsoids are drawn at the 50% probability level.

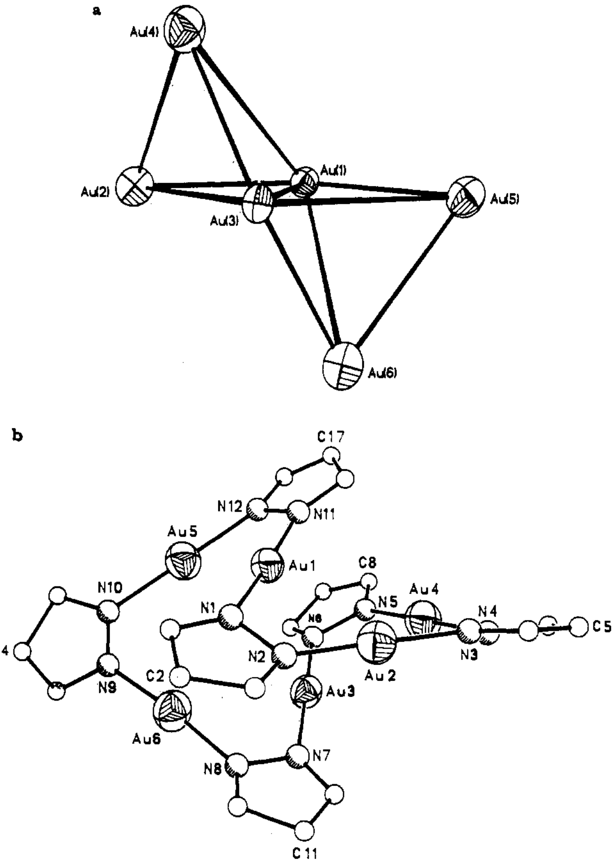

Figure 5. (a) Edge-sharing bitetrahedron formed by the six Au atoms of complex **4**. Lines between Au centers are not meant to represent bonding. (b) $Au_6(HC_3N_2)_6$ core (phenyl groups removed) of **4** with N(3)–N(4) and N(9)–N(10) depicting the 72.9° angle formed by Au(2)⋯Au(4) and Au(5)⋯Au(6) vectors. The thermal ellipsoids are drawn at the 50% probability level; N and C atoms have been given arbitrary radii.

(C_2 point symmetry) possesses a 2-fold symmetry axis passing through the Cu atom and bisecting the Br–Cu–Br and N–Cu–N angles. The Cu–N(1) and Cu–N(3) bonds are approximately equal in length, 2.005 (9) and 2.027 (10) Å, respectively. The difference between the two Cu–Br bond lengths, 2.360 (2), and 2.375 (2) Å, is statistically significant. As shown in Figure 1, the Cu center is neither square planar nor tetrahedral. An analysis of the six angles defined by two Cu-coordinated atoms (Br and N) and the copper center shows that the geometry of the copper center is intermediate between tetrahedral and square planar. Specifically, the trans Br(1)–N(3) and Br(2)–N(1) pairs abandon the square-planar geometry by moving in opposite directions toward a tetrahedral arrangement, thus relieving the steric crowding caused by the bulky cis pyrazoles. The trans angles Br(1)–Cu–N(3) and Br(2)–Cu–N(1) become 152.7 (3)°, and the planes that they define are mutually perpendicular (dihedral angle 89.1°). The angles between cis ligands range between 91.5 (3) and 96.3 (1). Geometric distortions of this type are commonly observed in four-coordinate Cu^{II} complexes with sterically demanding ligands.[25] The dihedral angle formed by the planar

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[25] (a) Holm, R. H.; O'Connor, M. S. *Prog. Inorg. Chem.* **1971**, *14*, 325. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry. A Comprehensive Text*, 3rd ed.; Wiley: New York, 1972; pp 912–913.

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ (**4**)

	x	*y*	*z*	*U*, $Å^2$
Au(1)	5730 (1)	7435 (1)	2180 (1)	54 (1)[a]
Au(2)	4242 (1)	6886 (1)	2742 (1)	77 (1)[a]
Au(3)	4232 (1)	8857 (1)	2155 (1)	55 (1)[a]
Au(4)	3293 (1)	7563 (1)	1667 (1)	75 (1)[a]
Au(5)	6545 (1)	8725 (1)	1642 (1)	74 (1)[a]
Au(6)	9168 (1)	4410 (1)	2289 (1)	78 (1)[a]
N(1)	5991 (18)	7470 (16)	2866 (9)	65 (10)[a]
N(2)	5254 (17)	7254 (17)	3093 (8)	63 (11)[a]
N(3)	3204 (17)	6460 (15)	2428 (9)	59 (10)[a]
N(4)	2762 (16)	6737 (14)	2089 (10)	57 (10)[a]
N(5)	3806 (20)	8406 (16)	1238 (9)	73 (12)[a]
N(6)	4291 (16)	8943 (14)	1474 (9)	57 (10)[a]
N(7)	4146 (15)	8833 (14)	2845 (8)	49 (9)[a]
N(8)	4859 (16)	9071 (14)	3088 (7)	46 (9)[a]
N(9)	6818 (16)	9807 (14)	2369 (8)	52 (9)[a]
N(10)	7135 (16)	9561 (14)	2010 (8)	51 (9)[a]
N(11)	5553 (16)	7324 (14)	1502 (9)	56 (10)[a]
N(12)	5963 (17)	7884 (13)	1267 (8)	53 (9)[a]
C(1)	6620 (17)	7705 (16)	3129 (10)	44 (10)[a]
C(2)	6342 (20)	7587 (21)	3569 (11)	63 (13)[a]
C(3)	5509 (19)	7256 (22)	3524 (12)	69 (14)[a]
C(4)	2732 (22)	5865 (17)	2579 (12)	64 (14)[a]
C(5)	2040 (18)	5796 (18)	2282 (10)	47 (11)[a]
C(6)	2110 (22)	6337 (18)	1969 (12)	62 (13)[a]
C(7)	3794 (18)	8510 (17)	796 (10)	49 (11)[a]
C(8)	4241 (17)	9106 (19)	749 (10)	47 (11)[a]
C(9)	4507 (16)	9380 (18)	1179 (10)	48 (11)[a]
C(10)	3603 (19)	8654 (21)	3114 (10)	59 (12)[a]
C(11)	3878 (22)	8723 (21)	3536 (12)	70 (14)[a]
C(12)	4735 (39)	8978 (21)	3493 (14)	120 (25)[a]
C(13)	7846 (20)	9935 (18)	1890 (12)	62 (13)[a]
C(14)	7915 (22)	10541 (23)	2241 (12)	72 (15)[a]
C(15)	7259 (24)	10471 (25)	2480 (15)	90 (18)[a]
C(16)	5180 (18)	6875 (18)	1204 (10)	49 (11)[a]
C(17)	5359 (21)	7149 (21)	758 (13)	66 (14)[a]
C(18)	5765 (23)	7750 (19)	812 (10)	58 (13)[a]
C*(11)	7728 (14)	7696 (11)	2612 (7)	68 (10)
C*(12)	8497	7979	2490	74 (11)
C*(13)	8871	8563	2737	123 (18)
C*(14)	8478	8864	3106	82 (11)
C*(15)	7709	8581	3228	85 (12)
C*(16)	7335	7997	2981	51 (8)
C*(21)	5338 (13)	7162 (15)	4352 (9)	99 (14)
C*(22)	4886	6963	4725	103 (15)
C*(23)	4094	6646	4663	82 (12)
C*(24)	3756	6529	4227	93 (13)
C*(25)	4208	6728	3855	64 (9)
C*(26)	5000	7044	3917	59 (9)
C*(31)	2462 (12)	5248 (15)	3295 (9)	106 (15)
C*(32)	2707	4804	3665	98 (14)
C*(33)	3531	4561	3719	74 (11)
C*(34)	4111	4761	3403	112 (16)
C*(35)	3866	5205	3033	79 (11)
C*(36)	3042	5448	2980	53 (8)
C*(41)	1324 (15)	7250 (11)	1461 (8)	73 (10)
C*(42)	791	7393	1087	102 (14)
C*(43)	422	6799	847	92 (13)
C*(44)	585	6062	982	85 (12)
C*(45)	1118	5920	1356	65 (9)
C*(46)	1487	6514	1596	58 (9)
C*(51)	2809 (17)	7441 (15)	596 (7)	92 (13)
C*(52)	2441	6967	271	120 (17)
C*(53)	2579	7083	−185	91 (13)
C*(54)	3084	7674	−316	138 (20)
C*(55)	3452	8148	9	111 (16)
C*(56)	3315	8031	465	54 (8)
C*(61)	5675 (15)	10194 (14)	986 (7)	85 (12)
C*(62)	6210	10797	1073	102 (14)
C*(63)	6117	11239	1455	78 (11)
C*(64)	5488	11078	1751	91 (13)
C*(65)	4952	10475	1664	55 (8)
C*(66)	5046	10033	1281	55 (8)
C*(71)	2288 (13)	8635 (11)	2594 (7)	52 (8)
C*(72)	1493	8366	2473	97 (14)
C*(73)	1167	7759	2704	86 (12)
C*(74)	1635	7421	3055	110 (16)
C*(75)	2429	7691	3176	92 (13)
C*(76)	2756	8297	2945	46 (8)
C*(81)	5089 (14)	8998 (15)	4323 (9)	92 (13)
C*(82)	5615	9190	4691	117 (17)
C*(83)	6337	9605	4626	101 (14)
C*(84)	6533	9827	4192	88 (12)
C*(85)	6007	9635	3824	69 (10)
C*(86)	5285	9220	3889	62 (9)
C*(91)	7692 (11)	11088 (14)	3253 (8)	59 (9)
C*(92)	7503	11545	3616	104 (15)
C*(93)	6686	11789	3666	86 (12)
C*(94)	6058	11577	3351	110 (16)
C*(95)	6247	11120	2988	84 (12)
C*(96)	7064	10876	2939	53 (8)
C(101)	8604 (15)	10369 (10)	1258 (8)	79 (11)
C(102)	9067	10223	880	78 (11)
C(103)	9252	9486	764	93 (13)
C(104)	8975	8895	1026	94 (13)
C(105)	8513	9040	1404	88 (12)
C(106)	8327	9777	1520	57 (9)
C(111)	4053 (17)	6002 (16)	1056 (7)	92 (13)
C(112)	3560	5383	1152	150 (23)
C(113)	3730	4965	1542	107 (15)
C(114)	4393	5165	1837	95 (14)
C(115)	4887	5783	1741	86 (12)
C(116)	4717	6202	1351	66 (9)
C(121)	6868 (14)	8731 (14)	546 (6)	73 (10)
C(122)	7154	9196	208	76 (11)
C(123)	6743	9208	−216	91 (13)
C(124)	6045	8755	−302	103 (14)
C(125)	5759	8291	37	93 (13)
C(126)	6170	8279	461	56 (8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Distances (Å) and Angles (deg) for $Cu(3,5\text{-}Ph_2pzH)_2Br_2$ (**1**)

	Distances		
Cu–Br(1)	2.360 (2)	N(1)–N(2)	1.34 (1)
Cu–Br(2)	2.375 (2)	N(3)–N(4)	1.37 (1)
Cu–N(1)	2.005 (9)	N(3)–C(4)	1.36 (1)
Cu–N(3)	2.027 (10)	N(1)–C(1)	1.36 (1)
	Angles		
Br(1)–Cu–Br(2)	96.3 (1)	Br(2)–Cu–N(3)	92.5 (3)
N(3)–Cu–N(1)	92.4 (4)	Br(1)–Cu–N(3)	152.7 (3)
Br(1)–Cu–N(1)	91.5 (3)	Br(2)–Cu–N(1)	152.7 (3)

pyrazole rings is 39.7°. A listing of important bond lengths and angles for **1** is given in Table VI.

$[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3\cdot 2THF$ (2). Unlike the gold analogue, which exhibits high symmetry in the solid state (vide infra), complex **2** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of the discrete silver trimer depicted in Figure 2 and two THF molecules. The nine-membered inorganic ring of silver and nitrogen atoms is neither regular in geometry nor planar. The three Ag positions do not form an equilateral triangle. The three Ag···Ag distances range from 3.486 (2) to 3.305 (2) Å, a difference of 0.181 (2) Å. The six nitrogen atoms of the three pyrazolate rings deviate from the plane defined by the Ag centers over the range +0.450 Å for N(4) to −0.489 Å for N(5). However, no significant deviation from linearity is observed in the coordination around Ag. Similarly the nine carbon atoms of the three pyrazolate rings deviate from this same plane over the range of +1.132 Å for C(5) to −1.013 Å for C(8). The three dihedral angles defined by the atoms Ag–N–N–Ag in complex **2** are Ag(1)–N(1)–N(2)–Ag(2) = −40.3°, Ag(2)–N(3)–N(4)–Ag(2) = 8.8° and Ag(3)–N(5)–N(6)–Ag(1) = 12.8°.

The distortion from an idealized geometry can be described as follows: one pyrazolate ring hinged "below" the plane of the Ag atoms [pz(8)] and one pyrazolate ring hinged "above" the plane [pz(5)] with the pyrazolate ring [pz(2)] having the greatest di-

Table VII. Distances (Å) and Angles (deg) for $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3\cdot 2THF$ (**2**)

Distances			
Ag(1)···Ag(2)	3.496 (2)	N(1)–N(2)	1.38 (2)
Ag(2)···Ag(3)	3.362 (2)	N(3)–N(4)	1.39 (2)
Ag(3)···Ag(1)	3.305 (2)	N(5)–N(6)	1.36 (2)
Ag(1)–N(1)	2.09 (1)	N(1)–C(1)	1.36 (2)
Ag(1)–N(6)	2.09 (1)	N(2)–C(3)	1.35 (2)
Ag(2)–N(2)	2.08 (1)	N(3)–C(4)	1.34 (2)
Ag(2)–N(3)	2.09 (1)	N(4)–C(6)	1.36 (2)
Ag(3)–N(4)	2.08 (1)	N(5)–C(7)	1.37 2)
Ag(3)–N(5)	2.08 (1)	N(6)–C(9)	1.37 (2)
Angles			
N(1)–Ag(1)–N(6)	174.7 (4)	Ag(1)–N(6)–C(9)	135 (1)
N(2)–Ag(2)–N(3)	176.3 (6)	N(1)–C(1)–C(2)	108 (2)
N(4)–Ag(3)–N(5)	175.6 (5)	C(2)–C(1)–C(16)	129 (1)
N(2)–N(1)–C(1)	109 (1)	N(2)–C(3)–C(2)	109 (2)
Ag(2)–N(3)–N(4)	118 (1)	C(1)–C(2)–C(3)	106 (1)
N(1)–N(2)–C(3)	108 (1)	C(4)–C(5)–C(6)	102 (1)
N(3)–N(4)–C(6)	108 (1)	C(7)–C(8)–C(9)	105 (2)
Ag(3)–N(5)–C(7)	133 (1)	C(9)–C(66)–C(61)	119.1 (7)

Table VIII. Distances (Å) and Angles (deg) for $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ (**4**)

Distances			
Au–N	1.978 (9)	C(1)–C(2)	1.42 (2)
Au···Au′	3.368 (1)	N–N′	1.38 (2)
N–C(1)	1.36 (2)	C(1)–C(16)	1.47 (2)
Angles			
N–Au–Au′	119.8 (3)	N–Au···Au′	59.8 (3)
N–Au–N′	179.6 (3)	Au–N–C(1)	131.7 (7)
Au–N–N′	120.2 (7)	C(1)–N–N′	108.1 (8)
N–C(1)–C	110 (1)	N–C(1)–C(16)	123 (1)
C(2)–C(1)–C(16)	126 (1)	C(1)–C(16)–C(15)	118.6 (6)
C(1)–C(16)–C(11)	121.4 (6)		

Table IX. Distances (Å) and Angles (deg) for $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ (**4**)

Distances			
Au(1)···Au(2)	3.128 (2)	Au(5)···Au(6)	3.631 (1)
Au(1)···Au(3)	3.495 (1)	Au(1)–N(1)	2.06 (3)
Au(1)···Au(4)	4.141 (1)	Au(1)–N(11)	2.03 (3)
Au(1)···Au(5)	3.121 (2)	Au(2)–N(2)	2.00 (3)
Au(1)···Au(6)	3.864 (1)	Au(2)–N(3)	2.02 (3)
Au(2)···Au(3)	3.925 (1)	Au(3)–N(6)	2.03 (3)
Au(2)···Au(4)	3.678 (1)	Au(3)–N(7)	2.06 (2)
Au(2)···Au(5)	6.010 (1)	Au(4)–N(4)	2.13 (3)
Au(2)···Au(6)	5.181 (1)	Au(4)–N(5)	2.16 (3)
Au(3)···Au(4)	3.085 (2)	Au(5)–N(10)	2.06 (3)
Au(3)···Au(5)	4.079 (1)	Au(5)–N(12)	2.07 (3)
Au(3)···Au(6)	3.149 (2)	Au(6)–N(8)	2.05 (3)
Au(4)···Au(5)	5.619 (1)	Au(6)–N(9)	2.04 (3)
Au(4)···Au(6)	5.998 (1)		
N(1)–N(2)	1.44 (4)	N(7)–N(8)	1.39 (3)
N(3)–N(4)	1.30 (4)	N(9)–N(10)	1.28 (4)
N(5)–N(6)	1.40 (4)	N(11)–N(12)	1.40 (4)
Angles			
N(2)–N(1)–Au(1)	108 (2)	N(9)–N(10)–Au(5)	120 (2)
N(1)–N(2)–Au(2)	121 (2)	N(12)–N(11)–Au(1)	112 (2)
N(4)–N(3)–Au(2)	128 (2)	N(11)–N(12)–Au(5)	118 (2)
N(3)–N(4)–Au(4)	120 (2)	N(1)–Au(1)–N(11)	174.7 (1)
N(6)–N(5)–Au(4)	112 (2)	N(2)–Au(2)–N(3)	175.6 (1)
N(5)–N(6)–Au(3)	114 (2)	N(6)–Au(3)–N(7)	176.7 (1)
N(8)–N(7)–Au(3)	115 (2)	N(4)–Au(4)–N(5)	178.9 (1)
N(7)–N(8)–Au(6)	116 (2)	N(10)–Au(5)–N(12)	179.3 (1)
N(10)–N(9)–Au(6)	130 (2)	N(8)–Au(6)–N(9)	176.0 (1)

Table X. Selected Dihedral Angles (deg) for $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ (**2**) and Deviations (Å) of Selected Atoms from the Ag(1)···Ag(2)···Ag(3) Plane

Dihedral Angles	
Ag(1)–N(1)–N(2)–Ag(2)	−40.3
Ag(2)–N(3)–N(4)–Ag(3)	8.8
Ag(3)–N(5)–N(6)–Ag(1)	12.8
N(3)–Ag(2)–Ag(3)–N(4)	3.6
N(5)–Ag(3)–Ag(1)–N(6)	5.3

Deviations of Atoms from Plane Defined by Ag(1)···Ag(2)···Ag(3)

Equation with Esd's in Parentheses for X, Y, and Z Fractional Coordinates: $(8.52\ (4))X + (3.79\ (1))Y + (12.7\ (2))Z = 5.84\ (1)$

N(1)	0.1413	C(1)	0.1816
N(2)	−0.3666	C(3)	−0.6618
N(3)	0.3373	C(4)	0.7383
N(4)	0.4504	C(6)	0.9165
N(5)	−0.4880	C(7)	−0.8740
N(6)	−0.3316	C(9)	−0.6391

hedral angle (Ag(1)–N(1)–N(2)–Ag(2)) being partly "above" and partly "below" the plane of Ag atoms. See Table X for a list of significant dihedral angles and the out-of-plane distances in complex **2**.

Overall, the distortions from idealized geometry observed in **2** could be obtained by twisting the molecule about an axis that passes through C(2) and Ag(3). This action will (a) put one pyrazolate above and the other below the plane defined by the silver atoms, (b) require the unique pyrazolate ring to span the longest Ag···Ag distance, (c) bring the phenyl groups C(41)–C(46) and C(51)–C(56) closest together, and (d) at the same time place the C(3) atom below and the C(5) atom above the plane defined by the three silver centers.

$[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ (3). The asymmetric unit consists of one-sixth of the gold pyrazolate trimer shown in Figure 3. Specifically, the asymmetric unit contains one Au center at half-occupancy as it resides on a 2-fold axis, one N, and one and one-half carbons (C(2) is on a 2-fold axis) along with one phenyl ring. The molecule sits on a 3_2 axis. The three two-coordinate Au^I centers are 3.368 (1) Å apart, a nonbonding distance, and form an equilateral triangle. The five atoms of the pyrazolate rings and the three gold atoms are in a plane with D_{3h} point group symmetry. The Au–N bond distance of 1.978 (9) Å in **3** is longer than the Au–N bonds in the CF_3 analogue,[10] 1.93 (3) Å. The planes of the phenyl rings are 45° to the plane of the inorganic nine-membered ring.

In the unit cell the discrete pyrazolate gold trimer molecules are coplanar and parallel to each other in the unit cell along the *c* axis. The closest intermolecular Au···Au and Au···N distances are 7.567 and 4.672 Å, respectively, clearly noninteracting. Unlike the case for the structurally similar Au carbeniato trimer ($[AuC(OEt){=}NC_6H_4Me]_3$) reported by Minghetti et al.,[20,26] the *intermolecular* Au···Au and Au···N distances in **1** are in excess of 2.25 times that of the *intramolecular* distances.

It should be noted that the synthesis of an insoluble material, mp 200 °C, has been reported by Banditelli et al.[27] and was assigned the molecular formula $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ on the basis of an elemental analysis and similar chemistry observed for differently substituted pyrazolates. In view of the very different physical properties (melting point, solubility) of the complex characterized here, it appears that the material synthesized by the Italian workers[27] may be a polymer of the form $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_n$, $n > 6$.

$[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ (4). The hexameric gold pyrazolate complex crystallizes in the monoclinic space group $P2_1/n$. All six gold centers observed in **4** are two-coordinate, nearly linear, N-bonded Au^I. The gold–nitrogen inorganic ring of **4** has the same Au–N–N repeat unit found in **3**, but the ring is 18-membered, twice that observed in complexes **2** and **3**. The grouping of the Au centers is best described as an edge-sharing bitetrahedron (Figure 5a). The Au(3) and Au(1) centers make up the common edge of the tetrahedra Au(1)–Au(2)–Au(3)–Au(4) and Au(1)–Au(3)–Au(5)–Au(6). The gold centers and the bridging pyrazolate rings, when considered together, can be described as a "two-bladed propeller", D_2 symmetry, with a pitch (dihedral angle between the best fit of the planes of pz(5) and pz(14) of 72.9°: Figure 5b depicts such a diagram. From this perspective it can be seen

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(26) Minghetti, G.; Bonati, F. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 429.
(27) Banditelli, G.; Bandini, A. L.; Bonati, F.; Goel, R. G.; Minghetti, G. *Gazz. Chim. Ital.* **1982**, *112*, 539.

that three types of pairs of gold centers exist: (a) gold centers bridged by one pyrazolate ligand, (b) gold centers separated by two pyrazolate ligands, and (c) gold centers separated by three pyrazolate ligands as followed along the Au–N–N 18-membered ring.

The particular view of **4** given in Figure 5a has been chosen because the Au(1)···Au(3) vector is unique. These gold centers are the closest (through space) metal centers (3.495 Å) that are separated by three pyrazolate ligands. The other two pairs of gold centers separated by three pyrazolate ligands (Au(2)–Au(6) andd Au(4)–Au(5)) are 5.181 (1) and 5.619 (1) Å apart, respectively. As viewed in Figure 5a, the bitetrahedron formed by the Au centers has a compressed "axis" (Au(1)···Au(3)) and a trapezoidal distortion (Au(2)···Au(6) = 5.181 (1) Å; Au(4)···Au(5) = 5.619 (1) Å) of the "equatorial plane". This trapezoidal distortion is also seen in the Au(5)···Au(6) and Au(2)···Au(4) distances (3.361 (1) and 3.678 (1) Å) versus the Au(1)···Au(2) and Au(3)···Au(6) distances (3.128 (2) and 3.149 (2) Å). In both cases these are distances between gold centers bridged by only one pyrazolate ligand. The geometrical constraints imposed on the Au···Au distances of the trimeric complex **3** are not present in **4**, allowing for differences in the long-range nonbonding distances between gold atoms. This is clearly seen in the four Au···Au distances 3.128 (2), 3.121 (2), 3.085 (2), and 3.149(2) Å, which are significantly shorter than the one measured in **3**. An overall deviation from an ideal geometry is observed in **4**. The coordination around gold atoms deviates as much as 5° from linearity, and a marked distortion of the pyrazolates is seen in the N–N bonds, 1.28 (4)–1.44 (4) Å, and the N–N–Au angles, 108 (2)–130 (2)° (Table IX).

Discussion

As all group 11 metals in the 1+ oxidation state can form linear two-coordinate species, we attempted to make neutral pyrazolato trimer species for Cu, Ag, and Au of the general formula [M(3,5-Ph_2pz)]$_3$. The initial successes we had with Au and Ag encouraged us to complete the series. Attempts to synthesize a Cu^I trimer from Cu^ICl and Na(3,5-Ph_2pz), reacted in a 1:1 ratio in CH_3CN, gave[28] an anionic Cu^{II} dimer bridged by four acetamide anions (hydration of acetonitrile) and containing an acetamide and a deprotonated acetamide in the terminal positions. A similar reaction between $Cu^{II}Br_2$ and Na(3,5-Ph_2pz) in THF gave $CuBr_2$(3,5-Ph_2pzH)$_2$ upon crystallization, a result of protonation by water. Despite the fact that we were unable to structurally characterize either Cu^I or Cu^{II} trimeric pyrazolato complexes, the copper(II) bis(pyrazole) adduct, **1**, is of interest as a precursor for heterometallic multinuclear species. As it was the only copper pyrazole complex isolated from these reactions, it is reported here.

The topologically unusual gold hexamer, **4**, crystallizes as a racemic mixture. Considering the $Au_6(pz)_6$ core without the 3,5-diphenyl substituents, enantiomeric interconversion of the observed complex (D_2 symmetry) would require a conformer of C_{2v} or higher symmetry containing improper rotation elements. In C_{2v} point group symmetry the interaction of two pyrazolate rings separated by two other pyrazolate rings (for example, the pz(8) and pz(18) or the pz(11) and pz(2) rings) eliminates this path for interconversion.

It is germane to this topological discussion of the hexameric gold(I) pyrazolate complex that an 18-membered ring of D_{3d} symmetry, having six Au–N–N repeat units and containing all-trans arrangements of the pyrazolate rings, can be constructed from Dreiding molecular models. This conformer resembles a crown containing the six gold atoms in a plane with six pyrazolates bridging alternately on either side of the Au_6 plane. With the 3,5-diphenylpyrazolate hexamer discussed here, a crown conformation would produce large phenyl–phenyl interactions between alternating pyrazolate rings. With unsubstituted or 4-substituted pyrazolate rings, such a geometry appears to be plausible. In fact, a planar Au_n geometry is found in the recently reported [Au(PhNNNPh)]$_4$ and [Au(o-$CH_3C_6H_4CS_2$)]$_6$ complexes.[29,30] An interconversion of the observed D_2 two-bladed propellar hexamer (containing two trans and four cis pyrazolate rings) through or to the crown to produce its enantiomer requires the cleavage of a Au–N bond followed by the rearrangement of four pyrazolates. As is illustrated in Figure 4, the pyrazolate rings pz(11)–pz(14), pz(14)–pz(17), pz(2)–pz(5), and pz(5)–pz(8) are in a cisoid relationship while the pz(8)–pz(11) and pz(2)–pz(7) rings are transoid. The formation of large rings is not common in inorganic chemistry. The 18-membered ring, [Au–N–N]$_6$, of complex **4** is one of the largest ones reported to date and has potential for use in electron microscopy.[31]

In the rather extensive Au-cluster chemistry[32] there are only two other examples[33,34] of a Au_6 edge-sharing bitetrahedral arrangement. The two gold centers forming the common edge of the bitetrahedron (Figure 5a) are not the two metal centers closest to each other; they are, however, the only ones that are spatially oriented for metal–metal formation. Model construction indicates that, in the gold pyrazolate polymer system [Aupz]$_n$, a face-to-face orientation of metal orbitals, such as seen between Au(1) and Au(3) in **4**, can only be achieved when n = 6, 9, 12, ..., etc. The combination of two factors, (a) two-coordinate linear geometry at the metal center and (b) the 120° angle formed by the σ orbitals on the N atoms of the pyrazolate anion, gives trimeric species for Au^I and Ag^I. Due to the ease of oxidation of Cu^I to Cu^{II}, characterizing the analogous first-row trimer has not yet been achieved. A comparative study of the behavior of the gold trimer and gold hexamer complexes, **3** and **4**, toward oxidation is in progress.

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Registry No. 1, 111495-78-4; **2**, 111495-80-8; **3**, 56178-37-1; **4**, 111315-04-9; Au(THT)Cl, 39929-21-0; $ClAuPPh_3$, 14243-64-2.

Supplementary Material Available: Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths, and bond angles for complexes **1–4** (15 pages); tables of observed and calculated structure factors for the four complexes (198 pages). Ordering information is given on any current masthead page.

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[28] Raptis, R. G.; Fackler, J. P., Jr., unpublished results. Acetonitrile was used in this reaction, as it is known to stabilize Cu^I: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry. A Comprehensive Text*, 3rd ed.; Wiley: New York, 1973; p 906. The pyrazolato anion presumably was the base (nonnucleophilic) that deprotonated the acetamide.

[29] Beck, J.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 95.

[30] Schuerman, J. A.; Fronczek, F. R.; Selbin, J. *J. Am. Chem. Soc.* **1986**, *108*, 336.

[31] Hainfield, J. F. *Science (Washington, D.C.)* **1987**, *236*, 450.

[32] King, R. B. *Inorg. Chim. Acta* **1986**, *116*, 109.

[33] (a) Van der Velden, J. W. A.; Bour, J. J.; Otterloo, B. F.; Bosman, W. P.; Noordik, J. H. *J. Chem. Soc., Chem. Commun.* **1981**, 583. (b) Van der Velden, J. W. A.; Bour, J. J.; Bosman, W. P.; Noordik, J. H. *Inorg. Chem.* **1983**, *22*, 1913.

[34] Briant, C. W.; Hall, K. P.; Mingos, D. M. P. *J. Organomet. Chem.* **1983**, *254*, C18.