

Notes

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**Synthesis and Crystal Structure of a Mixed-Valence,
Au^I₂/Au^{III}, Pyrazolato Complex Stable in Aqua Regia. X-ray
Photoelectron Study of Homo- and Heterovalent
Gold–Pyrazolato Trimers**

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Introduction

The chemical reactivity of trinuclear transition-metal complexes that contain metal atoms in a triangular arrangement not containing metal–metal bonds is a little studied area of chemistry. These arrays are constructed in such a manner that the metal atoms might be expected to undergo reaction chemistries at the three centers in a rather independent fashion. However, there is increasing evidence that various steric and electronic factors may influence the reactivities of the metal atoms in these compounds such that an independent reaction chemistry is not observed. The triangular complex of gold reported here, wherein the metal atoms are not bonded to each other but are separated by a relatively short nonbonding distance, turns out to be a rather striking example of this statement.

We have recently discussed¹ the syntheses and X-ray crystal structures of the metallocyclic pyrazolato complexes [M^I(μ-3,5-Ph₂p_z)₃]₂,² where M^I = Cu, Ag, Au. We are now studying the reaction chemistry of these metal trimers and report our work here on the Au compound.

As Balch reported,³ the trimeric Au^I complex [Au(μ-MeOCNMe)₃] can be oxidized by stoichiometric amounts of halogens to form [Au(μ-MeOCNMe)₃X_n], where X = Br or I, which contain Au^I₂/Au^{III} (n = 2), Au^I/Au^{III}₂ (n = 4), or Au^{III}₃ (n = 6) metal cores. The similar Au^I complex [Au(μ-EtOCNC₆H₄Me)₃] has been studied⁴ crystallographically; however, no structural data are available for the mixed-valence or Au^{III} trimers. In contrast to the aforementioned trigold system, the Au^I trimers [Au(μ-3,5-R₂p_z)₃], where R = alkyl, can only be oxidized^{5,6} by 1 equiv of I₂, yielding the Au^I₂/Au^{III} complex [Au(μ-3,5-R₂p_z)₃]₂. Bonati and Mingetti reported⁷ that further oxidation could be achieved by reaction of [Au(μ-3,5-Ph₂p_z)₃], with aqua regia, forming a dimeric [Au(μ-3,5-Ph₂-4-Cl-p_z)₂Cl₄] complex characterized by its elemental analysis IR and NMR spectra, and molecular weight. Our reinvestigation of this work gives a crystallographically characterized product that is a mixed-valence Au^I₂/Au^{III} complex in which the pyrazolato rings have been chlorinated. Here we present our efforts to synthesize Au^{III}-containing trinuclear pyrazolato complexes along with the XPS study of [Au(μ-3,5-Ph₂p_z)₃] (1) and [Au(μ-3,5-Ph₂p_z)₃Cl₂] (2) and the results of the crystallographic characterization of [Au(μ-3,5-Ph₂-4-Cl-p_z)₃Cl₂] (3).

Experimental Section

All reactions were carried out under an argon atmosphere unless otherwise stated. All solvents were distilled and stored over molecular sieves prior to use. 3,5-Diphenylpyrazole was purchased from Lancaster Ltd. and deprotonated with sodium hydride. Complexes 1 and AuCl₃py were prepared by literature^{1b,8} procedures.

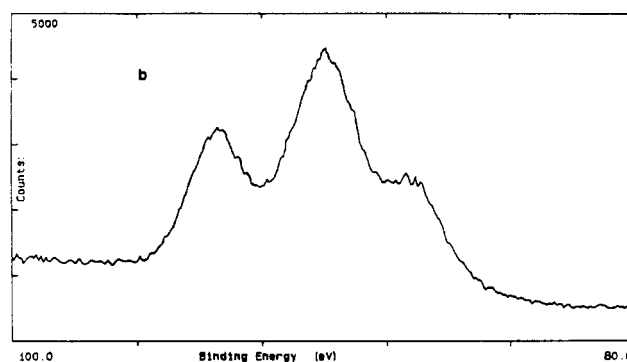
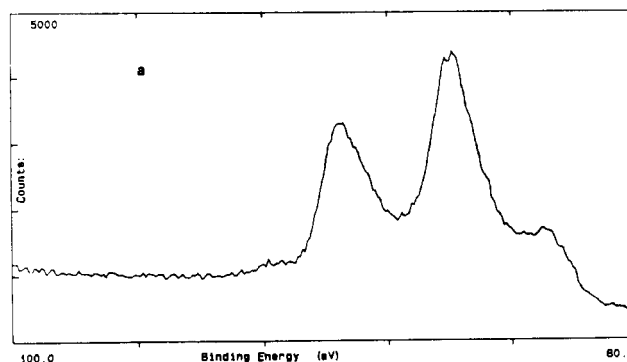


Figure 1. (a) XPS spectrum of the Au^I₃ complex 1. (b) XPS spectrum of the Au^I₂/Au^{III} complex 2. Due to the fact that the charging potential is different for the two observations made, the absolute bonding energies for spectra a and b are not comparable.

[Au(μ-3,5-Ph₂p_z)₃Cl₂] (2). To a solution of 50 mg (0.13 mmol) of AuCl₃py in 10 mL of thf was added 33 mg (0.14 mmol) of Na[3,5-Ph₂p_z], and the solution turned dark red immediately. It was allowed to stir for 6 h and filtered. Slow diffusion of Et₂O into this solution, in the dark, afforded red crystals of 2: mp 229–231 °C; yield 44 mg, 89%. Complex 2 has been characterized⁹ crystallographically.

[Au(μ-3,5-Ph₂-4-Cl-p_z)₃Cl₂] (3). To 30 mg (0.024 mmol) of 1 was added 3 mL of aqua regia in an open reaction vessel. The white solid of 1 turned red immediately, and the mixture was stirred for 6 h at room temperature without any further color change. The red solid was allowed to settle, the supernatant was decanted, and the solid product was washed three times with H₂O. The wet solid of 3 was dissolved in 3 mL of CH₂Cl₂. Slow diffusion of Et₂O into this solution afforded red crystals of 3 appropriate for an X-ray diffraction study. Yield: 19 mg, >50%.

Other Reactions. To an aqueous solution of 38 mg (0.10 mmol) of KAuCl₄ was added a stoichiometric amount of 3,5-Ph₂p_zH in an open beaker, and AuCl₃(3,5-Ph₂p_zH) was precipitated quantitatively as an orange solid soluble in organic solvents (a modification of the synthesis⁸

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- (2) Abbreviations used: 3,5-Ph₂p_z = 3,5-diphenylpyrazolato anion; 3,5-Ph₂p_zH = 3,5-diphenylpyrazole; 3,5-R₂p_z = 3,5-dialkylpyrazolato anion; py = pyridine; thf = tetrahydrofuran.
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Table I. Crystallographic Data for **3**

formula	C ₄₉ H ₄₀ Au ₃ Cl ₅ N ₆ O
fw	1497.07
space group	P2 ₁ /n (No. 14)
a, Å	20.798 (5)
b, Å	9.772 (3)
c, Å	24.224 (6)
β, deg	90.43 (2)
V, Å ³	4923 (2)
Z	4
d _{calc} , g/cm ³	2.02
μ(Mo Kα), cm ⁻¹	92.19
radiation (monochromated in Mo Kα (λ _{air} = 0.71069 Å) incident beam)	
temp, °C	22
trans factors: max: min	1.000: 0.274
R ^a	0.058
R _w ^b	0.059

$${}^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad {}^b R_w = \frac{[\sum \sqrt{w}(|F_o| - |F_c|)]}{\sum \sqrt{w}|F_o|}$$

$$w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2].$$

of AuCl₃py using pyrazole instead of pyridine). The product was filtered, washed with water, and air-dried. To a 2-mL CH₂Cl₂ solution of this material was added stoichiometric amount of tris(*n*-butyl)amine. The solution turned dark red immediately and then changed slowly to orange. It was stirred for 3 h and was diluted with 2 mL of CH₂Cl₂ and Et₂O was allowed to slowly diffuse into it at -5 °C. This afforded approximately equal amounts of physically separated crystals of **1** (light yellow) and **2** (red), identified by unit cell determination and low-angle X-ray diffraction data collection, respectively. The crystals of **1** prepared by this method had the 4-position of the pyrazolato rings partially (<20%) chlorinated. When a 10-fold excess of amine was used, the reaction mixture turned red immediately and then slowly decolorized. Only **1** was detected in the solid product.

X-ray Photoelectron Spectroscopy. The XP spectra of complexes **1** and **2** were obtained at 22 °C by using a Hewlett-Packard 5950A ESCA spectrometer with Al Kα radiation and a resolution of 0.8 eV. The powder samples were placed on gold stubs covered with double-stick Scotch tape. The sample of the mixed-valence complex **2** became charged during the experiment, necessitating the use of a flood gun and rendering the measured binding energies for **1** and **2** not comparable. Complex **1** shows a symmetric peak for the Au(4f_{7/2}) electrons with width-at-half height of 1.41 eV (Figure 1a), while the Au(4f_{7/2}) peak of **2** is asymmetric with a shoulder at the high-energy side, corresponding to the Au^{III} electrons binding energy, with a width at half-height of 2.01 eV (Figure 1b). The Au(4f_{5/2}) peaks behave similarly.

Crystallography. The X-ray analysis of **3** was carried out with a Nicolet R3m/E automated diffractometer and SHELXTL (Version 5.1) software implemented on a Eclipse S140 minicomputer. A single crystal of **3** appropriate for X-ray study was mounted atop a glass fiber for data collection. Initial cell parameters were determined by using orientation reflections obtained from photographic data and were confirmed by axial photographs and a Delaunay reduction. Accurate unit cell dimensions were calculated from the setting angles of 25 reflections with 25° < 2θ < 30°. Intensity data were collected for 6424 unique reflections, ±h, ±k, ±l with 0 < 2θ < 45°, by using the ω-scanning technique in bisecting geometry. No symmetry-equivalent reflections were measured. The intensity data were corrected for Lorentz and polarization effects and standard decay (ca. 12%). An empirical absorption correction based on azimuthal scans of medium-intensity reflections was applied. Initial positional parameters for the three gold atoms were obtained from the direct-methods program solution. The remaining non-hydrogen atoms were located in difference Fourier maps. An interstitial molecule of diethyl ether was found to occupy a position of no chemical importance. The gold, chlorine, oxygen, and carbon atoms of the pyrazolato rings were refined anisotropically. Hydrogen atoms were placed in calculated positions (C-H = 0.960 Å) and phenyl groups were treated as idealized rigid hexagons (C-C = 1.395 Å; C-C-C = 120°) to minimize parameterization. Structure refinement using all 6424 unique reflections gave a *R* value of 0.107. Refinement of 275 parameters using 3618 reflections with *F_o*² > 3σ(*F_o*²) converged to a conventional *R* value of 0.0579 with a goodness-of-fit indicator of 1.165. The highest peak of residual electron density, 1.81 e Å⁻³, appears at a distance of 1.14 Å from Au(2). Parameters pertaining to data collection and structure refinement are listed in Table I. Atomic coordinates and equivalent isotropic thermal parameters for **3** are given in Table II. 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 **3** have been deposited as supplementary materials.

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for [Au(μ-3,5-Ph₂-4-Cl-pz)]₃Cl₂·Et₂O (**3**)

atom	x	y	z	U _{iso} ^a
Au(1)	10031 (1)	1079 (1)	2696 (1)	37 (1)*
Au(2)	11561 (1)	1200 (1)	3159 (1)	38 (1)*
Au(3)	10372 (1)	1891 (1)	4032 (1)	42 (1)*
Cl(1)	10048 (3)	3362 (7)	2543 (3)	68 (3)*
Cl(2)	10025 (3)	-1216 (7)	2871 (3)	71 (3)*
Cl(3)	11683 (4)	737 (8)	784 (3)	69 (3)*
Cl(4)	12763 (4)	2477 (10)	5256 (3)	88 (4)*
Cl(5)	7607 (4)	1114 (11)	3833 (4)	104 (4)*
N(1)	10757 (8)	858 (16)	2156 (7)	31 (5)
N(2)	11374 (8)	914 (17)	2353 (7)	34 (5)
N(3)	11762 (9)	1565 (18)	3946 (7)	41 (5)
N(4)	11291 (8)	2082 (18)	4309 (7)	41 (5)
N(5)	9440 (8)	1595 (17)	3780 (7)	35 (5)
N(6)	9313 (9)	1299 (18)	3238 (8)	45 (5)
C(1)	10767 (10)	723 (23)	1601 (8)	35 (8)*
C(2)	11380 (11)	780 (20)	1431 (8)	37 (8)*
C(3)	11776 (9)	893 (20)	1906 (8)	28 (8)*
C(4)	12328 (12)	1592 (26)	4230 (11)	57 (11)*
C(5)	12229 (12)	2173 (30)	4737 (9)	57 (11)*
C(6)	11552 (13)	2461 (23)	4794 (8)	56 (10)*
C(7)	8917 (11)	1496 (29)	4074 (12)	67 (12)*
C(8)	8412 (11)	1232 (28)	3687 (11)	65 (11)*
C(9)	8678 (10)	1109 (26)	3182 (10)	53 (10)*
C(11)	10082 (8)	1503 (15)	817 (7)	63 (8)
C(12)	9548 (8)	1319 (15)	473 (7)	83 (10)
C(13)	9112 (8)	270 (15)	580 (7)	88 (10)
C(14)	9209 (8)	-596 (15)	1031 (7)	79 (9)
C(15)	9743 (8)	-412 (15)	1375 (7)	59 (7)
C(16)	10179 (8)	638 (15)	1268 (7)	47 (7)
C(31)	12750 (6)	2034 (13)	2306 (6)	41 (6)
C(32)	13415 (6)	2093 (13)	2377 (6)	48 (7)
C(33)	13805 (6)	1092 (13)	2141 (6)	65 (8)
C(34)	13529 (6)	34 (13)	1834 (6)	53 (7)
C(35)	12863 (6)	-25 (13)	1763 (6)	36 (6)
C(36)	12474 (6)	975 (13)	1999 (6)	36 (6)
C(41)	12967 (6)	-65 (15)	3684 (6)	44 (6)
C(42)	13549 (6)	-514 (15)	3466 (6)	53 (7)
C(43)	14105 (6)	265 (15)	3541 (6)	64 (8)
C(44)	14079 (6)	1494 (15)	3833 (6)	64 (8)
C(45)	13497 (6)	1944 (15)	4050 (6)	68 (8)
C(46)	12941 (6)	1164 (15)	3976 (6)	46 (6)
C(61)	10802 (10)	4136 (21)	5176 (7)	120 (14)
C(62)	10509 (10)	4746 (21)	5630 (7)	156 (17)
C(71)	8352 (10)	2516 (23)	4884 (10)	143 (16)
C(72)	8299 (10)	2716 (23)	5452 (10)	164 (19)
C(73)	8774 (10)	2218 (23)	5808 (10)	136 (15)
C(74)	9303 (10)	1520 (23)	5597 (10)	116 (13)
C(75)	9356 (10)	1319 (23)	5029 (10)	95 (11)
C(76)	8881 (10)	1817 (23)	4672 (10)	73 (9)
C(91)	8429 (8)	1780 (15)	2218 (7)	58 (7)
C(92)	8085 (8)	1608 (15)	1727 (7)	88 (10)
C(93)	7697 (8)	457 (15)	1652 (7)	94 (11)
C(94)	7654 (8)	-522 (15)	2069 (7)	80 (9)
C(95)	7998 (8)	-350 (15)	2561 (7)	87 (10)
C(96)	8386 (8)	801 (15)	2635 (7)	56 (7)
O*	8922 (13)	5973 (21)	1141 (10)	121 (12)*
C(1*)	8843 (19)	6116 (38)	2099 (15)	132 (15)
C(2*)	8942 (18)	5284 (37)	1638 (14)	115 (13)
C(3*)	9049 (18)	5290 (37)	641 (14)	117 (13)
C(4*)	8938 (26)	6215 (56)	204 (22)	246 (31)
C(63)	10592 (10)	4187 (21)	6156 (7)	91 (11)
C(64)	10968 (10)	3017 (21)	6227 (7)	126 (14)
C(65)	11261 (10)	2406 (21)	5773 (7)	99 (11)
C(66)	11178 (10)	2966 (21)	5248 (7)	54 (7)

^a An asterisk denotes the equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Discussion

We have attempted to synthesize trimeric Au^{III}-pyrazolato complexes by two procedures; by oxidation of a Au^I-pyrazolato trimer and by trimerization of Au^{III} monomeric complexes. Surprisingly, both procedures have a common type of product, the mixed-valence Au^I₂/Au^{III}-pyrazolato complexes. This observation suggests an unusual stability for the d¹⁰d¹⁰d⁸ configu-

Table III. Selected Distances (Å) and Angles (deg) for $[\text{Au}(\mu\text{-}3,5\text{-Ph}_2\text{-}4\text{-Cl-pz})_3\text{Cl}_2$ (**3**)

Distances			
Au(1)···Au(2)	3.3677 (6)	N(2)–C(3)	1.37 (3)
Au(1)···Au(3)	3.4011 (7)	N(3)–C(4)	1.36 (3)
Au(2)···Au(3)	3.3352 (7)	N(4)–C(6)	1.34 (3)
Au(1)–Cl(1)	2.262 (7)	N(5)–C(7)	1.31 (3)
Au(1)–Cl(2)	2.282 (7)	N(6)–C(9)	1.34 (3)
Au(1)–N(1)	2.02 (2)	C(1)–C(2)	1.34 (3)
Au(1)–N(6)	2.01 (2)	C(2)–C(3)	1.42 (3)
Au(2)–N(2)	2.01 (2)	C(4)–C(5)	1.37 (4)
Au(2)–N(3)	1.98 (2)	C(5)–C(6)	1.44 (4)
Au(3)–N(4)	2.03 (2)	C(7)–C(8)	1.43 (4)
Au(3)–N(5)	2.05 (2)	C(8)–C(9)	1.35 (4)
N(1)–N(2)	1.37 (2)	C(2)–Cl(3)	1.69 (2)
N(3)–N(4)	1.42 (3)	C(5)–Cl(4)	1.70 (2)
N(5)–N(6)	1.37 (3)	C(8)–Cl(5)	1.72 (3)
N(1)–C(1)	1.35 (3)		
Angles			
N(1)–Au(1)–N(6)	179.7 (7)	Cl(2)–Au(1)–N(6)	88.8 (5)
N(2)–Au(2)–N(3)	177.4 (7)	Au(1)–N(1)–N(2)	118 (1)
N(4)–Au(3)–N(5)	176.6 (7)	Au(2)–N(2)–N(1)	121 (1)
Cl(1)–Au(1)–Cl(2)	178.7 (3)	Au(2)–N(3)–N(4)	121 (1)
Cl(1)–Au(1)–N(1)	89.3 (5)	Au(3)–N(4)–N(3)	115 (1)
Cl(1)–Au(1)–N(6)	90.8 (5)	Au(3)–N(5)–N(6)	120 (1)
Cl(2)–Au(1)–N(1)	91.2 (5)	Au(1)–N(6)–N(5)	121 (1)

ration of the pyrazolato metalocycle.

The reactions of AuCl_3py with $\text{Na}[3,5\text{-Ph}_2\text{pz}]$ and of $\text{AuCl}_3(3,5\text{-Ph}_2\text{pzH})$ with $(n\text{-Bu})_3\text{N}$ yield trimeric metalocycles. This was expected in view of the known tendency of the pyrazolato ligands to be bidentate. Transition-metal complexes containing monodentate pyrazolato groups are rare. Two such complexes^{10,11} are known, $(\text{PPh}_3)_2(\text{CO})\text{Ir}(3,5\text{-Me}_2\text{pz})$ and $(\text{PPh}_3)_2\text{ClPt}(3,5\text{-Ph}_2\text{pz})$, and they both act as metalloligands toward other metals, forming¹² $\text{Ir}(\mu\text{-}3,5\text{-Me}_2\text{pz})\text{Au}$ and a series¹¹ of $\text{Pt}(\mu\text{-}3,5\text{-Ph}_2\text{pz})\text{M}$, $\text{M} = \text{Cu, Ag, or Au}$, heterobimetallic complexes, respectively. The reduction of two-thirds of the Au^{III} atoms in both reactions is not well understood. Obviously, the coordination of a pyrazolato ligand, $3,5\text{-Ph}_2\text{pz}^-$, is required for the reduction process; AuCl_3py is stable in solution until it is reacted with $\text{Na}[3,5\text{-Ph}_2\text{pz}]$ and so is $\text{AuCl}_3(3,5\text{-Ph}_2\text{pzH})$ until it is deprotonated by $(n\text{-Bu})_3\text{N}$. In both cases, the amines can be the reducing agents; however, the presence of stoichiometric amounts of either pyridine or tris(*n*-butyl)amine fail to reduce all three Au^{III} centers. It is not known whether $\text{Au}^{\text{III}} \rightarrow \text{Au}^{\text{I}}$ reduction precedes trimerization or vice versa.

The result of the reaction of **1** with aqua regia is most surprising. Aqua regia a reagent which dissolves metallic gold and is used as the ultimate cleaning solution for laboratory glassware, fails to oxidize **1** beyond the $\text{Au}^{\text{I}}_2/\text{Au}^{\text{III}}$ oxidation state of **3**. It can be argued that the oxidation of the first gold atom improves the π -acceptor ability of the two pyrazolato groups coordinated to it, so that they remove sufficient electron density from the remaining two Au^{I} atoms to prevent their oxidation. However, changes in the Au–N bond lengths of **3**, compared with those of **1**, which would have been consistent with this argument, were not observed in the structure of **3** (vide infra). A similar deactivation of one metal atom toward oxidation upon oxidation of another has been reported¹³ for some dirhodium and diiridium complexes containing bridging pyrazolato ligands. Halogens also fail to oxidize⁵ $[\text{Au}(\mu\text{-}3,5\text{-R}_2\text{pz})_3]$ complexes beyond the $\text{Au}^{\text{I}}_2/\text{Au}^{\text{III}}$ state. Although there appears to be no steric reason that three planar Au^{III} units cannot coexist in these structures, the presence of the one oxidized center clearly impedes oxidation at the other two

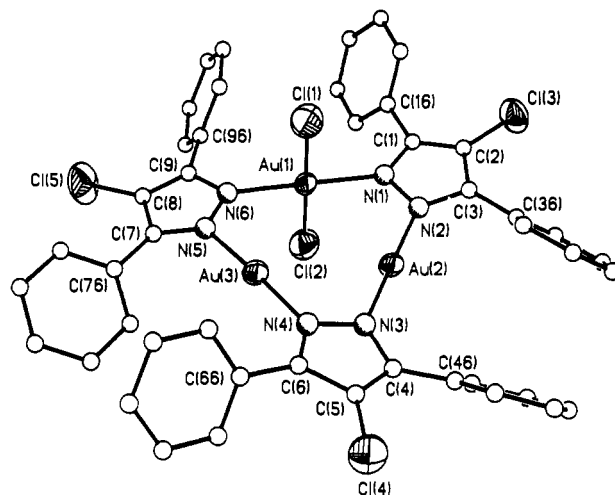


Figure 2. ORTEP drawing of $[\text{Au}(\mu\text{-}3,5\text{-Ph}_2\text{-}4\text{-Cl-pz})_3\text{Cl}_2$ (**3**) with the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Carbon and nitrogen atoms are of arbitrary radii for clarity. Solvent molecule is not shown.

centers in the molecule. Electronic communication through the pyrazolato ligands may be the origin of this effect. The halogenation of the 4-position of the pyrazolato rings of **3** is a commonly observed feature⁷ in the chemistry of pyrazoles and pyrazolates.

The XPS examination of **2** shows that the $\text{Au}(4f_{7/2})$ ionization of the Au^{I} and Au^{III} centers does not result in two resolved peaks. Instead, a broadening of the Au^{I} peak with a shoulder at the high-energy side is observed. The asymmetry of the spectrum of **2** represents the 1:2 ratio of $\text{Au}^{\text{III}}:\text{Au}^{\text{I}}$ in this complex. There is only one other XPS study¹⁴ of a mixed-valence gold complex, $\text{Au}^{\text{I}}[\mu\text{-}(\text{CH}_2)_2\text{PPh}_2]_2\text{Au}^{\text{III}}\text{Br}_2$, and its results are in agreement with the ones presented here. In that study, a broadening of the peak, with a width at half-height of 3.15 eV, was observed when its spectrum was compared with those of its Au^{I}_2 and Au^{III}_2 analogues, which showed widths at half-height of 1.62 and 1.93 eV, respectively. The $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ XPS peak study was symmetric due to the 1:1 ratio of $\text{Au}^{\text{I}}:\text{Au}^{\text{III}}$ centers.

The mixed-valence complex **3** crystallizes in the monoclinic space group $P2_1/c$ with a whole molecule of the gold trimer and an interstitial molecule of diethyl ether in the asymmetric unit. Some important bond lengths and angles for **3** are listed in Table III. The molecule consists of three gold atoms bridged by three pyrazolato ligands, forming a $(\text{Au-N-N})_3$ nine-membered, planar (within 0.15 Å) metalocycle (Figure 2). The carbon atoms of the pyrazolato rings deviate as much as 0.38 Å from the best-fit plane of the metalocycle, while the phenyl rings rotate freely out of this plane. Two of the metal atoms are two-coordinate linear Au^{I} centers and the third one is a square-planar trans Au^{III} . There is no statistically significant difference between the $\text{Au}^{\text{I}}\text{-N}$ and the $\text{Au}^{\text{III}}\text{-N}$ bond lengths of **3**, 1.98 (3)–2.05 (2) Å, just as it had been seen in the structure⁹ of **2**. The geometry of the pyrazolato rings of **3** is comparable to the geometries of the corresponding rings^{2,9} of **1** and **2**, with N–N, N–C, and C–C bond lengths ranging from 1.37 (3) to 1.42 (3) Å, 1.31 (3) to 1.37 (3) Å and 1.35 (4) to 1.44 (3) Å, respectively. Therefore, the chlorination of the 4-position of the pyrazolato rings has no observable influence of the rest of the structure. The small deviations from the ideal coordination geometries for the gold atoms and from perfect planarity for the nine-membered metalocycle cause the intramolecular $\text{Au}\cdots\text{Au}$ distances to be unequal, 3.3352 (7), 3.3677 (6), and 3.4011 (7) Å.

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Supplementary Material Available: Tables SI-SV, listing crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **3** (8 pages); Table SVI, listing observed and calculated structure factors for **3** (38 pages). Ordering information is given on any current masthead page.

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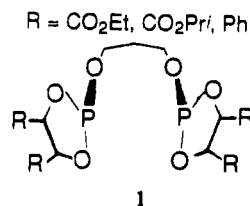
Practical Syntheses of Chelating Bis(dioxaphospholane) Ligands through Chlorodioxaphospholane Intermediates and Demonstration of Catalytic Competence of Bis(phosphite)rhodium Cations

Donald J. Wink,* Thomas J. Kwok, and Allen Yee

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The development of novel mono- and diphosphorus compounds, either for their inherent physical properties¹ or for application to catalysis² (in particular, asymmetric catalysis³) continues as an important area of synthetic phosphorus research. Most of the compounds that have been developed for catalytic applications are derivatives of aryl- or alkylphosphines; surprisingly little work has been done with less electron-rich ligands, such as phosphites or related species. These are a very tempting group of compounds for catalysis, since oxygenated phosphorus ligands may cause dramatic changes in the reactivity or selectivity of a catalyst by making the metal more electrophilic. In addition, appropriately functionalized chiral alcohols, particularly chiral diols, constitute a synthetically diverse means of quickly, (in some cases) without the need for a discrete resolution, synthesizing new chiral auxiliaries.⁴ Finally, the absence of a P-C bond in a ligand may permit the synthesis of catalysts that are not degraded by oxidative P-C bond cleavage, a significant problem in hydroformylation.⁵

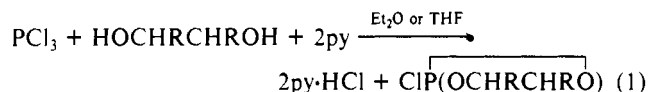
These advantages are balanced somewhat by certain important problems. A less electron-rich metal center may not undergo the oxidative-addition reactions that are the key to small molecule activation. Also, while the P-O bond may be more stable to simple oxidative-insertion reactions, it is still quite susceptible to hydrolysis, alcoholysis, or Arbuzov-type side reactions. In this paper, we report how we have successfully addressed this synthetic challenge in the moderate-scale synthesis of one group of compounds, bis(dioxaphospholane) ligands (**1**) derived from a chiral



diol side group and an achiral backbone.⁶ Moreover, cationic rhodium complexes of these ligands are indeed competent for the generation of both hydrogenation and hydroformylation catalysts.

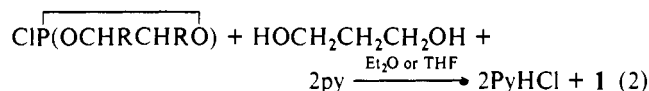
Results and Discussion

Simple chiral diols—we have worked with diisopropyl tartrate, diethyl tartrate, and (*R,R*)-dihydrobenzoin⁷—react readily with PCl₃ in the presence of base to give a chlorodioxaphospholane⁸ as a single stereoisomer (eq 1). In the case of the tartrate esters,



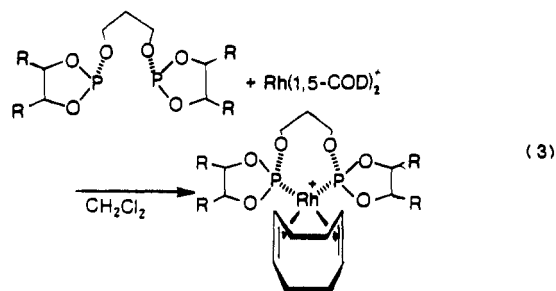
the product is purified by distillation in vacuo while the diphenyl derivative is obtained pure after crystallization from ether. All three compounds are obtained in analytically pure form in fair to good (46–93%) yield. They are sensitive to protic solvents but are indefinitely stable at ambient temperatures under dry nitrogen.

The formation of a bis(dioxaphospholane) could conceivably be performed with any other diol. However, reactions with aliphatic 1,2-diols such as ethylene glycol and pinacol are complicated by the decomposition reactions, presumably involving an equilibrium mixture of heterocyclic rings. Much better results are obtained with 1,3-propanediol, which affords good (71–90%) yields of the desired diphosphorus products as oils (eq 2) that can be



purified to spectroscopic and analytical purity from ether. The NMR spectra of these complexes are essentially the same as their acyclic analogues (shifts in the ³¹P NMR spectrum occur at ca. 145 ppm). They are thermally sensitive, but can be stored at low temperature and handled for short periods at ambient temperatures.

Our primary interest in these compounds is as auxiliaries for asymmetric catalysis, and indeed they easily form cationic rhodium precatalysts. Reaction with bis(1,5-cyclooctadiene)rhodium tetrafluoroborate gives good yields of analytically and spectroscopically pure complex salts (eq 3).⁹ These exhibit a charac-



teristic resonance in the ³¹P NMR spectrum at ca. 150 ppm with a coupling to rhodium of ca. 240 Hz, indicative of a phosphite-like ligand bound to Rh(I).¹⁰

The rhodium complexes are precatalysts for the hydrogenation of enamides. Reactions in acetone at atmospheric pressure and

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