Table I. Gas Products of Reaction Systems Containing $H_2N_2O_2$ in 5.0 M $HClO_4$ at 25 °C, with and without Added NO and with and without C_2H_5OH as Chain Inhibitor

	t, h	$n_{N_2O}/(n_{H_2N_2O_2})_0$	n_{N_2}/n_{N_2O}	$(n_{N_2}+n_{N_2O})/(n_{H_2N_2O_2})_0$	$10^5\Delta n_{NO}$, mol
	A. No C_2H_5OH Added[a]				
1. $(P_{NO})_0 = 0$; $10^5(n_{H_2N_2O_2})_0 = 5.93$	18	0.28	0.48	0.41	
	24	0.31	0.43	0.45	
	87	0.55	0.22	0.67	
2. $(P_{NO})_0 = 43.8$ torr; $10^5(n_{H_2N_2O_2})_0 = 4.44$	67	0.32	1.04	0.65	8.52
	98	0.32	1.56	0.83	4.98
	118	0.29	1.71	0.78	6.13
	166	0.29	1.77	0.81	6.80
	B. 0.5 mL of C_2H_5OH Added[a]				
1. $P_{NO}° = 0$; $10^5(n_{H_2N_2O_2})_0 = 4.42$	46	0.47	0.17	0.55	
	170	0.75	0.10	0.83	
	210	0.98	0.075	1.06	
2. $P_{NO}° = 50.9$ torr; $10^5(n_{H_2N_2O_2})_0 = 5.26$	42	0.49	0.11	0.54	2.53
	96	0.69	0.095	0.76	3.55
	163	0.79	0.080	0.85	2.92
	250	0.94	0.054	0.99	3.47

[a] Total solution volume 10.0 mL.

Table II. Mass Spectrometric Analyses of N_2O Product of $H_2N_2O_2$ Decomposition and Reaction with ^{15}NO (96.2%) in 5.0 M $HClO_4$ at 25 °C

	e/m	fraction of total N_2O	% ^{15}N in total N_2O
A. No C_2H_5OH Added			
$P_{NO}° = 45.0$ torr;	46	0.1725	
$10^5(n_{H_2N_2O_2})_0 = 4.59$; $t = 190$ h	45	0.4547	40.0
	44	0.3728	
B. 0.5 mL of C_2H_5OH Added			
$P_{NO}° = 36.0$ torr; $t = 250$ h	46	0.1542	
	45	0.0239	16.6
	44	0.8219	

In the absence of chain inhibition, the free radical OH may interact with ·ONNOH to yield NO (eq 7) and with NO to yield HNO_2 (eq 8). The latter will in turn be expected to undergo disproprotionation to yield NO and NO_3^- (eq 9), so that some nitrate should be found among the NO–$H_2N_2O_2$ reaction products (but has not been observed directly by us). The near randomness of isotopic distribution observed in N_2O in the non-chain-inhibited case indicates that it is produced largely by HNO dimerization, so that H atom abstraction on the part of unlabeled NO clearly comes into play on an important scale in this case (eq 10). This downgrades the importance of eq 4 as an N_2O source. To account for this and to identify the major source of the very abundant N_2 product, as well as of OH radicals, we postulate attack of NO at oxygen on ·ONNOH to produce these two products, plus NO_2 (eq 11). Through its expected disproportionative hydrolysis (eq 12), the NO_2 will become a further source of both HNO_2 and NO_3^-. The reaction pathway described above is summarized in eq 7–14 of Scheme I.

Scheme I

$$OH + \cdot ONNOH \rightarrow 2NO + H_2O \qquad (7)$$

$$^{15}NO + OH \rightarrow H^{15}NO_2 \qquad (8)$$

$$3H^{15}NO_2 \rightarrow 2^{15}NO + H^+ + NO_3^- + H_2O \qquad (9)$$

$$NO + HONNOH \rightarrow HNO + \cdot ONNOH \qquad (10)$$

$$NO + \cdot ONNOH \rightarrow ONONNOH \rightarrow NO_2 + N_2 + OH \qquad (11)$$

$$2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^- \qquad (12)$$

$$H^{15}NO + H^{15}NO \rightarrow {}^{15}N^{15}NO + H_2O \qquad (6)$$

$$H^{15}NO + HNO \rightarrow {}^1/_2{}^{15}NNO + {}^1/_2N^{15}NO + H_2O \qquad (13)$$

$$HNO + HNO \rightarrow N_2O + H_2O \qquad (14)$$

In addition to the above scheme, the possible reactions eq 15 and 16 have been postulated by Buchholz and Powell; however, these seem less plausible to us than eq 7–14.

$$HONNOH + NO \rightarrow HNO_2 + N_2 + OH \qquad (15)$$

$$HONNOH + \cdot ONNOH \rightarrow 2NO + N_2 + OH + H_2O \qquad (16)$$

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Synthesis and X-ray Structural Characterization of a Bimetallic Rh–Au Complex with Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

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Heterobimetallic complexes with bidentate phosphine and phosphine–pyridine type ligands to hold two metals in close proximity have received considerable attention in recent years.[1-10] Bifunctional ligands such as 2-(diphenylphosphino)pyridine, Ph_2Ppy, have proved to be particularly useful in constructing

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heterobimetallic species.[1-5] We recently reported the synthesis and structural characterization of several mono- and binuclear complexes of Rh and Ir with the potentially tridentate ligand, 2-[bis(diphenylphosphino)methyl]pyridine, $[Ph_2P]_2CHC_5H_5N$ = PNP.[11-13] We now report on the synthesis and X-ray structural characterization of a PNP-bridged heterobimetallic complex of Rh and Au, $[RhAu(\mu\text{-}PNP)_2]BF_4NO_3$, in which the phosphorus atoms are arranged cis on the rhodium atom and trans on the gold atom (vide infra). This is the first Rh–Au phosphine complex that has been characterized by single-crystal X-ray diffraction.

Experimental Section

Physical Measurements. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz at 25 °C with use of a Nicolet NT-300 spectrometer. The chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4, with positive shifts downfield. IR spectra were recorded on a Beckman Model 4250 grating spectrometer using KBr disks.

Preparation of Compounds. All manipulations were carried out under a purified N_2 atmosphere, using standard Schlenk techniques. $[Rh(nbd)(PNP)]BF_4$ (nbd = norbornadiene) and $Au(PPh_3)NO_3$ were prepared according to literature methods.[11,14]

$[Rh(PNP)_2]BF_4$ (**1**) was prepared by the reaction of $[Rh(nbd)(PNP)]BF_4$ with a stoichiometric amount of PNP ligand in acetone solution. The product was precipitated with diethyl ether and collected by filtration. Yellow crystals were obtained by solvent diffusion from methylene chloride and diethyl ether: yield 50%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 1.06 (d, J_{Rh-P} = 115.6 Hz); IR ν(py–CN) = 1588 cm^{-1}. Anal. Calcd for $C_{60}H_{50}BF_4N_2P_4Rh$: C, 64.75; H, 4.54; N, 2.52; P, 11.10. Found: C, 63.57; H, 4.56; N, 2.39; P, 10.81.

$[RhAu(PNP)_2]BF_4NO_3$ (**2**) was prepared by reaction of $[Rh(PNP)_2]BF_4$ with 2 equiv of $Au(PPh_3)NO_3$ in methylene chloride solution. The initial yellow solution immediately changed to orange-red upon addition of the $Au(PPh_3)NO_3$. Precipitation with diethyl ether gave an orange-red product: yield 82%; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 76.02 (d of sym 4-line mult separated by ca. 162 Hz, Int = 1), 60.29 (sym 4-line mult, Int = 1); IR ν(Pyr–CN) = 1600 cm^{-1}, $\nu(BF_4^-)$ = 1090 cm^{-1} (br), $\nu(NO_3^-)$ = 1335 cm^{-1} (br sh). Anal. Calcd for $C_{60}H_{50}BF_4N_3O_3P_4RhAu$: C, 52.54; H, 3.67; N, 3.06. Found: C, 51.71; H, 4.08; N, 3.37. The presence of both a BF_4 and a NO_3 anion was confirmed by the X-ray analysis (vide infra).

X-ray Structure Determination. Crystals of **2** suitable for X-ray analysis were obtained by slow solvent diffusion using an acetone and diethyl ether mixture. In this case, **2** crystallized as an acetone solvate.

Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data is presented in Table I. A crystal of **2** was secured to the end of a glass fiber with 5-min epoxy resin. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs.[15] The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and a decay of 10% was noted. A linear decay correction was applied such that the minimum, maximum, and average corrections were 1.00, 1.05, and 1.03. The data were corrected for Lorentz, polarization, and background effects. The effects of absorption were included using the empirical absorption program EAC (ψ-scan data).[15]

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The metal atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference-Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,[16] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers[17] values of $\Delta f'$ and $\Delta f''$. The final difference-Fourier map did not reveal significant residual electron density. The largest peak was 0.9 e/Å^3 and was located ca. 1 Å from the Au atom. Two nonequivalent $[RhAu(PNP)_2]BF_4NO_3$ molecules were found in the asymmetric unit along with one acetone solvate molecule. The two

Table I. Summary of Crystal Data and Intensity Collection for Compound 2

Crystal Parameters	
cryst syst	monoclinic
space gp	$P2_1/c$ (No. 14)
cryst dimens, mm^3	0.2 × 0.15 × 0.3
cell parameters	
a, Å	26.871 (8)
b, Å	19.693 (3)
c, Å	22.47 (1)
β, deg	98.52 (2)
V, Å^3	11760
Z	8
d(calcd), g cm^{-1}	1.582
abs coeff, cm^{-3}	29.30
max, min, av transmissn factors	1.0, 0.70, 0.92
formula	$C_{60}H_{50}BF_4N_3O_3P_4AuRh\cdot{}^1/_2C_3H_6O$
fw	1400.70
Measurement of Intensity Data	
diffractometer	CAD 4
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å) graphite monochromatized
scan type; range in 2θ, deg	ω–2θ; 0–40
no. of unique reflcns measd (region)	10 952 ($+h, +k, \pm l$)
no. of obsd reflcns[a]	5034 [$F_o^2 \geqslant 2\sigma(F_o^2)$]
refinement by full-matrix least squares	
no. of parameters	694
R[b]	0.062
R_w[b]	0.066
GOF[b]	1.53
p[a]	0.04

[a] The intensity data were processed as described in: "CAD4 and SDP-PLUS User's Manual"; B. A. Frenz & Associates, Inc., College Station, TX, 1982. The net intensity $I = [K/\mathrm{NPI})](C - 2B)$, where K = 20.1166(attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/\mathrm{NPI}))^2[C + 4B + (pI)^2]$ where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. the $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2[\sigma(I)/I]F_o$. [b] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o|)^2]^{1/2}$. The error in an observation of unit weight (GOF) is $[\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

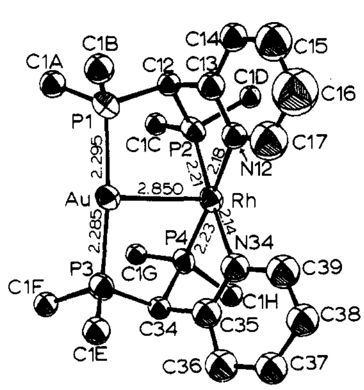

Figure 1. ORTEP view of one of the dications of $[RhAu(PNP)_2]^{2+}$. The other dication has the same stereochemistry and labeling scheme except that primed atom names are used. The phenyl rings have been omitted for clarity, and 50% probability boundaries have been used.

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Table II. Table of Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Au	−0.12294 (4)	0.21576 (6)	0.26840 (5)	3.43 (3)	Au′	0.38331 (4)	0.20786 (6)	0.17819 (5)	3.16 (2)
Rh	−0.15291 (8)	0.1529 (1)	0.37168 (9)	3.24 (5)	Rh′	0.36430 (8)	0.1234 (1)	0.07391 (9)	3.00 (5)
P1	−0.0684 (3)	0.2858 (4)	0.3281 (3)	3.7 (2)	P1′	0.4321 (3)	0.2809 (4)	0.1310 (3)	2.9 (2)
P2	−0.0770 (3)	0.1693 (4)	0.4224 (3)	3.6 (2)	P2′	0.4361 (3)	0.1548 (4)	0.0448 (3)	3.4 (2)
P3	−0.1654 (3)	0.1354 (4)	0.2074 (3)	3.8 (2)	P3′	0.3474 (3)	0.1264 (4)	0.2327 (3)	3.3 (2)
P4	−0.1468 (3)	0.0535 (4)	0.3261 (3)	3.3 (2)	P4′	0.3825 (3)	0.0357 (4)	0.1354 (3)	2.9 (2)
N12	−0.1589 (7)	0.254 (1)	0.4085 (9)	3.2 (5)*	N12′	0.3441 (7)	0.223 (1)	0.0270 (8)	3.2 (5)*
N34	−0.2286 (8)	0.139 (1)	0.3279 (9)	4.3 (5)*	N34′	0.2922 (7)	0.089 (1)	0.0853 (8)	3.1 (5)*
C12	−0.0681 (9)	0.260 (1)	0.409 (1)	2.8 (6)*	C12′	0.4333 (9)	0.253 (1)	0.052 (1)	3.4 (6)*
C13	−0.1159 (9)	0.289 (1)	0.425 (1)	3.7 (6)*	C13′	0.3811 (8)	0.264 (1)	0.0185 (9)	1.9 (5)*
C14	−0.1152 (9)	0.348 (1)	0.461 (1)	3.8 (6)*	C14′	0.376 (1)	0.317 (1)	−0.021 (1)	3.7 (6)*
C15	−0.159 (1)	0.373 (2)	0.472 (1)	6.5 (8)*	C15′	0.326 (1)	0.331 (1)	−0.050 (1)	5.7 (8)*
C16	−0.204 (1)	0.345 (2)	0.452 (2)	10 (1)*	C16′	0.287 (1)	0.291 (2)	−0.034 (1)	5.7 (7)*
C17	−0.202 (1)	0.285 (2)	0.414 (1)	6.9 (8)*	C17′	0.295 (1)	0.236 (1)	0.005 (1)	4.6 (7)*
C34	−0.1877 (9)	0.069 (1)	0.255 (1)	2.7 (6)*	C34′	0.3334 (9)	0.050 (1)	0.186 (1)	3.1 (6)*
C35	−0.237 (1)	0.100 (1)	0.277 (1)	4.4 (7)*	C35′	0.287 (1)	0.056 (1)	0.141 (1)	4.1 (7)*
C36	−0.286 (1)	0.081 (1)	0.246 (1)	5.4 (8)*	C36′	0.241 (1)	0.026 (1)	0.148 (1)	5.0 (7)*
C37	−0.327 (1)	0.105 (1)	0.274 (1)	4.9 (7)*	C37′	0.201 (1)	0.029 (1)	0.100 (1)	5.1 (7)*
C38	−0.320 (1)	0.146 (1)	0.327 (1)	5.0 (7)*	C38′	0.207 (1)	0.060 (2)	0.046 (1)	5.8 (8)*
C39	−0.270 (1)	0.160 (2)	0.353 (1)	5.5 (8)*	C39′	0.254 (1)	0.088 (1)	0.041 (1)	4.0 (7)*
C1A	−0.0051 (9)	0.276 (1)	0.312 (1)	3.6 (6)*	C1A′	0.4077 (9)	0.367 (1)	0.117 (1)	3.2 (6)*
C2A	0.037 (1)	0.314 (1)	0.344 (1)	5.8 (8)*	C2A′	0.367 (1)	0.388 (1)	0.144 (1)	4.9 (7)*
C3A	0.086 (1)	0.309 (2)	0.326 (1)	6.1 (8)*	C3A′	0.346 (1)	0.455 (1)	0.132 (1)	4.7 (7)*
C4A	0.089 (1)	0.265 (2)	0.276 (1)	6.6 (9)*	C4A′	0.370 (1)	0.495 (1)	0.099 (1)	5.0 (7)*
C5A	0.051 (1)	0.227 (2)	0.247 (1)	6.2 (8)*	C5A′	0.412 (1)	0.480 (1)	0.069 (1)	5.6 (8)*
C6A	0.001 (1)	0.234 (1)	0.262 (1)	4.9 (7)*	C6A′	0.432 (1)	0.411 (1)	0.083 (1)	4.1 (7)*
C1B	−0.0839 (9)	0.372 (1)	0.320 (1)	4.0 (7)*	C1B′	0.4950 (8)	0.288 (1)	0.169 (1)	3.1 (6)*
C2B	−0.123 (1)	0.394 (1)	0.279 (1)	4.0 (6)*	C2B′	0.5064 (9)	0.260 (1)	0.225 (1)	3.5 (6)*
C3B	−0.1348 (9)	0.464 (1)	0.266 (1)	3.5 (6)*	C3B′	0.556 (1)	0.261 (1)	0.257 (1)	4.1 (7)*
C4B	−0.107 (1)	0.515 (2)	0.307 (1)	5.8 (8)*	C4B′	0.595 (1)	0.294 (1)	0.231 (1)	5.2 (7)*
C5B	−0.070 (1)	0.496 (2)	0.353 (1)	5.9 (8)*	C5B′	0.586 (1)	0.326 (2)	0.176 (1)	5.8 (8)*
C6B	−0.058 (1)	0.425 (1)	0.361 (1)	4.7 (7)*	C6B′	0.533 (1)	0.323 (1)	0.143 (1)	4.5 (7)*
C1C	−0.0184 (9)	0.124 (1)	0.419 (1)	2.8 (6)*	C1C′	0.4300 (8)	0.152 (1)	−0.037 (1)	2.5 (5)*
C2C	0.0265 (9)	0.154 (1)	0.413 (1)	3.7 (6)*	C2C′	0.386 (1)	0.130 (1)	−0.075 (1)	4.3 (7)*
C3C	0.073 (1)	0.122 (1)	0.412 (1)	5.4 (8)*	C3C′	0.381 (1)	0.134 (1)	−0.138 (1)	5.0 (7)*
C4C	0.073 (1)	0.048 (2)	0.421 (2)	8 (1)*	C4C′	0.424 (1)	0.153 (1)	−0.165 (1)	5.2 (7)*
C5C	0.026 (1)	0.018 (2)	0.426 (1)	6.1 (8)*	C5C′	0.469 (1)	0.171 (1)	−0.130 (1)	5.1 (7)*
C6C	−0.020 (1)	0.054 (1)	0.429 (1)	4.1 (7)*	C6C′	0.474 (1)	0.171 (1)	−0.062 (1)	4.3 (7)*
C1D	−0.0782 (9)	0.170 (1)	0.504 (1)	2.7 (6)*	C1D′	0.4992 (8)	0.123 (1)	0.0707 (9)	1.5 (5)*
C2D	−0.120 (1)	0.146 (1)	0.527 (1)	4.6 (7)*	C2D′	0.5405 (9)	0.162 (1)	0.092 (1)	3.6 (6)*
C3D	−0.119 (1)	0.147 (2)	0.591 (1)	7.1 (9)*	C3D′	0.588 (1)	0.133 (1)	0.114 (1)	5.0 (7)*
C4D	−0.077 (1)	0.170 (1)	0.628 (1)	5.0 (7)*	C4D′	0.591 (1)	0.063 (1)	0.112 (1)	4.9 (7)*
C5D	−0.037 (1)	0.196 (1)	0.607 (1)	5.7 (8)*	C5D′	0.5503 (9)	0.020 (1)	0.093 (1)	3.7 (6)*
C6D	−0.035 (1)	0.196 (1)	0.540 (1)	5.8 (8)*	C6D′	0.502 (1)	0.053 (1)	0.072 (1)	3.9 (7)*
C1E	−0.2200 (9)	0.164 (1)	0.156 (1)	3.6 (6)*	C1E′	0.2915 (9)	0.147 (1)	0.263 (1)	3.3 (6)*
C2E	−0.240 (1)	0.229 (2)	0.167 (1)	6.7 (9)*	C2E′	0.265 (1)	0.094 (1)	0.287 (1)	5.4 (8)*
C3E	−0.284 (1)	0.250 (2)	0.129 (1)	6.1 (8)*	C3E′	0.219 (1)	0.116 (1)	0.318 (1)	5.1 (7)*
C4E	−0.304 (1)	0.207 (2)	0.080 (1)	7.6 (9)*	C4E′	0.209 (1)	0.184 (2)	0.319 (1)	6.4 (9)*
C5E	−0.285 (1)	0.144 (2)	0.070 (1)	7.2 (9)*	C5E′	0.234 (1)	0.235 (2)	0.298 (1)	6.5 (9)*
C6E	−0.243 (1)	0.120 (2)	0.109 (1)	6.4 (8)*	C6E′	0.276 (1)	0.216 (1)	0.264 (1)	5.1 (7)*
C1F	−0.1242 (9)	0.090 (1)	0.161 (1)	3.2 (6)*	C1F′	0.3887 (9)	0.101 (1)	0.298 (1)	3.0 (6)*
C2F	−0.131 (1)	0.021 (1)	0.146 (1)	5.6 (8)*	C2F′	0.4225 (9)	0.149 (1)	0.325 (1)	3.8 (6)*
C3F	−0.100 (1)	−0.007 (1)	0.110 (1)	5.3 (8)*	C3F′	0.457 (1)	0.133 (1)	0.378 (1)	4.9 (7)*
C4F	−0.064 (1)	0.035 (1)	0.085 (1)	4.4 (7)*	C4F′	0.458 (1)	0.070 (2)	0.402 (1)	5.9 (8)*
C5F	−0.055 (1)	0.102 (1)	0.101 (1)	5.2 (8)*	C5F′	0.423 (1)	0.017 (2)	0.373 (1)	6.0 (8)*
C6F	−0.0900 (9)	0.131 (1)	0.136 (1)	3.4 (6)*	C6F′	0.389 (1)	0.034 (1)	0.320 (1)	4.3 (7)*
C1G	−0.0906 (9)	0.019 (1)	0.306 (1)	2.7 (6)*	C1G′	0.4412 (8)	0.023 (1)	0.1874 (9)	1.8 (5)*
C2G	−0.054 (1)	0.062 (1)	0.287 (1)	4.0 (7)*	C2G′	0.452 (1)	−0.040 (1)	0.210 (1)	4.2 (7)*
C3G	−0.010 (1)	0.036 (1)	0.268 (1)	4.5 (7)*	C3G′	0.498 (1)	−0.047 (1)	0.246 (1)	4.7 (7)*
C4G	−0.000 (1)	−0.035 (1)	0.269 (1)	4.8 (7)*	C4G′	0.531 (1)	0.010 (1)	0.266 (1)	4.6 (7)*
C5G	−0.037 (1)	−0.076 (1)	0.289 (1)	4.4 (7)*	C5G′	0.517 (1)	0.074 (1)	0.241 (1)	4.0 (7)*
C6G	−0.0824 (9)	−0.054 (1)	0.304 (1)	3.6 (6)*	C6G′	0.4715 (9)	0.081 (1)	0.202 (1)	3.1 (6)*
C1H	−0.1789 (9)	−0.015 (1)	0.356 (1)	3.2 (6)*	C1H′	0.368 (1)	−0.052 (1)	0.105 (1)	4.6 (7)*
C2H	−0.204 (1)	−0.066 (1)	0.322 (1)	4.9 (7)*	C2H′	0.390 (1)	−0.071 (1)	0.060 (1)	3.9 (7)*
C3H	−0.229 (1)	−0.122 (2)	0.348 (1)	7.5 (9)*	C3H′	0.387 (1)	−0.140 (1)	0.041 (1)	4.2 (7)*
C4H	−0.230 (1)	−0.123 (2)	0.406 (2)	8 (1)*	C4H′	0.365 (1)	−0.187 (1)	0.071 (1)	5.1 (8)*
C5H	−0.204 (1)	−0.069 (2)	0.445 (2)	8 (1)*	C5H′	0.341 (1)	−0.167 (1)	0.119 (1)	4.6 (7)*
C6H	−0.178 (1)	−0.014 (2)	0.420 (1)	8 (1)*	C6H′	0.341 (1)	−0.098 (1)	0.138 (1)	4.6 (7)*

[a] Starred values indicate atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$. Primed atoms refer to the second nonequivalent molecule in the asymmetric unit.

nonequivalent molecules were not related by crystallographic symmetry of some higher order unit cell because close examination of long-range contacts showed them to be distinct. The BF_4^- anions showed signs of the usual rotational disorder, but refinement with isotropic thermal parameters gave acceptable distances and angles (supplementary material).[18] The final positional and thermal parameters of the refined atoms of the two dications appear in Table II and as supplementary material.[18]

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(18) See paragraph at end of paper regarding supplementary material.

Table III. Selected Distances and Angles in $[RhAu(\mu\text{-}PNP)_2]^{2+}$

Distances,[a] Å					
Au-Rh	2.850 (2)	2.857 (2)	P1-C12	1.89 (2)	1.86 (2)
Au-P1	2.295 (6)	2.308 (6)	P3-C34	1.84 (2)	1.84 (2)
Au-P3	2.285 (7)	2.313 (6)	P2-C12	1.84 (2)	1.94 (2)
Rh-P2	2.207 (7)	2.214 (7)	P4-C34	1.82 (2)	1.89 (2)
Rh-P4	2.227 (6)	2.221 (6)	N12-C13	1.35 (3)	1.32 (2)
Rh-N12	2.18 (2)	2.26 (2)	N12-C17	1.33 (3)	1.37 (2)
Rh-N34	2.14 (2)	2.10 (2)	N34-C35	1.38 (3)	1.44 (3)
P1-C1A	1.80 (2)	1.83 (2)	N34-C39	1.38 (3)	1.33 (2)
P1-C1B	1.76 (2)	1.79 (2)	C12-C13	1.49 (3)	1.51 (3)
P3-C1E	1.81 (2)	1.79 (3)	C34-C35	1.60 (3)	1.49 (3)
P3-C1F	1.86 (2)	1.77 (2)			
P2-C1C	1.83 (2)	1.83 (2)			
P2-C1D	1.85 (2)	1.82 (2)			
P4-C1G	1.77 (2)	1.84 (2)			
P4-C1H	1.78 (2)	1.87 (2)			

Angles,[a] deg					
P1-Au-P3	170.3 (3)	170.1 (3)	Au-Rh-P2	90.3 (2)	91.3 (2)
P1-Au-Rh	91.0 (2)	91.8 (2)	Au-Rh-P4	87.6 (2)	86.9 (2)
P3-Au-Rh	90.6 (2)	89.6 (2)	Au-Rh-N12	87.5 (3)	83.0 (3)
P2-Rh-N34	176.1 (5)	169.8 (5)	Au-Rh-N34	92.5 (3)	98.2 (3)
P4-Rh-N12	174.9 (6)	169.4 (5)	Au-P1-C12	108.4 (8)	110.0 (8)
P2-Rh-N12	77.5 (7)	77.3 (7)	Au-P3-C34	108.5 (6)	109.6 (6)
P4-Rh-N34	78.9 (6)	78.4 (6)	Rh-P2-C12	101.1 (6)	101.9 (5)
P2-Rh-P4	103.9 (3)	106.3 (3)	Rh-P4-C34	100.2 (7)	98.9 (7)
N12-Rh-N34	99.9 (8)	99.9 (7)	P1-C12-P2	116 (1)	113 (1)
Rh-N12-C13	117.7 (8)	117.7 (8)	P1-C12-C13	104 (2)	107 (2)
Rh-N34-C35	118.8 (8)	117.3 (9)	P3-C34-P4	115 (1)	111 (1)
Rh-N12-C17	124.8 (8)	119.3 (8)	P3-C34-C35	105 (2)	114 (2)
Rh-N34-C39	123.3 (9)	122.8 (8)			

[a] The first and second values refer to unprimed and primed atoms, respectively.

The labeling scheme for one dication of **2** is presented in Figure 1. The other has the same labeling scheme except that primed atom names are used. Tables of observed and calculated structure factor amplitudes are included as supplementary material.[18]

Results and Discussion

$[Rh(PNP)_2]BF_4$ (**1**) has not been previously reported and was synthesized by the reaction of $[Rh(nbd)(PNP)]BF_4$ with PNP ligand. The room-temperature $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2) indicated that all four phosphorus atoms were coordinated to Rh and are equivalent (one doublet resonance at δ 1.06, $J_{Rh-P} = 116$ Hz). The ν(py-CN) stretching frequency (1588 cm^{-1}, KBr disk) in the IR spectrum is consistent with unbound pyridyl N atoms.[11-13] The solution structure of **1** at room temperature is probably that of a $(PNP)_2$-chelated complex with dangling pyridyl groups.[19]

The reaction of $[Rh(PNP)_2]BF_4$ with 2 equiv of $Au(PPh_3)NO_3$ in CH_2Cl_2 solution resulted in the formation of the heterobimetallic complex $[RhAu(PNP)_2]BF_4NO_3$ (**2**). The byproduct of this reaction is $Au(PPh_3)_2NO_3$. The ^{31}P NMR spectrum of **2** (CH_2Cl_2) consisted of two complex multiplets of equal intensity (Experimental Section and included as supplementary material[18]). The IR showed a ν(py-CN) frequency of 1600 cm^{-1}, which indicates that the pyridyl nitrogen atoms are bound.[11-13] These data did not lead to an unambiguous determination of the structure of **2**, and therefore a single-crystal X-ray analysis was undertaken. There have been no previous X-ray structures reported for heterobimetallic PNP complexes. In addition, there is much current interest in the synthesis and structures of mixed-metal gold complexes with phosphine ligands.[9,20-23]

The crystal structure of **2** consisted of two well-separated $[RhAu(PNP)_2]^{2+}$ dications, two BF_4^- and NO_3^- anions, and one acetone solvate molecule in the asymmetric unit. The molecular structure of one of the dications is shown in the figure. The other dication has the same overall stereochemistry as the one shown in the figure and has the same labeling scheme except that primed atom names have been used. Selected distances and angles for both dications are shown in Table III and as supplementary material.[18]

The gold and the rhodium atoms are bridged by two PNP ligands such that the coordination geometry around the gold is T shaped ($\mathit{Au}\mathrm{RhP}_2$) while that around the rhodium is square-pyramidal ($\mathit{Rh}\mathrm{AuP}_2\mathrm{N}_2$), with the gold atom occupying the axial position. The phosphorus atoms are arranged cis around the rhodium atom and trans around gold, and therefore this structure represents a rare example of a *trans,cis*-bis(phosphine)-bridged binuclear complex.[13,24] The angles around the metal atoms within the coordination cores have values that are close to those of the idealized geometries. Around gold, the P1-Au-P3 angle is 170.3 (3)° and the Rh-Au-P1 and Rh-Au-P3 angles are 91.0 (2) and 90.6 (2)°, respectively. The corresponding values for the primed dication are the same within experimental error. Around rhodium, the atoms P2, P4, N12, and N34 form a nearly planar arrangement (maximum displacement from the least-squares plane is 0.14 Å), and the Rh atom is displaced only 0.02 Å from this plane. The Au-Rh vector is orthogonal to this plane (Au-Rh-P2, -P4, -N12, and -N34 angles are 90.3 (2), 87.6 (2), 87.5 (3), and 92.5 (3)°, respectively. Within the square plane around the Rh atom the angles deviate from their idealized values of 90° because the chelated five-membered ring "bite" angles P2-Rh-N12 and P4-Rh-N34 are constrained and thus small (77.5 (7) and 78.9 (6)°,

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(19) The low-temperature ^{31}P NMR spectra of **1** showed that the solution structure is more complex. The doublet resonance broadened and shifted significantly as the temperature was lowered. The doublet resonance became sharp again at about -90 °C, but it was shifted 6.7 ppm to higher field (δ -5.6 (d, $J = 116$ Hz)). This behavior is unusual and probably results from the presence of a five-coordinate N-bonded isomer that becomes thermodynamically favored at low temperature and exchanges with the four-coordinate isomer at a rate similar to the NMR time scale.

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respectively) while the P2–Rh–P4 and N12–Rh–N34 angles are opened to 103.9 (3) and 99.9 (8)°, respectively. The primed dication shows larger deviations from idealized square-pyramidal geometry around Rh′ (Table III and least-squares planes included as supplementary material[18]). This is not considered important and probably results from a difference in packing.

The two PNP ligands bridge the metal atoms, but the four P atoms are not coplanar as is commonly found in bis(phosphine)-bridged binuclear compounds.[12,24] The torsion angles P1–Au–Rh–P2 and P3–Au–Rh–P4 are −37 and 35°, respectively. The structure of **2** is very similar to that of $[Rh_2(CO)(\mu\text{-PNP})_2]^{2+}$ (**3**)[13] with the axial CO ligand removed. The corresponding torsion angles in **3** (P2–Rh1–Rh2–P3 and P1–Rh1–Rh2–P4) are −36 and 35°, respectively. The Au–P distances in **2** (average 2.300 (6) Å) are similar to values found in other gold–phosphine and mixed iridium–gold–phosphine clusters.[20-22] The Rh–P distances (average 2.217 (6) Å), which are trans to nitrogen atoms, are similar to values found in **3**.[13] The Rh–N bond distances in **2** (average 2.17 (2) Å) are similar to values found in **3** (2.15 (1) Å),[13] in $[Rh(nbd)PNP)]PF_6$ (2.15 Å),[11] and in $[Rh_2(CO)_2(\mu\text{-PNP})_2](PF_6)_2$ (2.19 Å).[12]

The average Au–Rh distance in **2** is 2.854 (2) Å. Since this is the first Rh–Au phosphine complex characterized by X-ray analysis, this distance cannot be compared to those in other similar compounds. However, several Ir–Au phosphine clusters have recently been subjected to X-ray analysis. In all of these compounds the Au–Ir distances are significantly shorter than the Au–Rh distance in **2**: $[(dppe)_2IrAuPPh_3](BF_4)_2$, 2.625 (1) Å;[25] $[(PPh_3)_3H_2Ir(\mu\text{-H})AuPPh_3]BF_4$, 2.765 (1) Å;[22] $[IrAu_2H(PPh_3)_4NO_3]BF_4$, 2.685 (1) Å.[21] The long distance in **2** is probably a result of the bridging PNP ligand.

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Registry No. **1**, 95936-60-0; **2**, 95936-62-2; $\mathbf{2}\cdot{}^1/_2C_3H_6O$, 95936-63-3; $[Rh(nbd)(PNP)]BF_4$, 86436-86-4; $Au(PPh_3)NO_3$, 14897-32-6; Au, 7440-57-5; Rh, 7440-16-6.

Supplementary Material Available: ^{31}P NMR spectrum of **2** and tables of positional and thermal parameters, least-squares planes, distances and angles, and observed and calculated structure factor amplitudes for **2** (45 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Magnetic Properties of the Linear-Chain Organic-Intercalated Chromium(II) Compound Tetramethylammonium Tribromochromate(II), $[(CH_3)_4N]CrBr_3$

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There has been a great deal of interest in the last few years in one-dimensional, 1D, transition-metal complexes, from both theoretical and experimental points of view, because they exhibit several unusual physical and chemical properties.[1,2]

In this context, the synthesis of new materials having quasi-1D physical properties appears to be an important challenge for a chemist.

Recently, we have synthesized and studied a series of two-dimensional ferromagnetic insulators of Cr(II), having general formula $(RNH_3)_2CrCl_4$, R = alkyl, whose structures are based on the tetragonal K_2NiF_4 lattice.[3,4] One of the salient chemical features of these Cr(II) compounds is that, when the bulkiness of the cation is increased, i.e. from the linear amine hydrochloride, RNH_3Cl, to the tetrahedral tetraalkylammonium chloride, R_4NCl, it is possible to obtain 1D Cr(II) compounds, having formula $[R_4N]CrCl_3$, where chains of Cr(II) octahedra, having faces in common, are present. Quite recently, in fact, we have described the synthesis, the crystal structure, and the magnetic properties of the first term of the series: tetramethylammonium trichlorochromate(II), $[(CH_3)_4N]CrCl_3$,[5] and we found that the compound shows 1D magnetic behavior and the crystal structure consists of linear chains of Cr(II) atoms bridged by three chloride ions.

In order to obtain more complete information on the physical properties of the series, we have carried out the synthesis of the corresponding bromide derivative. This note deals with the synthesis and the low-temperature magnetic behavior of tetramethylammonium tribromochromate(II), which shows antiferromagnetic exchange interactions.

Experimental Section

Tetramethylammonium bromide (BDH Chemical Ltd.) was used as supplied. Since the title compound is hygroscopic and very easily oxidized, the preparation and sample handling were carried out under nitrogen.[6]

Synthesis of $[(CH_3)_4N]CrBr_3$. Finely divided electrolytic chromium metal (0.647 g, 12.4 mmol) was placed in a three-necked 250-mL flask containing a Teflon-coated stirrer bar with 30 mL of glacial acetic acid, and nitrogen gas was bubbled for 20 min through the solvent. The chromium metal was completely dissolved by passing HBr gas under reflux, through the solvent, until a deep blue solution was obtained. The HBr addition was stopped, and a solution of $(CH_3)_4NBr$ (1.90 g, 12.4 mmol) in 50 mL of glacial acetic acid, degassed previously, was added dropwise to the Cr(II) solution. Immediately, a yellow crystalline product separated. The complex was then filtered and dried under vacuum with a Schlenk filtration apparatus.

The elemental analysis was performed by A. Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany, and by Laboratorio Microanalisi, CNR, Area della Ricerca di Roma.

Anal. Calcd for $C_4H_{12}NCrBr_3$: C, 13.13; H, 3.30; N, 3.83; Cr, 14.21; Br, 65.52. Found: C, 13.07; H, 3.15; N, 3.85; Cr, 14.15; Br, 65.30.

X-ray Powder Diffraction. The polycrystalline sample was sealed under nitrogen in a Lindemann tube, i.d. 0.3 mm, and diffraction patterns were collected with a Philips Debye-Scherrer camera (Ni-filtered Cu Kα radiation).

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements in the temperature range 1.8–297 K were determined by using the Faraday apparatus described elsewhere.[7] The polycrystalline sample was placed inside a quartz sphere, sealed under nitrogen with a drop of "Durofix" glue, and suspended by a fine silica wire from a Sartorius electronic vacuum microbalance. The magnetic field and the gradient were supplied by two superconducting solenoids. The magnetization measurements were made at field strengths up to 7 T. Temperature measurements were based on a calibrated Au, 0.03% atomic Fe vs. chromel thermocouple and gallium arsenide diodes. Temperatures below 4.2 K were achieved by pumping on the liquid He in the inner Dewar of the Faraday balance.

Electronic Spectra. Near-infrared and visible spectra were taken on a Beckman DK 2A recording spectrophotometer. Powdered samples

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