Notes

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Reactions of Carbon Monoxide with (Nitrato)(triphenylphosphine)gold(I). Crystal Structures of (Isocyanato)(triphenylphosphine)gold(I) ($AuC_{19}H_{15}NOP$) and (Fulminato)(triphenylphosphine)gold(I) ($AuC_{19}H_{15}NOP$)

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In an earlier paper[2] we described the synthesis of (fulminato)(triphenylphosphine)gold(I) ($AuPPh_3CNO$). This product was obtained by reacting $AuPPh_3NO_3$ with carbon monoxide in CH_2Cl_2 solution. It was shown that the fulminate ligand was most probably formed by a rather complicated reaction initiated by a two-step reduction of $AuPPh_3NO_3$ via $AuPPh_3NO_2$ to $AuPPh_3NO$ by carbon monoxide (see Scheme I). The nitrosyl compound, acting as a chloride scavenger, exchanges NO for Cl with CH_2Cl_2 obtaining formoxime a after rearrangement. Loss of HCl from compound a results in the formation of HCNO, which can react with starting material, yielding $AuPPh_3CNO$. In labeling experiments it was proven that the carbon in the fulminate did not originate from carbon monoxide but from methylene chloride.

In another experiment, the reaction of carbon monoxide with solid $AuPPh_3NO_3$ in the absence of solvent, a brown paramagnetic solid was obtained.[2] We now report that careful examination of this solid revealed the presence of a small quantity of $AuPPh_3NCO$. The two final compounds, $AuPPh_3NCO$ and $AuPPh_3CNO$, were characterized by two X-ray crystal structure analyses presented in this paper.

Experimental Section

Preparations and physical data of $AuPPh_3NCO$ and $AuPPh_3CNO$ were presented in an earlier paper.[2]

Scheme I

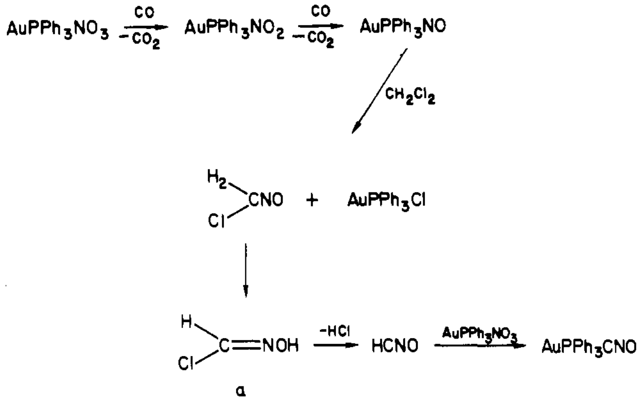

Table I. Summary of Crystal and Intensity Collection Data

compd	$AuPPh_3NCO$	$AuPPh_3CNO$
temp, K	298	298
appearance	colorless rectangular	colorless rectangular
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
cryst dimens, mm^3	0.47 × 0.12 × 0.17	0.50 × 0.14 × 0.22
cell params		
a, Å	10.782 (1)	10.891 (1)
b, Å	12.007 (1)	12.169 (1)
c, Å	13.077 (1)	12.871 (1)
V, Å^3	1682.9	1705.7
Z	4	4
d(calcd), g cm^{-3}	1.97	1.95
μ, cm^{-1}	89.9	89.8
formula	$AuC_{19}H_{15}NOP$	$AuC_{19}H_{15}NOP$
$F(000)$	952	952
F_w	501.27	501.27
diffractometer	Nonius CAD4	Nonius CAD4
radiation[a]	Mo Kα	Mo Kα
wavelength, Å	0.71069	0.71069
scan type	ω–2θ	ω–2θ
range in 2θ, deg	0–70	0–60
no. of reflcns collcd	16015	10399
data collcd	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
empirical abs cor[b]		
range cor factors	0.72–1.00	0.87–1.00
no. of obsd reflcns[c]	4473	2743
Bijvoet coeff	+0.99 (2)	−0.98 (2)
no. of Friedel pairs	843	498
empirical abs cor[d]		
range cor factors	0.69–1.14	0.66–1.12
no. of paras	253	67
R[e]	0.032	0.043
R_w	0.037	0.050

[a] Graphite monochromator. [b] Reference 5. [c] Space group symmetry-equivalent reflections were averaged, $R_{int} = \sum(I - \langle I\rangle)/\sum I = 0.044$ (I), 0.015 (II), respectively, resulting in 7442 (I) and 4959 (II) unique reflections, respectively, of which 4473 (I) and 2743 (II), respectively, were observed with $I > 3\sigma(I)$. [d] Reference 9. [e] The function minimized was $\sum w(F_o - F_c)$ with, in both cases, $w = (\sigma(F_o) + 0.0004F_o^2)^{-1}$ with $\sigma(F_o)$ from counting statistics.

Procedure for the Reaction of $AuPPh_3NO_3$ with CO and without Solvent. In a typical experiment 200 mg of powdered $AuPPh_3NO_3$ was placed under 8 atm of carbon monoxide pressure for 2 weeks. The white starting material turned brown slowly (visible after $^1/_2$ h), ending up dark brown after 2 weeks. The resulting solid was extracted twice with about 400 mL of diisopropyl ether, and the extract was then filtered over a silica gel column, absorbing all excess $AuPPh_3NO_3$. After evaporation, about 5 mg of a white solid remained, consisting of $AuPPh_3Cl$ and

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(1) Gladfelter, W. L. In *Organometallic Compounds: Synthesis, Structure and Theory*; Shapiro, B. L., Ed.; Texas A&M University: College Station, TX, 1983; p 281.
(2) Bos, W.; Bour, J. J.; Steggerda, J. J.; Pignolet, L. H. *Inorg. Chem.* **1985**, *24*, 4298.
(3) Lehman, M. S.; Larsen, F. K.; *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Gen. Theor. Crystallogr.* **1974**, *A30*, 580.
(4) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.*. **1978**, *11*, 114.
(5) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Gen. Theor. Crystallogr.* **1968**, *A24*, 351.
(6) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Van den Hark, T.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Gould, R. O.; Parthasarathi, V. *Conformation in Biology*; Srinivasan, R.; Sarma, R. H., Eds.; Adenine: New York, 1982; p 389.
(7) Sheldrick, G. M., *SHELX, ,A Program for Crystal Structure Determination*; University Chemical Laboratory: Cambridge, England, 1976.
(8) *International Tables for X-ray Crystallography* Kynoch: Birmingham, England, 1974; Vol. IV.
(9) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.
(10) Beurskens, G.; Noordik, J. H.; Beurskens, P. T. *Cryst. Struct. Commun.* **1980**, *9*, 23.
(11) Motherwell, W. D. S., *PLUTO, A Program for Plotting Molecular and Crystal Structures*, University Chemical Laboratory: Cambridge, England, 1976.
(12) Aarflot, K.; Ase, K. *Acta Chem. Scand., Ser. A.*, **1974**, *A28*, 137.
(13) Maresca, L.; Natile, G.; Marotti-Lanfredi, A. M.; Tiripicchio,A. *J. Am. Chem. Soc* **1982**, *104*, 7661.
(14) Nagel, U.; Peters, K.; von Schnering, H. G.; Beck, W. *J. Organomet. Chem.* **1980**, *185*, 427.
(15) Britton, D.; Dunitz, J. D. *Acta Crystallogr.* **1965**, *19*, 662.
(16) Rosenzweig, A.; Cromer, D. T. *Acta Crystallogr.* **1959**, *12*, 709.
(17) Bunker, P. R.; Landsberg, B. M.; Winnewisser, B. P. *J. Mol. Spectrosc.* **1979**, *74*, 9.
(18) Barrick, J. C.; Canfield, D.; Giessen, B. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 464.

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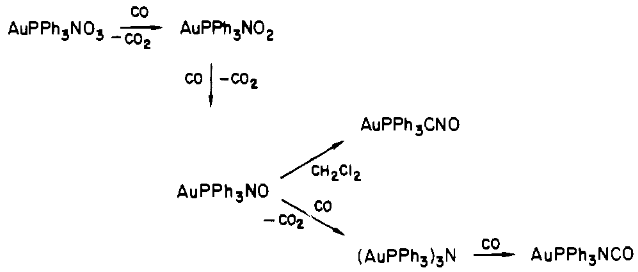
Scheme II



$AuPPh_3NCO$ according to the infrared spectrum. $AuPPh_3Cl$ was found to be a minor impurity in the starting material. The product could be purified by recrystallization from CH_2Cl_2/hexane; however, a completely pure isocyanate could not be obtained.

Identification of $AuPPh_3NCO$. IR (CsI pellet): 2204 (br, vs), 2146 cm^{-1} (sharp, s); 385 cm^{-1} (br, m); all characteristic for $AuPPh_3NCO$.[2,19,20] Peak matching of the parent mass peak: calcd *m/e* 501.054; found *m/e* 501.056.

X-ray Structure Determinations

Suitable crystals of the isocyanato compound (I) and of the isomeric and isomorphous fulminato compound (II) were obtained by slow diffusion of hexane into a methylene chloride solution.[2]

Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data is presented in Table I. The intensity of the primary beam was checked throughout the data collections by monitoring three reference reflections every 30 min. A random variation in the intensities of 3% for I and a decline in the intensities of 68% for II occurred over the course of the data collection. Smooth curves based on the reference reflections were used to correct for this drift. The reliability of the correction for II was proved by the subsequent averaging of symmetry-equivalent reflections and the result of the structure determination. On all reflections profile analysis was performed;[3,4] an empirical absorption correction was applied by using ψ scans,[5] Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|$ values.

Solution and Refinement of the Structure. For each structure the gold atom was found from the Patterson synthesis. The non-hydrogen atoms were found with DIRDIF.[6] The structures were refined by full-matrix least-squares on $|F|$ values by using SHELX.[7] Scattering factors were taken from ref 8, and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers[8] values of $\nabla f'$ and $\nabla f''$. Hydrogen atoms were found in the difference Fourier maps and were included. After completion of the isotropic refinement, empirical absorption corrections based on F_o–F_c differences were applied[9] and the Bijvoet coefficients were calculated.[10] The absolute structure for I was found to be correct. The structure for II had a negative Bijvoet coefficient and therefore was inverted before continuing the refinement. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined; the phenyl hydrogens of I were refined in riding mode (C–H = 1.08 Å), and the phenyl groups of II were refined as rigid groups with standard geometry (C–C = 1.40 Å; C–H = 1.08 Å). The hydrogen atoms had fixed isotropic temperature factors of 0.05 Å^2. In each case the final difference Fourier map showed no peaks higher than 2.0 e/Å^3 around the gold atom. Plots were made with PLUTO.[11]

Discussion

The discovery of $AuPPh_3NCO$ as product of the reaction of solid $AuPPh_3NO_3$ with carbon monoxide in the absence of solvent is interesting, as in methylene chloride solution it is completely absent, so its formation by isomerization of the fulminate can be excluded. In the absence of CH_2Cl_2 a further reduction of the $AuPPh_3NO$ may take place, yielding a nitrido compound, which upon addition of carbon monoxide leads to the formation of $AuPPh_3NCO$ (Scheme II).

Isocyanates of ruthenium carbonyl clusters have been reported[1] from a reaction of nitrosyls with CO with nitrido as intermediate. We think that such a route is also operative here. The fact that $AuPPh_3NCO$ is found in only small quantities is probably due to the unfavorable reaction conditions. Increase of the carbon monoxide pressure and longer reaction times served to increase the yield.

Table II. Fractional Positional and Thermal Parameters (with Esd's)

atom	*x*	*y*	*z*	$100U_{eq}$, Å^2
		a. $AuPPh_3NCO$		
Au1	0.35397 (2)	0.44786 (2)	0.24246 (2)	4.34 (1)
P1	0.54131 (12)	0.38430 (10)	0.28241 (10)	3.80 (4)
N1	0.1844 (5)	0.5041 (5)	0.2060 (5)	6.45 (20)
C1	0.0847 (6)	0.4754 (6)	0.1908 (5)	5.18 (20)
O1	−0.0200 (5)	0.4496 (6)	0.1749 (5)	9.41 (25)
C11	0.6074 (5)	0.2951 (4)	0.1848 (4)	3.88 (14)
C12	0.5305 (6)	0.2336 (5)	0.1238 (4)	4.86 (18)
C13	0.5776 (7)	0.1607 (6)	0.0513 (5)	5.60 (22)
C14	0.7034 (8)	0.1520 (6)	0.0394 (5)	6.28 (24)
C15	0.7816 (7)	0.2137 (7)	0.0986 (6)	6.26 (24)
C16	0.7359 (6)	0.2902 (6)	0.1714 (5)	5.13 (19)
C21	0.5384 (5)	0.3007 (4)	0.3975 (4)	4.00 (15)
C22	0.4589 (7)	0.3312 (6)	0.4757 (5)	5.94 (21)
C23	0.4520 (8)	0.2658 (7)	0.5637 (5)	6.84 (25)
C24	0.5201 (7)	0.1723 (6)	0.5725 (5)	6.26 (23)
C25	0.5994 (7)	0.1425 (6)	0.4946 (6)	6.80 (27)
C26	0.6080 (6)	0.2058 (6)	0.4064 (5)	5.29 (20)
C31	0.6552 (5)	0.4928 (4)	0.3010 (4)	4.06 (14)
C32	0.6726 (5)	0.5662 (5)	0.2203 (5)	5.23 (18)
C33	0.7611 (6)	0.6509 (5)	0.2298 (6)	6.35 (22)
C34	0.8284 (6)	0.6617 (6)	0.3168 (7)	6.60 (24)
C35	0.8112 (7)	0.5896 (6)	0.3962 (6)	6.92 (26)
C36	0.7232 (6)	0.5044 (6)	0.3893 (5)	5.60 (20)
		b. $AuPPh_3CNO$		
Au1	0.35367 (4)	0.43684 (3)	0.24220 (3)	5.02 (1)
P1	0.5456 (3)	0.3798 (2)	0.2861 (2)	4.48 (8)
C11	0.5387 (8)	0.2985 (5)	0.4046 (5)	4.3 (2)
C12	0.6056 (8)	0.2013 (5)	0.4127 (5)	6.9 (3)
C13	0.5939 (8)	0.1375 (5)	0.5021 (5)	8.5 (4)
C14	0.5152 (8)	0.1707 (5)	0.5817 (5)	6.9 (4)
C15	0.4483 (8)	0.2678 (5)	0.5718 (5)	8.1 (4)
C16	0.4601 (8)	0.3317 (5)	0.4824 (5)	7.4 (4)
C21	0.6158 (6)	0.2943 (5)	0.1890 (4)	4.2 (2)
C22	0.5411 (6)	0.2288 (5)	0.1263 (4)	5.6 (3)
C23	0.5938 (6)	0.1571 (5)	0.0545 (4)	5.6 (3)
C24	0.7212 (6)	0.1507 (5)	0.0455 (4)	6.3 (3)
C25	0.7959 (6)	0.2159 (5)	0.1082 (4)	6.8 (3)
C26	0.7431 (6)	0.2877 (5)	0.1799 (4)	5.5 (3)
C31	0.6542 (7)	0.4889 (5)	0.3066 (5)	4.5 (2)
C32	0.6714 (7)	0.5609 (5)	0.2235 (5)	5.5 (2)
C33	0.7544 (7)	0.6477 (5)	0.2325 (5)	5.7 (3)
C34	0.8198 (7)	0.6627 (5)	0.3245 (5)	7.6 (4)
C35	0.8025 (7)	0.5908 (5)	0.4076 (5)	7.7 (4)
C36	0.7197 (7)	0.5039 (5)	0.3986 (5)	6.0 (3)
C1	0.1866 (13)	0.4771 (10)	0.2068 (10)	6.4 (3)
N1	0.0840 (11)	0.4730 (8)	0.1847 (7)	6.1 (3)
O1	−0.0295 (12)	0.4682 (9)	0.1619 (9)	10.7 (4)

Table III. Bond Lengths (Å) with Esd's in Parentheses

		a. $AuPPh_3NCO$			
Au1–P1	2.222 (1)	C11–C12	1.368 (8)	C23–C24	1.346 (11)
Au1–N1	2.006 (5)	C11–C16	1.397 (8)	C24–C25	1.378 (11)
P1–C11	1.815 (5)	C12–C13	1.387 (9)	C25–C26	1.384 (9)
P1–C21	1.810 (5)	C13–C14	1.369 (10)	C31–C32	1.387 (8)
P1–C31	1.803 (5)	C14–C15	1.363 (11)	C31–C36	1.375 (8)
N1–C1	1.147 (8)	C15–C16	1.412 (9)	C32–C33	1.400 (9)
C1–O1	1.189 (8)	C21–C22	1.384 (8)	C33–C34	1.355 (11)
		C21–C26	1.370 (8)	C34–C35	1.365 (11)
		C22–C23	1.395 (9)	C35–C36	1.398 (9)
		b. $AuPPh_3CNO$			
Au1–P1	2.274 (3)	P1–C11	1.820 (6)	C1–N1	1.154 (15)
Au1–C1	1.939 (14)	P1–C21	1.797 (5)	N1–O1	1.272 (15)
		P1–C31	1.798 (6)		

Final positional and thermal parameters of $AuPPh_3NCO$ and $AuPPh_3CNO$ are given in Table II. Molecular geometry data are collected in Tables III and IV. Stereoviews of the molecules showing the molecular configuration are given in Figure 1. The crystallographic numbering schemes are given in Figure 2 (molecules in minimum overlap position). Lists of structure factors, coordinates of hydrogen atoms, and anisotropic parameters are available as supplementary material.

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(19) Nichols, D. I.; Charleston, A. S. *J. Chem. Soc., A* **1969**, 2581.
(20) Beck, W.; Fehlhammer, W. P.; Pollman, P.; Schachl, H. *Chem. Ber.* **1969**, *102*, 1976.

Table IV. Bond Angles (deg) with Esd's in Parentheses

		a. $AuPPh_3NCO$			
P1-Au1-N1	179.5 (1)	C14-C15-C16	121.4 (7)	C21-C26-C25	119.4 (6)
Au1-N1-C1	142.6 (6)	C11-C16-C15	117.2 (6)	C32-C31-C36	120.2 (5)
N1-C1-O1	177.6 (8)	C22-C21-C26	119.8 (6)	C31-C32-C33	119.0 (6)
C12-C11-C16	120.4 (6)	C21-C22-C23	119.6 (6)	C32-C33-C34	120.6 (6)
C11-C12-C13	121.2 (6)	C22-C23-C24	120.7 (6)	C33-C34-C35	120.3 (6)
C12-C13-C14	119.2 (7)	C23-C24-C25	119.5 (6)	C34-C35-C36	120.5 (7)
C13-C14-C15	120.5 (7)	C24-C25-C26	121.0 (6)	C31-C36-C35	119.3 (7)
		b. $AuPPh_3CNO$			
P1-Au1-C1	176.7 (4)	Au1-P1-C31	114.6 (3)	C11-P1-C31	107.8 (3)
Au1-P1-C11	109.7 (3)	Au1-C1-N1	162.9 (11)	C21-P1-C31	104.5 (3)
Au1-P1-C21	113.2 (3)	C11-P1-C21	107.8 (3)	Au1-C1-N1	179.1 (13)

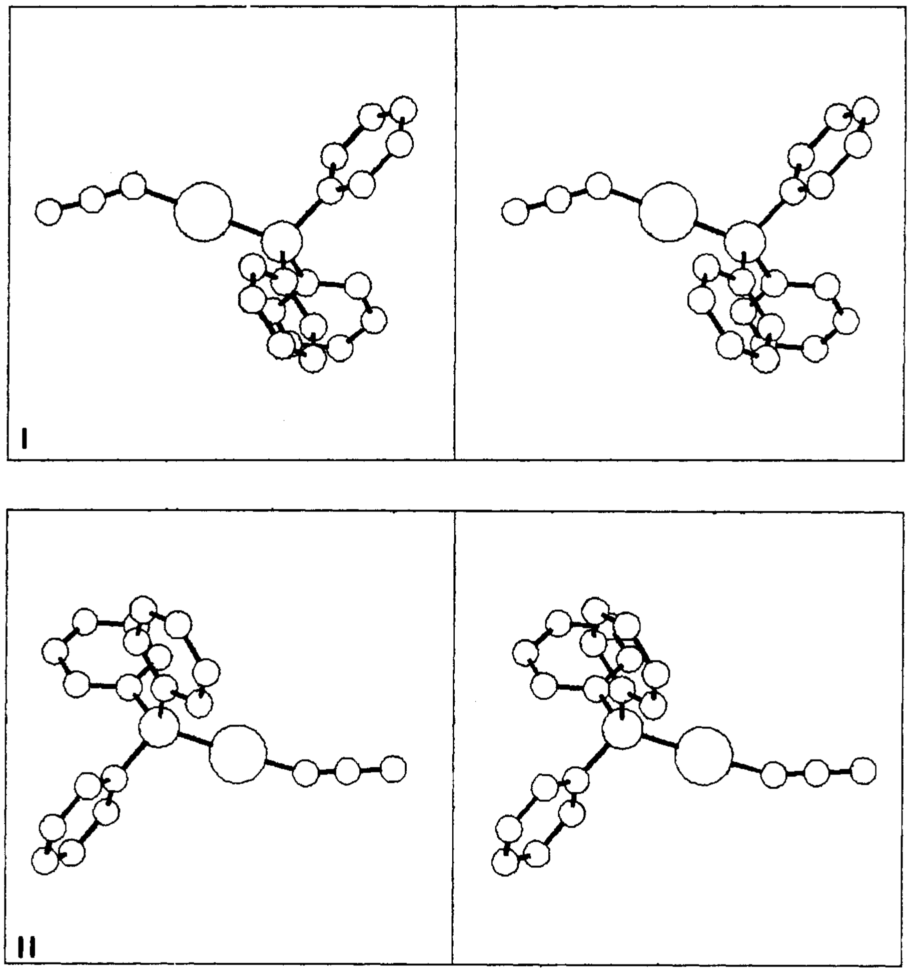

Figure 1. Stereoviews of the molecules: (I) isocyanato compound; (II) fulminato compound.

The Au-triphenylphosphine moiety of both compounds shows no unusual geometry. The Au-P distances are significantly different: 2.222 (1) Å for the isocyanato compound and 2.274 (3) Å for the fulminato compound.

$AuPPh_3NCO$. The metal-nitrogen-carbon angle of 142.6° in the isocyanato compound (I) is very small. To our knowledge it is the smallest angle ever found for metal-isocyanato compounds, not counting the 128° of AgNCO, which has bridging NCO ligands.[12] The closest value to this angle is found for the platinum-isocyanato complex $Pt(Me_2NCH_2CH_2NMe_2)(CONHCH_2CH_2)ClNCO$[13] (Pt-N-C = 147°). Normally the metal-nitrogen-carbon angle is found between 160 and 180°. The bond lengths N-C and C-O are 1.14 and 1.19 Å, respectively. These are in the normal ranges found for metal-isocyanates, N-C = 1.11-1.15 Å, and C-O = 1.18-1.23 Å.[21-29]

Table V. Angles (deg) and Distances (Å) for Fulminato Compounds

compd	Au-C-N	C-N-O	Au-C	C-N	N-O	ref
$AuPPh_3CNO$	163	179.1	1.94	1.15	1.27	
$[Au(CNO)_2]^-$	179	178	2.01	1.10	1.25	14
AgCNO		180	2.18	1.16	1.25	18
HCNO				1.17	1.20	17

$AuPPh_3CNO$. The angles and especially the bond lengths of the fulminate ligand have relatively large standard deviations. This

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(21) Pickardt, J.; Rautenberg, N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 1569.

(22) Hermann, W. A.; Bell, L. K.; Ziegler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39.

(23) Kepert, D. L.; Kucharski, E. S.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 1932.

(24) Anderson, S. J.; Brown, D. S.; Finney, K. J. *J. Chem. Soc. Dalton Trans.* **1979**, 152.

(25) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1970**, 605.

(26) Anderson, O. P.; Marshall, J. C. *Inorg. Chem.* **1978**, *17*, 1258.

(27) Brauer, D. J.; Burger, H.; Pawelke, G.; Flegler, K. H.; Haas, A. *J. Organomet. Chem.* **1978**, *169*, 389.

(28) Mergehenn, R.; Haase, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1877.

(29) Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 457.

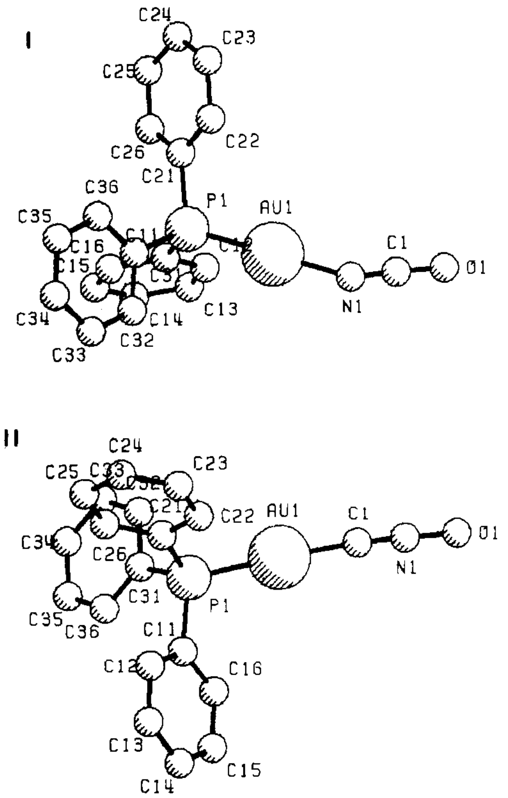

Figure 2. Crystallographic atomic numbering scheme: (I) isocyanato compound; (II) fulminato compound (molecules in minimum overlap position.

is probably caused by the decomposition that took place during the measurements.

Difference Fourier syntheses show significant rest-electron densities (up to 2 e/Å^3) in the neighborhood of the Au–CNO moiety. Therefore, the estimated standard deviations are not reliable. Refinement problems were also noted by others in solving the structures of the bis(fulminato)gold complex $AsPh_4[Au(CNO)_2]$[14] and AgCNO,[15] the only two other fulminates of which the crystal structures were determined. To investigate this problem, we exposed crystals of $AuPPh_3CNO$ to X-ray radiation for 24 h. The rotation photographs and the IR spectra of the crystal taken before and after the exposure did not show any significant changes, and we could not draw any conclusions about a possible rearrangement of the gold fulminate moiety during the decomposition. The bond lengths in the fulminate agree well with other known fulminates, (see Table V). In $AuPPh_3CNO$ the gold–carbon distance (1.939 (14) Å) is slightly shorter than in $AsPh_4[Au(CNO)_2]$ (2.01 (2) Å). This can be attributed to a trans effect of the triphenylphosphine. The same effect is observed when the Au–C distances of $KAu(CN)_2$ and $AuPPh_3CN$ are compared. Here a shortening is found from 2.12 to 1.85 Å.[16] In case of the fulminate this trans effect is apparently less pronounced.

Surprisingly the angle Au–C–N in $AuPPh_3CNO$ is 162.9 (11)°. One would expect this compound to be linear as is found for $AsPh_4[Au(CNO)_2]$. Due to this nonlinearity, the fulminate is isomorphous with the isocyanate. No unusual short intermolecular distances are found in $AuPPh_3CNO$. In this respect it is interesting that studies on fulminic acid, HCNO, have shown a remarkably low energy difference between the linear and bent structures.[17]

Acknowledgment is made to the Netherlands Foundation for Chemical Research (SON) and to NATO for an exchange grant to J.J.S.

Registry No. $AuPPh_3NCO$, 24169-91-3; $AuPPh_3CNO$, 98875-32-2; $AuPPh_3NO_3$, 14897-32-6; CO, 630-08-0.

Supplementary Material Available: Lists of structure factors, coordinates of hydrogen atoms, and anisotropic parameters (56 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Pulse-Radiolysis Study of the Reduction of VO^{2+} by the Hydrated Electron[1]

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The hydrated electron, e_{aq}^-, produced by the irradiation of water with an electron beam is a strong reductant. The half-cell potential of $H^+ + e_{aq}^- \rightarrow H$ is −2.3 eV.[3] This reductant reacts with a number of d and f transition-metal ions[4,5] and their compounds at rates that are essentially diffusion-controlled.

When the reduced species has a primary coordination sphere that is markedly altered from that of the original reactant, the initial product of the electron transfer may be formed in an excited electronic state and/or in an inappropriate coordination configuration. We have previously studied the change of coordination in the linear $O{-}^{+}Np{-}O$ ion upon reduction to the hydrated $Np^{4+}{}_{aq}$ ion[6] using transient conductivity detection. The results were interpreted in terms of a reaction scheme wherein there occurred a step in which the initial [O–Np–O] product rearranged to a hydrolyzed $Np^{4+}{}_{aq}$ ion. The present study was undertaken to determine if a similar process could be identified in the case of a d transition element where the bonding between metal ion and coordinated oxygen is markedly altered. The ion of choice, $VO^{2+}{}_{aq}$, has one "yl"-type oxygen, which has a relatively slow rate of exchange with bulk H_2O,[7] four equatorial H_2O molecules with residence times of 10^{-3} s,[8] and a trans H_2O molecule that is very labile.

Experimental Section

The preparation and standardization of the stock VO^{2+} perchlorate solutions have been previously described.[9] Fresh, unbuffered solutions of (2–5) × 10^{-4} M $VO(ClO_4)_2$ were prepared under an Ar atmosphere. Ethanol, 0.01–0.05 M, or *tert*-butyl alcohol, 0.12 M, was added to scavenge the OH radicals. The pH was adjusted to values between 3.8 and 4.6 by the addition of appropriate amounts of $HClO_4$.

The solutions were irradiated with 0.25-μs pulses from a 15-MeV linac. The dose (ca. 1.4 krad/pulse) was monitored for each pulse. The temperature was kept constant at 25 ± 0.2 °C during the measurement. The transient conductivity change was measured with an improved system described in ref 10. These changes were predominantly in the design of the irradiation cell assembly and improved shielding, which resulted in markedly improved signal-to-noise ratios.

Results and Discussion

When water is subjected to a pulse of ionizing radiation, a positive transient conductivity signal is observed as a result of the formation of H^+, e_{aq}^-, and OH^-. In the absence of a reducible ion, this signal decays rapidly to zero due to the reactions

$$H^+ + OH^- \rightarrow H_2O \qquad (1)$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (2)$$

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(3) Schwartz, H. A. *J. Chem. Educ.* **1981**, *58*, 101.

(4) M. Anbar, In *Solvated Electron*; Advances in Chemistry 50; American Chemical Society: Washington, DC, 1965.

(5) Sullivan, J. C.; Gordon, S.; Cohen, D.; Mulac, W.; Schmidt, K. H. *J. Phys. Chem.* **1976**, *80*, 1684.

(6) Schmidt, K. H.; Gordon, S.; Thompson, R. C.; Sullivan, J. C. *J. Inorg. Nucl. Chem.* **1980**, *42*, 611.

(7) Johnson, M. D.; Murman, R. K. *Inorg. Chem.* **1983**, *22*, 1068.

(8) Reuben, J.; Fiat, D. *Inorg. Chem.*, **1967**, *6*, 579.

(9) Watkins, K. O.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1974**, *13*, 1712.

(10) Schmidt, K. H.; Gordon, S.; Thompson, M.; Sullivan, J. C.; Mulac, W. A. *Radiat. Phys. Chem.* **1983**, *21*, 321.