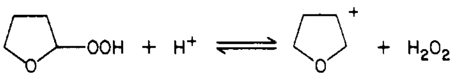
hydroperoxytetrahydrofuran. Again a yellow-green compound was obtained, which did not contain peroxides. However, addition of 30% H_2O_2 to a slurry of the THF cocondensate in THF again yielded a yellow solution to which addition of 18-crown-6 caused immediate precipitation of **3**.

The above results suggest the following interpretation. MoO_3 behaves as a free radical initiator for THF, leading to formation of α-hydroperoxytetrahydrofuran in the presence of O_2. Because these solutions are acidic, pH ca. 2, the tetrahydrofuran-substituted peroxide is in equilibrium with H_2O_2 as shown in eq 6. The peroxo

 (6)

ligand addition to the Mo then occurs through the reaction of the H_2O_2 with the molybdenum oxide species in solution.

The counterpart to eq 6 for *tert*-butylhydroperoxide is eq 7.

$$(CH_3)_3COOH + H^+ \rightleftharpoons (CH_3)_3C^+ + H_2O_2 \qquad (7)$$

That **3** does not occur upon the addition of *tert*-butylhydroperoxide implies the equilibrium for eq 7 must lie far to the left under our reaction conditions. This is apparently due to the instability of the *tert*-butyl cation under these conditions. Therefore in this case, without in situ H_2O_2 formation, **3** is not observed.

While the synthesis of a number of diperoxomolybdenum(VI) complexes have been reported by reacting oxomolybdenum(VI) complexes with H_2O_2,[25] we are aware of only one report of a diperoxomolybdenum(VI) complex synthesized without the addition of H_2O_2. This is the formation of diperoxo(tetraphenylporphinato)molybdenum(VI), $(O_2)_2Mo(TPP)$, from the reaction of *cis*-dioxo(tetraphenylporphinato)molybdenum(VI), $O_2Mo(TPP)$, with 2-propanol recently reported by Ledon, et al.[26] In his report, Ledon proposes that $O_2Mo(TPP)$ abstracts a hydrogen atom from the alcohol to form a free radical. The alcohol free radical interacts with dioxygen to form the alkylperoxide, which is in equilibrium with H_2O_2. Again, in situ H_2O_2 formation leads to a Mo peroxo complex.

Acknowledgment. The authors thank Robert Brown at the Albany Bureau of Mines for his assistance with the thermogravimetric analyses and Robert McCune at the Albany Bureau of Mines for his assistance with the X-ray powder diffraction analyses. Thanks are extended to Dr. A. B. Anderson for providing a copy of ref 16 prior to publication.

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Reactions of Gold(I) Compounds with Carbon Monoxide To Form Gold Clusters and Fulminates

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Au(I) compounds of the type $AuPPh_3X$, where X is a weak coordinated ligand like NO_3^-, ClO_4^-, BF_4^-, or OAc^-, react with carbon monoxide to form gold clusters of the type $Au_9(PPh_3)_8X_3$. The carbon monoxide is transformed to CO_2, probably via initial binding to gold. A precursor of the gold clusters could be detected in a $AuPPh_3NO_3$ matrix. When CH_2Cl_2 is used as a solvent, carbon monoxide and $AuPPh_3NO_3$ or $Au_9(PPh_3)_8{}^{3+}$ give a complicated reaction resulting in the formation of fulminates. In this way $AuPPh_3CNO$ and $Au_{11}(PPh_3)_8(CNO)_2{}^+$ are synthesized. Key in the formation of fulminate is the reaction of a reactive intermediate, probably $AuPPh_3NO$, with CH_2Cl_2. ^{13}CO-labeling experiments confirm the origin of the carbon in the fulminate to be CH_2Cl_2.

Introduction

Recently we described reactions of isocyanides with gold clusters, resulting in the synthesis of $Au_9(PPh_3)_6(i\text{-}PrNC)_2{}^{3+}$, the first gold cluster containing isocyanide ligands.[1] Since carbon monoxide and isocyanide are quite similar electronically, we decided to investigate reactions of gold(I) compounds and gold clusters with CO.

Only two gold–CO compounds are known today, $Au(CO)Cl$[2] and $Au_2(CO)Cl_4$,[3] but they are unstable in the presence of moisture even at room temperature. As this paper will show, weak coordination of CO to gold is responsible for the rapid reduction of gold compounds to gold clusters. Gold clusters are normally synthesized by using $NaBH_4$ as reducing agent[4] or by means of gold evaporation into a phosphine solution.[5] The introduction of CO as a reducing agent is very interesting in this respect, since CO has been shown to be very mild and selective.

During reduction experiments with CO we discovered the formation of gold–fulminato (Au–CNO) compounds. The formation of the fulminate is due to a complicated reaction involving CH_2Cl_2, which was used as solvent. Gold fulminate compounds are very rare. Two types are known, namely the bis(fulminato) complex $Au(CNO)_2{}^-$[6,7] and its oxidized form $Au(CNO)_2X_2{}^-$ (X = Br, I).[8] $Na[Au(CNO)_2]$ is obtained by reacting $AuCl_3$ with ethanol and nitric acid, analogous to the preparation of mercury fulminates.

Experimental Section

Instrumentation. C, H, and N analyses were carried out in the microanalytical department of the University of Nijmegen. The other analyses were measured by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany. Molecular weights were determined by using a Knauer

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[†] University of Nijmegen

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11.00 vapor pressure osmometer in acetone at 37 °C. Electrical conductivity measurements were performed with a Metrohm Konduktoskop using a Philips PR 9510/00 conductivity cell at 25 °C. ^{31}P NMR spectra were recorded on a Varian XL 100 FT at 40.5 MHz, infrared spectra on a Perkin-Elmer 283, and mass spectra on a VG 7070 E spectrometer. All materials were of reagent quality. $NH_4{}^{15}NO_3$ was obtained from Duphar, ^{13}CO from Stohler. $Na[Au(CNO)_2]$ was prepared according to the literature.[6]

General Safety Note. Fulminates of metal complexes can be explosive. Syntheses involving impurities or syntheses carried out on a scale larger than reported here should be treated with extreme caution.

Preparation of $AuPPh_3X$ ($X = NO_2$, NCO). The general procedure for the synthesis of $AuPPh_3X$ is as follows: A suitable salt of the ligand X is dissolved in methanol in large excess (2 g of $NaNO_2$ in 400 mL of MeOH; 1.2 g of KOCN in 200 mL of MeOH). To this is added a solution of 500 mg (0.96 mmol) of $AuPPh_3NO_3$ in 200 mL of MeOH. After the mixture is allowed to stand for 1 h, a double volume of water is added, upon which the product precipitates. The yields are quantitative.

$AuPPh_3NCO$ crystallizes as white needles and can be purified by slow diffusion of hexane into a CH_2Cl_2 solution. Anal. Calcd for $C_{19}H_{15}AuPNO$ ($M_r = 501.273$): C, 45.5; H, 3.0; N, 2.8. Found: C, 45.6; H, 3.0; n, 2.8. $^{31}P[^1H]$ NMR (CH_2Cl_2): a broad singlet (line width 20 Hz, room temperature) at 29.04 ppm downfield relative to TMP. IR (CsI pellet): 2204 (broad, very strong), 2146 (sharp, strong), 385 cm^{-1} (broad, medium), and peaks originating from PPh_3. In CH_2Cl_2 solution, only one IR peak at 2210 cm^{-1} (broad, very strong) is observed. The IR spectrum is consistent with literature values.[9,10] Melting point: 202 °C. Peakmatching of the parent mass peak: calcd, *m/e* 501.0557; found, *m/e* 501.0552.

$AuPPh_3NO_2$. The white powder obtained from the reaction is recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution, resulting in colorless rectangular crystals. Anal. Calcd for $C_{18}H_{15}AuPNO$ ($M_r = 505.269$): C, 42.8; H, 3.0; N, 2.8. Found: C, 43.2; H, 3.0; N, 2.7. $^{31}P[^1H]$ NMR (CH_2Cl_2): 24.54 ppm (singlet width 3 Hz) downfield relative to TMP. IR (CsI pellet): 1230 (broad, strong), 1040 (broad, strong), 370 cm^{-1} (broad, medium), and bands originating from PPh_3. The nitrite slowly decomposes under the influence of light and increased temperatures.

$AuPPh_3{}^{15}NO_3$. The same procedure is used as with the isocyanate and nitrite salts, using an excess of 5 equiv of $NH_4{}^{15}NO_3$. The resulting product is not purified further. In the infrared spectrum the nitrate is observed at 1495, 1340, and 1250 cm^{-1}, which are about 20 cm^{-1} lower than the bands of $^{14}NO_3$.

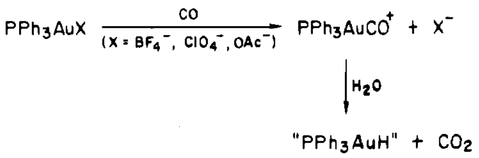
Preparation of $AuPPh_3CNO$. (1) From $AuPPh_3NO_3$. A 200-mg (0.38-mmol) sample of $AuPPh_3NO_3$ is dissolved in 20 mL of CH_2Cl_2. About 250 mL of CO gas is passed through the solution and the reaction vessel sealed. After being stirred for 1 h, the reaction mixture contains 10–38 mg of $AuPPh_3CNO$ and 160–170 mg of $AuPPh_3Cl$. This yield can be increased by converting the $AuPPh_3Cl$ back to $AuPPh_3NO_3$ by treatment of the product with 2 equiv of $AgNO_3$ in methanol, as with the synthesis of $AuPPh_3NO_3$.[4] After AgCl and excess $AgNO_3$ are filtered off, the crude mixture is redissolved in CH_2Cl_2 and CO is passed through the solution again. In this way the reaction with CO is performed in four cycles. The crude reaction product is filtered off over silica gel with diethyl ether to remove small amounts of gold clusters and gold bis(phosphine). $AuPPh_3CNO$ is isolated by chromatography over a silica gel column using toluene for the elution of $AuPPh_3Cl$ followed by diethyl ether to recover all $AuPPh_3CNO$. Yield: 38%.

(2) From $Au(PPh_3)_2NO_3$ and $Na[Au(CNO)_2]$. A 19.8-mg (0.065-mmol) sample of $Na[Au(CNO)_2]$ is dissolved in 20 mL of DMF. To this is added slowly a solution of 51 mg (0.065 mmol) of $Au(PPh_3)_2NO_3$ in 20 mL of DMF with stirring. The white product is precipitated by adding water and is filtered off. Yield: 80%.

$AuPPh_3CNO$ can be recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution. Anal. Calcd for $C_{19}H_{15}AuPNO$ ($M_r = 501.273$): C, 45.5; H, 3.0; N, 2.8. Found: C, 45.5; H, 3.0; N, 2.8. $^{31}P[^1H]$ NMR (CH_2Cl_2): singlet (line width 6 Hz) at 36.25 ppm downfield relative to TMP. IR (CsI pellet): 2405 (sharp, weak), 2156 (sharp, very strong), 1208 (sharp, very strong), 332 cm^{-1} (weak), and peaks originating from PPh_3. Melting point: 174–174.5 °C. Mass spectrum (FAB): *m/e* 501 (M^+), 486, 459. Peakmatching: calcd, *m/e* 501.0557; found, *m/e* 501.0564. $AuPPh_3CNO$ does not explode by stroke or heating.

Preparation of $Au_{11}(PPh_3)_8(CNO)_2NO_3$. (1) From $Au_9(PPh_3)_8(NO_3)_3$. A 250-mg (0.062-mmol) sample of $Au_9(PPh_3)_8(NO_3)_3$ is dissolved in 40 mL of CH_2Cl_2 and placed under 7 atm of CO pressure at room temperature in the dark for 3 weeks. During this time the color changes from red-brown to orange-red and some gold metal precipitates. After filtration and evaporation to dryness, the orange-red product is purified by chromatography over a Sephadex LH-60 gel filtration column using acetone as eluent. Yield calculated on gold: 18%.

Scheme I



(2) From $Au_8(PPh_3)_8(NO_3)_2$. A 110-mg (0.029-mmol) sample of $Au_8(PPh_3)_8(NO_3)_2$ is dissolved in 20 mL of DMF. To this is added slowly a solution of 8.8 mg (0.029 mmol) of $Na[Au(CNO)_2]$ in DMF with stirring. After $^1/_2$ h water is added and the precipitate filtered off by using Kieselguhr. The purification is carried out as described above. Yield calculated on gold: 24%.

(3) From $Au_8(PPh_3)_7(NO_3)_2$. A 50-mg (0.014-mmol) sample of $Au_8(PPh_3)_7(NO_3)_2$ and 15 mg (0.028 mmol) of $AuPPh_3CNO$ are dissolved in 2 mL of CH_2Cl_2. After standing for 2 weeks in the dark, the reaction is complete. The purification can be conducted as above by chromatography over Sephadex LH-60 using acetone as eluent. Yield calculated on gold: 41%.

$Au_{11}(PPh_3)_8(CNO)_2NO_3$ can be recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution, giving red parallelepiped crystals. Anal. Calcd from $C_{149}H_{120}Au_{11}N_3O_5P_8$ ($M_r = 4411.02$): C, 39.8; H, 2.7; N, 1.0; P, 5.6; O, 1.8; Au, 49.1. Found: C, 39.5; H, 2.7; N, 1.0; P, 5.6; Au, 49.4. The molecular weight determined in an acetone solution by using an osmometric pressure procedure is 4400, assuming a 1:1 electrolyte. The electrical conductivity measured in MeOH at 25 °C and 10^{-3} M dilution is $\Lambda = 112\ \Omega^{-1}\ cm^2\ mol^{-1}$, consistent with a 1:1 electrolyte of mass 4400. $^{31}P[^1H]$ NMR (CH_2Cl_2): sharp singlet at 42.53 ppm (line width 3 Hz) downfield relative to TMP. IR (CsI pellet: 2137 cm^{-1} (broad, medium) and bands originating from PPh_3.

General Procedure for the Reduction of $AuPPh_3NO_3$ by CO or H_2. A 500-mg (0.96-mmol) sample of $AuPPh_3NO_3$ is dissolved in 250 mL of EtOH. During $^1/_2$ h a slow stream of CO or H_2 is passed through the solution, after which the reaction vessel is sealed. An instantaneous brown color can be observed with CO, whereas H_2 reacts considerably slower. The CO reaction is complete after this time and can be worked up according to the normal synthesis of $Au_9(PPh_3)_8(NO_3)_3$ using $NaBH_4$.[4] The H_2 reaction mixture must be stirred for several days before workup. Yields calculated on gold: with CO, 45%; with H_2, 60%.

Results and Discussion

Reactions of $AuPPh_3X$ with CO. Whether or not $AuPPh_3X$ reacts with CO depends on the character of the ligand X. With strongly coordinating ligands like Cl^-, SCN^-, or CN^- no reaction can be observed in any solvent. With weakly coordinated ligands like NO_3^-, ClO_4^-, BF_4^-, or OAc^-, by using the solvents EtOH, THF, acetone, toluene, or diethyl ether, CO is capable of reducing the gold. The resulting products are the gold clusters $Au_9(PPh_3)_8{}^{3+}$ and $Au_8(PPh_3)_7{}^{2+}$ together with $Au(PPh_3)_2{}^+$. The overall reaction can be written as in (1). The presence of $Au_8(PPh_3)_7{}^{2+}$ is as

$$10AuPPh_3X + 3CO + 3H_2O \rightarrow Au_9(PPh_3)_8X_3 + Au(PPh_3)_2X + 3CO_2 + 6HX$$

$$X = NO_3^-, BF_4^-, ClO_4^-, \text{or } OAc^- \tag{1}$$

expected from the equilibrium[11] (2). Although the reaction must

$$Au_9(PPh_3)_8{}^{3+} \rightleftarrows Au_8(PPh_3)_7{}^{2+} + AuPPh_3{}^+ \tag{2}$$

be very complicated, it is very fast even at room temperature. In ethanol an instantaneous brown color can be observed as soon as the first CO bubble is passed through the solution. In solvents like toluene or diethyl ether, in which the gold clusters do not dissolve, a direct precipitation of $Au_9(PPh_3)_8{}^{3+}$ and $Au_8(PPh_3)_7{}^{2+}$ occurs.

The reduction to gold clusters could also be performed with H_2, by using EtOH as a solvent. In this case the reaction is considerably slower, but a better yield of $Au_9(PPh_3)_8{}^{3+}$ could be

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obtained. It seems likely that the reduction by CO occurs via coordination of CO to gold (Scheme I). This is supported by the fact that only gold triphenylphosphines with weakly coordinated ligands react with CO, since CO is believed to have only a minor interaction with gold.

There is an interesting difference in reaction speed between $AuPPh_3NO_3$ and $Au(PPh_3)_2NO_3$ reacting with CO. Where $AuPPh_3NO_3$ reacts rapidly, the bis(phosphine)gold compound shows almost no conversion over a long period of time. In the latter case no free bonding site on gold is present and therefore the addition of CO is blocked. When one uses $AuPPh_3Cl$ or $AuPPh_3CN$, the same problem arises. Therefore only compounds with ligands that can be substituted easily will react with CO (or H_2). After addition of CO, a reaction with H_2O seems likely, resulting in oxygen transfer from H_2O to CO. When the experiment is carried out in absolutely dry solvents, no reaction is observed. Because of the generation of HX, the solution grows strongly acidic.

The mechanism for the formation of gold clusters is not well understood. We suggest that PPh_3Au or PPh_3AuH is intermediate. These highly reactive species congregate to form larger particles via $Au_2(PPh_3)_2$. The growth of the gold cluster is continued as long as the total number of PPh_3 ligands is less than 8. When this amount is reached, no more room is available for additional triphenylphosphines and the growth stops.[11]

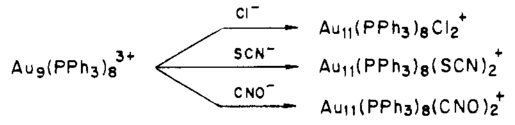
Powdered $AuPPh_3NO_3$ also reacts with carbon monoxide in the absence of solvent. The white starting product turns brown slowly while generating CO_2. The resulting dark brown powder shows a single ESR signal with $g = 2.004$ and forms $Au_9(PPh_3)_8(NO_3)_3$ and $Au_8(PPh_3)_7(NO_3)_2$ when dissolved in solvents like CH_2Cl_2, EtOH, toluene, THF, or acetone. One could look upon this substance as a reactive precurser to gold clusters. This is the first time such a species is obtained in a stable form, although still in a $AuPPh_3NO_3$ matrix. Further investigations in this direction are in progress and are needed to show more details about this species.

Reaction of $AuPPh_3NO_3$ with CO in CH_2Cl_2. The reaction with carbon monoxide was also carried out in CH_2Cl_2. From $AuPPh_3X$ where X = BF_4^- or ClO_4^- were formed gold clusters as in the other solvents. However, with $AuPPh_3NO_3$ no gold clusters were formed but instead more than 80% of the reaction product consisted of $AuPPh_3Cl$, showing that the solvent participated in the reaction. The reaction product also contained a small and variable amount (usually between 2 and 10%) of $AuPPh_3CNO$ (Scheme V). Its yield could be increased by treatment of the crude mixture with $AgNO_3$ to convert the excess $AuPPh_3Cl$ back to $AuPPh_3NO_3$. The mixture was again reacted with carbon monoxide. After four such cycles a yield of 38% $AuPPh_3CNO$ could be obtained. The reaction only took place when traces of water were present. With carefully dried CH_2Cl_2 and starting material, either no reaction or a very incomplete reaction occurred. It is not known if water is needed in catalytic or stoichiometric quantities. To reveal the origin of the carbon atom in the fulminate ligand, the experiment was also performed by using ^{13}CO. It showed that carbon-13 was present in $^{13}CO_2$ and not in the fulminate ligand. ^{15}N labeling of the nitrate resulted in the formation of ^{15}N-labeled fulminate (eq 3).

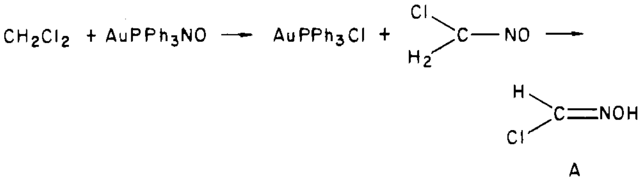
$$AuPPh_3{}^{15}NO_3 \xrightarrow[CH_2Cl_2]{^{13}CO} AuPPh_3Cl + AuPPh_3C^{15}NO + {}^{13}CO_2 \qquad (3)$$

Reactions of $Au_9(PPh_3)_8(NO_3)_3$ with CO in CH_2Cl_2. In comparison with the reaction of $AuPPh_3NO_3$ with CO in CH_2Cl_2, reactions with $Au_9(PPh_3)_8(NO_3)_3$[4] were also carried out. In addition to $AuPPh_3Cl$ and a very small amount (~1%) of $AuPPh_3CNO$, three gold clusters were formed, with ^{31}P NMR signals at 50.12, 51.43, and 52.53 ppm downfield relative to TMP. Only the last signal persisted after a long reaction period. This gold cluster was identified as $Au_{11}(PPh_3)_8(CNO)_2NO_3$. The reactive species is probably $AuPPh_3NO_3$, present because of equilibrium 2. As its equilibrium concentration is small, the reaction will be slow, as observed. The generated $AuPPh_3CNO$ (eq 3) will react with $Au_8(PPh_3)_7(NO_3)_2$ to form $Au_{11}(PPh_3)_8(CNO)_2NO_3$. This was verified by reacting 2 equiv of $AuPPh_3CNO$ with $Au_8(PPh_3)_7(NO_3)_2$ directly. Indeed, $Au_{11}(PPh_3)_8(CNO)_2NO_3$ could be obtained in good yield (eq 4).

Scheme II



Scheme III



$$2AuPPh_3CNO + Au_8(PPh_3)_7(NO_3)_2 \rightarrow Au_{11}(PPh_3)_8(CNO)_2NO_3 \qquad (4)$$

Vollenbroek et al.[12] showed that Au_{11} clusters were formed by reacting $Au_9(PPh_3)_8^{3+}$ with strongly coordinating anions like Cl^- and SCN^-. In fact, we were able to carry out the same type of reaction using CNO^- (Scheme II).

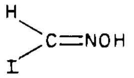
Formation of the Fulminate. We suggest that the first step in the formation of the fulminate is the reduction of $AuPPh_3NO_3$ to $AuPPh_3NO_2$ by CO (eq 5). Two reasons for this assumption

$$AuPPh_3NO_3 \xrightarrow{CO} AuPPh_3NO_2 + CO_2 \qquad (5)$$

can be put forward. First, the reaction to fulminates also takes place starting from $AuPPh_3NO_2$, and second, when the reaction is carried out by using H_2 instead of CO, $AuPPh_3NO_2$ is the ultimate product. The fact that $AuPPh_3NO_2$ by itself is not able to react with CH_2Cl_2 to produce fulminate (^{13}CO experiments mentioned earlier showed that the carbon in the fulminate originates from CH_2Cl_2) shows that the reaction with CO does not stop at this point. No example for the reduction of nitrate to nitrite by CO is known to us from the literature. Thermodynamically this conversion is favorable. The further reduction from nitrite to nitrosyl by CO (eq 6) seems likely since many examples with

$$CO + AuPPh_3NO_2 \rightarrow AuPPh_3NO + CO_2 \qquad (6)$$

various metals like Mn, Fe, Ru, Os, and Ni[13-16] are known. The nitrosyl compound must be very reactive. Reaction with CH_2Cl_2 could lead to formoxime A (Scheme III) and $AuPPh_3Cl$. The hypothetical formoxime is similar to the known formoximes I and II.[17] These are formed by treating $Hg(CNO)_2$ with HI and Cl_2,



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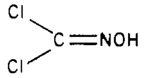

II

respectively. Compound I is stable in ethereal solution below −20 °C. Addition of a suitable base, like triethylamine, generates fulminic acid, HCNO. In our case the role of triethylamine can be taken over by $AuPPh_3NO_3$, which is good chloride scavenger (eq 7). $AuPPh_3Cl$ and HNO_3 are reaction products that are

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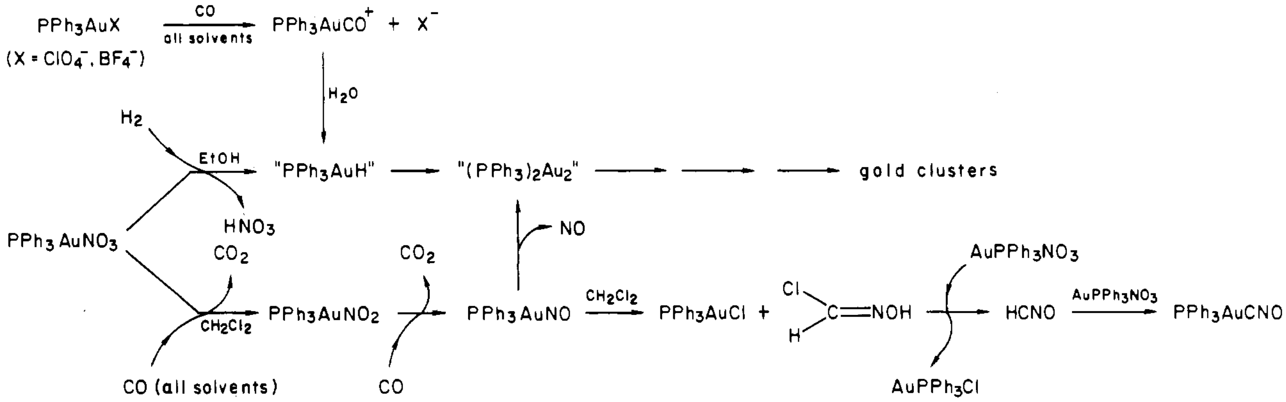
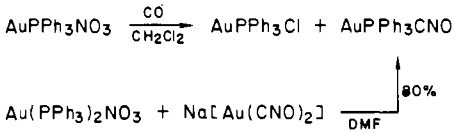
(17) Grundmann, C.; Grünanger, P. In "The Nitrile Oxides"; Springer-Verlag: Berlin, 1971; pp 33–40.

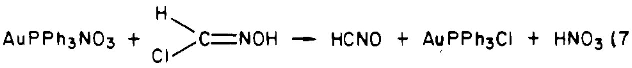
Scheme IV



Scheme V



observed. The last step in the reaction sequence could simply be the reaction of HCNO with $AuPPh_3NO_3$ to form the final product $AuPPh_3CNO$ (eq 8). Earlier it was mentioned that the reaction

 (7)

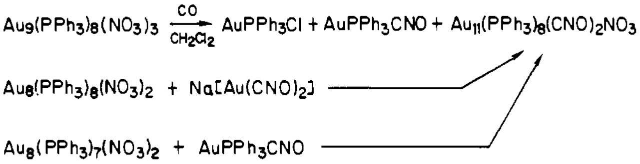
$$AuPPh_3NO_3 + \mathrm{H(Cl)C{=}NOH} \rightarrow HCNO + AuPPh_3Cl + HNO_3 \quad (7)$$

$$HCNO + AuPPh_3NO_3 \rightarrow AuPPh_3CNO + HNO_3 \quad (8)$$

did not run without a trace of water. Possibly the reaction needs water only in a catalytic quantity, and because no real mechanism is given, the role of water is not apparent. The reaction schemes in CH_2Cl_2 and other solvents are combined in Scheme IV.

Identification of Fulminato Compounds. $AuPPh_3CNO$, which is present in only small amounts after reacting $AuPPh_3NO_3$ with CO in CH_2Cl_2, was detected because of its very strong infrared absorptions at 2156 and 1210 cm^{-1}. It was clear that the compound contained gold, triphenylphosphine, and an unknown ligand. Experiments with ^{15}N-labeled $AuPPh_3NO_3$ showed that the vibration at 2156 cm^{-1} shifted to 2119 cm^{-1} (whereas the other remained unchanged), indicating the presence of nitrogen in the unknown ligand. The parent peak of the mass spectrum was peakmatched to $AuPC_{19}H_{15}NO$, consistent with $AuPPh_3$ with one carbon, nitrogen, and oxygen. The fragmentation pattern further indicated the oxygen to be situated on the outside of the unknown ligand, because it could be split off. To distinguish between the two remaining possibilities, isocyanate (–NCO) and fulminate (–CNO), $AuPPh_3NCO$ was synthesized. Both IR and NMR spectra were totally different. Final chemical proof was obtained when the compound could also be synthesized from $Au(PPh_3)_2NO_3$ and the explosive $Na[Au(CNO)_2]$ in good yield (Scheme V).

Scheme VI



Safety Note: Pure $Na[Au(CNO)_2]$ explodes with a sharp bang when heated with a flame. Otherwise, the compound is fairly stable with no considerable decomposition at room temperature during 1 day. The compound did not detonate by stroke.

The crystal structures have been determined for both $AuPPh_3CNO$ and $AuPPh_3NCO$.[18]

The fulminate vibration of $Au_{11}(PPh_3)_8(CNO)_2^+$ is found at 2135 cm^{-1} (medium) and is somewhat broader than the fulminate absorption of $AuPPh_3CNO$. $Au_{11}(PPh_3)_8(CNO)_2^+$ could also be synthesized by reacting $Au_8(PPh_3)_8^{2+}$ with $Na[Au(CNO)_2]$ and by reacting $Au_8(PPh_3)_7(NO_3)_2$ with $AuPPh_3CNO$ (Scheme VI).

Although it was possible to obtain crystals of $Au_{11}(PPh_3)_8(CNO)_2NO_3$, we were unable to perform an X-ray crystal structure determination because of twin-crystal problems.

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Registry No. $Au_{11}(PPh_3)_8(CNO)_2NO_3$, 98921-33-6; $Au_9(PPh_3)_8(NO_3)_3$, 37336-35-9; $Au_8(PPh_3)_8(NO_3)_2$, 81283-09-2; $Au_8(PPh_3)_7(NO_3)_2$, 81283-10-5; $AuPPh_3NCO$, 24169-91-3; $AuPPh_3NO_2$, 98875-31-1; $AuPPh_3NO_3$, 14897-32-6; $AuPPh_3CNO$, 98875-32-2; $Au(PPh_3)_2NO_3$, 98875-33-3; $Na[Au(CNO)_2]$, 98875-34-4; CO, 630-08-0; H_2, 1333-74-0; CH_2Cl_2, 75-09-2.

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[18] Submitted for publication in *Inorg. Chem.*