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# Reaction of CO and an Isonitrile with $PtAu_8(PPh_3)_8{}^{3+}$. Crystal Structure of $Pt(CO)(AuPPh_3)_8(NO_3)_2 \cdot 2C_4H_{10}O \cdot 2CH_2Cl_2$

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$Pt(AuPPh_3)_8{}^{2+}$ (1) reacts with CO and CN-*i*-Pr to form $Pt(CO)(AuPPh_3)_8{}^{2+}$ (2) and $Pt(CN-i-Pr)(AuPPh_3)_8{}^{2+}$ (3), respectively, in which CO and CN-*i*-Pr are bonded to the central Pt, which thus acquires 9-coordination. Excess of CN-*i*-Pr gives substitution of a peripheral PPh₃ yielding $Pt(CO)(AuPPh_3)_7(AuCN-i-Pr)^{2+}$ (2a) and $Pt(CN-i-Pr)(AuPPh_3)_7(AuCN-i-Pr)^{2+}$ (3a). $Pt(CO)(AuPPh_3)_8(NO_3)_2$ was characterized by IR and ³¹P and ¹³C NMR spectroscopy and single-crystal X-ray diffraction (monoclinic, $C2/c$, $a$ = 23.579 (3) Å, $b$ = 24.117 (3) Å, $c$ = 31.008 (6) Å, $\beta$ = 109.23 (3)°, $V$ = 16 649.0 Å³, $Z$ = 4; the residuals are $R$ = 0.051 and $R_w$ = 0.076 for 8426 observed reflections and 226 variables; Cu K$\alpha$ radiation). In the metal cluster the central Pt is surrounded by eight Au atoms in a structure similar to two (100) planes of an fcc packing. CO is $\mu_1$ bonded to Pt on top of this pseudo (100) plane. The phosphines are attached to the Au atoms, giving a steric shielding of the PtCO moiety. The clusters 3, 2a, and 3a should, according to their IR and NMR spectra, have similar structures.

## Introduction

Gold cluster compounds are known with cluster composition $Au_{n+1}(PR_3)_{n-x}X_x$ (X = Cl, Br, I, CN, SCN, CNR; $n$ between 7 and 12 and $x$ between 0 and 3), which have a central Au surrounded by $n$ peripheral $AuPR_3$ or AuX groups.[1,2] The formula $Au(AuPR_3)_{n-x}(AuX)_x$ that we will use here focuses attention on the connectivity of the central atom. Peripheral interactions, although important in the bonding of the cluster, are not indicated in such formulas. $Au(PR_3)(AuPR_3)_7{}^{2+}$ is the only known cluster where in addition to seven Au atoms one $PR_3$ is directly bonded to the center. This cluster reversibly loses $PR_3$ as shown in reaction 1. $Au(AuPPh_3)_7{}^{2+}$ reacts with CN-*t*-Bu to form $Au(PPh_3)$-

$$Au(AuPR_3)_7{}^{2+} + PR_3 \rightleftharpoons Au(PR_3)(AuPR_3)_7{}^{2+} \quad (1)$$
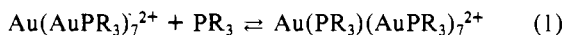
$(AuCN-t-Bu)(AuPPh_3)_6{}^{2+}$, probably via $Au(CN-t-Bu)$-$(AuPPh_3)_7{}^{2+}$ as an intermediate.[3] In such addition reactions the $S^2P^4$ cluster orbital configuration is completely filled to $S^2P^6$.[4,5] Addition compounds of the type $Au(X)(AuPR_3)_8$ could not be detected up till now, although such compounds could be possible on steric ground and on the basis of the fact that $Au(AuPR_3)_8{}^{3+}$ can be reduced to $Au(AuPR_3)_8{}^+$ with the $S^2P^6$ configuration.[6] $PtAu_n$ metal clusters have been known for a few years. In these compounds, Pt is the central atom but there is a greater variety of peripheral groups. In addition to AuPPh₃ in $Pt(AuPPh_3)_8{}^{2+}$[7] and in the other known $PtAu_n$ clusters, there is PPh₃ in $Pt(PPh_3)(AuPPh_3)_6{}^{2+}$,[8] PPh₃ and C≡C-*t*-Bu in $Pt(PPh_3)(C≡C-t-Bu)(AuPPh_3)_6{}^+$,[9] PPh₃ and NO₃ in $Pt(PPh_3)_2(NO_3)(AuPPh_3)_2{}^+$,[8] and PPh₃ and H in $Pt(H)(PPh_3)(AuPPh_3)_7{}^{2+}$.[7] In this paper we report the addition of CO and CN-*i*-Pr to $Pt(AuPPh_3)_8{}^{2+}$ (1), in which $Pt(CO)(AuPPh_3)_8{}^{2+}$ (2) and $Pt(CN-i-Pr)(AuPPh_3)_8{}^{2+}$ (3) are formed, respectively.

## Experimental Section

**Measurements.** C, H, and N analysis were carried out in the microanalytical department of the University of Nijmegen. The other analysis were measured by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany. Proton-decoupled ³¹P NMR spectra were recorded in CH₂Cl₂

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on a Varian XL 100 FT instrument at 40.5 MHz with TMP reference, ¹³C NMR spectra were recorded on a Bruker WM 200 instrument $CD_2Cl_2$ vs TMS, ¹H NMR spectra were recorded on a Bruker WH 90 instrument in $CD_2Cl_2$ vs TMS, and infrared spectra were recorded on a Perkin-Elmer 283 instrument in CsI pellets.

**Preparation of the Compounds. $Pt(CO)(AuPPh_3)_8(NO_3)_2$ (2).** A 200-mg (500-μmol) sample of 1 was dissolved in 50 mL of acetone. CO was bubbled through the solution at room temperature and atmospheric pressure, turning the brown-red solution immediately into a bright red one. The acetone solution was evaporated to dryness, and the remaining red solid was washed with diethyl ether and dried in vacuo; yield 200 mg (50 μmol). The isotopically labeled $Pt(^{13}CO)(AuPPh_3)_8(NO_3)_2$ was prepared by the same procedure, using ¹³CO gas.

Anal. Calcd for $PtAu_8P_8C_{145}H_{120}N_2O_7$ (mol wt 4021.20): C, 43.31; H, 3.01; N, 0.70. Found: C, 42.96; H, 3.13; N, 0.71. IR: $\nu$(CO) 1940 cm⁻¹, $\nu$(¹³CO) 1900 cm⁻¹. ³¹P NMR: $\delta$ = 51.3 (singlet) with Pt satellites ²$J$(Pt-P) = 391 Hz. ¹³C NMR: ¹³CO $\delta$ = 210.7 (nonet) with ¹$J$(Pt-C) = 1256 Hz and ³$J$(P-C) = 11 Hz. The ³¹P NMR spectrum of the ¹³CO-labeled compound showed a doublet at $\delta$ = 51.3 with ³$J$(P-C) = 11 Hz and Pt satellites with ²$J$(Pt-P) = 391 Hz. Crystals suitable for X-ray analysis could be obtained by slow diffusion of diethyl ether into a dichloromethane solution of $Pt(CO)(AuPPh_3)_8(NO_3)_2$. The red crystals contained 2 mol of diethyl ether and 2 mol of dichloromethane/mol of cluster, as was determined by ¹H NMR spectroscopy. The solvent molecules were readily lost when in contact with air, destroying the crystallinity of the sample.

**$Pt(CN-i-Pr)(AuPPh_3)_8(NO_3)_2$ (3).** A 120-mg (30-μmol) sample of 1 was dissolved in 10 mL of $CH_2Cl_2$, and 2 mg (30 μmol) of CN-*i*-Pr was added under vigorous stirring at −20 °C, to avoid substitution of PPh₃ by CN-*i*-Pr, turning the brown-red solution immediately into a bright red one. After the solution was allowed to warm to room temperature, the product was precipitated by pouring the $CH_2Cl_2$ solution into diethyl ether. Further purification was achieved by repeated dissolution in $CH_2Cl_2$ and reprecipitation by slow diffusion of diethyl ether.

Anal. Calcd for $PtAu_8P_8C_{148}H_{127}N_3O_6$ (mol wt 4062.30): C, 43.76; H, 3.15; N, 1.03. Found: C, 43.29; H, 3.14; N, 1.03. IR: characteristic CNR absorption at 2102 cm⁻¹. ³¹P NMR: AuP $\delta$ = 50.4 (singlet), ²$J$(Pt-P) = 397 Hz.

**$Pt(CN-i-Pr)(AuPPh_3)_7(AuCN-i-Pr)(NO_3)_2$ (3a).** A 120-mg (30-μmol) sample of 1 was dissolved in 10 mL of $CH_2Cl_2$, and 6 mg (90 μmol) of CN-*i*-Pr was added with stirring at room temperature, turning the brown-red solution immediately into a bright red one. After 0.5 h the mixture was poured into diethyl ether and the resulting precipitate was purified by recrystallization from $CH_2Cl_2$/diethyl ether.

Anal. Calcd for $PtAu_8P_7C_{134}H_{119}N_4O_6$ (mol wt 3869.07): C, 41.60; H, 3.10; N, 1.45. Found: C, 40.92; H, 3.14; N, 1.45. IR: Characteristic CNR absorptions at 2187 and 2111 cm⁻¹. ³¹P NMR: AuP $\delta$ = 51.9 (singlet), ²$J$(Pt-P) = 378 Hz. ¹H NMR: AuCN-*i*-Pr CH(C$H_3$)₂ $\delta$ = 0.90 (doublet), ³$J$(H-H) = 6.6 Hz, C$H$(CH₃)₂ $\delta$ = 3.45 (septet), ³$J$(H-H) = 6.6 Hz, PtCNR CH(C$H_3$)₂ $\delta$ = 0.61 (doublet), ³$J$(H-H) = 6.4 Hz, C$H$(CH₃)₂ $\delta$ = 3.24 (septet), ³$J$(H-H) = 6.4 Hz.

**$Pt(CO)(AuPPh_3)_7(AuCN-i-Pr)(NO_3)_2$ (2a).** A 60-mg (15-μmol) sample of 2 was dissolved in 10 mL of $CH_2Cl_2$, and 1.0 mg (15 μmol) of CN-*i*-Pr was added with stirring at room temperature. The mixture was poured into diethyl ether, and the resulting precipitate was recrystallized from $CH_3OH$/diethyl ether.

Anal. Calcd for $PtAu_8P_7C_{131}H_{112}N_3O_7$ (mol wt 3828.01): C, 41.10; H, 2.95; N, 1.10. Found: C, 40.40; H, 2.97; N, 1.14. IR: characteristic CNR absorption at 2192 cm⁻¹ and $\nu$(CO) at 1951 cm⁻¹. ³¹P NMR: $\delta$

**Table I.** Crystal Data for
Pt(CO)(AuPPh3)8(NO3)2·2C4H10O·2CH2Cl2

| $M_r$ | 4117.2 | $\beta$ | 109.23 (3) |
|---|---|---|---|
| space group | C2/c | $V$, Å$^3$ | 16649.0 |
| a, Å | 23.579 (3) | $\rho$(calcd), g cm$^{-3}$ | 1.641 |
| b, Å | 24.117 (3) | $\mu$(Cu Kα), cm$^{-1}$ | 160.23 |
| c, Å | 31.008 (6) | | |

= 53.1 (singlet), $^2J$(Pt–P) = 372 Hz.

**1** was prepared by published methods.[10] The other reagents were obtained from commercial sources and were used without further purification. Solvents were dried prior to use by standard procedures.

**Structure Determination of Pt(CO)(AuPPh3)8(NO3)2·2C4H10O· 2CH2Cl2. Collection and Reduction of Crystallographic Data.** Since single crystals decomposed very quickly upon removal from the solvent mixture, a red crystal (0.2 × 0.4 × 0.7 mm) was mounted in a capillary together with a drop of a mixture of dichloromethane and diethyl ether. X-ray data were measured on a Nonius CAD4 diffractometer at 293 K, using monochromated Cu Kα radiation. The unit cell dimensions were calculated from the setting angles of 25 reflections with 38° < 2θ < 66°. The crystal data are listed in Table I. The data were collected by using the ω–2θ mode with a variable scan speed and a maximum scan time of 15 s/reflection. A total of 12 958 reflections with 6° < 2θ < 120° were recorded ($h,k,\pm l$). Three standard reflections were measured after every 1800 s of X-ray exposure time. After the intensities had decreased to 66% of their initial values, due to decomposition of the crystal, a new crystal was mounted. With this a total of 13 018 reflections were recorded ($h,-k,\pm l$). The intensities of the standard reflections then decreased to 83% of their initial values. The two reflection sets were scaled. After correction for Lorentz and polarization effects, the equivalent reflections were averaged ($R^{av} = [\sum(||F_o|-|F_c||)/\sum|F_o|] = 0.057$, including all reflections). A total of 12 324 reflections remained, of which 8426 had $F > 6\sigma(F)$ ($\sigma(F)$ was based on counting statistics). No extinction correction was performed.

**Solution and Refinement of the Structure.** The positions of the heavy atoms (Au, Pt, and P) were found automatically by PATSYS,[11] which combines the Patterson part of SHELXS-86[12] and DIRDIF.[13] The remaining carbon atoms and phenyl carbons were positioned from three successive difference Fourier maps. The phenyl rings were treated as regular hexagons, and their hydrogen atoms were placed at ideal positions. The structure was refined by full-matrix least squares on $F$ values, using SHELX.[14] Scattering factors were taken from ref 15. Isotropic refinement converged to $R = 0.103$. At this stage an empirical absorption correction was applied,[16] resulting in a further decrease of $R$ to 0.094 (correction factors were in the range of 0.81–1.38). A large number of peaks, found at positions between the cluster ions (at distances more than 3.5 Å from any atom), could not be unambiguously be interpreted. They are ascribed to a mixture of (disordered) NO3 ions (expected: one independent ion) and solvent molecules (expected: one dichloromethane molecule and one diethyl ether molecule). Some of these peaks suggested the geometry of NO3 or the solvent molecules; but none of them were found well enough to warrant inclusion in the refinement. (There are at least six positions between the cluster ions that are large enough to accommodate NO3 or CH2Cl2). During the final stage of the refinement the anisotropic parameters of the gold, platinum, and phosphorus atoms were refined. The phenyl groups were treated as rigid groups during the refinement. The hydrogen atoms were given fixed isotropic temperature factors of 0.05 Å$^2$. The refinement converged to an $R$ value ($=\sum(||F_o|-|F_c||)/\sum|F_o|$) of 0.051 and an $R_w$ value ($=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$) of 0.076 for the 8426 "observed" reflections and 226 variables. The function minimized was $\sum w(F_o-F_c^2)$ with $w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$ with $\sigma(F_o)$ from counting statistics. Positional and thermal parameters are given in Table II, and selected bond distances and angles

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

| atom | x | y | z | $U_{eq}$(×100), Å$^2$ |
|---|---|---|---|---|
| Pt | 0.50000 | 0.36415 (3) | 0.25000 | 2.92 (3) |
| Au2 | 0.38282 (3) | 0.37613 (3) | 0.23997 (2) | 4.39 (3) |
| Au3 | 0.45319 (3) | 0.27359 (3) | 0.27318 (2) | 4.06 (3) |
| Au4 | 0.57653 (3) | 0.31592 (3) | 0.32549 (2) | 3.90 (3) |
| Au5 | 0.48118 (4) | 0.32809 (3) | 0.32809 (2) | 4.98 (3) |
| P2 | 0.2903 (2) | 0.4149 (2) | 0.2297 (2) | 5.7 (2) |
| P3 | 0.4101 (2) | 0.1956 (2) | 0.2919 (2) | 5.1 (2) |
| P4 | 0.6433 (2) | 0.2895 (2) | 0.3952 (2) | 4.3 (2) |
| P5 | 0.4741 (2) | 0.4321 (2) | 0.3905 (2) | 5.6 (2) |
| C1 | 0.50000 | 0.443 (1) | 0.25000 | 6.2 (7) |
| O1 | 0.50000 | 0.489 (1) | 0.25000 | 9.7 (7) |

**Table III.** Selected Bond Lengths (Å) and Bond Angles (deg) (with Esd's)

| | | | |
|---|---|---|---|
| Pt–Au2 | 2.692 (1) | Au3–Au3' | 3.005 (1) |
| Pt–Au3 | 2.651 (1) | Au3–Au4' | 3.079 (1) |
| Pt–Au4 | 2.703 (1) | Au4–Au5 | 2.833 (1) |
| Pt–Au5 | 2.654 (1) | Au4–Au4' | 4.881 (1) |
| Au2–Au3 | 2.967 (1) | Au2–P2 | 2.299 (5) |
| Au2–Au5 | 2.954 (1) | Au3–P3 | 2.302 (4) |
| Au2–Au5' | 4.387 (1) | Au4–P4 | 2.306 (4) |
| Au2–Au4' | 2.903 (1) | Au5–P5 | 2.285 (4) |
| Au3–Au4 | 3.004 (1) | Pt–Cl | 1.896 (29) |
| Au3–Au5 | 3.150 (1) | Cl–O1 | 1.126 (30) |
| Au2–Pt–Au3 | 67.46 (3) | Au4–Pt–Au4' | 129.02 (3) |
| Au2–Pt–Au4 | 120.88 (3) | Au4–Pt–Au5' | 127.62 (4) |
| Au2–Pt–Au5 | 67.08 (3) | Au5–Pt–Au5' | 157.27 (4) |
| Au2–Pt–Au2' | 167.68 (4) | Pt–Au2–P2 | 162.04 (13) |
| Au2–Pt–Au3' | 124.07 (4) | Pt–Au3–P3 | 178.49 (13) |
| Au2–Pt–Au4' | 65.11 (3) | Pt–Au4–P4 | 170.22 (11) |
| Au2–Pt–Au5' | 110.31 (3) | Pt–Au5–P5 | 161.61 (13) |
| Au3–Pt–Au4 | 68.25 (3) | Au2–Pt–Cl | 83.84 (4) |
| Au3–Pt–Au5 | 72.86 (3) | Au3–Pt–Cl | 145.47 (4) |
| Au3–Pt–Au3' | 69.05 (3) | Au4–Pt–Cl | 115.49 (3) |
| Au3–Pt–Au4' | 70.21 (3) | Au5–Pt–Cl | 78.64 (3) |
| Au3–Pt–Au5 | 128.28 (3) | Pt–Cl–O1 | 180.0 |
| Au4–Pt–Au5 | 63.84 (3) | | |

are provided in Table III. Structure factor tables and the positional parameters of the phenyl carbon and hydrogen atoms and of the residual peaks between the clusters are available as supplementary material.

## Results and Discussion

**Synthesis and Characterization of 2.** A solution of **1** in acetone reacts rapidly with CO, giving **2** in high yield. **2** was characterized by elemental analysis and by IR, $^{31}$P NMR, and $^{13}$C NMR spectroscopy, and its solid-state structure was determined by a single-crystal X-ray analysis (vide infra). The cluster ion has a central Pt atom attached to CO and eight AuPPh3 groups as shown in Figure 1b. The $^{31}$P NMR spectrum of **2** is in agreement with this structure and consists of a singlet at $\delta = 51.3$ with Pt satellites at $^2J$(Pt–P) = 391 Hz. These data are similar to those of **1** ($\delta = 55.3$ and $^2J$(Pt–P) = 497 Hz). The low value of $J$(Pt–P) indicates it to be a $^2J$ coupling, which proves Pt to be the central atom in the cluster. The singlet nature of the P resonance could be due to a fast fluxionality of the cluster equilibrating the phosphines, a phenomenon often observed in the analogous homonuclear Au clusters.[17]

The $^{13}$C NMR spectrum of isotopically labeled Pt($^{13}$CO)(AuPPh3)8(NO3)2 shows a nonet at $\delta = 210.7$ with $^3J$(P–C) = 10.9 Hz and Pt satellites at $^1J$(Pt–C) = 1256.5 Hz. These data show that CO is bonded to the central Pt atom. The CO stretching frequency, as observed in the IR spectrum, is at 1940 cm$^{-1}$ (for $^{13}$CO at 1900 cm$^{-1}$). This is very close to the 1930 cm$^{-1}$ found for Pt(PPh3)3(CO), and it is at the lower limit of the range found for the terminal CO in homonuclear Pt carbonyl cluster compounds of the type [Pt3(CO)6]$_n$$^{2-}$.[18] This suggests that the charge

(17) Vollenbroek, F. A.; van den Berg, J. P.; van der Velden, J. W. A.; Bour, J. J. *Inorg. Chem.* **1980**, *19*, 2685.

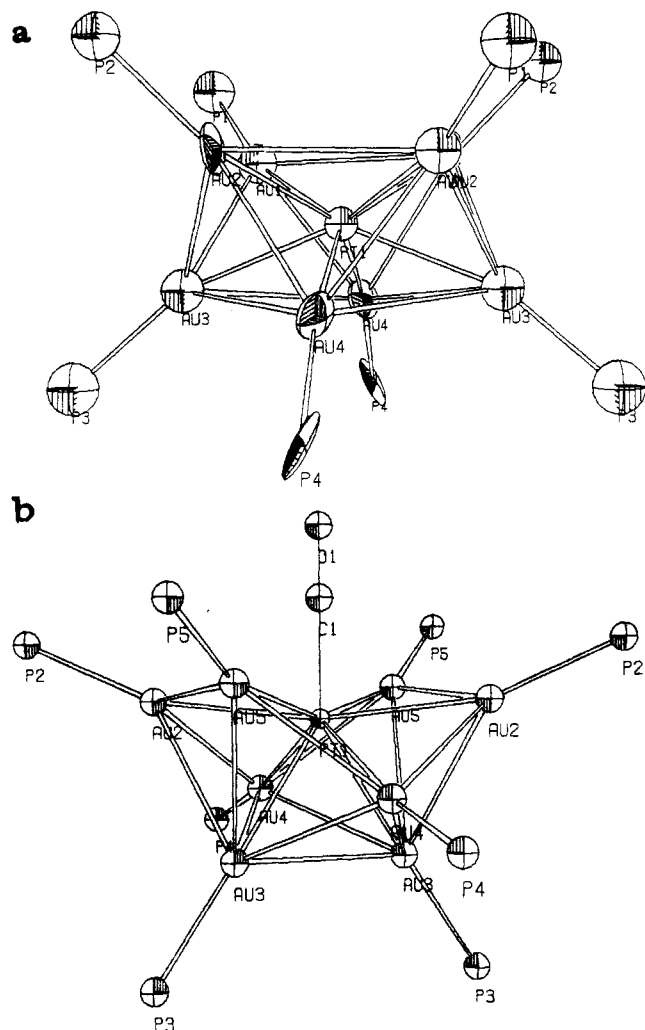**Figure 1.** X-ray structures of **1** (a)[10] and **2** (b). Phenyl groups are omitted for the sake of clarity.

**Table IV.** C–N Vibrational Frequencies (in cm⁻¹) of CN-*i*-Pr Bonded to Au and Pt

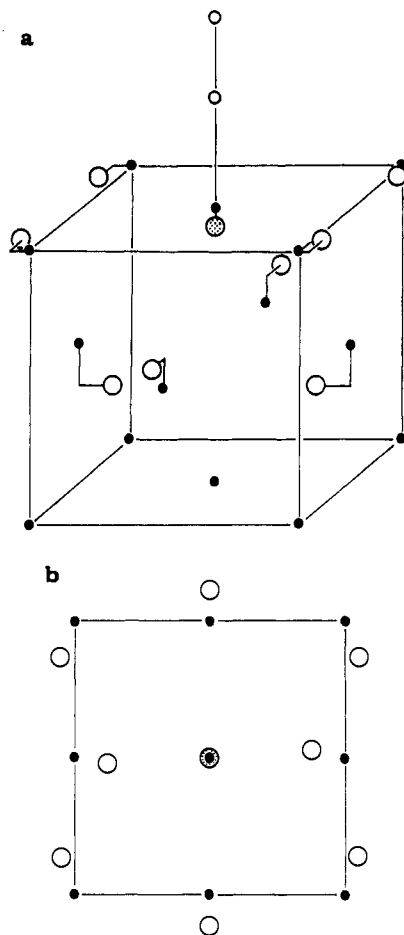| complex | Au-(CN-*i*-Pr) | Pt-(CN-*i*-Pr) | ref |
|---|---|---|---|
| Au(AuPPh₃)₆(AuCN-*i*-Pr)₂³⁺ | 2200 | | 19 |
| [Au(AuPPh₃)₇(AuCN-*i*-Pr)₂(AuI)]²⁺ | 2180 | | 3 |
| Au(AuPPh₃)₆(AuCN-*i*-Pr)(AuI)₃ | 2180 | | 3 |
| Pt(CO)(AuPPh₃)₇(AuCN-*i*-Pr)²⁺ | 2192 | | a |
| Pt(CN-*i*-Pr)(AuPPh₃)₈²⁺ | | 2102 | a |
| Pt(CN-*i*-Pr)(AuPPh₃)₇(AuCN-*i*-Pr)²⁺ | 2187 | 2111 | a |

*a* This work.



**Figure 2.** Similarity of **2** and the face-centered cubic lattice: (a) perspective sketch; (b) scaled projection on (100); O = ideal lattice point.

on the Pt atom is very low or even negative.

The fast reaction of **1** with CO to give **2** is in striking contrast with the case of isoelectronic Au(AuPPh₃)₈³⁺, which shows no reaction with CO. We think that this inertness is not caused by more severe steric hindrance around the central atom but is mainly due to electronic differences. In **2** the frontier orbitals are at higher energy than they are in Au(AuPPh₃)₈³⁺, as concluded from the 0.5 V lower $E_{1/2}$ value for its reduction.[7,19] The frontier orbitals in **2** therefore better match the CO π and π* orbital energies. In this respect these cluster compounds reflect the great difference in stability of the mononuclear Pt and Au carbonyl complexes.

**Synthesis and Characterization of 3, 2a, and 3a.** A solution of **1** in CH₂Cl₂ mixed with an equimolecular amount of CN-*i*-Pr produces **3**. Its elemental analysis is in accord with the composition PtAu₈(PPh₃)₈(CN-*i*-Pr)(NO₃)₂. The isonitrile could be bonded either to Au or to Pt. The ³¹P NMR spectrum showed one singlet (at 50.4 ppm) with a ²J(Pt–P) coupling (of 397 Hz). This indicates that PPh₃ is not bonded to Pt and that, as in the parent compound **1** and the CO analogue **2**, each Au has a bonded PPh₃. The isonitrile is thus bonded to Pt. This is in accord with the CN vibrational frequency found at 2102 cm⁻¹, well beyond the range of 2180–2200 cm⁻¹ for CN-*i*-Pr bonded to Au (see Table IV). Compound **3** is therefore formulated as Pt(CN-*i*-Pr)(AuPPh₃)₈²⁺, and it is formed by an addition reaction of CN-*i*-Pr to **1**, just as **2** is formed by the addition of CO to **1**. The reaction of CNR (R = *i*-Pr and *t*-Bu) with Au(AuPPh₃)₈³⁺ does not yield a simple addition product, but the disubstituted Au(AuCNR)₂(AuPPh₃)₆³⁺ is formed via a complicated reaction path.[20] Au(AuPPh₃)₇²⁺ adds

CNR, but the addition product is unstable and rearranges rapidly to Au(PPh₃)(AuCNR)(AuPPh₃)₆²⁺. So PPh₃ seems to be preferred over CNR as a basic ligand for the central Au atom in these compounds.[3,20]

Clusters **2a** and **3a** are formed when **2** and **3**, respectively, are exposed to an excess of CN-*i*-Pr. For **3a** two different CN-*i*-Pr sites can be detected in the IR spectrum with characteristic absorptions at 2187 and 2111 cm⁻¹. These are assigned to CN-*i*-Pr bonded to Au and Pt, respectively (see Table IV). These two bonding sites are also evident in the ¹H NMR spectrum (CH₃ at 0.90 and 0.61 ppm and CH(CH₃)₂ at 3.45 and 3.24 ppm, respectively). The ³¹P NMR spectrum of **3a** (singlet at 51.9 ppm, ²J(Pt–P) = 378 Hz) is very similar to those of **2** (δ = 51.3 ppm, ²J(Pt–P) = 391 Hz) and **3** (δ = 50.4 ppm, ²J(Pt–P) = 397 Hz).

The IR spectrum of **2a** shows ν(CO) at 1951 cm⁻¹ and ν(CN-*i*-Pr) at 2192 cm⁻¹. The ³¹P NMR data (δ = 53.1 ppm, ²J(Pt–P) = 372 Hz) are very similar to those of **2** and **3a**. In conclusion, we think that, in the reaction of **2** and **3** with excess CN-*i*-Pr, one of the phosphines bonded to a peripheral Au is substituted by a

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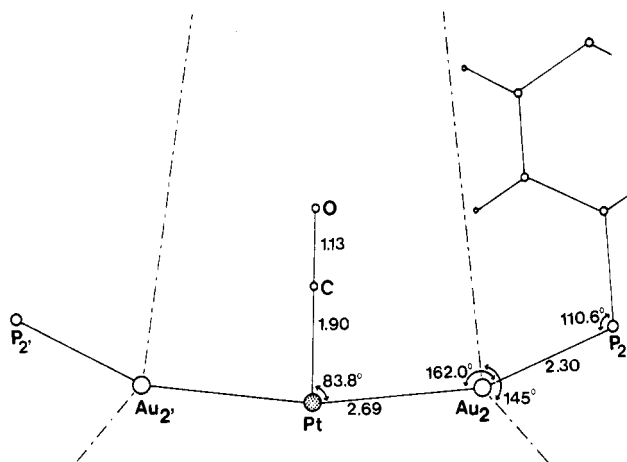
**Figure 3.** Steric hindrance of the phosphines indicated by Tolman cones.

CN-*i*-Pr. So far we have not observed indications for a complicated reaction path as was found[3] for the substitution reaction of Au(AuPPh₃)₈³⁺. A further substitution of PPh₃ by CN-*i*-Pr in **2a** and **3a** must be very slow, since no other products could be detected even after prolonged exposure to an excess of CN-*i*-Pr.

**The X-ray-Determined Structure of 2.** The molecular structure of the cluster ion is shown in Figure 1. The NMR study has given evidence that the central atom is Pt. CO is attached to the central Pt, which is further bonded to eight Au atoms, giving the Pt atom a coordination number of 9. PPh₃ groups with normal bond lengths and angles are bonded to each of the peripheral Au atoms. The Pt–Au bond lengths are 2.65–2.70 Å and are definitely longer than those in the parent cluster **1** (2.63–2.64 Å), but still shorter than the intermetallic distances in Pt–Au alloys (2.77–2.88 Å).[21] The distances between adjacent Au atoms are in the range 2.83–3.15 Å, longer than in **1**, where they are 2.80–2.86 Å. Au–P bond lengths are 2.285–2.306 Å, slightly longer than in **1** (2.25–2.29 Å). The Pt–C bond distance is 1.896 Å, similar to 1.86 Å found for Pt(PPh₃)₃(CO),[22] which has also about the same $\nu$(CO). In the homonuclear Pt carbonyl clusters [Pt₃(CO)₆]ₙ²⁻, the Pt–C bond distances for the terminal carbonyls are significantly shorter[23] (1.77–1.88 Å), although their $\nu$(CO) values are higher. The C–O bond length in **2** (1.126 Å) is in the normal range found for metal carbonyls. The structure of **2** is interesting in comparison

with that of **1**. Both structures are shown in Figure 1. The CO causes the AuPPh₃ groups to bend outward, thus lowering the $S_8$ symmetry of **1** into $C_2$. The toroidlike **1** is changed into the more spherically filled cluster **2**, which is in accord with the change in cluster electron configuration from S²P⁴ into S²P⁶. The increased coordination number of Pt results in a weakening of the metal interactions, as reflected in the increased bond lengths and in the decrease of ²*J*(Pt–P) from 497 Hz in **1** to 391 Hz in **2**. The metal framework of **2** is reminiscent of the (100) plane of the face-centered cubic lattices of Pt and Au (with lattice constants of 3.92 and 4.07 Å, respectively). This is shown in Figure 2, where deviations from the ideal lattice points are indicated in a perspective sketch and in a scaled projection on (100). Although the deviations are significant, the overall similarity is striking. The steric hindrance of the phosphines is illustrated in Figure 3, where a sketch is made along the pseudo (011) plane (that is, the plane through Au2, Pt, Au2', C, and O). Tolman cones[24] are shown around the Au–P vector with a cone angle of 145°. There is less restriction in the (010) and (001) planes, thus allowing the Pt–C–O moiety to be exposed in these directions to external reagents. The stretching frequency of CO adsorbed at various crystal faces of platinum metal is found at 2060–2125 cm⁻¹.[25] These are assigned to CO chemisorbed at steps and terraces. At low coverage of CO on Pt(111), absorptions are found in the range 1810–1860 cm⁻¹, and these are assigned to chemisorption in bridges and on sites of 3-fold symmetry.[26] The $\nu$(CO) found for the linear terminal CO in **2** is at 1940 cm⁻¹, just between both ranges.

Crystal structures are not available at the moment for **2a, 3**, and **3a**. Spectroscopic data, however, give support to the view that their structures are very similar to that of **2**. In **3** and **3a** the central Pt is attached to the CN-*i*-Pr, and in **2a** and **3a** one of the eight peripheral Au atoms has a bonded CN-*i*-Pr in place of a PPh₃. The reactivity of these and analogous compounds is under study and will be reported later.

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