

**GOLD CLUSTERS: SYNTHESIS AND CHARACTERIZATION OF  
 $[\text{Au}_8(\text{PPh}_3)_7(\text{CNR})]^{2+}$ ,  $[\text{Au}_9(\text{PPh}_3)_6(\text{CNR})_2]^{3+}$  AND  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CNR})_2\text{I}]^{2+}$   
 AND THEIR REACTIVITY TOWARDS AMINES. THE CRYSTAL  
 STRUCTURE OF  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-}i\text{-Pr})_2\text{I}](\text{PF}_6)_2$**

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**Summary**

In the reactions of  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ ,  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  with RNC (R = isopropyl and t-butyl) in dichloromethane  $[\text{Au}_8(\text{PPh}_3)_7\text{CNR}]^{2+}$  is initially, and is then converted into  $[\text{Au}_9(\text{PPh}_3)_6(\text{CNR})_2]^{3+}$  via various intermediates.  $[\text{Au}_9(\text{PPh}_3)_6(\text{CNR})_2]^{3+}$  reacts with  $\text{I}^-$  at low temperature ( $-78^\circ\text{C}$ ) in methanol to yield  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CNR})_2\text{I}]^{2+}$ , but when the reaction is carried out at room temperature  $\text{Au}_{11}(\text{PPh}_3)_6(\text{CNR})\text{I}_3$  is formed. The cluster compounds have been characterised by elemental analysis,  $^{31}\text{P}\{^1\text{H}\}$  NMR, conductivity measurements, IR and  $^{197}\text{Au}$  Mössbauer spectroscopy. The reactions of the clusters with amines to form carbene clusters are very slow, and the reasons for this are considered.

The structure of  $[\text{Au}_{11}\text{C}_{134}\text{H}_{112}\text{IN}_2\text{P}_7](\text{PF}_6)$  was determined by X-ray diffraction.  $M_r = 3796.39$  cubic, space group  $143d$ ,  $a$  37.955(12) Å,  $V$  54677.2 Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 2.21$  Mg m<sup>-3</sup>, Mo- $K_\alpha$  radiation (graphite crystal monochromator,  $\lambda$  0.71069 Å),  $\mu(\text{Mo-}K_\alpha)$  125.2 cm<sup>-1</sup>,  $F(000) = 33510.3$ ,  $T$  293 K. Final conventional  $R$ -factor = 0.048,  $R_w = 0.062$  of 1867 unique reflections and 198 variables. The Au-skeleton is the same as in  $\text{Au}_{11}(\text{PPh}_3)_8\text{I}_3$  having  $C_{3v}$  symmetry with one central and 10 peripheral Au atoms.

**Introduction**

The synthesis of gold(I) and gold(III) isocyanide complexes and their reactions with nucleophiles such as amines and alcohols have been much studied [1–4]. The reactions of gold clusters with isocyanides, however, have been little investigated, although we previously described the synthesis of the first isocyanide gold cluster

$[\text{Au}_9(\text{PPh}_3)_6(\text{CNR})_2]^{3+}$  [5]. We now describe the synthesis, properties and structure of three new isocyanide gold cluster compounds,  $[\text{Au}_8(\text{PPh}_3)_7(\text{CN-t-Bu})]^{2+}$ ,  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-i-Pr})_2\text{I}]^{2+}$  and  $\text{Au}_{11}(\text{PPh}_3)_6(\text{CN-i-Pr})\text{I}_3$ .

Since formation of carbenes from isocyanide and amines is an interesting property of the  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  compounds, this reaction has also been studied for the gold cluster compounds.

## Experimental

### Instrumental

C, H and N analysis were carried out in the microanalytical department of the University of Nijmegen and the other analyses by Dr. A. Bernhardt, Elbach über Engelskirchen, F.R.G. Electrical conductivity measurements were performed with a Metrohm Konduktoskop and a Philips PR 9510/00 conductivity cell at 25°C.  $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian XL 100 FT at 40.5 MHz, infrared spectra on a Perkin-Elmer 283 spectrophotometer, and  $^{197}\text{Au}$  Mössbauer spectra at 4.2 K with an apparatus described earlier [6,7]. All materials were of reagent grade.

### Preparations

$[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ ,  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  were synthesized by standard procedures [8].

#### $[\text{Au}_8(\text{PPh}_3)_7(\text{CN-t-Bu})](\text{NO}_3)_2$

To a solution of 200 mg (0.056 mmol) of  $[\text{Au}_8(\text{PPh}_3)_7](\text{NO}_3)_2$  in 10 ml of dichloromethane was added 0.1 ml (2 mmol) t-BuNC. After 2 min the mixture was added to 50 ml ether and the precipitate was filtered off, washed with ether, and dried in vacuo. Yield 200 mg (90%). Anal. Found: C, 42.48; H, 3.16; N, 1.06.  $M = 3619.03$ .  $\text{Au}_8\text{C}_{131}\text{H}_{114}\text{N}_3\text{P}_7\text{O}_6$  calcd.: C, 43.48; H, 3.18; N, 1.16%. IR  $\nu(\text{CN})$  2186 and  $\nu(\text{NO}_3^-)$  1360  $\text{cm}^{-1}$ . (CsI pellet).  $^{31}\text{P}\{^1\text{H}\}$ NMR 52.8 ppm in  $\text{CH}_2\text{Cl}_2$  relative to TMP. Conductivity in methanol at 25°C  $\Lambda_0$  168  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ .

#### $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2](\text{PF}_6)_2$

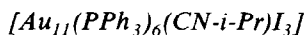
This was prepared as described previously [5].

#### $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-t-Bu})_2](\text{NO}_3)_3$

To a solution of 200 mg (0.056 mmol)  $[\text{Au}_9(\text{PPh}_3)_6](\text{NO}_3)_3$  in 20 ml of dichloromethane was added 0.1 ml (2 mmol) t-BuNC. After 14 d the mixture was added to 50 ml ether and the precipitate was filtered off, then dissolved in 3 ml of dichloromethane. The solution was chromatographed through a silica column (Kieselgel 60 230–400 mesh ASTM) and eluted with a 0.02 M  $\text{KNO}_3$  in methanol. The last band was evaporated to dryness, and the solid redissolved in  $\text{CH}_2\text{Cl}_2$ . The solution was filtered, and red square-pyramidal crystals were obtained by slow diffusion of ether into the solution. Anal. Found: C, 37.63; H, 2.97; N, 1.85.  $M = 3698.76$ .  $\text{Au}_9\text{C}_{118}\text{H}_{108}\text{P}_6\text{N}_5\text{O}_9$  calcd.: C, 38.32; H, 2.94; N, 1.90%. IR  $\nu(\text{CN})$  2175,  $\nu(\text{NO}_3^-)$  1360  $\text{cm}^{-1}$  (CsI pellet).  $^{31}\text{P}\{^1\text{H}\}$  53.3 ppm in  $\text{CH}_2\text{Cl}_2$  relative to TMP.

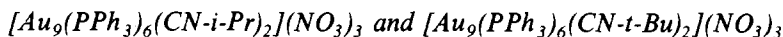


A solution of 137 mg (0.037 mmol) of  $[Au_9(PPh_3)_6(CN-i-Pr)_2](NO_3)_2$  in 6 ml methanol was cooled to  $-78^\circ C$  and a cold ( $-78^\circ C$ ) solution of 124 mg (0.34 mmol)  $Bu_4NI$  in 3 ml methanol was added. After 10 min the mixture was added to a cold ( $-78^\circ C$ ) solution of 55 mg (0.34 mmol)  $NH_4PF_6$  in 14 ml methanol, and the orange-red precipitate was filtered off and washed with 2 ml methanol. Yield 141 mg. Red crystals were obtained by slow diffusion of hexane into an acetone solution. Anal. Found: Au, 49.45; C, 35.55; H, 2.60; N, 0.40; P, 6.52; F, 4.71.  $M = 4557.74$ .  $Au_{11}C_{132}H_{119}N_2P_9F_{12}I$  calcd.: Au, 47.54; C, 35.3; H, 2.63; N, 0.61; P, 6.12; F, 5.00%. IR  $\nu(CN)$  2180,  $\nu(PF_6)$  840  $cm^{-1}$  (CsI pellet).  $^{31}P\{^1H\}NMR$  52.3 ppm relative to TMP in  $CH_2Cl_2$ . Conductivity:  $\Lambda_0$  300  $ohm^{-1} cm^2 mol^{-1}$  at  $25^\circ C$  in acetone.



To a solution of 50 mg (0.015 mmol) of  $[Au_9(PPh_3)_6(CN-i-Pr)_2](NO_3)_3$  in 25 ml of methanol was added a solution of 50 mg (0.15 mmol)  $Bu_4NI$  in 25 ml methanol. After 5 d the solution was colourless and red crystals had formed. The crystals were washed with methanol and dried in vacuo. Anal. Found: C, 34.13; H, 2.46; N, 0.40.  $M = 4169.61$ .  $Au_{11}C_{112}H_{97}NP_6I_3$  calcd.: C, 32.26; H, 2.35; N, 0.34. IR  $\nu(CN)$  2180  $cm^{-1}$  (CsI pellet).  $^{31}P\{^1H\}NMR$  49.2 ppm in  $CH_2Cl_2$  relative to TMP.

#### X-ray analyses



Attempts to solve the crystal structures of these compounds by X-ray diffraction were not successful. The reflections were recorded in the same way as described below for the  $Au_{11}$  cluster. The two compounds appeared to have cubic symmetry; systematic extinctions were compatible with FM3M;  $Z = 4$ ;  $a$  24.08(1) and a 24.35(1) Å for the i-Pr and t-Bu compound, respectively. Intensity data for i-Pr (for t-Bu in parenthesis): measured 3942 (9840); after symmetry averaging 135 (297), of which 97 (213) observed with  $I > 3\sigma$ . The two compounds gave almost identical Patterson syntheses, the highest peaks of which were entirely consistent with a centered-cube  $Au_9$  cluster.

Further structure elucidation was not possible because of disorder.



A crystal obtained by recrystallization from an acetone hexane solution was used. Mo- $K_\alpha$  radiation was used with a graphite crystal monochromator on a Nonius CAD4 single crystal diffractometer ( $\lambda$  0.71069 Å). The cubic unit cell dimensions,  $a$  37.955(12) Å,  $V$  54677 Å<sup>3</sup>, were determined from the angular settings of 25 reflections with  $14^\circ < \theta < 16^\circ$ .  $Z = 16$ . The space group was determined to be  $I\bar{4}3d$  from the reflection conditions:  $hkl$ :  $h + k + l = 2n$ ;  $0kl$ :  $k + l = 2n$ ;  $hhl$ :  $2h + l = 4n$ ;  $h00$ :  $h = 4n$  and the structure determination. The intensity data of 25505 reflections, (the half sphere up to  $\theta$  45°), were measured, using the  $\omega - 2\theta$  scan technique, with a scan angle of 1.10° and a variable scan rate with a maximum scan time of 20 s per reflection. The intensity of the primary beam was checked by monitoring three reference reflections every 30 min. The final drift correction factors were between 0.98 and 1.04. A smooth curve based on the reference reflections was used to correct

for this drift. For all reflections a profile analysis was performed [9,10]; an empirical absorption correction was applied, using psi scans [11],  $\mu(\text{Mo-K}\alpha)$  125.2 cm<sup>-1</sup> (correction factors were in the range 0.42 to 1.00). Laue symmetry equivalent reflections were averaged,  $R_{\text{int}} = \Sigma(I - \langle I \rangle) / \Sigma I = 0.119$ , resulting in 3112 unique reflections of which 1867 had  $I > 3\sigma(I)$ . Lorentz and polarization corrections were applied and the data were reduced to  $|F_0|$ -values.

An automated combination [12] of SHELX84 [13] and DIRDIF [14] was used to investigate all possible space groups ( $Im\bar{3}m$ ,  $I\bar{4}3m$ ,  $I\bar{4}3d$ ,  $I432$  and  $I4_132$ ) assuming that the space group can largely be explained by the high symmetry of the gold cluster. Only  $I\bar{4}3m$  and  $I\bar{4}3d$  led to a possible gold cluster and expansion in  $I\bar{4}3d$  gave the solution of the structure. The structure was refined by full-matrix least-squares on  $|F|$  values, using SHELX [15]. Scattering factors were taken from ref. 16 and the effects of anomalous dispersion were included in  $F_c$  by using Cromer and Ibers values of  $\nabla f'$  and  $\nabla f''$ . Hydrogen atoms were found in the difference Fourier maps and were included in idealized positions at 1.08 Å from the carbon atom to which they are bonded. During the evaluation of the structure it became apparent that the iodine atoms and the two i-PrNC groups occupy positions which are related by a crystallographic threefold axis. This disordered situation was refined with 1/3 occupancy for the iodine and 2/3 for the atoms of the i-PrNC ligand. The hexafluorophosphate ions were also found to be disordered; the occupancy factors were refined (see Table 2) using fixed temperature factors. If one PF<sub>6</sub> is present on each P-site, there are 2<sup>1/4</sup> PF<sub>6</sub> ions per Au<sub>11</sub> cluster, so the P-sites must be partially occupied. The weighted sum of the refined occupancy factors gives 1.6 PF<sub>6</sub> ions per Au<sub>11</sub> clusters, but this is not a very accurate value because of disorder and correlations with temperature factors. There is chemical evidence for the presence of 2 PF<sub>6</sub> ions per cluster. Isotropic refinement converged to  $R = 0.063$ .

At this stage empirical absorption correction was applied [17] resulting in a further decrease of  $R$  to 0.061 (correction factors were in the range 0.888–1.044). After completion of the isotropic refinement the Bijvoet coefficient was calculated [18], resulting in a value of +0.86(5), based on 32 Friedel pairs, showing that the absolute structure is correct. During the final stages of the refinement the positional parameters of all atoms and the anisotropic thermal parameters of the nonhydrogen atoms were refined; the phenyl groups were refined as rigid group with standard geometry. Owing to the disorder effects, the bond lengths of the atoms of the isocyanide fragment and those of the atoms of the hexafluorophosphate fragments were fixed at normal lengths. The hydrogen atoms had fixed isotropic temperature factors of 0.08 Å<sup>2</sup>. The final conventional agreement factors were  $R = 0.048$  and  $R_w = 0.062$  for the 1867 'observed' reflections and 198 variables. The function minimized was  $\Sigma w(F_0 - F_c)^2$  with  $w = 1/(\sigma^2(F_0) + 0.00016F_0^2)$  with  $\sigma(F_0)$  from counting statistics. The maximum shift to error ratio in the last full matrix least-squares cycle was less than 0.5. The final difference Fourier map showed no peaks higher than 1 e/Å<sup>3</sup> (found in the neighbourhood of the gold atoms). Plots were made with PLUTO [19].

## Results and discussion

### *The formation and structure of [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>(CNR)]<sup>2+</sup>*

The reaction of [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup>, [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup> and [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> with RNC

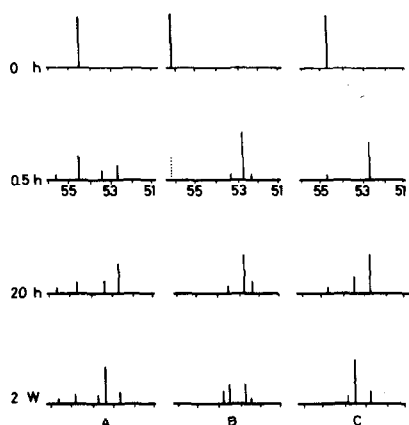
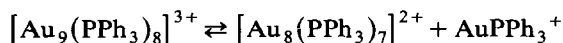
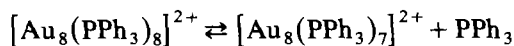


Fig. 1. Time-dependent  $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in  $\text{CH}_2\text{Cl}_2$  relative to TMP in ppm. (A)  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  + CN-t-Bu; (B)  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  + CN-t-Bu; (C)  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  + CN-t-Bu.

which ultimately leads to the formation of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CNR})_2]^{3+}$  is not straightforward, and follows a complicated path. The time dependent  $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of CN-t-Bu with  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ ,  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  are shown in Fig. 1. The reaction with  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  is slow; initially a compound with a peak at 52.8 ppm is the main product, but after 2 weeks this has largely been converted into  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-t-Bu})_2]^{3+}$ , which was identified by its peak at 53.3 ppm.

$[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  reacts much faster. It is completely converted after 0.5 h, the compound with a peak at 52.8 ppm is again the main intermediate, after 2 weeks it is partially converted into  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-t-Bu})_2]^{2+}$ .

The progression of the reaction of  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  with CN-t-Bu is roughly in between the reactions of  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  and  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ . From the NMR data we conclude that the reaction rates fall in the sequence  $[\text{Au}_8(\text{PPh}_3)_7]^{2+} > [\text{Au}_8(\text{PPh}_3)_8]^{2+} > [\text{Au}_9(\text{PPh}_3)_8]^{3+}$ . The reacting species is probably  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ , which is formed in the following reversible reactions:



From this point of view it was of interest to record the  $^{31}\text{P}$  NMR spectra of  $\text{CH}_2\text{Cl}_2$  solutions of (i) a mixture of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  with  $[\text{Au}_9(\text{P}(p\text{-tol})_3)_8]^{3+}$  and (ii) a mixture of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  with  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ . That of the first solution shows a rapid broadening and splitting of the peaks of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  and  $[\text{Au}_9(\text{P}(p\text{-tol})_3)_8]^{3+}$ , but that of the second shows only sharp peaks of the initial clusters.

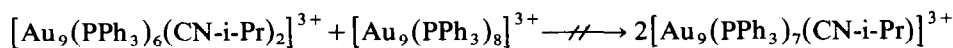
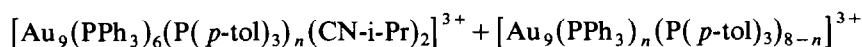
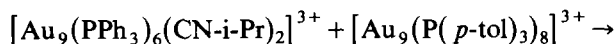


TABLE 1  
 MÖSSBAUER DATA

	Au-site <sup>a</sup>	<i>QS</i> (mm s <sup>-1</sup> )	<i>IS</i> (mm s <sup>-1</sup> )	Ref.
t-BuNCAuCl	—	8.0	2.2	5
PPh <sub>3</sub> AuCl	—	7.5	2.9	5
[Au <sub>9</sub> (PPh <sub>3</sub> ) <sub>6</sub> (CN-i-Pr) <sub>2</sub> ] <sup>3+</sup>	Au <sub>c</sub>	0	2.9	5
	Au <sub>p</sub> -P	6.8	1.8	
	Au <sub>p</sub> -CN-i-Pr	6.8	0.9	
[Au <sub>8</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>2+</sup>	Au <sub>c</sub> -P	0	2.4	20
	Au <sub>p</sub> -P	6.7	1.9	
	Au <sub>c</sub> -P	0	2.3	
[Au <sub>8</sub> (PPh <sub>3</sub> ) <sub>7</sub> (CN-t-Bu)] <sup>2+</sup>	Au <sub>p</sub> -P	6.9	2.0	
	Au <sub>p</sub> -CN-t-Bu	5.9	0.9	
	Au <sub>c</sub>	0	2.9	20,21
	Au <sub>p</sub> -P	6.6	1.6	
[Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>7</sub> I <sub>3</sub> ]	Au <sub>p</sub> -I	4.1	0.0	
	Au <sub>c</sub>	0	2.7	this work
	Au <sub>p</sub> -P	6.7	1.6	
	Au <sub>p</sub> -CN-i-Pr	6.0	0.4	
[Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>7</sub> (CN-i-Pr) <sub>2</sub> I] <sup>2+</sup>	Au <sub>p</sub> -I	not found, probably due to low intensity		
	Au <sub>c</sub>	0	2.9	this work
	Au <sub>p</sub> -P	6.3	1.5	
	Au <sub>p</sub> -CN-i-Pr	6.8	2.2	
Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>6</sub> (CN-i-Pr)I <sub>3</sub>	Au <sub>p</sub> -I	4.8	-0.2	
	Au <sub>c</sub>	0	2.9	
	Au <sub>p</sub> -P	6.3	1.5	
	Au <sub>p</sub> -CN-i-Pr	6.8	2.2	

<sup>a</sup> Au<sub>c</sub> = central gold atom, Au<sub>p</sub> = peripheral gold atom.

These results indicate that although the phosphines PPh<sub>3</sub> and P(*p*-tol)<sub>3</sub> exchange rapidly, the CN-i-Pr does not so with PPh<sub>3</sub>. This observation supports our view that the reaction of [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>3+</sup> with RNC goes via the coordinatively unsaturated [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup>.

The compound with the 52.8 ppm signal was isolated and identified as [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>(CN-t-Bu)](NO<sub>3</sub>)<sub>2</sub>. The value of  $\nu(\text{CN})$  2186 cm<sup>-1</sup>, is about 40 cm<sup>-1</sup> higher in frequency than that for the free CN-t-Bu ligand, as is usual. The conductivity in methanol ( $\Lambda_0$  168 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) indicates a 2/1 electrolyte.

The Mössbauer spectrum of [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>(CN-t-Bu)]<sup>2+</sup> could be fitted to 5 lines for 3 gold sites (Table 1). In line with former studies [20–22] these can be identified

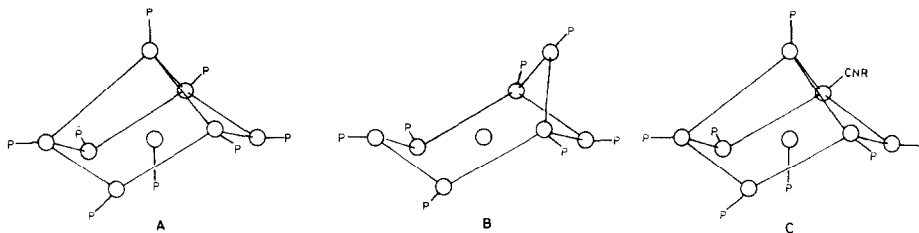


Fig. 2. [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup> (A) as determined by X-ray analysis; [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>2+</sup> (B) as determined by X-ray analysis; [Au<sub>8</sub>(PPh<sub>3</sub>)<sub>7</sub>(CNR)]<sup>2+</sup> (C) as indicated by Mössbauer data. The position of CNR at one of the seven peripheral gold atoms is arbitrary.

as a central gold phosphine site ( $IS\ 2.3$ ,  $QS\ 0\ \text{mm s}^{-1}$ ), a peripheral gold isocyanide site ( $IS\ 0.9$ ,  $QS\ 5.9\ \text{mm s}^{-1}$ ), and a peripheral gold phosphine site ( $IS\ 2.0$ ,  $QS\ 6.9\ \text{mm s}^{-1}$ ). As the central gold phosphine site and the peripheral gold phosphine site have Mössbauer parameters very close to those of  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ , we conclude that their gold skeletons are rather similar.  $[\text{Au}_8(\text{PPh}_3)_7(\text{CN-t-Bu})]^{2+}$  is thus not a simple addition product of  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  and CN-t-Bu, because some rearrangement must have taken place, the CN-t-Bu being bonded not to the vacant coordination site of the central gold atom but to one of the peripheral gold atoms. The single signal for the central Au-site indicates that there has been a rearrangement of the Au skeleton to that of  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  (see Fig. 2).

*The structure of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$*

We prepared crystals of the previously described  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  cluster [5] which were apparently suitable for X-ray structure determination, but it turned out that because of disorder only the gold skeleton could be determined, and a complete structure determination was impossible. The gold skeleton was found to be a centered cube with edge  $\text{Au-Au} = 2.9$  (in  $Fm\bar{3}m$ :  $\text{Au}_1 = 0, 0, 0$ ;  $\text{Au}_2 = 0, 0, 0.061$ ) The isostructural  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-t-Bu})_2](\text{PF}_6)_2$  cluster gives the same result.

(Continued on p. 394)

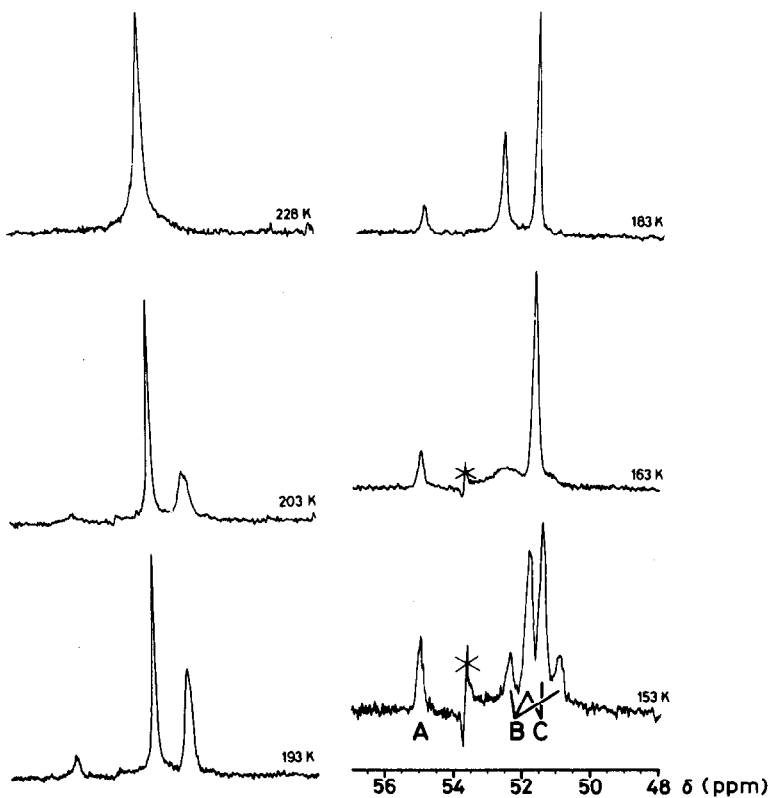


Fig. 3. Temperature-dependent  $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  in  $\text{CH}_2\text{Cl}_2$  relative to TMP.

TABLE 2

FRACTIONAL POSITIONAL AND THERMAL PARAMETERS (with esd's) FOR  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-}i\text{-Pr})_2\text{I}]^{2+}$ 

Atom	x	y	z	$U_{\text{eq}} (\times 100)$ ( $\text{\AA}^2$ )
Au(1)	0.28730(5)	0.28730(5)	0.28730(5)	4.21(6)
Au(2)	0.21889(5)	0.27486(6)	0.27655(6)	5.73(9)
Au(3)	0.33411(6)	0.24879(6)	0.32415(6)	6.46(10)
Au(4)	0.25169(6)	0.34305(6)	0.26163(6)	6.76(10)
Au(5)	0.32727(5)	0.32727(5)	0.32727(5)	5.32(6)
I	0.2180(4)	0.3996(4)	0.2340(4)	6.9(6)
P(2)	0.1594(4)	0.2697(4)	0.2711(4)	5.4(6)
P(3)	0.3790(4)	0.2184(4)	0.3493(4)	6.2(6)
P(5)	0.3617(3)	0.3617(3)	0.3617(3)	5.0(4)
C(21)	0.1118(7)	0.2758(7)	0.2150(8)	4.4(14)
C(22)	0.1018(7)	0.2707(7)	0.1800(8)	6.2(17)
C(23)	0.1250(7)	0.2549(7)	0.1563(8)	8.4(18)
C(24)	0.1583(7)	0.2441(7)	0.1677(8)	5.5(15)
C(25)	0.1683(7)	0.2491(7)	0.2027(8)	4.8(13)
C(26)	0.1451(7)	0.2650(7)	0.2264(8)	4.9(15)
C(27)	0.1626(7)	0.2173(9)	0.3184(9)	8.9(20)
C(28)	0.1513(7)	0.1891(9)	0.3391(9)	9.6(20)
C(29)	0.1173(7)	0.1758(9)	0.3351(9)	5.1(14)
C(2A)	0.0946(7)	0.1906(9)	0.3103(9)	5.7(14)
C(2B)	0.1058(7)	0.2188(9)	0.2896(9)	6.2(16)
C(2C)	0.1398(7)	0.2322(9)	0.2936(9)	6.7(17)
C(2D)	0.1509(8)	0.3387(11)	0.2815(10)	8.5(20)
C(2E)	0.1356(8)	0.3705(11)	0.2920(10)	9.7(14)
C(2F)	0.1034(8)	0.3703(11)	0.3097(10)	10.2(33)
C(2G)	0.0866(8)	0.3384(11)	0.3169(10)	11.5(25)
C(2H)	0.1019(8)	0.3067(11)	0.3064(10)	9.9(22)
C(2I)	0.1341(8)	0.3069(11)	0.2887(10)	4.4(14)
C(31)	0.4322(10)	0.2527(9)	0.3922(8)	10.8(23)
C(32)	0.4616(10)	0.2745(9)	0.3947(8)	8.6(21)
C(33)	0.4759(10)	0.2896(9)	0.3644(8)	9.2(20)
C(34)	0.4608(10)	0.2829(9)	0.3316(8)	9.5(20)
C(35)	0.4314(10)	0.2610(9)	0.3290(8)	10.2(21)
C(36)	0.4170(10)	0.2459(9)	0.3593(8)	5.2(14)
C(37)	0.4323(9)	0.1732(9)	0.3258(8)	7.8(16)
C(38)	0.4464(9)	0.1466(9)	0.3048(8)	8.3(20)
C(39)	0.4251(9)	0.1291(9)	0.2805(8)	11.6(23)
C(3A)	0.3897(9)	0.1382(9)	0.2772(8)	11.6(24)
C(3B)	0.3755(9)	0.1648(9)	0.2983(8)	6.5(16)
C(3C)	0.3969(9)	0.1823(9)	0.3225(8)	6.2(15)
C(3D)	0.3871(8)	0.1690(9)	0.4037(10)	5.9(16)
C(3E)	0.3796(8)	0.1554(9)	0.4370(10)	11.1(27)
C(3F)	0.3513(8)	0.1688(9)	0.4563(10)	12.1(29)
C(3G)	0.3306(8)	0.1958(9)	0.4424(10)	13.1(29)
C(3H)	0.3382(8)	0.2094(9)	0.4091(10)	8.8(20)
C(3I)	0.3664(8)	0.1960(9)	0.3897(10)	6.3(16)
C(41)	0.2340(7)	0.3878(4)	0.2401(7)	6. (3)
N(4)	0.2215(10)	0.4144(8)	0.2294(14)	0.5(21)
C(42)	0.2145(15)	0.4482(8)	0.2129(15)	32. (9)
C(43)	0.190 (3)	0.4490(27)	0.1789(25)	26. (7)
C(44)	0.2406(27)	0.4792(11)	0.220 (4)	30. (9)
C(51)	0.3113(9)	0.4143(8)	0.3584(7)	6.3(16)



TABLE 2 (continued)

Atom	x	y	z	$U_{eq}$ ( $\times 100$ ) ( $\text{\AA}^2$ )	Occupation factor
C(52)	0.2946(9)	0.4451(8)	0.3698(7)	5.5(15)	
C(53)	0.3060(9)	0.4619(8)	0.4004(7)	6.7(17)	
C(54)	0.3340(9)	0.4480(8)	0.4197(7)	6.8(17)	
C(55)	0.3507(9)	0.4172(8)	0.4084(7)	4.9(14)	
C(56)	0.3393(9)	0.4003(8)	0.3777(7)	6.8(18)	
C(56)	0.3393(9)	0.4004(8)	0.3778(7)	6.8(17)	
P(7)	0.2500	0.5048(7)	0.5000	8.0	0.36(2)
F(71)	0.2792(8)	0.4848(11)	0.4896(14)	8.0	0.36(4)
F(72)	0.2478(16)	0.5193(9)	0.4661(4)	8.0	0.45(4)
F(73)	0.2724(10)	0.5322(10)	0.5104(13)	8.0	0.30(4)
F(74)	0.2276(10)	0.4773(10)	0.4897(13)	8.0	0.33(5)
P(8)	0.1250	0.5000	0.2500	8.0	0.11(1)
F(81)	0.0881(11)	0.5000	0.2500	8.0	0.14(3)
F(82)	0.1250	0.4631(11)	0.2500	8.0	0.30(4)

TABLE 3

BOND ANGLES ( $^\circ$ ) (with esd's)

Au(2)–Au(1)–Au(3)	128.7(1)	Au(2)–Au(4)–I	54.7(1)	Au(3)–P(3)–C(3C)	114.9(11)
Au(2)–Au(1)–Au(4)	66.1(1)	Au(4)–Au(5)–I	136.6(3)	Au(3)–P(3)–C(3I)	113.4(12)
Au(2)–Au(1)–Au(5)	138.7(1)	Au(1)–Au(2)–P(2)	173.6(4)	Au(5)–P(5)–C(56)	113.1(11)
Au(3)–Au(1)–Au(4)	161.0(1)	Au(2)–Au(4)–P(2)	118.7(4)	Au(4)–C(41)–N(4)	174.7(7)
Au(3)–Au(1)–Au(5)	68.4(1)	Au(1)–Au(3)–P(3)	172.1(4)	C(26)–P(2)–C(2C)	104.1(15)
Au(4)–Au(1)–Au(5)	92.6(1)	Au(3)–Au(5)–P(3)	123.7(4)	C(26)–P(2)–C(2I)	105.2(16)
Au(2)–Au(1)–Au(2)	69.7(1)	Au(1)–Au(5)–P(5)	180.0	C(2C)–P(2)–C(2I)	102.6(16)
Au(1)–Au(2)–Au(4)	57.3(1)	Au(3)–Au(5)–P(5)	123.2(1)	C(36)–P(3)–C(3C)	104.5(16)
Au(1)–Au(3)–Au(5)	54.7(1)	Au(4)–Au(5)–P(5)	135.6(1)	C(36)–P(3)–C(3I)	107.6(17)
Au(1)–Au(4)–Au(2)	56.6(1)	Au(1)–Au(4)–C(41)	169.5(8)	C(3C)–P(3)–C(3I)	102.6(16)
Au(1)–Au(4)–Au(5)	43.0(1)	Au(2)–Au(4)–C(41)	133.4(8)	C(51)–P(5)–C(51')	105.6(16)
Au(2)–Au(4)–Au(5)	93.1(1)	Au(5)–Au(4)–C(41)	130.3(8)	C(41)–N(4)–C(42)	101.2(1)
Au(1)–Au(5)–Au(3)	56.8(1)	Au(2)–P(2)–C(26)	113.3(11)	N(4)–C(42)–C(43)	118.2(1)
Au(1)–Au(5)–Au(4)	44.4(1)	Au(2)–P(2)–C(2C)	115.5(12)	N(4)–C(42)–C(44)	118.4(1)
Au(3)–Au(5)–Au(4)	101.2(1)	Au(2)–P(2)–C(2I)	114.8(12)	C(43)–C(42)–C(44)	119.6(1)
Au(1)–Au(4)–I	177.7(3)	Au(3)–P(3)–C(36)	112.9(13)		

TABLE 4

BOND LENGTHS ( $\text{\AA}$ ) (with esd's)

Au(1)–Au(2)	2.670(3)	Au(2)–P(2)	2.276(14)	P(3)–C(3C)	1.84(4)
Au(1)–Au(3)	2.692(2)	Au(3)–P(3)	2.270(14)	P(3)–C(3I)	1.81(4)
Au(1)–Au(4)	2.693(2)	Au(5)–P(5)	2.266(21)	P(3)–C(3I)	1.18(4)
Au(1)–Au(5)	2.627(4)	Au(4)–C(41)	2.000(1)	P(5)–C(56)	1.80(4)
Au(2)–Au(2')	3.051(3)	P(2)–C(26)	1.79(3)	C(41)–N(4)	1.118(1)
Au(2)–Au(4)	2.927(3)	P(2)–C(2C)	1.82(4)	N(4)–C(42)	1.453(1)
Au(3)–Au(5)	2.992(3)	P(2)–C(2I)	1.83(4)	C(42)–C(43)	1.584(1)
Au(4)–I	2.709(14)	P(3)–C(36)	1.82(4)	C(42)–C(44)	1.559(1)

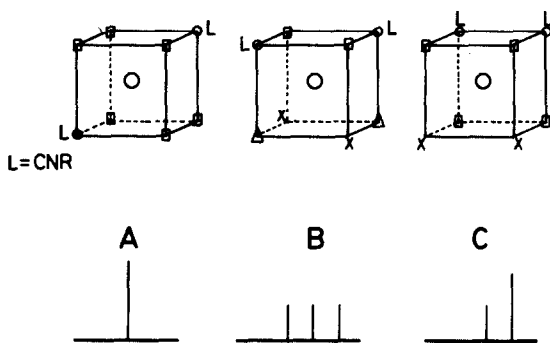


Fig. 4. The three isomers **A**, **B** and **C** proposed for  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{2+}$ .

$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (see Fig. 3) at room temperature shows one sharp peak, but as the temperature is lowered new peaks grow. The spectra can be explained by the assumption that there are three isomers, **A**, **B** and **C** (see Fig. 4), with one, three and two phosphorus sites respectively. At room temperature the isomers are interconverted by fast intramolecular movements. In the temperature range 210–170 K the single peak found at room temperature is split into three signals, one from each of the three isomers, which are no longer interconvertible at these temperatures, but still undergo rapid equilibration of their phosphine ligands. At 155 K this fluxionality is also blocked, and all the phosphine sites can be detected. Some coincidence of signals from **B** and **C** is assumed, as indicated in Fig. 3.

#### *Formation and properties of $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-i-Pr})_2\text{I}]^{2+}$*

The reaction of  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  with halide or pseudohalide ion ( $\text{X}$ ) leads to the formation of  $[\text{Au}_{11}(\text{PPh}_3)_8\text{X}_2]^+$  [8] and so it seemed of interest to examine the reaction of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  with halide ion. With  $\text{I}^-$  in methanol at 200 K  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-i-Pr})_2\text{I}]^{2+}$  was formed; the product was identified by chemical analyses, conductivity measurements ( $\Lambda_0$  300  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  at 25°C in acetone; indicating a 2/1 electrolyte) and IR spectroscopy ( $\nu(\text{CN})$  2180  $\text{cm}^{-1}$ ; indicating coordination of *i*-PrNC).

The Mössbauer spectrum of this compound can be fitted to 5 lines for three gold sites: (see Table 1) a central gold ( $\text{Au}_c$ ) with a single resonance line at  $IS$  2.7  $\text{mm s}^{-1}$ , a peripheral gold phosphine ( $\text{Au}_p\text{-P}$ ) site with a quadrupole pair  $IS$  1.6 and  $QS$  6.7  $\text{mm s}^{-1}$ , and a peripheral gold isocyanide ( $\text{Au}_p\text{-CN-i-Pr}$ ) site with a quadrupole pair  $IS$  0.4 and  $QS$  6.0  $\text{mm s}^{-1}$ . No gold-iodide site could be found probably because of the expected low intensity.

Its structure was determined by X-ray analysis and was found to be nearly the same as that of  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$  [23].

#### *The X-ray structure of $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-i-Pr})_2\text{I}](\text{NO}_3)_2$*

Fractional positional parameters, selected bond angles and bond distances are listed in Tables 2, 3 and 4. The dicationic cluster ion has one central and 10 peripheral gold atoms, which are situated at the centre and the vertices of an icosahedron with one triangular face replaced by a single vertex (Fig. 5). The metal framework is thus very similar to that in other  $\text{Au}_{11}$  clusters:  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$  [23],

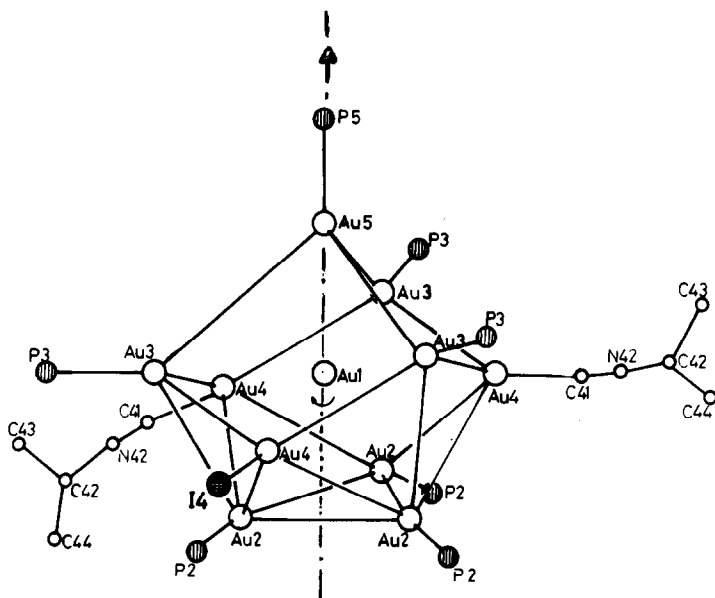


Fig. 5. Structure of  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-}i\text{-Pr})_2\text{I}]^{2+}$  and the atomic numbering scheme.

$\text{Au}_{11}(\text{PPh}_3)_7(\text{SCN})_3$  [24],  $\text{Au}_{11}(\text{P}(p\text{-ClC}_6\text{H}_4)_3)_7\text{I}_3$  [25] and  $\text{Au}_{11}(\text{P}(p\text{-FC}_6\text{H}_4)_3)_7\text{I}_3$  [26], all with symmetry  $C_{3v}$ .

The positions of the iodine and the two isopropylisocyanide ligands in the crystal are related by a crystallographic threefold axis, leading to disorder. The Au–C distance was fixed at 2.000 Å during the refinement procedure because of this disorder.

The relevant bond parameters are listed in Table 5, along with those of  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$  for comparison. The distances between central and peripheral Au atoms are in the range 2.627–2.693 Å and those between peripheral Au atoms between 2.927–3.051 Å. These distances and the values of the main bond angles are

TABLE 5

A COMPARISON OF BOND ANGLES ( $^\circ$ ) AND BOND DISTANCES (Å) IN  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$  AND  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-}i\text{-Pr})_2\text{I}]^{2+}$

	$[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-}i\text{-Pr})_2\text{I}]^{2+}$	$\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$ [3]
Au(1)–Au(5)–P(5)	180.0	178.5
Au(1)–Au(2)–P(2)	173.6	170.4–175.6
Au(1)–Au(3)–P(3)	172.1	171.1–177.3
Au(1)–Au(4)–I(4)	177	175.4–177.6
Au(1)–Au(2,3,4,5)	2.627(4)–2.693(3)	2.634(1)–2.732(2)
Au(2)–Au(4)	2.927(3)	2.877(1)–3.145(2)
Au(2)–Au(2)	3.051(3)	3.031(2)–3.083(1)
Au(3)–Au(5)	2.992(3)	2.919(1)–2.963(1)
Au(2,3,5)–P	2.266(21)–2.276(14)	2.289(63)–2.455(74)
Au(4)–I(4)	2.709(14)	2.616(13)–2.623(14)

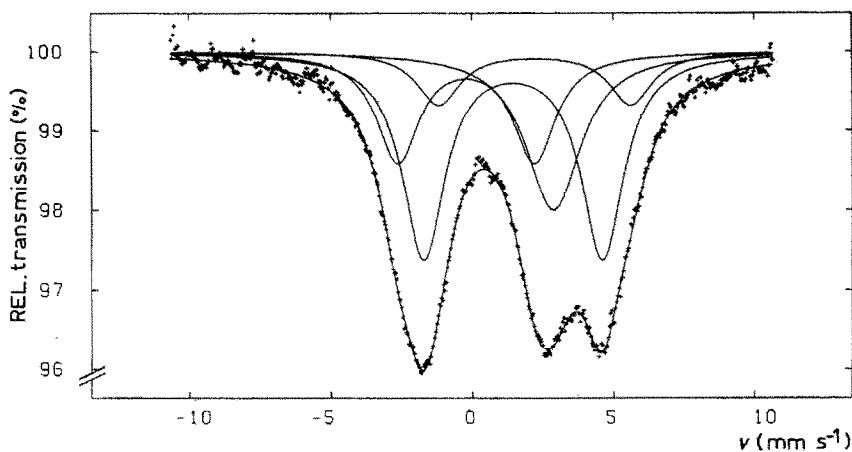


Fig. 6. Mössbauer spectrum of  $\text{Au}_{11}(\text{PPh}_3)_6(\text{CN-i-Pr})\text{I}_3$ .

very close to those found in  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$  (see Table 5). The Au–I bond distance is 2.709 Å, which is 0.1 Å longer than that in  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$ .

#### *Formation and properties of $\text{Au}_{11}(\text{PPh}_3)_6(\text{CN-i-Pr})\text{I}_3$*

When the reaction of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  with  $\text{I}^-$  in methanol is carried out at room temperature,  $\text{Au}_{11}(\text{PPh}_3)_6(\text{CN-i-Pr})\text{I}_3$  was formed. The product was identified by chemical analysis and by its solubility in benzene, which indicates an unchanged cluster molecule. In the IR spectra  $\nu(\text{CN})$  appears at  $2180\text{ cm}^{-1}$ , the same frequency as in  $[\text{Au}_{11}(\text{PPh}_3)_7(\text{CN-i-Pr})_2\text{I}]^{2+}$ .

The  $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a benzene solution shows a single signal at 49.2 ppm relative to TMP, which is in the usual region for uncharged  $\text{Au}_{11}$  clusters (47.5–50.0 ppm) [27].

The Mössbauer spectrum (Fig. 6) can be fitted to 7 lines for 4 gold sites, a central gold site with a single resonance line at  $IS\ 2.9\text{ mm s}^{-1}$ , a peripheral gold phosphine site with a quadrupole pair at  $IS\ 1.5$  and  $QS\ 6.3\text{ mm s}^{-1}$ , a peripheral gold iodide site with a quadrupole pair at  $IS\ 0.2$  and  $QS\ 4.8\text{ mm s}^{-1}$ , and a gold isopropylisocyanide site with a quadrupole pair at  $IS\ 2.2$  and  $QS\ 6.8\text{ mm s}^{-1}$ . These data are all in expected range and so are confident that  $\text{Au}_{11}(\text{PPh}_3)_6(\text{CN-i-Pr})\text{I}_3$  is similar to the well known  $\text{Au}_{11}(\text{PPh}_3)_7\text{I}_3$ , but with one phosphine replaced by CN-i-Pr.

#### *The reaction with amines*

The addition of primary amines to gold(I) isocyanide complexes leads to formation of formamidine complexes [1–4]. The magnitude of the  $\nu(\text{CN})$  shift seems to be significant for the reactivity of the isocyanide ligand. Carbene formation from  $\text{Au}^{\text{I}}$  complexes is influenced by the electron-withdrawing effect of the gold atoms, which is reflected in the  $\nu(\text{CN})$  frequency, and carbene formation generally only takes place if the frequency of the coordinated ligand is at least  $60\text{ cm}^{-1}$  higher than that of the free ligand.

Although the shifts of 40 to  $60\text{ cm}^{-1}$  for the  $\text{Au}_9$  isocyanide clusters seem low, these clusters do react with primary amines to form carbene cluster compounds. However, these reactions are very slow (30 days were needed for a reasonable extent

of conversion) and complex. We could not isolate pure products, and so abandoned this aspect of the investigation for the time being. There are probably three factors giving rise to this very slow carbene formation. First, the effective charge of the gold atoms in a gold cluster is smaller than that in Au<sup>I</sup> compounds, and this certainly result in slower carbene formation. Second, there is steric hindrance to the approach of the amine from the bulky phosphines. Third, the equilibrium  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+} \rightleftharpoons [\text{Au}_8(\text{PPh}_3)_6(\text{CN-i-Pr})]^{2+} + (\text{AuCN-i-Pr})^+$  could play a role, since  $(\text{AuCN-i-Pr})^+$  reacts with amine and the carbene could add to the Au<sub>8</sub> cluster. However, the <sup>31</sup>P{<sup>1</sup>H}NMR experiments with mixtures of  $[\text{Au}_9(\text{PPh}_3)_6(\text{CN-i-Pr})_2]^{3+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ , mentioned above, indicate that the rates of the reactions giving rise to this equilibrium are unfavourably low.

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