Preparation and Properties of Cyano(triphenylphosphoniomethanide)-gold(I) and its Oxidative-addition Products with Halogens

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The 1 : 1 complex $[Au(CN)(CH_2PPh_3)]$ has been obtained from the reaction between triphenylphosphoniomethanide and gold(I) cyanide. This undergoes oxidative-addition reactions with halogens X_2 to give the gold(III) complexes *trans*-$[AuX_2(CN)(CH_2PPh_3)]$. The complexes have been characterized by conductivity measurements, n.m.r., and vibrational spectroscopy, and contain a stable bond between the ylidic carbon and the gold atom.

Due to the presence of a neighbouring onium centre, the Au–C σ bond in ylide complexes of gold is considerably more stable than that in other organogold complexes.[1,2] Examples of mononuclear gold(I) ylide complexes reported previously are $CH_3-Au-CH_2PR_3$,[3] $[R_3P-Au-CH_2PR_3]^+$,[3,4] and $[R_3PCH_2-Au-CH_2PR_3]^+$(R = CH_3 or Ph).[3,4]

In the present work the reaction of gold(I) cyanide, AuCN, with triphenylphosphoniomethanide, Ph_3PCH_2, has been examined. The 1 : 1 reaction could conceivably lead to the neutral complex $[Au(CN)(CH_2PPh_3)]$ or an ionic complex $[Au(CH_2PPh_3)_2][Au(CN)_2]$. This reaction has been studied in order to find out more about the properties of ylide complexes of gold, and about the co-ordination chemistry of AuCN, since very few complexes of this compound have been studied to date. An additional aim was to study the oxidative-addition reactions of the ylide–gold cyanide complex with halogens. These are expected, by analogy with the results of previous studies, to lead to square-planar dihalogenogold(III) compounds,[5] although under certain conditions Au–Au bonded binuclear gold(II) complexes have been found.[6]

Experimental

Preparation of Compounds.—All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Triphenylphosphoniomethanide, Ph_3PCH_2, was prepared by a method similar to that described in the literature [7] using methyltriphenylphosphonium iodide and sodium amide. The product was recrystallized from benzene–pentane and characterized by its ^1H n.m.r. spectrum.

Cyano(triphenylphosphoniomethanide)gold(I), $[Au(CN)(CH_2PPh_3)]$. A solution of Ph_3PCH_2 (1.2 g, 4.3 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred suspension of AuCN (1.0 g, 4.5 mmol) in tetrahydrofuran (10 cm^3) over a period of 8 min. This mixture was left to stir for 22 h. The crude product was filtered off, washed twice with tetrahydrofuran, and dried *in vacuo*. Yield 1.70 g. This was redissolved in chloroform (16 cm^3) and the resulting solution was filtered to remove a small amount of green residue. The volume of the filtrate was reduced to 3—4 cm^3 under vacuum and an equal volume of diethyl ether was added to the cooled solution (– 10 °C). The product is an air-stable crystalline solid with a slight violet colouration, m.p. 185—188 °C. Yield 1.61 g (75%) (Found: C, 47.55; H, 3.50. Calc. for $C_{20}H_{17}AuNP$: C, 48.10; H, 3.45%). N.m.r. ($CDCl_3$): ^1H, 1.88 [CH_2, d, $^2J(PH)$ = 13.6 Hz] and 7.7 p.p.m. (phenyl protons, complex multiplet); ^{31}P-{^1H}, 33.8 p.p.m. (s); ^{13}C-{^1H}, 6.79 [CH_2, d, $^1J(PC)$ = 40.0], 125.4 [phenyl C^1, d, $^1J(PC)$ = 85.9 Hz], 128.9, 129.7, 132.3, 133.0, 133.3 (phenyl carbons, singlets), and 153.8 p.p.m. (CN, s). The solution in $CDCl_3$ is not indefinitely stable. After standing for several days, new lines appear in the ^1H n.m.r. spectrum in the CH_2 region. I.r.: ν(CN) at 2 142 cm^{-1}. Raman: ν(CN) at 2 140 cm^{-1}. The molar conductivity of a 9.333×10^{-4} mol dm^{-3} solution in nitromethane is 2.4 S cm^2 mol^{-1}.

trans-*Dibromocyano*(*triphenylphosphoniomethanide*)*gold*(III), $[AuBr_2(CN)(CH_2PPh_3)]$. The compound $[Au(CN)(CH_2PPh_3)]$ (0.33 g, 0.50 mmol) was dissolved in chloroform (5 cm^3) and a solution of bromine (0.11 g, 0.68 mmol) in chloroform was added with stirring. The volume of the solution was reduced to 2 cm^3 and a yellow solid began to separate. The mixture was allowed to stand for about 15 min and diethyl ether (2 cm^3) was added. The product was collected, washed with chloroform–ether (1 : 1), and vacuum dried. M.p. 165—170 °C, yield 0.42 g (96%) (Found: C, 35.90; H, 2.65. Calc. for $C_{20}H_{17}AuBr_2NP$: C, 36.45; H, 2.60%). ^1H N.m.r. (CD_2Cl_2): 3.33 [CH_2, d, $^2J(PH)$ = 11.6 Hz] and 7.7 p.p.m. (phenyl protons, complex multiplet). I.r.: ν(AuBr) at 252 cm^{-1}. Raman: ν(CN) at 2 143 and 2 164, ν(AuBr) at 201 cm^{-1}. The molar conductivity of a 1.133×10^{-3} mol dm^{-3} solution in nitromethane is 3.7 S cm^2 mol^{-1}.

trans-*Dichlorocyano*(*triphenylphosphoniomethanide*)*gold*(III), $[AuCl_2(CN)(CH_2PPh_3)]$. This was prepared by a method analogous to that given above for the bromo-complex, using chlorine gas (50 cm^3, 2.0 mmol) with rapid removal of excess of Cl_2 by pumping. The product was a pale yellow solid, m.p. 198—205 °C, yield 0.35 g (92%) (Found: C, 41.80; H, 3.20. Calc. for $C_{20}H_{17}AuCl_2NP$: C, 42.15; H, 3.00%). I.r.: ν(AuCl) at 363 cm^{-1}. Raman: ν(CN) at 2 162 and ν(AuCl) at 340 cm^{-1}.

trans-*Cyanodi-iodo*(*triphenylphosphoniomethanide*)*gold*(III), $[AuI_2(CN)(CH_2PPh_3)]$. This was prepared by a method analogous to those given above for the chloro- and bromo-complexes, using iodine (0.17 g, 0.67 mmol). The product was an orange-brown solid, m.p. 143—147 °C, yield 0.46 g (92%) (Found: C, 31.90; H, 2.30. Calc. for $C_{20}H_{17}AuI_2NP$: C, 31.75; H, 2.55%). I.r.: ν(AuI) at 197 cm^{-1}.

Conductivity Measurements.—Conductivity measurements were carried out using a Beckman RC-18A conductivity bridge.

Spectroscopy.—Far-i.r. spectra (50—400 cm^{-1}) were obtained on a Grubb-Parsons Cube MKII interferometer fitted with a 6.25-μm Mylar-film beam splitter. They were run on petroleum jelly mulls between polythene plates, and calibrated by using the spectrum of water vapour. Far-i.r. spectra were also run at *ca.* 125 K in a Grubb-Parsons GMR 01 low-temperature cell cooled with liquid nitrogen. Spectra were Fourier transformed and printed using an interfaced CBM microcomputing system. I.r. spectra were obtained on a Perkin-Elmer 597 spectrometer. They were run on Nujol mulls between KBr plates, and were calibrated using the spectrum of polystyrene.

Raman spectra were obtained on a Jasco R300 Raman spectrometer and were excited with a Coherent CR4 argon-ion laser (514.5-nm line), with powers between 20 and 50 mW. The spectra were run on polycrystalline samples in glass capillary tubes.

Discussion

The reaction of triphenylphosphoniomethanide, Ph_3PCH_2, with AuCN produces a 1 : 1 complex which is thermally stable in the solid state and which decomposes only very slowly in chloroform solution. The complex shows ν(CN) bands in the i.r. and Raman spectra at 2 142 and 2 140 cm^{-1} respectively. These values are almost coincident, in contrast with the situation for $[Au(CN)_2]^-$, for which ν(CN) occurs at 2 146 and 2 164 cm^{-1} in the i.r. and Raman respectively.[8] The cyano-carbon chemical shift is 153.8 p.p.m., which is very close to that of $[Au(CN)_2]^-$ (154.2 p.p.m.).[9] The ylidic protons show a downfield chemical shift and a characteristic increase in the $^2J(PH)$ coupling constant relative to the uncomplexed ylide,[7] and the ^1H n.m.r. parameters for these protons are similar but not identical to those of $[Au(CH_2PPh_3)_2]Cl$.[4] The ionic formulation $[Au(CH_2PPh_3)_2][Au(CN)_2]$ for the present compound is excluded by the conductivity results, which show that the complex is effectively a non-conductor in nitromethane ($\Lambda = 2.4$ S cm^2 mol^{-1}, or 4.8 S cm^2 mol^{-1} based on the double empirical formula, compared with 60—115 S cm^2 mol^{-1} expected for a 1 : 1 electrolyte [10]), so it must therefore be formulated as the neutral complex $[Au(CN)(CH_2PPh_3)]$. This is to our knowledge the first example of an organogold(I) cyanide complex. Its high thermal stability again emphasizes the stabilizing effect of the neighbouring phosphonium centre on the metal–ylide carbon bond. This is further demonstrated by the lack of reactivity of the complex in $CHCl_3$ solution with dry HCl. [The Au–C bond in alkylgold(I) complexes is readily cleaved by HCl.[11]] There are very few complexes of gold(I) cyanide with which to compare the properties of the compound described here. Complexes of AuCN with PPh_3,[12,13] PMe_3,[14,15] and CH_3NC [16] are known, and both molecular [12,14,16] and ionic [13,15] formulations have been reported.

Attempts to prepare a copper(I) analogue of $[Au(CN)(CH_2PPh_3)]$ resulted in a compound of much lower thermal stability which did not analyze satisfactorily for a complex of 1 : 1 or any other simple stoicheiometry. The lower thermal stability of complexes of Ph_3PCH_2 with Cu^I and Ag^I relative to those of Au^I has been noted previously.[4,17]

The compound $[Au(CN)(CH_2PPh_3)]$ undergoes oxidative-addition reactions with chlorine, bromine, and iodine. The products are non-conductors in nitromethane and are therefore formulated as the neutral gold(III) complexes $[AuX_2(CN)(CH_2PPh_3)]$ (X = Cl, Br, or I). Assuming the usual square-planar co-ordination about gold(III), there are two possible structures for this complex depending on whether the halogen atoms are mutually *cis* or *trans*. It has previously been found that dialkyldihalogenogold(III) complexes, $[AuR_2X_2]^-$, show a marked preference for *cis* stereochemistry, whereas dicyanodihalogenogold(III) $[AuX_2(CN)_2]^-$ complexes have so far only been found with the *trans* configuration. Information about the stereochemistry can be obtained from the i.r. and Raman spectra in the ν(AuX) region.[18,19] The far-i.r. and low-frequency Raman spectra of $[AuBr_2(CN)(CH_2PPh_3)]$ are shown in the Figure. These show strong bands assigned to ν(AuBr) at 252 and 201 cm^{-1} respectively, which compare with the values 258 and 209 cm^{-1} respectively we have calculated from the previously published force constants for *trans*-$[AuBr_2(CN)_2]^-$ [the frequency of the Raman-active ν(AuBr) mode has not been reported].[19] In the present case the bands are not rigorously mutually exclusive, weak bands appearing at 197 and 250 cm^{-1} in the i.r. and Raman spectra respectively (Figure). This is consistent with the absence of an inversion centre for this complex. However, the near mutual exclusion and the wavenumbers of the bands clearly indicate a *trans* arrangement of the bromine atoms. Similar results were obtained for the corresponding chloro- and iodo-complexes, the ν(AuX) frequenices coinciding almost exactly with those of the appropriate $[AuX_2(CN)_2]^-$ species.[19] The observation of a *trans* configuration for these oxidative-addition products is in line with results obtained for other ylide complexes of gold.[5,6]

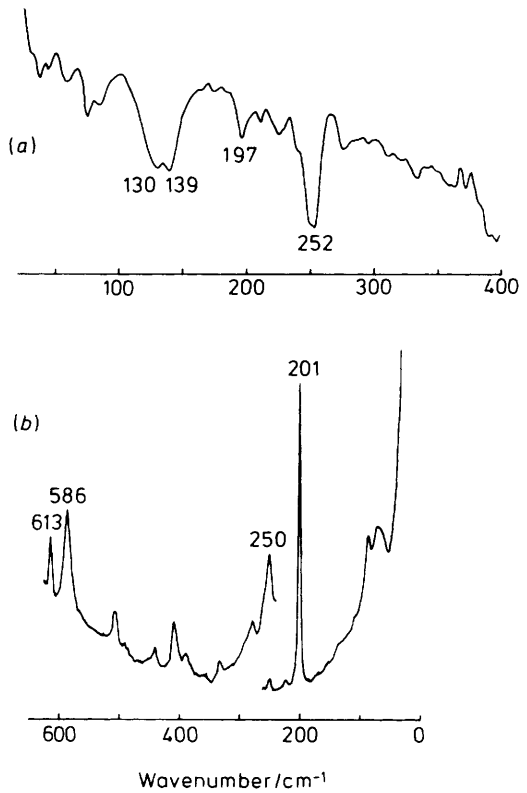

Figure. Far-i.r. (*a*) and Raman (*b*) spectra of *trans*-$[AuBr_2(CN)(CH_2PPh_3)]$

A reaction of $[Au(CN)(CH_2PPh_3)]$ with 0.5 mol equivalent of bromine was carried out in order to investigate the possible formation of an Au–Au bonded binuclear gold(II) complex similar to those which have been observed in the reaction of cyclic binuclear gold(I) ylide complexes with halogens.[6] Examination of the product of this reaction by ^1H n.m.r. spectroscopy showed that it consisted of about 30% of unreacted $[Au(CN)(CH_2PPh_3)]$, 30% of the 1 : 1 adduct $[AuBr_2(CN)(CH_2PPh_3)]$, and about 40% of a mixture of at least three different compounds with $\delta(CH_2)$ in the range 2.2—3.9 p.p.m. and $^2J(PH)$ in the range of 9—13 Hz. This mixture was too complex to characterize further, however.

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