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Monomeric to polymeric gold(I) complexes from bifunctional ligands $R_2PC\equiv CH$

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Abstract

Oligomeric and polymeric gold(I) complexes in which gold(I) centers are bridged by $R_2PC\equiv C^-$ ligands are reported. The new ligand ${}^iPr_2PC\equiv CH$ was prepared by reaction of iPr_2PCl with $HC\equiv CMgBr$. Displacement of SMe_2 from $[AuCl(SMe_2)]$ by $R_2PC\equiv CH$ gave $[AuCl(R_2PC\equiv CH)]$, $R = Ph$ or iPr , which were characterized spectroscopically and, for $R = {}^iPr$, by single crystal X-ray diffraction analysis [triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.229(2)$, $b = 9.345(1)$, $c = 7.654(1)$ Å, $\alpha = 112.79(1)$, $\beta = 105.49(1)$, $\gamma = 99.33(1)^\circ$, $V = 559.7(2)$ Å³]. Treatment of $[AuCl(R_2PC\equiv CH)]$ with NaOMe gave elimination of HCl with formation of $[Au(R_2PC\equiv C)]_x$. When $R = Ph$, the product is insoluble in all common organic solvents and is presumed to be polymeric but, when $R = {}^iPr$, the product is partially soluble in chlorinated organic solvents and is suggested to exist as a mixture of cyclic oligomers and linear polymer.

1. Introduction

Although the interesting ligands $R_2PC\equiv CH$ (e.g., $R = Ph, Et$) were reported some years ago [1], their coordination chemistry has not received much attention. There are several possible bonding modes for the ligands. For example, they can act as monodentate neutral ligands via the phosphorus lone pair or the $C\equiv C$ bond, as neutral bridging ligands with the formation of both metal–phosphorus and metal–acetylene bonds, as anionic monodentate ligands with the formation of metal–acetylide bonds, as bridging ligands with the formation of both metal–phosphorus and metal–acetylide bonds or as triply bridging ligands with the formation of metal–phosphorus, metal–acetylide and metal–acetylene bonds. The terminal acetylene can also be transformed into carbene, carbyne or vinylidene ligands and so another range of bonding modes is accessible. Only a few of the possible coordination modes have been observed. For example, Demerseman and co-workers [2] have recently reported the synthesis of $[(\eta^6\text{-arene})RuCl_2(PPh_2C\equiv CH)]_x$, arene = 4-MeC₆H₄-

CHMe₂, and $[(\eta^6\text{-C}_6\text{Me}_6)Cl(PMe_3)Ru=C(OMe)CH_2\text{-PPh}_2RuCl_2(\eta^6\text{-arene})]^+$, while Bruce and co-workers [3] have prepared several ruthenium cluster complexes containing the $\mu^5\text{-C}_2\text{PPh}_2$ ligand.

We are interested in the development of synthetic routes to novel macromolecules. There are many examples of metal-containing polymers in which the metal centers are bridged by bidentate ligands via the formation of two metal–ligand sigma bonds (e.g., $[L_nM(C\equiv C-Ar-C\equiv C)]_x$) [4] or two metal–ligand coordination bonds (e.g., $[L_nM(C\equiv N-Ar-N\equiv C)]_x$) [5]. Macromolecules with well-known ligands such as CN- or SCN- bridging metal centers are also known [6]. However organometallic polymers with ligands designed to give one sigma and one coordinate bond to the metal centers in the backbone of the polymer chain are rare [7]. Since metal–phosphorus and metal–acetylide bonds are often strong, it was expected that polymers of the type $[L_nM(PR_2C\equiv C)]_x$ could be produced and that they might have useful properties. For example, since the polymer backbone would contain both unsaturated organic fragments and inorganic elements, such as phosphorus and gold, with valence d-orbitals available for π -bonding, the polymers might display interesting properties such as electrical conductivity or optical

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non-linearity. The properties of the resulting polymers could be easily tuned by changing the substituents of the phosphines. In this regard, it is interesting to note that hydroboration of $\text{Ph}_2\text{PC}\equiv\text{CH}$ with $[\text{H-B}(\text{mes})_2]_2$ gives $\text{Ph}_2\text{PCH}=\text{CHB}(\text{mes})_2$ which exhibits second order optical nonlinearity [8].

This paper describes the synthesis and characterization of several monomeric and oligomeric or polymeric gold(I) compounds derived from the ligands $\text{R}_2\text{PC}\equiv\text{CH}$, where $\text{R} = \text{Ph}$ or ^iPr . Gold(I) was chosen as the metal center because it tends to form simple two-coordinated linear complexes [9], thus favoring the formation of linear polymers rather than cyclic dimers or oligomers, and because alkynyl complexes of the formula $[\text{Au}(\text{C}\equiv\text{CR})(\text{L})]$ ($\text{L} =$ phosphine, arsine, stibine, isocyanide and amine) are amongst the most stable organogold complexes and are known to have linear geometry [10–12]. Examples of gold complexes with bidentate ligands having both a 2-electron and a 1-electron donor, but which are not polymeric, are the interesting cyclic (dimer, or trimer) derivatives prepared from pyrazoles, 2-pyridyllithium, imidazoles, orthometalated arylphosphines or isocyanide precursors [9,13]. Clearly, the synthetic methodology developed below is not limited to gold(I) or to these particular ligands, but could be extended to include other metals and ligands with longer extended organic conjugated fragments.

2. Experimental section

All chemicals were used as purchased from Aldrich unless otherwise stated. Gold metal was purchased from Johnson Matthey while $[\text{AuCl}(\text{SMe}_2)]$ [14], and $\text{Ph}_2\text{PC}\equiv\text{CH}$ [1] were prepared by modified literature methods.

NMR spectra were collected on a Varian 200 or 300 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard. IR spectra were recorded on a Bruker IFS32 spectrometer with Nujol mulls. DSC analyses were carried out under a nitrogen atmosphere by using a Dupont 9900 DSC thermal analyzer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

2.1. $^i\text{Pr}_2\text{PC}\equiv\text{CH}$

To a solution of $\text{HC}\equiv\text{CMgBr}$ in THF solution (44 ml, 0.5 M, 22 mmol) cooled at -78°C was slowly added neat $(^i\text{Pr})_2\text{PCl}$ (3.2 ml, 20 mmol). The mixture was warmed to room temperature and stirred for one hour. The THF was distilled out and the colorless ligand was then distilled under vacuum. ^{31}P NMR in CDCl_3 :

$\delta -14.8$. ^1H NMR in CDCl_3 : δ 0.99 (dd, $J = 17.2, 7.0$ Hz, 6H, CH_3), 1.04 (dd, $J = 11.7, 7.1$ Hz, 6H, CH_3), 1.78 (m, 2H, CH), 2.68 (s, 1H, $\text{C}\equiv\text{CH}$). ^{13}C NMR in CDCl_3 : δ 18.9 (d, $J = 5.5$ Hz, CH_3), 19.5 (d, $J = 19.3$ Hz, CH), 23.3 (d, $J = 6.3$ Hz, CH_3), 77.0 (s $\text{C}\equiv\text{C}-\text{H}$), 93.2 (d, $J = 4.6$ Hz, $\text{P}-\text{C}\equiv\text{C}$). IR (neat) 3301 (s, $\nu(\text{CC}-\text{H})$), 2031 (m, $\nu(\text{C}\equiv\text{C})$) cm^{-1} . The compound appears unstable when stored at room temperature for a prolonged period and it slowly turned brown in color.

2.2. $[\text{AuCl}(\text{Ph}_2\text{PC}\equiv\text{CH})]$

A mixture of $[\text{AuCl}(\text{SMe}_2)]$ (0.30 g, 1.02 mmol) and $\text{Ph}_2\text{PC}\equiv\text{CH}$ (0.23 g, 1.09 mmol) in dichloromethane (20 ml) was stirred at room temperature for 0.5 h. The dichloromethane and SMe_2 were removed under vacuum. The residue was redissolved in dichloromethane and the resulting solution was passed through silica gel (*ca.* 2.4 cm) to give a colorless solution. The solvent was removed completely to give a white solid. Yield: 0.32 g, 71%. ^{31}P NMR in CDCl_3 : δ 21.3. ^1H NMR in CDCl_3 : δ 3.45 (d, $J = 8.6$ Hz, 1H, $\text{C}\equiv\text{CH}$), 7.2–7.5 (m, 10H, Ph). IR (Nujol) 3229 (s, $\nu(\text{CC}-\text{H})$), 2056 (m, $\nu(\text{C}\equiv\text{C})$) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{AuClP}$: C, 37.99; H, 2.51. Found: C, 37.63; H, 2.55%.

2.3. $[\text{AuCl}(^i\text{Pr}_2\text{PC}\equiv\text{CH})]$

A mixture of $[\text{AuCl}(\text{SMe}_2)]$ (0.30 g, 1.02 mmol) and $^i\text{Pr}_2\text{PC}\equiv\text{CH}$ (0.15 g, 1.06 mmol) in dichloromethane (20 ml) was stirred at room temperature for 0.5 h. The dichloromethane and SMe_2 were removed completely under vacuum. The residue was redissolved in dichloromethane (5 ml) and hexane (5 ml) and the solvents were allowed to evaporate slowly at room temperature to give colorless crystals. Yield: 0.33 g, 86%. ^{31}P NMR in CDCl_3 : δ 29.2. ^1H NMR in CDCl_3 : δ 1.22 (dd, $J = 7.0, 5.8$ Hz, 6H, CH_3), 1.32 (dd, $J = 7.0, 2.9$ Hz, 6H, CH_3), 2.22 (m, 2H, CH), 3.08 (d, $J = 8.0$ Hz, 1H, $\text{C}\equiv\text{CH}$). IR (Nujol) 3287 (s, $\nu(\text{CC}-\text{H})$), 2056 (s, $\nu(\text{C}\equiv\text{C})$) cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{15}\text{AuClP}$: C, 25.65; H, 4.04. Found: C, 25.73; H, 4.22%.

2.4. $\{[\text{Au}(\text{Ph}_2\text{PC}\equiv\text{C})]_x\}$

To a solution of $[\text{AuCl}(\text{Ph}_2\text{PC}\equiv\text{CH})]$ (0.20 g, 0.45 mmol) in THF (30 ml) was added NaOMe (50 mg, 0.92 mmol) in MeOH (5 ml). A white solid formed immediately. The mixture was stirred for 1 h and the resulting white precipitate was collected by filtration. The solid was washed with THF, MeOH, H_2O and MeOH and dried under vacuum. Yield: 0.16 g, 88%. The compound is insoluble in common organic solvents. The same compound is also obtained starting from $[\text{AuCl}(\text{SMe}_2)]$, $\text{Ph}_2\text{PC}\equiv\text{CH}$ and NaOMe. IR (Nujol) 2068 (s, $\nu(\text{C}\equiv\text{C})$) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{AuP}$: C, 41.40; H, 2.48. Found: C, 40.96; H, 2.18%.

2.5. $\{[Au(^iPr)_2PC\equiv C]\}_x$

To a solution of $[AuCl(^iPr)_2PC\equiv CH]$ (0.15 g, 0.40 mmol) in MeOH (30 ml) was added NaOMe (50 mg, 0.92 mmol). A white solid formed immediately. The mixture was stirred for 1 h and the resulting white precipitate was collected by filtration. The solid was washed with MeOH, H₂O and MeOH and dried under vacuum. Yield: 0.12 g, 89%. ³¹P NMR in CDCl₃: δ 32.9–34.8 (m). ¹H NMR in CDCl₃: δ 1.35 (br m, 12H, CH₃), 2.15 (br m, 2H, CH), IR (Nujol) 2072 (s, $\nu(C\equiv C)$) cm⁻¹. Anal. Calcd for C₈H₁₄AuP: C, 28.42; H, 4.17. Found: C, 28.54; H, 4.48%. The same product was obtained from the reaction in a mixed solvent of THF/MeOH (4:1). Anal. Calcd for C₈H₁₄AuP: C, 28.42; H, 4.17. Found: C, 28.21; H, 4.42%.

2.6. X-Ray structure determination for $[AuCl(^iPr)_2PC\equiv CH]$

A colorless needle-like crystal was cut and mounted in air on a glass fibre with epoxy cement. An Enraf-Nonius CAD4F diffractometer with graphite monochromated Mo K α radiation [15] was employed to collect the data at 23°C. The cell constants and an orientation matrix were obtained from photo and automatic indexing routines, followed by least squares fits of 21 accurately centered reflections ($27.0 \leq 2\theta \leq 42.3^\circ$). Intensity data were recorded in the θ - 2θ mode, at variable scan speeds (0.97 to 4.1 deg min⁻¹) and a scan width of $0.80 + 0.35 \tan \theta$, with a maximum time per datum of 60 s. Static background measurements were made at the end points of the width $0.9 + 0.35 \tan \theta$. Three standard reflections (010, 200 and 002) were monitored every 180 min of X-ray exposure time and showed 8.3% decay over the total period of 39.9 h. In all 3801 reflections and 63 standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, background radiation effects and decay using the Structure Determination Package [16] running on a PDP11/23 + computer. Eight faces were identified for the data crystal and the distances among them were measured on a microscope. An absorption correction was applied using the program ABCOR [17]. Equivalent reflections were averaged ($R_f = 0.015$) to give 3253 data for structure solution and refinements. A p value of 0.04 was applied to the data [18]. The structure was readily solved by MULTAN [19] and subsequent difference Fourier techniques. Refinement was by full-matrix least-squares techniques on F , using the SHELX-76 software [20] running on a Sun 3/80 workstation. Scattering factors for neutral, non-hydrogen atoms were taken from ref. 21. Anisotropic thermal parameters were assigned for all the non-hydrogen atoms and were refined. The hydrogen atoms were placed in ideal positions (C–H =

TABLE 1. Crystal data and experimental details

Compound, formula weight	C ₈ H ₁₅ Au ₁ Cl ₁ P ₁ , 374.603
Crystal system, space group	Triclinic, $P\bar{1}$
Cell dimensions (Å)	$a = 9.229(2)$, $b = 9.345(1)$ $c = 7.654(1)$, $\alpha = 112.79(1)$ $\beta = 105.49(1)$, $\gamma = 99.33(1)^\circ$
Cell volume (Å ⁻³), Z	559.7(2), 2
Density, g cm ⁻³ calcd.	2.223
F(000)	348
Diffractometer, monochromator	Enraf Nonius CAD4F; graphite
Radiation, wavelength (Å)	Mo K α , 0.71073
Approx. crystal dimens (mm)	0.50 × 0.11 × 0.10
Crystal volume (mm ⁻³)	5.34×10^{-3}
No. of faces, face indices	8, {100}, {110}, { $\bar{1}$ 10}, {10 $\bar{2}$ } & { $\bar{1}$ 1 $\bar{1}$ }
Index	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-1 \leq l \leq 10$
θ ranges	$0 \leq 2\theta \leq 60^\circ$
Abs coeff (cm ⁻¹)	130.1
Absorption max., min.	40.58, 20.10
No of unique data	2705
No. of observ., variables	2323 ($I \geq 3\sigma(I)$), 105
Final model; R and R _w	0.0404, 0.0457
Extinction parameter	$4.7(4) \times 10^{-3}$
Residual electron density range (e Å ⁻³)	2.33 to -2.03

0.95 Å) and were included for the structure factor calculations only. A common thermal parameter was assigned to all the hydrogen atoms and refined in the least-squares cycles. The refinement of 105 variables and 2323 ($I \geq 3\sigma(I)$) observations converged at agreement factors $R = 0.0404$, $R_w = 0.0457$ for the weighting scheme of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 0.4556$ and $g = 0.004$. In the final difference Fourier synthesis the top three peaks with electron density in the range 2.33 to 2.27 e.Å⁻³ were associated with Au atom at distances 0.84–0.91 Å. The rest of the peaks were below the electron density 0.825 e.Å⁻³ and of no chemical significance. The experimental details and crystal data, the positional and $U(\text{equiv})$ thermal parameters are given in Tables 1 and 2. Tables of anisotropic thermal parameters, calculated hydrogen atom parameters, torsion angles and structure amplitudes have been deposited.

3. Results and discussion

3.1. Ligand synthesis

The ligand Ph₂PC≡CH was prepared by the reaction of Ph₂PCl with one equivalent of HC≡CMgBr (eqn. 1, R = Ph), [1] and the new ligand ⁱPr₂PC≡CH was prepared similarly as a colorless liquid (eqn. (1), R = ⁱPr).
 $R_2PCl + HC\equiv CMgBr \longrightarrow R_2PC\equiv CH + MgBrCl$ (1)

TABLE 2. Atomic positional ($\times 10^4$) and thermal ($\times 10^3$) parameters

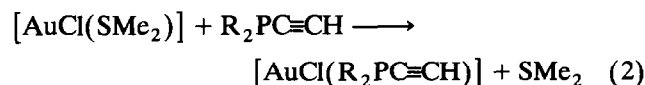
Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
Au	6867.3(4)	101.9(4)	-2146.8(4)	43.9(1)
Cl	5714(4)	-1973(4)	-5387(4)	71(1)
P	8002(3)	1961(3)	1094(3)	39(1)
C(1)	10062(9)	2722(11)	1868(13)	46(3)
C(2)	11478(10)	3255(14)	2502(19)	68(4)
C(3)	7384(10)	3812(10)	1774(13)	45(3)
C(4)	7749(12)	4675(11)	536(15)	55(4)
C(5)	5638(13)	3399(14)	1441(20)	66(5)
C(6)	7781(11)	1098(10)	2839(12)	43(3)
C(7)	8469(14)	-330(12)	2417(17)	62(4)
C(8)	8487(15)	2371(13)	5038(14)	66(4)

All the parameters were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

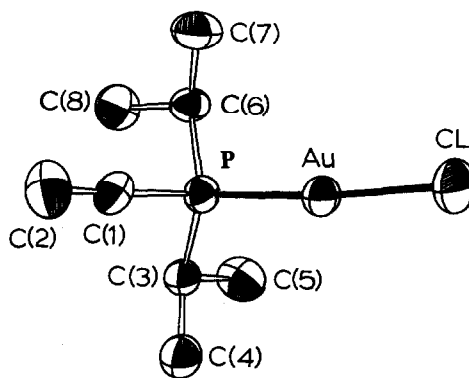
The compound ${}^1\text{Pr}_2\text{PC}\equiv\text{CH}$ appears unstable when stored at room temperature and turned to a brown color when stored for a prolonged period. The ligand was readily characterized spectroscopically. In particular, the ${}^{31}\text{P}$ NMR spectrum displays one singlet at -14.8 ppm and the chemical shift is very close to that of ${}^1\text{Pr}_2\text{PC}\equiv\text{CR}$ (-13.2 ppm, $\text{R} = \text{Me}$; -13.9 ppm, $\text{R} = \text{n-Bu}$) [22]. The IR spectrum displays IR bands assignable to $\nu(\text{C}\equiv\text{C})$ (2031 cm^{-1}) and $\nu(\text{CC-H})$ (3301 cm^{-1}). Two sets of methyl signals were observed since the two methyl groups of each ${}^1\text{Pr}$ group are inequivalent (diastereotopic), and there was one signal for the acetylenic and the P-CH protons, in both ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra (see data in Experimental section).

3.2. Preparation of mononuclear complexes

Reaction of $[\text{AuCl}(\text{SMe}_2)]$ with one equivalent of $\text{R}_2\text{PC}\equiv\text{CH}$ ($\text{R} = \text{Ph}$, ${}^1\text{Pr}$) produced $[\text{AuCl}(\text{R}_2\text{PC}\equiv\text{CH})]$ (eqn. (2), $\text{R} = \text{Ph}$ or ${}^1\text{Pr}$).

TABLE 3. Selected bond distances (\AA) and angles (deg)

Au-Cl	2.286(2)	Au-P	2.222(2)
P-C(1)	1.759(8)	P-C(3)	1.833(8)
P-C(6)	1.842(8)	C(1)-C(2)	1.204(7)
C(3)-C(4)	1.526(13)	C(3)-C(5)	1.519(13)
C(6)-C(7)	1.526(12)	C(6)-C(8)	1.510(12)
P-Au-Cl	175.2(2)	C(1)-P-Au	113.0(3)
C(3)-P-Au	115.9(3)	C(3)-P-C(1)	103.0(4)
C(6)-P-Au	111.9(3)	C(6)-P-C(1)	102.9(4)
C(6)-P-C(3)	109.0(4)	C(2)-C(1)-P	176.5(10)
C(4)-C(3)-P	110.2(7)	C(5)-C(3)-P	110.3(6)
C(5)-C(3)-C(4)	110.9(8)	C(7)-C(6)-P	108.6(6)
C(8)-C(6)-P	112.1(6)	C(8)-C(6)-C(7)	113.2(8)

Fig. 1. A view of the structure of $[\text{AuCl}({}^1\text{Pr}_2\text{PC}\equiv\text{CH})]$.

The ${}^{31}\text{P}$ resonances for the Au complexes shifted (55 ppm for $\text{R} = \text{Ph}$ and 44 ppm for $\text{R} = {}^1\text{Pr}$) downfield compared to the free ligands. The downfield shift is in the range reported for the phosphine coordination chemical shifts of $[\text{AuCl}(\text{PR}_3)]$ complexes; for example, 38.7 ppm for $[\text{AuCl}(\text{PPh}_3)]$ and 55.0 ppm for $[\text{AuCl}(\text{PPhEt}_2)]$ [23]. The IR spectrum displays bands assignable to $\nu(\text{C}\equiv\text{C})$ (at 2056 cm^{-1} for both $\text{R} = \text{Ph}$ and ${}^1\text{Pr}$) and $\nu(\text{CC-H})$ (at 3229 cm^{-1} for $\text{R} = \text{Ph}$, 3287 cm^{-1} for $\text{R} = {}^1\text{Pr}$). The ${}^1\text{H}$ NMR spectra exhibit $\text{C}\equiv\text{C-H}$ signals at 3.45 ppm (d, $J(\text{P-H}) = 8.6$ Hz) for $\text{R} = \text{Ph}$ and at 3.08 ppm (d, $J(\text{P-H}) = 8.0$ Hz) for $\text{R} = {}^1\text{Pr}$, beside the signals for Ph or iso-propyl groups. Like the free ligand ${}^1\text{Pr}_2\text{PC}\equiv\text{CH}$, the ${}^1\text{H}$ NMR spectrum of $[\text{AuCl}({}^1\text{Pr}_2\text{PC}\equiv\text{CH})]$ displays two sets of methyl signals and one signal for the acetylenic and the P-CH proton (see data in Experimental section).

3.3. Description of the molecular structure of $[\text{AuCl}({}^1\text{Pr}_2\text{PC}\equiv\text{CH})]$

The molecular structure of $[\text{AuCl}({}^1\text{Pr}_2\text{PC}\equiv\text{CH})]$ is shown in Fig. 1 and selected bond lengths and angles are presented in Table 3.

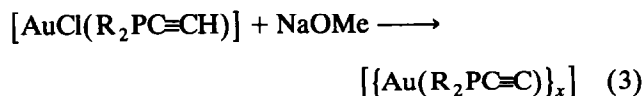
The bond distances and angles within each molecule are unexceptional and there are no very significant intermolecular bonding interactions. Of greatest interest in terms of the use of the complex as a precursor for organometallic polymers (see later) are the bond angles about phosphorus and gold. As expected, the angles $\text{P}-\text{Au}-\text{Cl} = 175.2(2)$ and $\text{P}-\text{C}(1)-\text{C}(2) = 176.5(10)^\circ$ are close to linear while $\text{C}(1)-\text{P}-\text{Au} = 113.0(3)^\circ$ is close to tetrahedral. There are no short intermolecular $\text{Au} \cdots \text{Au}$ contacts [shortest $\text{Au} \cdots \text{Au} = 5.38 \text{ \AA}$], although such contacts are common in other gold(I) complexes. The bulky ^iPr groups hinder such association.

The conformation adopted by the isopropyl substituents in the solid state is such that all methyl groups are inequivalent. The bulkier methyl substituents are staggered with respect to the other substituents on phosphorus. The methyl groups of the ^iPr groups straddle the linear substituents alkynyl [$\text{C}(1)-\text{P}-\text{C}(6)-\text{C}(7) = -64.9(8)^\circ$, $\text{C}(1)-\text{P}-\text{C}(6)-\text{C}(8) = 60.9(9)^\circ$] and AuCl [$\text{Au}-\text{P}-\text{C}(3)-\text{C}(4) = -59.9(7)^\circ$, $\text{Au}-\text{P}-\text{C}(3)-\text{C}(5) = 62.8(8)^\circ$] in order to minimize steric repulsions.

3.4. Synthesis of polymeric or oligomeric Au(I) complexes

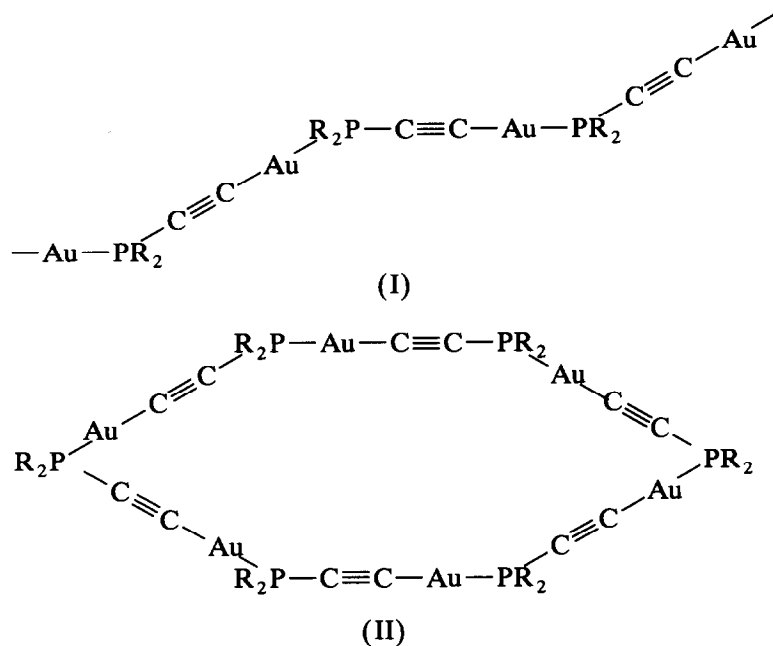
It has been shown that alkynylgold phosphine complexes $[\text{Au}(\text{C}\equiv\text{CR}')(\text{PR}_2)_2]$ can be prepared by the reaction of $[\text{AuCl}(\text{PR}_2)_2]$ with $\text{R}'\text{C}\equiv\text{CH}$ in the presence of a base such as sodium alkoxide [11,24]. In agreement, it was found that treatment of $[\text{AuCl}(\text{Ph}_2\text{PC}\equiv\text{CH})]$ with NaOMe in THF/MeOH immediately produced a white precipitate which analyzed for $[\{\text{Au}(\text{Ph}_2\text{PC}\equiv\text{C})\}_x]$ (eqn.

(3), $\text{R} = \text{Ph}$).



The product is insoluble in common organic solvents and therefore it could not be characterized by NMR spectroscopy. The IR spectrum of the white solid displays a strong band at 2068 cm^{-1} assignable to $\nu(\text{C}\equiv\text{C})$ and no bands for $\nu(\text{CC}-\text{H})$ around 3300 cm^{-1} . The IR spectrum, analytical and solubility data strongly suggest that an oligomeric or polymeric gold(I) phosphine acetylide complex is formed. In particular, the insolubility of the product implies that either linear or cyclic polymeric species $[\{\text{Au}(\text{Ph}_2\text{PC}\equiv\text{C})\}_x]$ (see below) are formed in the reaction. Unfortunately, the low solubility prevented the determination of the molecular weight or the NMR properties.

Treatment of $[\text{AuCl}(^i\text{Pr}_2\text{PC}\equiv\text{CH})]$ with NaOMe in MeOH or a mixed THF/MeOH solvent mixture also immediately produced a white precipitate which analyzed for $[\{\text{Au}(^i\text{Pr}_2\text{PC}\equiv\text{C})\}_x]$ (eqn. (3), $\text{R} = ^i\text{Pr}$). The IR spectrum of the product displays a strong band at 2072 cm^{-1} assignable to $\nu(\text{C}\equiv\text{C})$ and no bands for $\nu(\text{CC}-\text{H})$ around 3300 cm^{-1} . The isopropyl phosphine gold acetylide complex is insoluble in most organic solvents but slightly soluble in halogenated solvents such as dichloromethane and chloroform. Consistent with the formation of the acetylide complex, broad multiplets assignable for both CH_3 (at *ca.* 1.35 ppm) and $\text{P}-\text{CH}$ (at *ca.* 2.25 ppm) but no signal assignable for $\text{C}\equiv\text{C}-\text{H}$ were observed in the ^1H NMR spectrum of the product



in chloroform. The ^{31}P NMR spectrum shows overlapped broad peaks in the region 32.9–34.8 ppm, shifted downfield compared to the parent chloride gold(I) complex ($\delta = 29.2$ ppm). This is in agreement with the reported observation that the ^{31}P chemical shift for an alkyngold PPh_3 complex is slightly downfield from that of the parent chlorogold complex [24]. The broadness of the NMR signals, together with the low solubility of the product, indicates that either a polymeric or a mixture of oligomeric species $[\{\text{Au}(\text{}^i\text{Pr}_2\text{PC}\equiv\text{C})\}_x]$ is produced. Unfortunately, the solid is not soluble enough to obtain the molecular weight in solution.

The insoluble product could adopt a linear chain (I) or cyclic (II) polymeric structure. The presence of species of different ring-sizes in the chloroform solution of a partially soluble sample of the product could explain the multiplicity of resonances in the ^{31}P NMR spectrum. Since ^{31}P NMR chemical shifts are greatly affected by ring-size, a change in ring-size would change the chemical shift [25]. A strain-free planar ring should be formed by combination of n $-\text{Au}-\text{PR}_2-\text{C}\equiv\text{C}-$ units where $n = 360/(180 - \alpha)$ and α is the $\text{Au}-\text{P}-\text{C}$ angle, assuming that the $\text{C}\equiv\text{C}-\text{Au}-\text{P}$ unit is linear. In the X-ray structure of $[\text{ClAu}(\text{}^i\text{Pr}_2\text{PC}\equiv\text{CH})]$, the $\text{Au}-\text{P}-\text{C}$ angle is found to be 113° and hence the ideal value of $n = 5.5$ and cyclic species with formulae close to $[\{\text{Au}(\text{}^i\text{Pr}_2\text{PC}\equiv\text{C})\}_{5-6}]$ are likely to be formed along with linear polymers. The data are also consistent with a mixture of cyclic and low molecular weight linear oligomers. The insoluble portion probably has higher molecular weight with linear polymer chains as in (I).

The thermal properties of the oligomeric or polymeric compounds $[\{\text{Au}(\text{R}_2\text{PC}\equiv\text{C})\}_x]$ ($\text{R} = \text{Ph}, \text{}^i\text{Pr}$) have been studied using differential scanning calorimetry, DSC. Each displays a significant endothermic transition over a wide temperature range 30–160°C, consistent with a glass transition. At higher temperature, both $[\{\text{Au}(\text{Ph}_2\text{PC}\equiv\text{C})\}_x]$ and $[\{\text{Au}(\text{}^i\text{Pr}_2\text{PC}\equiv\text{C})\}_x]$ decomposed before melting, with the onset of decomposition occurring at 210°C and 250°C respectively. In both cases, the final decomposition product is metallic gold and TGA indicates the expected weight loss for formation of pure gold.

4. Supplementary materials available

Tables S1 (anisotropic thermal parameters), S2, (calculated H-atom parameters), S3 (torsion angles) and S4 (structure amplitudes) are available from the authors.

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