Macromolecular complexation of poly(methylenephosphine) to gold(I): a facile route to highly metallated polymers†

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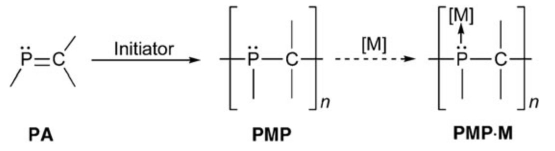
Alternating phosphorus–carbon polymers are found to be effective ligands for gold(I) to afford [MesP(AuCl)–CPh$_2$]$_n$, a new class of macromolecule with high gold content.

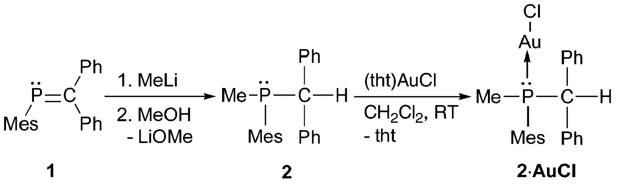
Macromolecules possessing phosphorus atoms in the main chain possess unique chemical functionality and attractive properties. Importantly, phosphorus polymers are of interest for their specialty applications as electroluminescent devices, sensors, biomaterials, and as catalyst supports.[1,2] The difficulty in finding suitable methods to incorporate phosphorus atoms into long chains is the major challenge for researchers in this area. We are tackling this problem by developing the addition polymerization of phosphaalkenes (PA) to afford homo- or co-polymers (Scheme 1).[3–6] The resultant polymers, called poly(methylenephosphine)s (PMP), are an unprecedented class of macromolecule which possess alternating phosphorus and carbon atoms.



Scheme 1 The addition polymerization of a phosphaalkene (PA) to afford poly(methylenephosphine) (PMP) and the proposed functionalization of the polymer through coordination to transition metal to give PMP-M.

An appealing feature of PMP is its potential chemical functionality through the phosphine moieties. We are particularly interested in exploiting PMP as a precursor to well-defined metal-containing macromolecules PMP-M.[7] When choosing target metals for coordination studies, gold(I) attracted our attention. Gold(I) has a high affinity for phosphine ligands and exhibits a tendency to form linear P–Au–X complexes which would permit high Au loadings in the densely substituted PMP-M. Moreover, gold-containing polymers are attracting considerable interest due to their exciting potential applications in nanochemistry, catalysis, and chemosensors.[8,9] Herein, we report the preparation of soluble gold-containing macromolecules with high gold loadings through the macromolecular complexation of PMP to Au(I).

We evaluated the potential for PMP to act as a ligand for transition metals by studying the reactivity of the molecular model **2** with Au(I). Model compound **2**, which was prepared from **1**,[10] was treated with (tht)AuCl (tht = tetrahydrothiophene) in CH$_2$Cl$_2$ solution. Monitoring the reaction progress by ^{31}P NMR spectroscopy showed that the signal for **2** at −23.0 ppm was consumed and replaced by a new signal at 16.0 ppm assigned to the coordination compound **2·AuCl** (see Fig. 1(a) and (b)).‡ Slow diffusion of EtOH into a concentrated CH$_2$Cl$_2$ solution of the product afforded analytically pure **2·AuCl** which was characterized by elemental analysis, EI MS (M$^+$, *m*/*z* = 564) and X-ray crystallography. The ^{1}H and ^{13}C NMR spectra of the crystals in C$_6$D$_6$ solution are consistent with the formulated structure of **2·AuCl**.



The molecular structure of **2·AuCl** (Fig. 2) displays similar metrical parameters to model compound **2**.§ One interesting feature of **2·AuCl** is that electron group geometry about the P atom is close to tetrahedral as evidenced by a widening of the C–P–C bond angles with respect to **2** [**2·AuCl**: avg. = 107.0(3)° *vs.* **2**: avg. = 102.7(1)°]. The P–Au and Au–Cl bonds [P(1)–Au(1) = 2.257(1) Å; Au(1)–Cl(1) = 2.305(1) Å) are at the long end of the range observed for similar gold(I)–phosphine complexes [Au–Cl: 2.21–2.26 Å; Au–Cl: 2.23–2.31 Å].[11] Interestingly, the P–Au–Cl bond angle deviates slightly from linearity [P(1)–Au(1)–Cl(1) = 175.69(4)°] with the Cl bending towards the less hindered P–Me moiety. The closest Au···Au contact of 9.47 Å in **2·AuCl** is much longer than would be expected if aurophilic interactions were present (*ca.* 3 Å).[12] These observations are not surprising since bulky gold(I) phosphines show bent Cl–Au–P angles [*e.g.* (*m*-tolyl)$_3$PAuCl: Cl–Au–P = 175.1(1)°] and often do not show aurophilic interactions.[13] However, the absence of *intermolecular* Au···Au interactions in the solid state structure of **2·AuCl** does not rule out the possibility of *intramolecular* aurophilic interactions in gold(I) polymer **3·AuCl**.

With model complex **2·AuCl** in hand, our next objective was to study the metallation of the polymer. The anionic polymerization of **1** in glyme using *n*-BuLi as the initiator afforded

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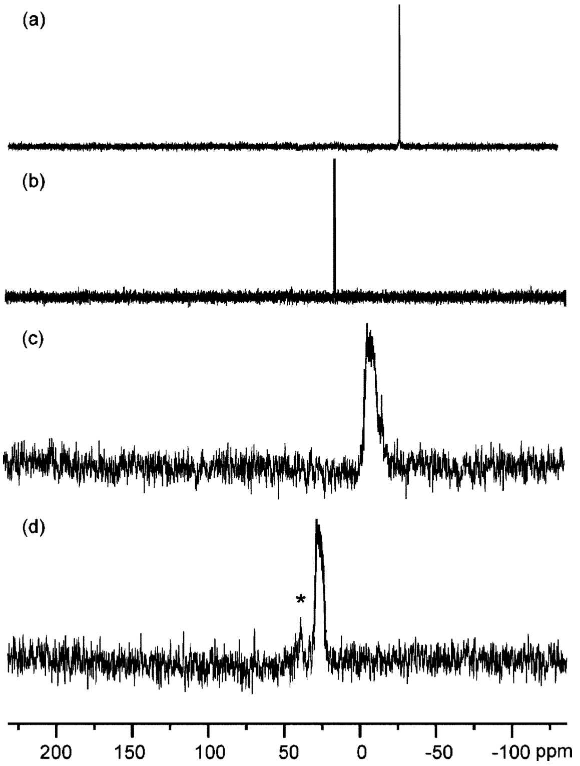
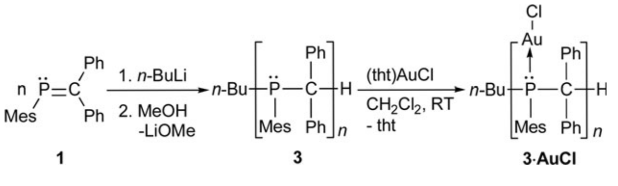


Fig. 1 ^{31}P NMR (CD_2Cl_2, 300 K) spectra of (a) model compound **2**, (b) gold complex **2·AuCl**, (c) polymer **3** and (d) coordinated polymer **3·AuCl**. * Tentatively assigned to phosphine oxide moieties (*cf.* **3**·O $\delta_{^{31}P}$ = 47; see ref. 3).

PMP **3** (M_n = 38 900 g mol^{-1}, PDI = 1.34).[4] In an attempt to prepare complexed polymer **3·AuCl**, the phosphine polymer **3** was treated with (tht)AuCl (1 equiv. per P) at room temperature in CH_2Cl_2 solution.¶ After 1 h, an aliquot was removed from the reaction mixture and analyzed by ^{31}P NMR spectroscopy. Remarkably, the broad resonance for the uncomplexed polymer **3** (δ = −7; Fig. 1(c)) was entirely consumed and was replaced by a new broad resonance assigned to **3·AuCl** (δ = 25; Fig. 1(d)). For comparison, a similar downfield shift is observed for the model compound (**2** *vs.* **2·AuCl**: $\Delta\delta$ = 39; **3** *vs.* **3·AuCl**: $\Delta\delta$ = 32). The gold-containing polymer **3·AuCl** was purified by precipitation of a concentrated CH_2Cl_2 solution with hexanes. The resultant white powder was further characterized by ^{1}H and ^{13}C NMR spectroscopy.



The novel gold-containing polymer **3·AuCl** was also characterized by triple detection GPC in THF solution. Importantly, the absolute number average molecular weight for **3·AuCl** (M_n = 71 600 g mol^{-1}) increased substantially upon coordination to gold (*cf.* **3**: M_n = 38 900 g mol^{-1}). The molecular weight of **3·AuCl** is the highest yet observed for a PMP-based polymer and is consistent with a high degree of P-metallation. The polydispersity indices for **3** and **3·AuCl** are both narrow (**3**: PDI = 1.34; **3·AuCl**: PDI = 1.29) which suggests that the integrity of the backbone is retained upon coordination. Thermogravimetric analysis of **3·AuCl** revealed an onset temperature of polymer degradation (T_{onset} = 325 °C) which is considerably higher than that for uncomplexed **3** (T_{onset} = 265 °C).[3] Remarkably, after heating to 1000 °C a shiny, lustrous residue was obtained. The residue was 40% of the initial mass of **3·AuCl** which is consistent with the expected gold content (36%). We speculate that this residue is composed primarily of elemental gold. Further studies are under way to confirm this hypothesis and to investigate the potential use of these polymers as polymer-supported catalysts or precursors to well-defined gold nanostructures.

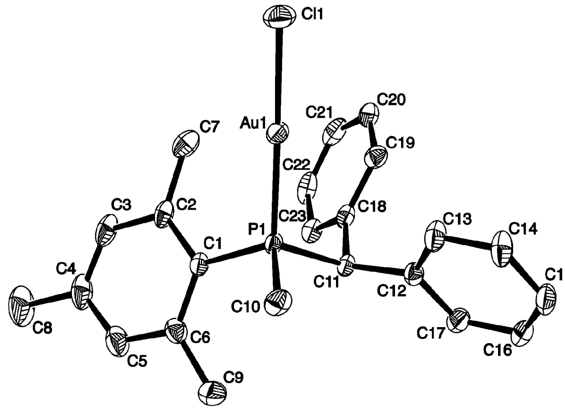


Fig. 2 Molecular structure of **2·AuCl** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P(1)–C(1) = 1.852(4); P(1)–C(10) = 1.833(4); P(1)–C(11) = 1.875(4); P(1)–Au(1) = 2.257(1); Au(1)–Cl(1) = 2.305(1). Selected bond angles (°): C(1)–P(1)–C(10) = 109.0(2); C(1)–P(1)–C(11) = 105.7(2); C(10)–P(1)–C(11) = 106.3(2); C(1)–P(1)–Au(1) = 115.2(1); C(10)–P(1)–Au(1) = 107.1(1); C(11)–P(1)–Au(1) = 113.2(1); P(1)–Au(1)–Cl(1) = 175.69(4).

Notes and references

‡ *Synthesis* of [Mes(Me)(CPh_2)P·AuCl] (**2·AuCl**): To a stirred solution of (tht)AuCl[14] (20 mg, 0.06 mmol) dissolved in CH_2Cl_2 (1 mL) was added model compound **2**[10] (21 mg, 0.06 mmol) in CH_2Cl_2 (4 mL). The reaction was monitored by ^{31}P NMR spectroscopy (δ = 16.0) and after 1 h the solvent was removed *in vacuo* leaving a white residue. The product was extracted with toluene (3 × 2 mL) and the solvent removed *in vacuo* to afford **2·AuCl** as a colourless solid (33 mg, 94%). X-Ray quality crystals were obtained from slow diffusion of EtOH into a concentrated solution of **2·AuCl** in CH_2Cl_2. ^{31}P NMR (CD_2Cl_2, 162 MHz): δ (ppm): 16.0 (s). ^{1}H NMR (C_6D_6, 400.13 MHz): δ (ppm): 7.65 (d, $^{2}J_{HH}$ = 8 Hz, 2H, Ph-*H*), 7.17 (m, 2H, Ph-*H*), 7.04 (m, 3H, Ph-*H*), 6.84 (m, 3H, Ph-*H*), 6.45 (br s, 2H, *m*-Mes-*H*), 4.52 (d, $^{2}J_{PH}$ = 16 Hz, 1H, P–CPh_2*H*), 2.23 (s, 6H, *o*-CH_3-Mes), 1.89 (s, 3H, *p*-CH_3-Mes), 1.15 (d, $^{2}J_{PH}$ = 9 Hz, 3H, P–CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz) (assignments made with the aid of HMQC experiments) δ (ppm): 143.3 (d, $^{1}J_{CP}$ = 10 Hz, *i*-Mes-*C*), 142.1 (br s, Mes-*C*), 137.7 (s, Mes-*C*), 136.7 (s, Mes-*C*), 132.1 (d, *J* = 9 Hz, Ph-*C*), 130.1–127.8 (m, Ph-*C*), 52.8 (d, $^{1}J_{CP}$ = 32 Hz, P-*C*H), 25.7 (d, $^{3}J_{CP}$ = 9 Hz, *o*-Mes-CH_3), 21.2 (s, *p*-Mes-CH_3), 16.8 (d, $^{1}J_{CP}$ = 35 Hz, P-CH_3). MS (EI, 70 eV): *m*/*z* (%) = 564 (0.4) [M^+], 332 (50) [M^+ − AuCl], 167 (100) [$CHPh_2^+$], 165 (50) [$PMeMes^+$], 119 (15) [Mes^+]. Anal. Calc. for $C_{22}H_{21}PAuCl$: C, 48.91; H, 4.46. Found: C, 50.38; H, 4.75%.

§ *Crystal data* for **2·AuCl**: $C_{23}H_{25}PAuCl·1/2CH_2Cl_2$, *M* = 607.28, monoclinic, space group *C*2/*c* (#15), *a* = 17.031(1), *b* = 7.7689(5), *c* = 35.310(3) Å, α = 90, β = 93.431(4), γ = 90°, *V* = 4663.5(6) $Å^3$,

T = 173(2) K, Z = 8, μ(Mo Kα) = 66.13 cm^{-1}, d_{calc} = 1.730 g cm^{-3}, 30781 reflections measured, 5534 unique reflections (R_{int} = 0.0524) which were used in all calculations. The final $R_1(F)$ was 0.0304, wR_2 (on $F2$) was 0.0722. CCDC 665759. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719199e.

¶ *Synthesis* of n-Bu(MesP(AuCl)CPh$_2$)$_n$H (**3·AuCl**). To a stirred solution of (tht)AuCl (45 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added polymer **3**[4] (45 mg, M_n = 38 900 ± 800 g mol^{-1}, PDI = 1.34 ± 0.03) in CH_2Cl_2 (5 mL). The reaction was monitored by ^{31}P NMR (δ = 24) and after 1.5 h the solvent was removed *in vacuo* leaving a yellow solid. The polymer was precipitated from CH_2Cl_2 (1 mL) and cold hexanes (15 mL). After filtration, the solvent was removed *in vacuo* affording **3·AuCl** as a pale yellow solid (58 mg, 74%). ^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ (ppm): 24 (br). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 9.0–6.5 (Ar-*H*), 2.4–1.7 (Me-*H*). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm): 146.5 (br, Mes-*C*), 142.2 (br, Mes-*C*), 138.0 (br, Mes-*C*), 132–124 (br mult, Ph-*C*), 52.1 (br, P-*C*-P), 23.1 (br, *o*-CH_3), 28.2 (br, *p*-CH_3). GPC-LLS (g mol^{-1}): M_w = 71 600 ± 600 g mol^{-1}, PDI = 1.29 ± 0.01), dn/dc = 0.16 (as determined by 100% mass recovery methods). Satisfactory elemental analyses could not be obtained.

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