# Notes

## Synthesis and Nuclear Magnetic Resonance Spectroscopy of the Platinum–Gold Clusters $[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]^+$ and $[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]^+$

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The platinum–gold cluster complexes $[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]^+$ and $[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]^+$ were obtained by treatment of $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$ or $[PtH\{N(CH_2CH_2PPh_2)_3\}]^+$ with $[AuCl(PPh_3)]$, isolated as $BPh_4^-$ salts, and characterized by $^{31}P$ and $^{195}Pt$ NMR spectroscopy. They contain five-co-ordinate platinum and two-co-ordinate gold fragments.

Platinum–gold cluster compounds have attracted much recent attention.[1–20] Most of these complexes involve gold as a bridging ligand between two or more metal atoms. There are only a few examples for clusters in which gold forms two-centre two-electron bonds which are not ligand bridged: $[Pt(AuPPh_3)Cl(PPh_3)_2]$ was prepared by oxidative addition of $[AuCl(PPh_3)]$ to $[Pt(PPh_3)_4]$;[21] $[Pt(AuPPh_3)Me_2(bipy)]^+$ (bipy = 2,2′-bipyridine) was formed by a donor–acceptor interaction of the electron-rich platinum(II) complex $[PtMe_2(bipy)]$ and $[Au(PPh_3)]^+$;[6] $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, was obtained by mixing $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$ with $[Au(NO_3)(PPh_3)]$ and AgCl.[7] We report here on two further examples of this category, the binuclear complexes $[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]^+$ and $[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]^+$, which were obtained from $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$ or $[PtH\{N(CH_2CH_2PPh_2)_3\}]^+$ and $[AuCl(PPh_3)]$. The new compounds can be regarded as isolobal analogues to the hydrides $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$[22] and $[PtH\{N(CH_2CH_2PPh_2)_3\}]^+$.[23] The isolobal mercury complexes $[Pt(HgR)\{N(CH_2CH_2PPh_2)_3\}]^+$ (R = Me or Ph)[24,25] and $[Pt(HgPh)\{P(CH_2CH_2PPh_2)_3\}]^+$[25] have been synthesized very recently.

### Experimental

NMR spectra were measured on a Bruker WP-80 spectrometer; chemical shifts are quoted relative to 85% $H_3PO_4$ or to aqueous $Na_2[PtCl_6]$ and all $J$ values are given in Hz. Chemical analyses were performed by the Institut für Physikalische Chemie der Universität Wien.

The starting materials $[PtCl\{N(CH_2CH_2PPh_2)_3\}]Cl$,[26] $[PtCl\{P(CH_2CH_2PPh_2)_3\}]Cl$[27] and $[AuCl(PPh_3)]$[28] were prepared as described previously; all other reagents are commercially available. The following reactions were carried out in a nitrogen atmosphere.

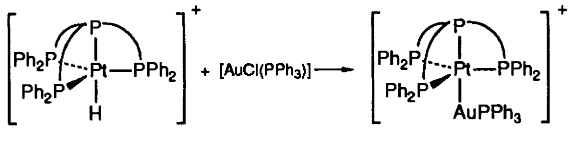
*Syntheses.*—$[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ **1**. A mixture of $[PtCl\{P(CH_2CH_2PPh_2)_3\}]Cl$ (93.7 mg, 0.1 mmol) and $NaBH_4$ (37.8 mg, 1 mmol) in MeOH (0.4 $cm^3$) and $CH_2Cl_2$ (0.4 $cm^3$) was stirred for 30 min, evaporated to dryness under reduced pressure, redissolved in $CH_2Cl_2$ (0.5 $cm^3$) and water (0.3 $cm^3$) and stirred for 10 min. The $CH_2Cl_2$ phase was separated off, washed with saturated aqueous NaCl solution (2 × 0.3 $cm^3$) and water (2 × 0.3 $cm^3$), treated with $[AuCl(PPh_3)]$ (52.6 mg, 0.1 mmol) and allowed to stand for 4 weeks. The mixture was evaporated to dryness and treated with MeOH (0.7 $cm^3$). The product precipitated upon addition of $NaBPh_4$ (27.4 mg, 0.08 mmol) in MeOH (0.1 $cm^3$) was filtered off, washed with water (2 × 0.3 $cm^3$) and MeOH (2 × 0.3 $cm^3$) and recrystallized from $CH_2Cl_2$–MeOH. Yield 78.9 mg (48%). As shown by $^{31}P$ NMR spectroscopy, the yield of the product was > 90%, but this has not been optimized. M.p. 191–195 °C (decomp.) (Found: C, 61.0; H, 4.6. Calc. for $C_{84}H_{77}AuBP_5Pt$: C, 61.35; H, 4.70%).

$[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]BPh_4$ **2**. A mixture of $[PtCl\{N(CH_2CH_2PPh_2)_3\}]Cl$ (92.0 mg, 0.1 mmol) and $NaBH_4$ (37.8 mg, 1.0 mmol) in MeOH (0.8 $cm^3$) was stirred for 30 min, evaporated to dryness under reduced pressure, treated with tetrahydrofuran (0.5 $cm^3$) and $[AuCl(PPh_3)]$ (52.6 mg, 0.1 mmol) and stirred for 30 min. The product was precipitated and purified as described for compound **1**. Yield 68.5 mg (41%). As shown by $^{31}P$ NMR spectroscopy, the yield of the product was > 90%, but this has not been optimized. M.p. 182–185 °C (decomp.) (Found: C, 60.7; H, 4.6; N, 0.8. Calc. for $C_{84}H_{77}AuBNP_4Pt{\cdot}0.5CH_2Cl_2$: C, 60.80; H, 4.70; N, 0.85%).

$[Pt(P_XPh_3)\{P_B(CH_2CH_2P_APh_2)_3\}][O_3SCF_3]_2$. A mixture of $[PtCl\{P(CH_2CH_2PPh_2)_3\}]Cl$ (93.7 mg, 0.1 mmol) and $PPh_3$ (26.2 mg, 0.1 mmol) in MeOH (0.4 $cm^3$) and $CH_2Cl_2$ (0.4 $cm^3$) was treated with $Tl(O_3SCF_3)$ (77.7 mg, 0.22 mmol) in MeOH (0.1 $cm^3$), stirred for 10 min, and then filtered off. According to $^{31}P$ NMR spectroscopy, the product is formed quantitatively: $\delta(P_B)$ 126.3, $\delta(P_A)$ 25.3, $\delta(P_X)$ −7.8, $J(PtP_B)$ 1717, $J(PtP_A)$ 2450, $J(PtP_X)$ 2077, $J(P_AP_X)$ 31, $J(P_BP_X)$ 298 Hz.

### Results and Discussion

The reaction of metal hydrides with gold(I) derivatives resulting in the isolobal substitution of $[AuL]^+$ for $H^+$ is a common synthetic method for the formation of gold–metal bonds.[7]



(1)

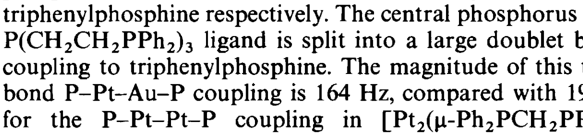
1

Treatment of $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$ with $[AuCl(PPh_3)]$ produces the cluster $[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]^+$ [equation (1)], which was isolated as its tetraphenylborate salt.

The structure of **1** in solution, as determined by NMR spectroscopy, consists of a trigonal bipyramidal environment of platinum, which is fixed by the tetradentate $P(CH_2CH_2PPh_2)_3$ ligand. The central phosphorus of the $P(CH_2CH_2PPh_2)_3$ ligand and the gold atom occupy the axial positions, while the three terminal phosphorus atoms of the $P(CH_2CH_2PPh_2)_3$ ligand lie in the equatorial positions. The two-co-ordinate gold is bound to platinum and triphenylphosphine. The complex was studied by $^{195}Pt$ and $^{31}P$ NMR spectroscopy: the $^{195}Pt$-$\{^1H\}$ NMR spectrum of **1** is a first-order doublet of doublets of 1:3:3:1 quartets at −5673 ppm. The larger doublet separation (1808 Hz) and the quartet separation (3130 Hz) are attributed to the one-bond couplings involving the central and terminal phosphorus atoms of the $P(CH_2CH_2PPh_2)_3$ ligand. The smaller doublet separation (232 Hz) is attributable to the two-bond coupling involving the triphenylphosphine ligand. The $^{31}P$-$\{^1H\}$ NMR spectrum shows signals at 155.5, 39.1 and 54.7 ppm which are attributed to the central and terminal phosphorus atoms of the $P(CH_2CH_2PPh_2)_3$ ligand and to triphenylphosphine respectively. The central phosphorus of the $P(CH_2CH_2PPh_2)_3$ ligand is split into a large doublet by the coupling to triphenylphosphine. The magnitude of this three-bond P–Pt–Au–P coupling is 164 Hz, compared with 195 Hz for the P–Pt–Pt–P coupling in $[Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(PPhMe_2)_2]^{2+}$.[29] The one-bond Pt–P coupling constant of the apical phosphorus atom of the tripod ligand is 1808 Hz compared to the following values for $[Pt\{P(CH_2CH_2PPh_2)_3\}X]^{n+}$ ($n$ = 1 or 2): 1369 Hz for X = $P(C_6H_{11})_2$,[30] 1452 Hz for X = Me,[31] 1467 Hz for X = H,[22] 1618 Hz for X = $P(OMe)_3$,[32] 1793 Hz for X = HgPh,[25] 1827 for X = $SnCl_3$,[33] 2077 Hz for X = $PPh_3$ (see below) and 2516 Hz for X = Cl.[34]

In order to assert the presence of the Pt–Au bond we have synthesized the corresponding 'gold free' complex $[Pt(PPh_3)\{P(CH_2CH_2PPh_2)_3\}]^{2+}$ for which the same spin system as for **1** is expected. This compound, which was previously believed to not exist 'as a consequence of the six phenyl groups in the equatorial positions of the $P(CH_2CH_2PPh_2)_3$ ligand which prevent the approach of a sterically hindered fifth ligand',[32] exhibits however clearly different NMR parameters (see Experimental section).

The complex $[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]^+$ was obtained according to equation (2) and was isolated as its tetraphenylborate salt.



(2)

2

The $^{195}Pt$-$\{^1H\}$ NMR spectrum of **2** consists of a doublet of 1:3:3:1 quartets at −4227 ppm as a result of coupling to triphenylphosphine (510 Hz) and to three equivalent terminal phosphorus atoms of the $N(CH_2CH_2PPh_2)_3$ ligand (3403 Hz). This demonstrates the trigonal bipyramidal environment of the platinum atom.

The two-bond Pt–Au–P coupling constant is considerably larger than that of **1**. This difference is possibly related to the *trans* influence[35–37] defined as the extent to which a ligand weakens a bond *trans* to it. For example a phosphorus ligand exerts a larger *trans* influence on the Pt–P bond in a linear P–Pt–P bond sequence than a nitrogen ligand in P–Pt–N. It seems that a similar correlation also exists in linear bond arrangements *via* two metals, *e.g.* P–Pt–Au–P (present in **1**) and N–Pt–Au–P (present in **2**). A similar correlation has been noted for two-bond Pt–Pt–P coupling constants in $[Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)(PR_3)L]^{n+}$ ($n$ = 1 or 2).[38] The triphenylphosphine $^{31}P$ resonance of **2** is at 36.3 ppm compared with 54.7 ppm for **1** and 4.2 ppm for $[Pt(AuPPh_3)Me_2(bipy)]^+$. The resonance of the phosphorus atoms of the $N(CH_2CH_2PPh_2)_3$ ligand in **2** is at 30.2 ppm.

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