Pergamon

0277–5387(95)00382–7

Polyhedron Vol. 15, No. 8, pp. 1309–1314, 1996

0277–5387/96 $15.00+0.00

THE SYNTHESIS OF PALLADIUM–GOLD AND PLATINUM–GOLD BIMETALLIC COMPLEXES BASED UPON TRIPOD TRIDENTATE PHOSPHINE AND ARSINE LIGANDS

ANDREW F. CHIFFEY, JOHN EVANS and WILLIAM LEVASON*

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

(*Received* 8 *August* 1995; *accepted* 11 *August* 1995)

Abstract—The planar complexes $MLCl_2$ [M = Pd or Pt; L = $MeC(CH_2PPh_2)_3$, $MeC(CH_2AsPh_2)_3$, $MeC(CH_2AsMe_2)_3$, $MeC(CH_2SMe)_3$ or $MeC(CH_2SeMe)_3$] have been prepared. In all cases spectroscopic data show that the tripod ligands are coordinated as *cis* bidentates. The complexes of $MeC(CH_2PPh_2)_3$ and $MeC(CH_2AsPh_2)_3$ react with $AuCl(SMe_2)$ in CH_2Cl_2 to form bimetallics $MLAuCl_3$ with the gold coordinated to the third donor group. All five tridentates react with $Au(SMe_2)Cl$ or Au(tetrahydrothiophen)Cl to form $L(AuCl)_3$ complexes.

Coordination complexes containing two different metal centres are of interest as possible precursors to bimetallic catalysts. We have recently reported[1] several palladium–gold and platinum–gold bimetallics based upon bis(diphenylarsino)methane of types *trans*-$[M(Ph_2AsCH_2AsPh_2AuX)_2X_2]$, *trans*-$[Pd(Ph_2AsCH_2AsPh_2AuX_3)_2X_2]$ and *trans*-$[Pt(Ph_2AsCH_2AsPh_2AuX_3)_2X_4]$ (M = Pd or Pt, X = Cl or Br), which have M : Au ratios of 1 : 2. Here, we report some examples based upon tripodal tridentate ligands $MeC(CH_2EPh_2)_3$ [E = P (ttp) or As (tta)], which have a 1 : 1 M : Au ratio.

EXPERIMENTAL

Physical measurements were made as described previously.[2] $MeC(CH_2PPh_2)_3$ (ttp) was obtained from Strem and used as-received. $MeC(CH_2AsPh_2)_3$ (tta) was obtained from sodium, $AsPh_3$ and $MeC(CH_2Cl)_3$ in liquid ammonia[3] and recrystallized from ethanol. ^1H NMR ($CDCl_3$): 0.95 (s, 1H), 2.31 (s, 2H), 7.1–7.4 (m, 10H). $MeC(CH_2AsMe_2)_3$ (ttam) was prepared from $NaAsMe_2$ and $MeC(CH_2Cl)_3$ in tetrahydrofuran.[4] ^1H NMR ($CDCl_3$): 0.95 (s, 6H), 1.05 (s, 1H), 1.70 (s, 2H); lit.[4] 0.95, 1.06, 1.71. $MeC(CH_2SMe)_3$[5] and $MeC(CH_2SeMe)_3$[6] were also made by literature methods. $MeC(CH_2SMe)_3$ ^1H NMR ($CDCl_3$): 1.10 (s, 1H), 2.15 (s, 3H), 2.65 (s, 2H); lit.[5] 1.15, 2.1, 2.5. $MeC(CH_2SeMe)_3$ ^1H NMR ($CDCl_3$): 1.15 (s, 1H), 2.0 [s, 3H, $^2J(^1H–^{77}Se) = 10$ Hz], 2.75 (s, 2H, $^2J(^1H–^{77}Se) = 9$ Hz]; $^{77}Se\{^1H\}$: δ 22.6; lit.[6] 1.15, 2.0, 2.75, δ (^{77}Se) = 23.

The Pd^{II} and Pt^{II} complexes were made by the same general method, described below for $Pd(ttp)Cl_2$.

$Pd(ttp)Cl_2$

A solution of $Pd(MeCN)_2Cl_2$ (0.05 g, 0.2 mmol) in CH_2Cl_2 (5 cm^3) was added to ttp (0.13 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) under nitrogen and the mixture stirred for 30 min. The solution was concentrated to *ca* 3 cm^3 and diethyl ether (20 cm^3) added slowly. The white precipitate was filtered off and dried *in vacuo*. Yield 0.14 g (91%). Found: C, 61.0; H, 5.0. $C_{41}H_{39}Cl_2P_3Pd$ requires: C, 61.4; H, 4.9%. FAB MS (3-NOBA matrix): *m*/*z* 800, calc. for $C_{41}H_{39}{}^{35}Cl_2P_3{}^{106}Pd^+$ 800; *m*/*z* 765, calc. for $C_{41}H_{39}{}^{35}ClP_3{}^{106}Pd^+$ 765. ^1H NMR ($CDCl_3$): 0.51 (s, 3H), 2.0 (s, 2H), 2.45 (m, 4H), 7.1–7.5 (m, 30H). $^{31}P\{^1H\}$ ($CDCl_3$ relative to 85% H_3PO_4): δ −28.9, +17.2. IR (Nujol mull): ν(Pd—Cl) 308, 293 cm^{-1}.

---

*Author to whom correspondence should be addressed.

UV–vis (CH_2Cl_2), $E_{max}/10^3$ cm^{-1} ($\varepsilon_{mol}/dm^{-1}$ mol cm^{-1}): 31.0 (4500), 37.7 (20,800).

Pt(ttp)Cl_2

Yield 85%. Found: C, 55.3; H, 4.6. $C_{41}H_{39}Cl_2P_3Pt$ requires: C, 55.3; H, 4.4%. FAB-MS: *m/z* 889, calc. for $C_{41}H_{39}{}^{35}Cl_2P_3{}^{95}Pt^+$ 889; *m/z* 854, calc. for $C_{41}H_{39}{}^{35}ClP_3{}^{195}Pt^+$ 854. ^1H NMR ($CDCl_3$): 0.49 (s, 3H), 2.0 (s, 2H), 2.53 (m, 4H), 7.1–7.6 (m, 30H). $^{31}P\{^1H\}$: δ −28.8 (s), −1.3 [$^1J(^{195}Pt–^{31}P) = 3430$ Hz]. ^{195}Pt (relative to $PtCl_6^{2-}$ in water): δ −4607. IR: ν(Pt—Cl) 314, 294 cm^{-1}. UV–vis (CH_2Cl_2): 32.8 (1400), 36.5 (7600), 39.5 (17,400).

Pd(tta)Cl_2

Yield 81%. Found: C, 51.6; H, 3.5. $C_{41}H_{39}As_3Cl_2Pd$ requires: C, 52.7; H, 4.2%. ^1H NMR ($CDCl_3$): 0.84 (s, 3H), 2.11 (s, 2H), 2.35 (m, 4H), 7.2–7.5 (m, 30H). IR: ν(Pd—Cl) 310, 295 cm^{-1}. UV–vis (CH_2Cl_2): 28.7 (5000), 36.8 (20,300).

Pt(tta)Cl_2

Yield 83%. Found: C, 47.3; H, 3.1. $C_{41}H_{39}As_3Cl_2Pt$ requires: C, 48.1; H, 3.8%. ^1H NMR ($CDCl_3$): 0.83 (s, 3H), 2.10 (s, 2H), 2.38 (m, 4H), 7.2–7.6 (m, 30H). ^{195}Pt: δ −4497. IR: ν(Pt—Cl) 312, 299 cm^{-1}. UV–vis: 29.6 (2000), 33.7 (5800).

Pd(ttam)Cl_2

Yield 81%. Found: C, 22.5; H, 5.0. $C_{11}H_{27}As_3Cl_2Pd$ requires: C, 23.5; H, 4.8%. IR: ν(Pd—Cl) 315, 310 cm^{-1}. UV–vis (CH_2Cl_2): 29.1 (4900), 38.8 (17,500).

Pt(ttam) Cl_2

Yield 80%. Found: C, 20.7; H, 4.8. $C_{11}H_{27}As_3Cl_2Pt$ requires: C, 20.3; H, 4.2%. ^{195}Pt NMR ($CDCl_3$): δ −4709. IR: ν(Pt—Cl) 310, 306 cm^{-1}. UV–vis (CH_2Cl_2): 35.2 (4600), 41.1 (10,200).

Pd(ttp)$AuCl_3$

Pd(ttp)Cl_2 (0.08 g, 0.1 mmol) in CH_2Cl_2 (10 cm^3) was treated with a solution of AuCl(SMe_2) (0.03 g, 0.1 mmol) in CH_2Cl_2 (10 cm^3) under a nitrogen atmosphere. The solution was concentrated to small volume, diethyl ether (20 cm^3) added and the white solid formed, filtered off, rinsed with diethyl ether and dried *in vacuo*. Yield 0.1 g (87%). FAB-MS: *m/z* 996, calc. for $C_{41}H_{39}{}^{197}Au^{35}Cl_2P_3{}^{106}Pd^+$ 997. Found: C, 46.4; H, 3.8. $C_{41}H_{39}AuCl_3P_3Pd$ requires: C, 47.6; H, 3.8%. ^1H NMR ($CDCl_3$): 0.72 (s, 3H), 2.36 (m, 2H), 2.68 (m, 4H), 7.1–7.6 (m, 30H). $^{31}P\{^1H\}$: 15.9 (s), 17.0 (s). IR: ν(Pd—Cl) 315, 293 cm^{-1}; ν(Au—Cl) 328 cm^{-1}. UV–vis (CH_2Cl_2): 31.3 (6100), 37.2 (22,300).

The following were prepared by the same general method.

Pt(ttp)$AuCl_3$

Yield 85%. FAB-MS: *m/z* 1124, $C_{41}H_{39}{}^{197}Au{}^{35}Cl_3P_3{}^{106}Pt^+$ 1121. Found: C, 44.0; H, 3.6. $C_{41}H_{39}AuCl_3P_3Pt$ requires: C, 43.8; H, 3.5%. ^1H NMR ($CDCl_3$): 0.72 (s, 3H), 2.33 (m, 2H), 2.67 (m, 4H), 7.1–7.6 (m, 30H). $^{31}P\{^1H\}$: −2.1 [$^1J(^{31}P–^{195}Pt) = 3410$ Hz], 15.0. ^{195}Pt: δ −4613. IR: ν(Pt—Cl) 301, 294 cm^{-1}; ν(Au—Cl) 321 cm^{-1}. UV–vis: 33.0 (1900), 36.5 (8300), 37.5 (10,300).

Pd(tta)$AuCl_3$

Yield 93%. Found: C, 41.0; H, 2.9; $C_{41}H_{39}As_3AuCl_3Pd$ requires: C, 42.0; H, 3.3%. ^1H NMR ($CDCl_3$): 0.86 (s, 3H), 2.1–2.6 (m, 6H), 7.1–7.6 (m, 30H). IR: ν(Pd—Cl) 311, 296 cm^{-1}; ν(Au—Cl) 322 cm^{-1}. UV–vis: 28.1 (5000), 34.6 (18,700).

Pt(tta)$AuCl_3$

Yield 94%. Found: C, 38.1; H, 2.5; $C_{41}H_{39}As_3AuCl_3Pt$ requires: C, 39.2; H, 3.1%. ^1H NMR ($CDCl_3$): 0.88 (s, 3H), 2.3–2.8 (m, 6H), 7.1–7.9 (m, 30H). ^{195}Pt: −4505. IR: ν(Pt—Cl) 311, 296 cm^{-1}; ν(Au—Cl) 321 cm^{-1}. UV–vis: 33.3 (1230), 39.1 (10,000).

Pd(ttt)Cl_2

Yield 71%. Found: C, 24.3; H, 4.1. $C_8H_{18}Cl_2PdS_3$ requires: C, 24.8; H, 4.6%. ^1H NMR ($CDCl_3$ 295 K): 1.24 (s, 3H), 2.14 (s, 3H), 2.6–3.5 (m, 12H). IR: ν(Pd—Cl) 327, 305 cm^{-1}. UV–vis: 25.4 (1400), 31.2 (2700), 37.5 (17,800).

Pt(ttt)Cl_2

Yield 75%. Found: C, 20.1; H, 3.5; $C_8H_{18}Cl_2PtS_3$ requires: C, 20.2; H, 3.8%. ^1H NMR (CD_2Cl_2, 295 K): 1.25 (s, 3H), 2.15 (s, 3H), 2.7–3.05 (m, 12H). ^{195}Pt (CH_2Cl_2): −3600, −3627, −3634. IR: ν(Pt—Cl) 322, 313 cm^{-1}. UV–vis: 26.7 (330), 33.4 (1200), 38.5 (2500).

Pd(ttse)Cl$_2$

Yield 82%. Found: C, 18.0; H, 2.9. $C_8H_{18}Cl_2PdSe_3$ requires: C, 18.2; H, 3.4%. ^1H NMR ($CDCl_3$, 295 K): 1.31 (s, 3H), 2.10 (3H), 2.68 (s, 6H), 2.78 (s), 2.95 (s, 6H). $^{77}Se\{^1H\}$ (CH_2Cl_2, 233 K): 34.0, 175.5, 177.5, 185.0, 190.0. IR: ν(Pd—Cl) 316, 303 cm^{-1}. UV–vis: 25.0 (1200), 31.5 (4300), 36.1 (15,400).

Pt(ttse)Cl$_2$

Yield 75%. Found: C, 15.4; H, 2.6. $C_8H_{18}Cl_2PtSe_3$ requires: C, 15.6; H, 2.9%. ^1H NMR ($CDCl_3$, 223 K): 1.31 (s, 3H), 2.09 (s), 2.10 (s, 3H), 2.75 (s), 2.78 (s, 6H), 2.80–3.3 (m, 6H). $^{77}Se\{^1H\}$ (CH_2Cl_2): 35.1, 153.9 [$^1J(^{77}Se–^{195}Pt) = 430$ Hz], 157.6 (490), 163.9 (490). ^{195}Pt (CH_2Cl_2): δ −3691, −3751, −3755. IR: ν(Pt—Cl) 318, 310 cm^{-1}. UV–vis: 25.8 (350), 30.5 (1100), 33.6 (15,000).

The gold complexes were made by the same general route.

(AuCl)$_3$(ttp)

AuCl(tetrahydrothiophen) (0.10 g, 0.3 mmol) in CH_2Cl_2 (10 cm^3) was added slowly to a solution of ttp (0.06 g, 0.1 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 30 min, concentrated to 2 cm^3 and treated with diethyl ether (15 cm^3) to afford a white precipitate. The solid was filtered off, rinsed with ether (15 cm^3) and dried *in vacuo*. Yield 0.11 g (86%). Found: C, 37.4; H, 3.1. $C_{41}H_{39}Au_3Cl_3P_3$ requires: C, 37.2; H, 3.0%. ^1H NMR ($CDCl_3$): 0.91 (s, 3H), 3.35 (m, 6H), 7.3–7.9 (m, 30H). $^{31}P\{^1H\}$: 17.6 (s, 2P), 18.7 (s, P). IR: ν(Au—Cl) 331, 325 (sh) cm^{-1}.

(AuCl)$_3$(tta)

Yield 82%. Found: C, 33.2; H, 2.5. $C_{41}H_{39}As_3Au_3Cl_3$ requires: C, 33.8; H, 2.7%. ^1H ($CDCl_3$): 1.05 (s, 3H), 3.28 (s, 6H), 7.2–8.1 (m, 30H). IR: ν(Au—Cl) 325 cm^{-1}.

(AuCl)$_3$(ttam)

Yield 89%. Found: C, 12.1; H, 2.2. $C_{11}H_{27}As_3Au_3Cl_3$ requires: C, 12.2; H, 2.5. IR: ν(Au—Cl) 321 cm^{-1}.

(AuCl)$_3$(ttt)

Yield 80%. Found: C, 10.9; H, 2.1. $C_8H_{18}Au_3Cl_3S_3$ requires: C, 10.6; H, 2.0%. ^1H NMR ($CDCl_3$): 1.18 (s, 3H), 2.34 (s, 9H), 2.92 (s, 6H). IR: ν(Au—Cl) 324 cm^{-1}.

(AuCl)$_3$(ttse)

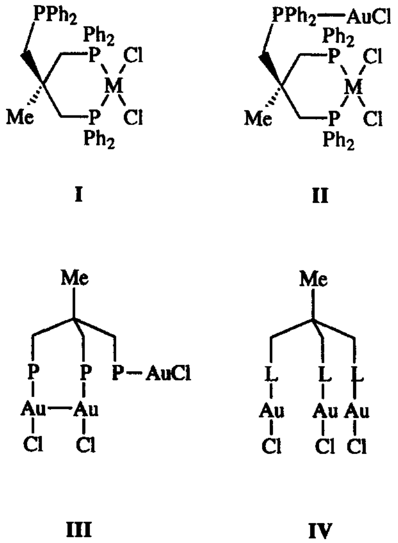
Yield 85%. Found: C, 9.5; H, 1.4. $C_8H_{18}Cl_3Se_3$ requires: C, 9.2; H, 1.7%. ^1H NMR ($CDCl_3$): 0.95 (s, 3H), 2.15 (s, 9H), 3.3 (s, 6H). IR: ν(Au—Cl) 327 cm^{-1}.

RESULTS AND DISCUSSION

Tripodal tridentate ligands $MeC(CH_2ER_n)_3$ (E = P or As, $n = 2$; E = S or Se, $n = 1$) usually coordinate all three donor atoms to octahedral, tetrahedral or five-coordinate metal centres,[7] for example in $CoCl_3\{MeC(CH_2PMe_2)_3\}$,[8] Pd(CO)$\{MeC(CH_2PPh_2)_3$,[9] or $Ru(CO)_2\{MeC(CH_2PPh_2)_3\}$.[10] However, the steric constraints of the ligands only allow coordination as bidentates to square planar metal centres as in $PtMe_2\{MeC(CH_2PPh_2)_3\}$[11] or $NiCl_2\{MeC(CH_2PPh_2)_3\}$.[12] Hence our strategy was to prepare the square planar complexes M(tripod)Cl$_2$ with Cl_2E_2 donor sets, and then to attempt to attach an AuCl group to the free E donor atom.

Palladium and platinum complexes of ttp, tta *and* ttam

The reaction of ttp with M(MeCN)$_2$Cl$_2$ gave high yields of the M(ttp)Cl$_2$ complexes. These were formulated as *cis* square planar (**I**) with P_2Cl_2 donor sets on the basis of the IR, UV–vis and particularly NMR spectroscopic data (Experimental section).



Scheme 1.

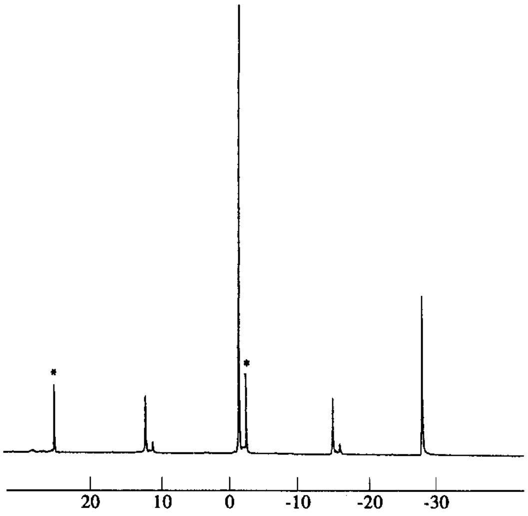


Fig. 1. The $^{31}P\{^{1}H\}$ NMR spectrum of $Pt(ttp)Cl_2$ in $CDCl_3$. The lines marked with an asterisk are due to phosphine oxide impurity.

The $^{31}P\{^{1}H\}$ NMR spectra show two resonances* in the ratio 2 : 1 due to coordinated and free PPh_2 groups (Fig. 1), and the ^{1}H NMR spectra show the corresponding two methylene resonances with ill-defined couplings. The $^{195}Pt\{^{1}H\}$ spectrum of $Pt(ttp)Cl_2$ contains a triplet at δ −4602 [$^{1}J(^{195}Pt-^{31}P) = 3440$ Hz] typical of a *cis* planar Pt^{II} complex.[13] The complexes of $MeC(CH_2AsPh_2)_3$ have very similar spectroscopic properties and are assigned a similar structure. For both the ttp and tta complexes, exchange between the free and coordinated donor groups was not evident in the ^{1}H or ^{31}P NMR spectra. The $M(ttam)Cl_2$ complexes are poorly soluble in chlorocarbon solvents, and the ^{1}H NMR spectra are complex due to the overlap of AsMe and $AsCH_2$ resonances. However, the IR and UV–vis spectra, and for $Pt(ttam)Cl_2$, the ^{195}Pt NMR resonance at δ −4709, are consistent with planar complexes with As_2Cl_2 donor sets.

Pd/Pt–Au *bimetallics*

The reaction of $M(ttp)Cl_2$ with $AuCl(SMe_2)$ in CH_2Cl_2 produced white powders which had Pd(Pt) : Au ratios of 1 : 1 as determined by EDX measurements, and microanalytical data were consistent with the formula $M(ttp)AuCl_3$. The FAB mass spectrum of the platinum complex showed a multiplet corresponding to the parent ion, but for the palladium complex the highest mass fragments observed corresponded to loss of one chlorine. The clearest evidence that the AuCl moiety has attached to the "free" PPh_2 group is provided by the $^{31}P\{^{1}H\}$ NMR spectra, which show two resonances (Fig. 2) due to coordinated phosphines, consistent with structure **II**. Coordination of the AuCl group has a minimal effect on the MP_2Cl_2 groups, as shown by the UV–vis and IR spectra. The ^{195}Pt chemical shift of $Pt(ttp)AuCl_3$ is only 7 ppm, different from that of $Pt(ttp)Cl_2$, which demonstrates the absence of any Pt···Au interaction. Unfortunately, repeated attempts to obtain suitable crystals of either complex to confirm this by an X-ray study have been unsuccessful.

The complexes $M(tta)AuCl_3$ were obtained in a similar manner; coordination of the AuCl to the "free" —CH_2AsPh_2 groups was evident by a shift of the appropriate methylene ^{1}H NMR resonance from *ca* δ 2.1 to *ca* 2.4, with minimal changes to the spectroscopic fingerprints of the MAs_2Cl_2 moieties. Surprisingly, the reaction of $M(ttam)Cl_2$ with $AuCl(SMe_2)$ in CH_2Cl_2 at ambient temperatures resulted in the rapid appearance of gold mirrors. Conducting the reactions at low temperatures (*ca* −30°C) in the dark resulted in the $M(ttam)Cl_2$ complexes being recovered unchanged.

Palladium and platinum complexes of ttt *and* ttse

The $M(ttse)Cl_2$ complexes have been described previously,[14] and the $M(ttt)Cl_2$ complexes were

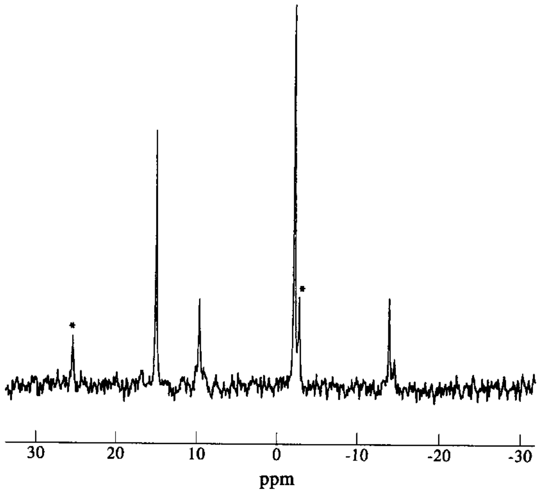


Fig. 2. The $^{31}P\{^{1}H\}$ NMR spectrum of $Pt(ttp)AuCl_3$ in $CDCl_3$. The lines marked with an asterisk are due to phosphine oxide impurity.

---

* The ligand ttp is air-sensitive and samples often show weak resonances at −24.7 (PPh_2) and +28.7 (O═PPh_2) due to the presence of MeC $(CH_2PPh_2)_2(CH_2PPh_2O)$. The uncoordinated —$PPh_2$ group in the planar complexes also seems to oxidize on prolonged exposure to air, and weak resonances due to this oxidized form $M\{MeC(CH_2PPh_2)_2(CH_2PPh_2O)\}Cl_2$ are present in the spectra of old samples.

readily obtained from $M(MeCN)_2Cl_2$ and the ligand in CH_2Cl_2. The IR and UV–vis spectra of these complexes are consistent with planar complexes, and hence with bidentate coordination by the ttt and ttse ligands. When these ligands coordinate as bidentates four diastereoisomers result, two *meso* and two *DL* (Fig. 3), which interconvert by pyramidal inversion at the group 16 atom. Hope *et al.*[14] identified all four invertomers in dimethyl sulphoxide solutions of $Pt(ttSe)Cl_2$, but found that at room temperature the $Pd(ttse)Cl_2$ was inverting rapidly, showing only two $^{77}Se\{^1H\}$ resonances due to coordinated and free SeMe groups, respectively. Our data from CH_2Cl_2 solutions are broadly in agreement, although the invertomer population in the platinum complex varies between solvents, and moderate solvent shifts are present in both the $^{77}Se\{^1H\}$ and ^{195}Pt spectra. In addition, we obtained the $^{77}Se\{^1H\}$ spectrum of $Pd(ttse)Cl_2$ at 233 K, at which temperature inversion had slowed, and four resonances due to coordinated SeMe groups were present, confirming the structure. The ^1H NMR spectra (Experimental section) are consistent with the proposed structures, but too complex to assign the resonances of individual invertomers. The ^1H NMR spectra of the $M(ttt)Cl_2$ complexes in $CDCl_3$ at 295 K show simple patterns with separate resonances due to MeC—, coordinated and uncoordinated SMe groups and a broad SCH_2 resonance consistent with fast pyramidal inversion. Inversion barriers decrease in the order $S < Se$ and are low in six-membered rings.[15] The spectra show complex resonance patterns on cooling as inversion slows. Exchange between free and coordinated SMe groups, however, is slow on the NMR time scale at room temperature. The ^{195}Pt NMR spectrum of $Pt(ttt)Cl_2$ in CD_2Cl_2 at 295 K contained three resonances, consistent with the three invertomers expected (Fig. 3). Unfortunately, neither the ttt nor ttse complexes reacted with $AuCl(SMe_2)$ to produce bimetallic complexes. No reaction appeared to occur on mixing the reagents in CH_2Cl_2 at room temperature, and on standing for several hours the mixtures deposited gold mirrors.

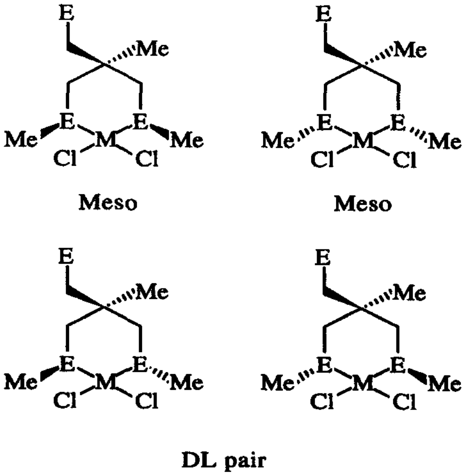


Fig. 3. Possible isomers (invertomers) of $M(ttt)Cl_2$ and $M(ttse)Cl_2$ complexes.

Gold complexes of ttp, tta, ttam, ttt *and* tttse

The reaction of three equivalents of $Au(SMe_2)Cl$ or Au(tetrahydrothiophen)Cl with one equivalent of the tripod ligand in CH_2Cl_2 produced white $L(AuCl)_3$ complexes. The X-ray structure $(AuCl)_3(ttp)$ was reported[16] some time ago, but no spectroscopic data were provided. The structure contains one AuCl unit bonded to each phosphine group, and unusually two of the gold units are linked by a long Au—Au bond (**III**). The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ contains two singlets at δ 17.6 and 18.7 in the ratio 2 : 1, and the ^1H NMR spectrum contains overlapping multiplet CH_2 resonances, which suggests that structure **III** is retained in solution.

The $(AuCl)_3(L)$ (L = ttam, tta, ttt and ttse) complexes all contain single sharp ν(Au—Cl) vibrations in the range 320–330 cm^{-1}, typical of linear LAuCl moieties.[17] The $(AuCl)_3(ttam)$ complex was insoluble in chlorocarbons, but the ^1H NMR spectrum of $(AuCl)_3(tta)$ contains a single sharp δ (CH_2) resonance, indicating that all three gold environments are the same, and hence the absence of an Au—Au bond (**IV**). $(AuCl)_3(ttt)$ and $(AuCl)_3(ttse)$ also showed singlet δ (Me) and δ (CH_2) resonances in their ^1H NMR spectra, consistent with structure **IV**, but unfortunately a ^{77}Se NMR spectrum of $(AuCl)_3(ttse)$ could not be obtained due to poor solubility. The ready displacement of the SMe_2 or tetrahydrothiophen from the starting materials by ttt and ttse contrasts with the failure of these two ligands to form the Pd/Pt–Au bimetallics described above. The reason for this different behaviour is unclear, possibly in the coordination of ttt or ttse to Pd^{II} or Pt^{II}, although the third —S(Se)Me group is neither coordinated nor undergoing fast exchange with the bound groups, electronic effects reduce its donor power. Similar effects would be less significant in ttp or tta complexes, where the group 15 centres are stronger σ-donors.

Acknowledgements—We thank EPSRC and B.P. Chemicals Ltd for a CASE award (A.F.C).

REFERENCES

1. A. F. Chiffey, J. Evans, W. Levason and M. Webster, *Polyhedron*, 1996, **15**, 591.

2. A. F. Chiffey, J. Evans, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.* 1994, 2835.
3. W. Hewertson and H. R. Watson, *J. Chem. Soc.* 1962, 1490.
4. R. D. Feltham, A. Kasenally and R. S. Nyholm, *J. Organomet. Chem.* 1967, **7**, 285.
5. R. Ali, S. J. Higgins and W. Levason, *Inorg. Chim. Acta* 1984, **84**, 65.
6. D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter and G. L. Marshall, *J. Chem. Soc., Perkin II* 1984, 429.
7. L. Sacconi and F. Mani, *Transition Met. Chem. (N.Y.)* 1982, **5**, 190.
8. K. Kashiwabara, M. Kita, J. Fujita, S. Kurachi and S. Ohba, *Bull. Chem. Soc. Japan* 1994, **67**, 2145.
9. J. Grevin, P. Kalck, J. C. Daran, J. Vaissermann and C. Bianchini, *Inorg. Chem.* 1993, **32**, 4965.
10. S. V. Hommeltoft and M. C. Baird, *Organometallics* 1986, **5**, 190.
11. R. E. Kirchner, R. G. Little, K. D. Tau and D. W. Meek, *J. Organomet. Chem.* 1978, **149**, C15.
12. P. Zanello, A. Cinquantini, C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and A. Bencini, *J. Chem. Soc., Dalton Trans.* 1990, 3761.
13. E. G. Hope, W. Levason and N. A. Powell, *Inorg. Chim. Acta* 1986, **115**, 187.
14. E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.* 1985, 2185.
15. E. W. Abel, K. G. Orrell and S. K. Bhargava, *Prog. Inorg. Chem.* 1984, **32**, 1.
16. M. K. Cooper, K. Henrick, M. McPartlin and J. L. Latten, *Inorg. Chim. Acta* 1982, **65**, L185.
17. D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton and J. G. Smith, *J. Chem. Soc. (A)* 1970, 545.