Transition Metal–Carbon Bonds. Part XXXV.[1] Internal Metallation of t-Butyldi-*o*-tolylarsine and Di-t-butyl-*o*-tolylarsine by Platinum †

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t-Butyldi-*o*-tolylarsine (L′) and di-t-butyl-*o*-tolylarsine (L″) have been prepared. K_2PtCl_4 with L′ (2 mol) gives *trans*-[$PtCl_2L'_2$] but when $PtCl_2(PhCN)_2$ was treated with L′ (2 mol proportions) in boiling n-propanol the mono-metallated species [PtCl(As′–C)L′] was formed. With one mole proportion of L′ $PtCl_2(PhCN)_2$ gives the chloro-bridged species [$Pt_2Cl_2(As'–C)_2$] [As′–C≡ *o*(t-butyl-*o*-tolylarsino)benzyl]. The complexes [Pt_2(acetate)$_2$(As′–C)$_2$], [Pt_2(benzoate)$_2$ (As′–C)$_2$], [Pt(acac)(As′–C)], and [PtCl(As′–C)Q] (Q = pyridine, PMe_2Ph, or $AsMe_2Ph$) and [Pt(As′–C) ($PMe_2Ph)_2$]Cl were prepared. On heating [$PtCl_2(PhCN)_2$] with L″[$Pt_2Cl_2(As''–C)_2$] forms {As″–C≡$Bu^t_2AsC_6H_3CH_2$–}. Palladium complexes *trans*-[$PdCl_2L'_2$] and *trans*-[$PdCl_2L''_2$] were also prepared but could not be induced to internally metallate. ^1H n.m.r. and i.r. data are given.

THERE is much interest in internal metallation reactions of transition metal complexes.[2] Nearly all the studies have been with N- or P-donors but in spite of the very large amount of work on tertiary arsine–transition metal compounds the internal metallation of an As-donor ligand has not hitherto been observed. We have shown that bulky substituents on P-donor ligands promote unusual chemistry including metallation.[3] It was therefore of interest to see if bulky tertiary arsine ligands would behave similarly. Previously the *o*-tolyl methyl groups of $PBu^t(o\text{-tolyl})_2$ and of $PBu^t_2(o\text{-tolyl})$ were found to be readily metallated by platinum to give five-membered chelate rings[4] and we have now studied the corresponding arsines $AsBu^t(o\text{-tolyl})_2$ (L′) and $AsBu^t_2(o\text{-tolyl})$ (L″). These ligands were prepared by treating the chlorides $AsBu^tCl_2$ or $AsBu^t_2Cl$ with *o*-tolyl-lithium (see Experimental section).

TABLE 1

Colours, melting or decomposition points, % yields, and microanalytical and molecular weight data

Compound	Colour	M.p./°C	Yield (%)	Analytical data [a] C	H	Cl	M [a,b]
trans-[$PtCl_2L'_2$]	Yellow	173—177	70	48·4 (48·35)	5·1 (5·2)	7·8 (7·95)	
trans-[PtCl(As′–C)L′]	White	190—193	87	50·4 (50·4)	5·2 (5·3)	4·3(4·15)	
[PtCl(As″–C)L″]	White	206—210	44	44·5 (44·6)	6·2 (6·25)	4·8 (4·5)	
[$Pt_2Cl_2(As'–C)_2$]	White	290 [c]	79	40·05 (39·75)	4·05 (4·1)	6·7 (6·5)	
[$Pt_2(OAc)_2(As'–C)_2$],$\frac{1}{2}C_6H_{12}$	Pale yellow	144—148	56	45·65 (45·3)	5·15 (5·15)		
[$Pt_2(OBz)_2(As'–C)_2$]	Pale yellow	195—200	80	48·05 (47·8)	4·4 (4·3)		982 (1258) [d]
[$Pt_2Cl_2(As''–C)_2$]	White	270	65	35·2 (35·35)	4·85 (4·75)	6·9 (6·95)	
[$Pt_2(OBz)_2(As''–C)_2$]	Pale yellow	190—195 [c]	75	44·3 (44·35)	4·9 (4·9)		
[PtCl(As′–C)py], [e] mixed isomers	White	192—195	85	44·3 (44·35)	4·4 (4·35)	5·5 (5·7)	620 (623)
[PtCl(As′–C)PMe_2Ph], mixed isomers	White	170—174	85	45·9 (45·8)	5·0 (4·9)	5·4 (5·2)	695 (682)
[PtCl(As′–C)($AsMe_2Ph$], mixed isomers	White	160—165	92	43·55 (43·0)	4·55 (4·6)	4·7 (4·9)	714 (726)
[Pt(acac)(As′–C)]	White	132—133	74	45·9 (45·45)	4·75 (4·8)		611 (607)
[Pt(As′–C)($PMe_2Ph)_2$]BPh_4	White	154—157	95	62·95 (63·1)	5·75 (5·85)		
[PtCl(As″–C)py] [f]	White	270 [c]	86	40·0 (40·8)	4·85 (4·95)	6·35 (6·0)	598 (589)
[PtCl(As″–C)(PMe_2Ph)]	White	170—171	73	42·35 (42·65)	5·25 (5·45)	5·4 (5·45)	643 (648)
[PtCl(As″–C)($AsMe_2Ph$)]	White	146—150	88	39·65 (39·95)	4·9 (5·1)	5·1 (5·1)	668 (692)
[Pt(acac)(As″–C)]	Pale yellow	172—174	80	42·75 (41·9)	5·2 (5·45)		591 (573)
trans-[$PdCl_2L'_2$]	Yellow	174—181	100	53·9 (53·65)	5·8 (5·75)	9·05 (8·8)	
trans-[$PdCl_2L''_2$]	Deep orange	250 [c]	87	47·2 (48·8)	6·7 (6·8)	9·85 (9·6)	

[a] Theoretical values in parentheses. [b] In chloroform solution. [c] Decomposes without melting. [d] Presumably decomposes in solution. [e] Nitrogen analysis: 2·3 (2·25)%. [f] Nitrogen analysis: 2·55 (2·4)%.

Potassium chloroplatinite (1 mol) when treated in warm aqueous ethanol with $AsBu^t(o\text{-tolyl})_2$ (2 mol) readily gave *trans*-[$PtCl_2L'_2$], characterized by micro-analysis and i.r. and n.m.r. data (see Tables 1 and 2). When $PtCl_2(PhCN)_2$ was treated with L′ (2 mol) in n-propanol for 3 h it gave the mono-metallated product [PtCl(As′–C)L′]. This probably has the *trans*-configuration from the low value of ν(Pt–Cl) (Table 2) and by analogy with the corresponding phosphorus analogue {As′–C≡ the mono-metallated chelate $AsBu^t(o\text{-tolyl})C_6H_3CH_2$}.

When a mixture of [$PtCl_2(PhCN)_2$] (1 mol) and L′ (1 mol) were heated in 2-methoxyethanol for 10 min the chloro-bridged internally metallated complex [$Pt_2Cl_2(As'–C)_2$] was readily obtained. Thus $PBu^t(o\text{-tolyl})_2$ and $AsBu^t(o\text{-tolyl})_2$ behave similarly towards internal metallation by platinum(II), possibly the arsine reacting a little more slowly than the phosphine. [$Pt_2Cl_2(As'–C)_2$] underwent reactions typical of a chloro-bridged platinum(II) complex, see Scheme. The chloride ligands were readily replaced by acetate or benzoate on

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[1] Part XXXIV, B. E. Mann, R. Pietropaolo, and B. L. Shaw, preceding paper.

[2] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[3] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

[4] A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 860.

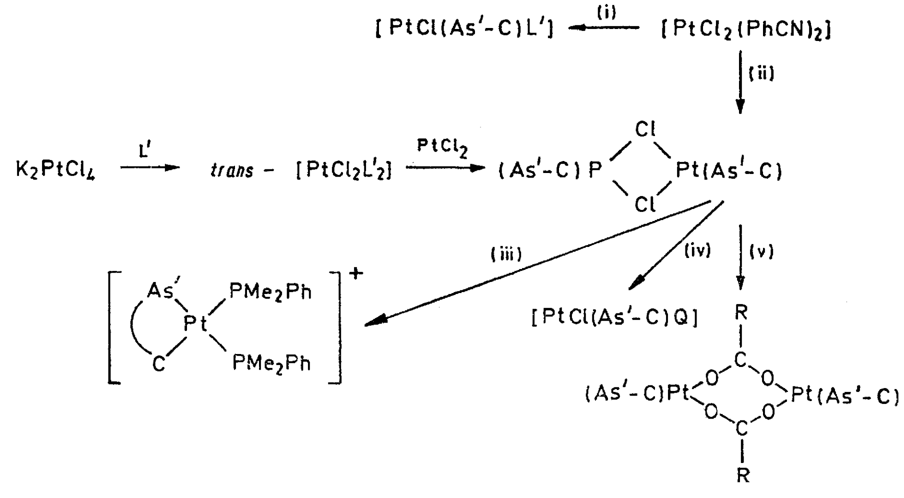
treatment with silver acetate or benzoate, respectively. $[Pt_2(OAc)_2(As'{-}C)_2]$ crystallized with cyclohexane of crystallization as did the corresponding phosphine complex and this is probably a consequence of cavities in the crystal caused by the bulkiness of the ligands. The chloro-bridges could be split by neutral ligands (Q = pyridine, PMe_2Ph, or $AsMe_2Ph$) to give mononuclear complexes $[PtCl(As'{-}C)Q]$ as *cis-trans*-mixtures. With an excess of dimethylphenylphosphine in boiling benzene the salt $[Pt(As'{-}C)(PMe_2Ph)_2]Cl$ formed; the cation also was isolated as the BPh_4^- salt. The mononuclear acetylacetonato-complex $[Pt(As'{-}C)(acac)]$ was prepared from $[Pt_2Cl_2(As'{-}C)_2]$ and thallium acetylacetonate. For convenience the various conversions of the platinum(II)–$AsBu^t(o\text{-tolyl})_2$ systems have been summarized in the Scheme.

TABLE 2

^1H N.m.r.[a] and i.r.[b] data

	$\tau(Bu^t)$	τ(tolylMe)	$\tau(CH_2)$ [c]		$\nu(Pt{-}Cl)/cm^{-1}$
trans-$[PtCl_2L'_2]$	8·35	7·42			335s or 318s
trans-$[PtCl(As'{-}C)L']$	8·39, 8·45	7·79, 7·68	7·53, 7·57		268s
$[PtNO_3(As'{-}C)L']$	8·41	7·67, 7·61	7·22		
$[PtCl(As''{-}C)L'']$	8·41, 8·52 8·54	7·13, 7·1	6·91 6·63		
$[Pt_2Cl_2(As'{-}C)_2]$ [d]					277s, 241s
$[Pt_2(OAc)_2(As'{-}C)_2]$	8·73	8·03	6·64		
$[Pt_2(OBz)_2(As'{-}C)_2]$	8·61	8·14	6·7, 6·97		
$[Pt_2Cl_2(As''{-}C)_2]$					279s, 240m
$]Pt_2(OBz)_2(As''{-}C)_2]$	8·77, 8·46		6·67, 6·56		
$[PtCl(As'{-}C)py]$ [e] mixed isomers	8·68, 8·4	7·65, 7·44	6·59, 6·35		293s, 276s
$[PtCl(As'{-}C)PMe_2Ph]$ [f] mixed isomers	8·67, 8·46	7·58	6·93, 6·63		270s
$[PtCl(As'{-}C)AsMe_2Ph]$ [g] mixed isomers	8·61, 8·39	7·8	6·73, 6·37		287w, 268s
$[Pt(acac)(As'{-}C)]$	8·57	7·21	6·53	8·15s 8·08s (acac methyls)	
$[Pt(As'{-}C)(PMe_2Ph)_2]Cl$	8·37	7·84	6·62br	8·2—8·6 [h] PMe_2Ph	
$[Pt(As'{-}C)(PMe_2Ph)_2]BPh_4$	8·4	7·86	6·03	8·4—8·74 [h] PMe_2Ph	
$[PtCl(As''{-}C)(py)]$	8·47		6·77		267s
$[PtCl(As''{-}C)(PMe_2Ph)]$	8·55		7·0 J(PH) 6	8·23d J(PH) 10·1	277s
$[PtCl(As''{-}C)(AsMe_2Ph)]$	8·53		6·86	8·34 ($AsMe_2Ph$ methyls)	280s
$[Pt(acac)(As''{-}C)]$	8·57		6·67 J(PtH) 109	8·18, 8·11 (acac methyls)	
trans-$[PdCl_2L'_2]$	8·41	7·39			353s
trans-$[PdCl_2L''_2]$	8·42	6·8			335s

[a] In CH_2Cl_2, τ-values ± 0·02, J values ± 0·5 Hz. [b] As Nujol mulls. [c] The methylene protons would be non-equivalent and should presumably give second order spectra with satellites due to coupling with platinum. However the resonances were generally weak and broadened ($w_{\frac{1}{2}}$ *ca.* 2—5 Hz). Only the stronger 'lines' were observed and in only one case was coupling to platinum-195 observed. [d] Too insoluble for n.m.r. studies. [e] Isomers present in *ca.* 1 : 1 ratio. [f] Isomers present in *ca.* 1 : 9 ratio. [g] Isomers present in *ca.* 4 : 6 ratio. [h] Partially obscured by Bu^t peaks.



Some reactions of t-butyldi-*o*-tolylarsine with platinum(II); (i), 2L', 100 °C; (ii), L', 124 °C; (iii), an excess of PMe_2Ph; (iv), pyridine, PMe_2Ph, or $AsMe_2Ph$; (v), AgOCOR

We have also prepared the dichloro-bridged complex $[Pt_2Cl_2(As''{-}C)_2]$ where $As''{-}C \equiv Bu^t_2AsC_6H_3CH_2$ by heating $[PtCl_2(PhCN)_2]$ with L'' in 2-methoxyethanol for 10 min. This binuclear complex reacted with neutral ligands, L, to give mononuclear species [PtCl(As''–C)L]. From the ^{1}H n.m.r. data only one isomer was produced but we do not know if it is of *cis*- or *trans*-configuration. The bridged chloride was converted into the mononuclear acetylacetonate.

We have also prepared the palladium complexes *trans*-$[PdCl_2L'_2]$ and *trans*-$[PdCl_2L''_2]$. The configuration follows from the occurrence of only one palladium–chlorine stretching frequency in the i.r. and at a high value (>330 cm^{-1}) characteristic of chlorine *trans* to chlorine. When these complexes were heated in n-propanol, conditions under which the corresponding phosphorus complexes metallated, they decomposed to give palladium mirrors and we have been unable to prepare internally palladated derivatives of $AsBu^t(o\text{-tolyl})_2$ and $AsBu^t_2(o\text{-tolyl})$.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Spectra were obtained as follows: i.r. 4000—400 cm^{-1}, Perkin-Elmer 457 spectrometer; i.r. 500—200 cm^{-1} Grubb-Parsons DM4 spectrometer; ^{1}H n.m.r., Perkin-Elmer R12 60 MHz spectrometer. Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus in chloroform (at 30 °C).

*t-Butyldi-*o*-tolylarsine.*—A diethyl ether solution of *o*-tolyl-lithium (0·525 mol in 470 ml) was added to a solution of dichloro-t-butylarsine [5] (28·9 g, 0·142 mol) in ether (150 ml) at *ca.* −40° over 30 min. The mixture was then heated under reflux for 45 min, cooled, and hydrolysed with degassed water (*ca.* 400 ml). The dried ethereal layer was evaporated under reduced pressure and the residue recrystallized from methanol. It formed very pale yellow *needles* (30·5 g, 68%), m.p. 80°. It was characterized by its ^{1}H n.m.r. spectrum $\tau(Bu^t)$ 8·78s, $\tau(o\text{-}CH_3)$ 7·68 in benzene.

*Di-t-butyl-*o*-tolylarsine.*—This was similarly prepared from *o*-tolyl-lithium (0·032 mol in 120 ml) and chlorodi-t-butylarsine [5] (6·89 g, 0·031 mol) with a reflux time of 2 h. The colourless product distilled at 128°, 0·2 mmHg and was characterized by its ^{1}H n.m.r. spectrum in benzene $\tau(Bu^t)$ 8·77s, $\tau(o\text{-}CH_3)$ 7·45s.

trans-*Dichlorobis(t-butyldi-*o*-tolylarsine)platinum*(II).— A solution of t-butyldi-*o*-tolylarsine (0·63 g, 2·0 mmol) in warm ethanol (*ca.* 2 ml) was added to a solution of potassium chloroplatinite (0·403 g, 0·95 mmol) in water (10 ml). The mixture was then agitated at *ca.* 25° in the dark for *ca.* 24 h. The resultant yellow precipitate gave the required product from dichloromethane–methanol as prisms (0·59 g, 0·66 mmol).

*Chloro{*o*-(t-butyl-*o*-tolylarsino)benzyl}(t-butyldi-*o*-tolylarsine)platinum*(II).—A mixture of *trans*-dichlorobis(benzonitrile)platinum(II) (0·45 g; 0·95 mmol) and t-butyldi-*o*-tolylarsine [0·63 g; 2·0 mmol in n-propanol (70 ml)] was heated under reflux for *ca.* 3 h to give a clear pale yellow solution. The solvent was evaporated to low volume under reduced pressure to give the product as *prisms* (0·71 g; 0·83 mmol).

*Chloro{*o*-(di-t-butylarsino)benzyl}(di-t-butyl-*o*-tolylarsine)-platinum*(II).—This was prepared in a similar manner to give the product as prisms.

*Di-μ-chloro-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum*(II).—A mixture of *trans*-dichlorobis(benzonitrile)platinum(II) (0·731 g; 1·55 mmol) and t-butyldi-*o*-tolylarsine (0·53 g; 1·68 mmol) in 2-methoxyethanol (50 ml) was heated under reflux for *ca.* 10 min, when the product was deposited as *prisms* (0·668 g; 0·615 mmol).

*Di-μ-chloro-bis{*o*-(di-t-butylarsino)benzyl}diplatinum*(II).—This was prepared in a similar manner from *trans*-dichlorobis(benzonitrile)platinum(II) and di-t-butyl-*o*-tolylarsine, to give the product as *prisms.*

*Di-μ-acetato-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum*(II).—A suspension of di-μ-chloro-bis{*o*-(tolylbutyl-*o*-tolylarsino)benzyl}diplatinum(II) (0·223 g; 0·21 mmol) and silver acetate (0·076 g; 0·45 mmol) in acetone (8 ml) was shaken in the dark overnight. The resultant slurry was filtered and the solvent removed under reduced pressure from the filtrate to give the product as *prisms* (0·133 g; 0·117 mmol) from dichloromethane–cyclohexane.

*Di-μ-benzoato-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum*(II).—This was similarly prepared as *prisms* from dichloromethane–cyclohexane (yield 80%).

*sym-Di-μ-benzoatobis{*o*-(di-t-butylarsino)benzyl}diplatinum*(II).—This was prepared in a similar manner to give the product as prisms from dichloromethane–cyclohexane (yield 55%).

*Chloro{*o*-(t-butyl-*o*-tolylarsino)benzyl}pyridine-platinum*(II) (*Mixed Isomers*).—Pyridine (48 μl; 0·3 mmol) was added to a suspension of di-μ-chloro-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum(II) (0·162 g; 0·15 mmol) in chloroform (10 ml). The mixture was set aside overnight, then the solvent removed under reduced pressure to give the product as *prisms* (0·158 g, 0·254 mmol) from benzene–n-hexane.

*Chloro{*o*-(di-t-butylarsino)benzyl}pyridineplatinum*(II).—This was prepared in a similar manner to give the product as *prisms* from benzene–n-hexane.

*Chloro{*o*-(t-butyl-*o*-tolylarsino)benzyl}dimethylphenylphosphineplatinum*(II) (*Mixed Isomers*).—Dimethylphenylphosphine (92 μl; 0·67 mmol) was added to a suspension of di-μ-chloro-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum(II) (0·356 g; 0·328 mmol) in benzene and the mixture shaken at *ca.* 25 °C for 3 h. The solvent was removed under reduced pressure to give the product as *prisms* (0·38 g; 0·557 mmol) from benzene–light petroleum (b.p. 40—60 °C).

*{*o*-(t-Butyl-*o*-tolylarsino)benzyl}bis(dimethylphenylphosphine)platinum*(II) *Chloride.*—Dimethylphenylphosphine (172 μl; 1·27 mmol) was added to a suspension of di-μ-chloro-bis{*o*-(t-butyl-*o*-tolylarsino)benzyl}diplatinum(II) (0·034 g; 0·29 mmol) in benzene (15 ml) and the mixture was heated under reflux for *ca.* 1 h. The resultant colourless solution was cooled at 0 °C to give the product as *needles* (0·452 g; 0·552 mmol).

*{*o*-(t-Butyl-*o*-tolylarsino)benzyl}bis(dimethylphenylphosphine)platinum*(II) *Tetraphenylborate.*—A solution of sodium tetraphenylborate (0·055 g; 0·162 mmol) in methanol (1 ml) was added to a solution of {*o*-(t-butyl-*o*-tolylarsino)-benzyl}bis(dimethylphenylphosphine)platinum(II) chloride (0·1 g; 0·147 mmol) in methanol (8 ml).

The solution was then set aside at *ca.* 25 °C for *ca.* 1 h when the product crystallised as *prisms* (0·11 g; 0·1 mmol).

*Chloro{*o*-(di-t-butylarsino)benzyl}dimethylphenylphosphine-platinum*(II).—Dimethylphenylphosphine (90 μl; 0·65 mmol) was added to a suspension of di-μ-chloro-bis{*o*-(di-t-butylarsino)benzyl}diplatinum(II) (0·3 g; 0·295 mmol) in benzene (15 ml) and the mixture heated under reflux for *ca.* 10 min.

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[5] A. Tzschach and W. Lange, *Z. anorg. Chem.*, 1964, **330**, 317.

The solvent was removed under reduced pressure to give the product as *prisms* (0·277 g; 0·428 mmol) from benzene–light petroleum (b.p. 40—60 °C).

Chloro{o-(*t-butyl*-o-*tolylarsino*)*benzyl*}*dimethylphenylarsine-platinum*(II) (*Mixed Isomers*).—This was similarly prepared as *prisms* from benzene–light petroleum (b.p. 40—60 °C) (yield 83%).

trans-*Dichlorobis*(*t-butyldi*-o-*tolylarsine*)*palladium*(II).—A solution of t-butyldi-*o*-tolylarsine (3·51 g; 11·2 mmol) in warm ethanol (35 ml) was added to a solution of sodium chloropalladite (1·588 g; 5·33 mmol) in methanol (30 ml). The solution was shaken and cooled to room temperature over *ca.* 0·5 h when the product crystallised as *prisms* (4·35 g; 5·33 mmol).

trans-*Dichlorobis*(*di-t-butyl*-o-*tolylarsine*)*palladium*(II) was prepared similarly.

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