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ASPECTS OF TRANSMETALLATION REACTIONS OF 2-$Me_2NCH_2C_6H_4$- AND 2,6-$(Me_2NCH_2)C_6H_3$-METAL (Pd, Pt, Hg, Tl) COMPLEXES WITH METAL CARBOXYLATES AND LOW-VALENT METAL (Pd, Pt) COMPLEXES

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Summary

A study has been made of reactions involving organometallic compounds containing *ortho*-Me_2NCH_2 substituted aryl ligands. The single step syntheses of the new compounds $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$, $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$, $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$, $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$ and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl]$ are described. Stable internal N—Tl coordination at low temperatures has been established for the C-chiral thallium compounds. Reactions of the other Tl and Hg compounds and of $[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Hg]$ with $Pd(O_2CMe)_2$, and also of the reverse reaction of *cis*-$[(2\text{-}Me_2\text{-}NCH_2C_6H_4)_2Pd]$ with $Hg(O_2CR)_2$ or $Tl(O_2CR)_3$, gave transmetallation of one organo ligand and led to a single mono-organopalladium compound and corresponding by-products. Reaction of *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ with $Pd(O_2CR)_2$ gave the dimeric compound $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2]$. *cis*-$[(2\text{-}Me_2\text{-}NCH_2C_6H_4)_2Pt]$ did not react with $Pd(O_2CMe)_2$, while reaction of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ or *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ with $Pd(O_2CMe)_2$ resulted in decomposition. Upon heating, *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ was isomerized to *cis*-isomer. A redox reaction between $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ and $[Pt(COD)_2]$ (COD = 1,5-cyclo-octadiene) and $[Pd_2(DBA)_3]$ (DBA = dibenzylideneacetone) gave the *cis*-isomers of $[(2\text{-}Me_2NCH_2C_6H_4)_2M]$ (M = Pd, Pt).

The results are discussed in terms of influence of internal coordination of the CH_2NMe_2 group. It is concluded that although internal coordination of the CH_2NMe_2 ligand can stabilize metal—carbon bonds it cannot prevent cleavage of such bonds by electrophiles. In this respect, there is no difference in the behaviour of $Hg(O_2CR)_2$ and $Tl(O_2CR)_3$. The reactions are influenced by the metal—nitrogen bond strength, which follows the order Pt—N > Pd—N > Hg—N,

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Tl—N. The reactivity of Pt compounds is greatly influenced by their structure and the type of ligand. It is proposed that cleavage of Pd—C bonds occurs mainly by a mechanism involving direct electrophilic attack at the carbon centre.

Introduction

In recent articles [1,2] we described reactions of cyclometallated platinum(II) compounds with mercury(II) and thallium(III) carboxylates, which gave distinctly different results. Reactions of the compounds *cis*- and *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] (I and II), *cis*-[(2-$Me_2NC_6H_4CH_2)_2Pt$] (III) and [{2,6-$(Me_2NCH_2)_2C_6H_3$}PtBr] (IV) with $Hg(O_2CR)_2$ involved formation of intermediates with a Pt-to-Hg bond. In the case of I, III and IV stable heterodinuclear Pt-Hg compounds were obtained in which the Pt—Hg bond is bridged by one carboxylato group. In contrast, a similar compound could not be isolated from the reactions of II, instead, elimination of Hg^0 and formation of the platinum(IV) compounds *trans-C*- and *trans-N*-[(2-$Me_2NCH_2C_6H_4)_2Pt(O_2CR)_2$] occurred. The latter products were also obtained from the reaction of II with $Tl(O_2CR)_3$, which occurred with $Tl(O_2CR)$ elimination. Reaction of IV with $Tl(O_2CR)_3$ gave both elimination of $Tl(O_2CR)$ with formation of *cis-O*-[{2,6-$(Me_2NCH_2)_2C_6H_3$}$(RCO_2)_2Pt^{IV}$Br] and exchange of one carboxylato group, resulting in formation of [{2,6-$(Me_2NCH_2)_2C_6H_3$}$Pt^{II}(O_2CR)$]. No evidence for Pt—Tl bonded intermediates in these reactions was obtained.

It is important to note that cleavage of platinum—carbon σ bonds, a process of fundamental importance in organometallic chemistry [3], did not occur. In general, arylation or alkylation of mercury(II) halides by organo-transition metal complexes occurs readily, and the cleavage of transition metal—alkyl and —aryl σ bonds by HgX_2 is of current interest, especially from a mechanistic point of view [3,4]. The reverse reactions have also been investigated and organomercurials have found useful application in the synthesis of σ- and π-bonded organic derivatives of transition metals [5]. It is now possible that the absence of transmetallation in the above reaction between organoplatinum compounds and mercury and thallium salts results both from the ability of organomercury compounds to undergo transmetallation with transition metal compounds and from the fact that there is internal N-coordination of the organic ligand(s) to platinum. In this respect, it is noteworthy that cleavage of metal—carbon bonds by electrophiles is promoted by phosphine ligands [6] and has also been reported for phosphorus containing cyclometallated platinum and palladium compounds [7].

In order to obtain more insight into the effect of this stabilization of metal—carbon bonds by internal nitrogen-coordination we have explored a number of reactions involving organic compounds containing *ortho*-CH_2NMe_2 substituted aryl groups. In this paper we describe i) transmetallation reactions of the diorganopalladium compound *cis*-[(2-$Me_2NCH_2C_6H_4)_2Pd$] with mercury(II) and thallium(III) carboxylates, ii) the synthesis of some new aryl-mercury and -thallium compounds containing *ortho*-CH_2NMe_2 substituents and iii) transmetallation reactions of these compounds with zerovalent metal complexes, as well as

the behaviour of cyclometallated platinum and palladium complexes towards $Pd(O_2CR)_2$.

Experimental

^1H and ^{13}C NMR spectra were recorded on Varian T60 and Bruker WP80 spectrometers. The IR spectra were measured on a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht. Molecular weights were determined with a Hewlett-Packard vapour-pressure osmometer, model 320B.

The compounds *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$, *cis*- and *trans*-$[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Pt]$ [8], $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$, $[(2\text{-}Me_2NCH_2C_6H_4)Hg(O_2CMe)]$ [9] and *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ [10] were prepared by published methods.

Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl]$

A freshly prepared solution of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Li]$ (7.5 mmol) in ether (25 ml) was slowly added to a solution of $HgCl_2$ (2.03 g, 7.5 mmol) in THF (30 ml) at 0°C, and the mixture was stirred for 2 h, while slowly warming up to room temperature. The solution was then filtered and the filtrate evaporated to dryness. Recrystallization of the residue from CH_2Cl_2/pentane gave $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl]$. Yield 2.25 g, 70%.

Synthesis of $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$

A solution of $TlCl_3$ (0.78 g, 2.5 mmol) in THF (20 ml) was added dropwise to a solution of $[(2\text{-}Me_2NCH_2C_6H_4)Li]$ (1.06 g, 7.5 mmol) in THF (20 ml) at −70°C. The resulting lemon yellow suspension was stirred for 1 h, then allowed to warm to room temperature and stirred for an additional hour. A brownish precipitate was filtered off, and the filtrate evaporated to dryness. The residue was washed with pentane and dried in vacuo, resulting in pure $[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2TlCl]$. Yield 0.26 g, 20%.

Synthesis of $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$

$[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$ was prepared by a procedure similar to that described above for $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$, starting from $TlCl_3$ and 2 equivalents of $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}Li]$ [9] in diethyl ether. Yield 25%.

Synthesis of $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$

$[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$ (0.20 mmol) and $TlCl_3$ (0.21 mmol) were stirred in CH_2Cl_2 (5 ml) for 10 min. The solution was filtered and evaporated to dryness. The residue was washed with pentane and dried in vacuo to give pure $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$. Yield 90%.

Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$

A freshly prepared solution of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_4\}Li]$ (7.5 mmol) in ether (25 ml) was slowly added to a suspension of $TlCl_3$ (2.35 g, 7.5 mmol) in ether (25 ml) at −70°C. The mixture was stirred for 1 h, warmed to room temperature, again stirred for 1 h, and filtered. The filtrate was evaporated to dryness and the residue recrystallized from ether. The yield of pure $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$ was 0.97 g, 28%.

Reaction of $Hg(O_2CMe)_2$ with cis-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$

A solution of $Hg(O_2CMe)_2$ (0.127 g, 0.4 mmol) and *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2\text{-}Pd]$ (0.150 g, 0.4 mmol) in chloroform (10 ml) was stirred for 1 h; THF (10 ml) was then introduced by slow diffusion. After 2 days yellow cubic crystals had been formed, and these isolated by decantation and identified as $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)\}_2]$. Yield 0.042 g, 35%.

Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe) \cdot TlClBr(O_2CMe)]$

A solution of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$ (0.235 g, 0.5 mmol) and $Pd(O_2CMe)_2$ (0.112 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was stirred for 24 h, and then concentrated to 2 ml. $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe) \cdot TlClBr(O_2CMe)]$ was precipitated by addition of pentane (10 ml), filtered off, washed with pentane and dried in vacuo. Yield 0.170 g, 50%.

Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe)]$

A solution of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl]$ (0.233 g, 0.5 mmol) and $Pd(O_2CMe)_2$ (0.112 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was stirred for 24 h, then filtered and concentrated to 2 ml. The precipitate, obtained by addition of pentane (10 ml) and isolated by filtration and vacuum drying, was identified as $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe)]$. Yield 0.090 g, 55%.

Synthesis of $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)\}_2]$

A solution of $Pd(O_2CMe)_2$ (0.056 g, 0.25 mmol) and *cis*-$[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Pd]$ (0.094 g, 0.25 mmol) in chloroform was stirred for 24 h, the reaction being monitored by ^1H NMR spectroscopy. Addition of pentane (10 ml) gave $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)\}_2]$ as yellow crystals. Yield 0.135 g, 90%.

Reaction of $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ with $Pd_2(DBA)_3$ (DBA = dibenzylideneacetone)

$[Pd_2(DBA)_3]$ (0.182 g, 0.2 mmol) was added to a solution of $[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Hg]$ (0.187 g, 0.4 mmol) in toluene (5 ml) and the mixture was stirred for 3 days. The mercury was filtered off and the filtrate evaporated to dryness. Dissolution of the residue in dichloromethane (1.5 ml) and addition of pentane (10 ml) gave a white precipitate, which was filtered off, dried in vacuo, and identified as *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ by comparison of its ^1H NMR spectrum with that of an authentic sample [8]. Yield 0.10 g, 67%.

Attempted reaction of $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ with $[Pt(DBA)_2]$

$[Pt(DBA)_2]$ was added to $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ in a procedure similar to that described above for $[Pd_2(DBA)_3]$. Work-up after the mixture had been stirred for 5 days gave the unchanged starting compounds.

Reaction of $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ with $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene)

$[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ (0.092 g, 0.2 mmol) was added to a solution of $[Pt(COD)_2]$ (0.082 g, 0.2 mmol) in toluene (5 ml). The mixture was stirred for 2 h then dichloromethane (5 ml) was added. The mixture was filtered and the filtrate evaporated to dryness. The residue was washed with pentane and dried in vacuo to give pure *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$. Yield 0.048 g, 52%.

Trans/cis conversion of [(2-$Me_2NCH_2C_6H_4)_2Pt$]

[(2-$Me_2NCH_2C_6H_4)_2Pt$] (*cis* or *trans*, 200 mg) was heated at 150°C under nitrogen for 5 hours. The product was dissolved in $CDCl_3$ (1.0 ml), and the solution was filtered and the ^1H NMR spectrum recorded. Both spectra were identified as that of the *cis*-isomer, whereas the integrals were reduced by 5% and 30%, respectively. Differential temperature analysis (DTA) experiments showed that both *cis*- and *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] started to sublime at about 150°C, though decomposition occurred at slightly higher temperatures (170°C).

Ligand exchange reactions between organometallic complexes and metal carboxylates

Reactions of palladium(II), mercury(II) and thallium(III) carboxylates with organometallic compounds of palladium, platinum, mercury and thallium, having organo-amine ligands, were performed in deuteriochloroform and monitored by ^1H and ^{13}C NMR spectroscopy. No attempt was made to isolate pure compounds from the reaction mixtures, the products being identified by comparison of their ^1H and ^{13}C NMR spectra with those of authentic samples or with data reported in the literature. Further details are given in the Results section.

Results

Synthesis of organomercury and organothallium compounds

The organothallium compounds [{2,6-$(Me_2NCH_2)_2C_6H_3$}TlClBr] and [(2-$Me_2NCH_2C_6H_4)_2TlCl$] were isolated from the 1 : 1 and 1 : 2 reactions of $TlCl_3$ with [{2,6-$(Me_2NCH_2)_2C_6H_3$}Li] and [(2-$Me_2NCH_2C_6H_4$)Li], respectively:

$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Li] + TlCl_3 \xrightarrow{LiBr} [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr] + 2\ LiCl \quad (1)$$

$$2[(2\text{-}Me_2NCH_2C_6H_4)Li] + TlCl_3 \rightarrow [(2\text{-}Me_2NCH_2C_6H_4)_2TlCl] + 2\ LiCl \quad (2)$$

Formation of the bromide product in reaction (1) is due to exchange with LiBr which is present as a consequence of the synthesis of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Li] from Li metal and 2,6-$(Me_2NCH_2)_2C_6H_3Br$ [11]. The use of excess of Li reagent in reaction (2) gave only the bis-substituted compound. The tris-compound [(2-$Me_2NCH_2C_6H_4)_3Tl$] was not isolated. Similar results were obtained in the synthesis of the corresponding indium compounds [12,13].

[{(*S*)-2-$Me_2NCH(Me)C_6H_4$}$_2$TlCl] was obtained by a similar procedure from $TlCl_3$ and [{(*S*)-2-$Me_2NCH(Me)C_6H_4$}Li]. [{(*S*)-2-$Me_2NCH(Me)C_6H_4$}$TlCl_2$] was synthesized via the ligand exchange reaction between [{(*S*)-2-$Me_2NCH(Me)$-C_6H_4}$_2$TlCl] and $TlCl_3$ (eq. 3);

$$[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl] + TlCl_3 \rightarrow 2[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2] \quad (3)$$

The organomercury compound [{2,6-$(Me_2NCH_2)_2C_6H_3$}HgCl] was prepared

by the 1 : 1 reaction of $HgCl_2$ with $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Li]$:

$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Li] + HgCl_2 \rightarrow [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl] + LiCl \quad (4)$$

The synthesis of the related compounds $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ and $[(2\text{-}Me_2NCH_2C_6H_4)HgCl]$ have been reported elsewhere. It has been demonstrated that a Hg—N bond is present at low temperature and that this bond is absent or labile at ambient temperatures [9].

The new thallium and mercury compounds were identified by elemental analyses (Table 1), molecular weight determinations (which indicate that the compounds exist as discrete monomeric species in chloroform), and ^1H and ^{13}C NMR spectroscopy. The presence of a direct aryl—metal bond was indicated by the coupling constants of the various hydrogen and carbon atoms with thallium and mercury, respectively (Tables 2 and 3). However, coordination of nitrogen to the respective metal centres cannot be deduced from these data. Though the NMe_2 groups show coupling with thallium for both the carbon and hydrogen atoms, long range coupling constants with thallium are quite normal [14], e.g. 114 Hz ($^5J(^{203,205}Tl—^{13}C)$) and 66 Hz ($^6J(^{203,205}Tl—^1H)$) in $p\text{-}MeC_6H_4\text{-}Tl(O_2CCF_3)_2$ [15]. Furthermore, the low temperature ^{13}C NMR spectra of $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$ showed only broadened resonances, on the basis of which no conclusions concerning the presence of Tl—N bonds in these complexes could be made.

In contrast, the dynamic ^{13}C NMR spectra of the monomeric compounds $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$ and $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$, which contain a stable chiral benzylic carbon centre, provided unambiguous evidence for Tl—N coordination. At low temperature two anisochronous resonances,

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Anal. Found (calcd.) (%)				Mol. wt.	Colour
	C	H	N	Other		
$[\{2,6\text{-}Me_2NCH_2)_2C_6H_3\}HgCl]$	32.36 (33.72)	4.46 (4.48)	5.99 (6.48)			White
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$	27.48 (28.19)	3.59 (3.75)	5.33 (5.48)	6.64 [a, b] (6.94)	502 [d] (511)	White
$[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$	42.22 (42.47)	4.84 (4.72)	5.25 (5.51)		546 [d] (508)	White
$[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl]$	44.21 (44.79)	5.14 (5.26)	4.84 (5.22)		587 [e] (536)	White
$[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$	28.35 (28.36)	3.21 (3.33)	3.33 (3.31)		480 [d] (423)	White
$[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)\}_2]$	43.20 (44.09)	4.94 (5.01)	4.51 (4.68)	10.82 [c] (10.68)		Yellow
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe)]$	46.38 (47.14)	6.18 (6.14)	7.45 (7.86)	8.55 (8.98) [c]		White
$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe)\text{-}TlClBr(O_2CMe)]$	25.39 (26.12)	3.27 (3.42)	3.74 (3.81)	8.07 [c, f] (8.70)		Cream

[a] Cl analysis. [b] Br 11.99 (15.67) %. [c] O analysis. [d] In chloroform. [e] In benzene. [f] Br 13.04 (10.88) %.

TABLE 2

^{1}H NMR DATA [a]

A: Thallium compounds	Aryl group				$NCH_{1,2}$	NCH_3		CCH_3
	ortho	*metha*	*para*	*metha'*				
$[(CN_2)TlClBr]$		7.06	7.30		3.63	2.48		
		(350)	(90)		(51)	(6)		
$[Ar_2TlCl]$	7.60	7.16	7.11	7.14	4.86	2.40		
	(470)	(169)	(45)	(138)	(46)			
$[ArTl(O_2CMe)_2]$	7.25	7.20	7.25	7.25	3.63	2.46		
	(928)	(376)	(106)	(312)	(34)	(12)		
$[ArTl(O_2CEt)_2]$	7.25	7.17	7.30	7.30	3.66	2.46		
	(920)	(385)	(106)	(314)	(34)	(12)		
$[\{(S)\text{-}Ar\}_2TlCl]$	7.60	7.23	7.20	7.23	3.97	2.39		1.35
	(419)	(180)	(43)	(127)	(61)			(12)
$[(S)\text{-}ArTlCl_2]$	7.60	7.20	7.20	7.20	3.33	2.13 [d]	1.90 [d]	1.13
	(880)	(384)	(104)	(302)	(34)	(12)	(18)	(12)

B: Palladium and mercury compounds	Aryl (*m*)	NCH_2	NCH_3	$CH_{1,2}$	CH_3
$[(CN_2)HgCl]$	7.03	3.33 (15)	2.27		
$[Ar_2Hg]$	7.20	3.43 (15)	2.25		
$[ArHgO_2CMe]$	7.20	3.41	2.30		2.06
$[ArHgO_2CEt]$	7.20	3.40	2.28	2.30	1.16
$[ArHgO_2C\text{-}i\text{-}Pr]$	7.13	3.38	2.28	2.50	1.21
cis-$[Ar_2Pd]$	6.90, 7.40	3.80	3.58		
$[(ArPdO_2CMe)_2]$	6.90	3.03, 3.62,	2.03 [d], 2.78 [d]		2.03
in C_6D_6:	7.0	2.55, 3.35	1.87 [d], 2.26 [d]		2.03
$[(ArPdO_2CEt)_2]$	6.90	3.06, 3.62	2.03 [d], 2.77 [d]	2.40	1.13
$[(ArPdO_2C\text{-}i\text{-}Pr)_2]$	6.82	3.06, 3.65	2.01 [d], 2.75 [d]		1.09
$[(CN_2)PdBr]$	6.83	4.01	2.98		
$[(CN_2)PdO_2CMe)$	6.80	3.97	2.86		2.17
$[(CN_2)Pd(O_2CMe)\text{-}Tl(O_2CMe)ClBr]$	6.80	3.99	2.89		2.13
$[(CN_2)PtBr]$	6.90	3.99 (46)	3.03 (34)		

[a] In $CDCl_3$, $\delta(^1H)$ in ppm relative to TMS; $J(^{203,205}Tl\text{--}^1H)$ and $J(^{199}Hg\text{—}^1H)$ between parentheses where appropriate: CN_2 = 2,6-$(Me_2NCH_2)_2C_6H_3$, Ar = 2-$Me_2NCH_2C_6H_4$, (*S*)-Ar = (*S*)-2-$Me_2NCH_2(Me)C_6H_4$. [d] $\delta(CH_3)$ 2.03. [c] $\delta(CH_2)$ 2.40, $\delta(CH_3)$ 1.13. [a] Diastereotopic methyl groups.

both with Tl couplings, are observed for the C atoms of the NMe_2 group. This points to coordination of the N atoms to Tl resulting in blocking of the inversion at nitrogen on the NMR time scale, because only in this situation is the N atom in a stable tetrahedral array, so producing diastereotopic Me groups. Upon raising the temperature the two signals start to coalesce, resulting in one isochronous resonance at ambient temperature for $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2\text{-}TlCl]$, suggesting occurrence of a fast NMR process involving dissociation of the Tl—N bond, pyramidal inversion at nitrogen, and concomittant rotation around the H_2C—N bond followed by recoordination. This process renders the methyl groups homotopic. For $[\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}TlCl_2]$ the NMe_2 groups show one broad resonance at room temperature, indicating that the above described process has not yet reached the fast exchange limit.

On the basis of these results we conclude that at low temperature Tl—N coordination is present for all compounds, and is inert on the NMR time scale.

TABLE 3

^{13}C NMR DATA [a, b]

Compound	Aryl group					NCH(R)	NCH_3	α-CH_3	Carboxylato group	
	C(2)	C(3)	C(4)	C(5)	C(6)				CO_2	CH_3
[$(CN_2)TlClBr$]	140.2	127.3	130.2			61.8	45.2			
	(379)	(736)	(115)			(443)	(61)			
[Ar_2TlCl]	138.7	131.3	128.3	127.6	133.7	64.9	45.2			
	(391)	(524)	(78)	(490)	(214)	(195)	(29)			
[$ArTl(OAc)_2$]	138.1	130.6	130.0	127.7	134.9	62.4	44.8		178.5	21.5
	(434)	(853)	(155)	(865)	(487)	(479)	(52)			
[$\{(S)\text{—}Ar\}_2TlCl$]	149.0	128.4	128.6	126.9	136.5	64.6	42.4	15.9		
	(205)	(438)	(76)	(447)	(289)	(190)	(32) [c]	(16)		
[$(S)\text{-}ArTlCl_2$]	145.2	130.1	130.4	127.6	135.6	64.6	— [d]	19.6		
	(430)	(856)	(154)	(837)	(478)	(432)		(37)		
[$(CN_2)HgCl$]	144.7	127.7	128.0			65.6	44.5			
		(180)				(112)				
[Ar_2Hg]	147.1	128.4	126.6	126.2	138.0	67.1	45.0			
	(37)	(70)		(113)	(94)	(63)				
[$ArHgOAc$]	144.2	129.0	128.5	127.2	137.5	64.8	44.6		177.0	22.9
		(170)	(32)	(213)	(133)	(110)	(10)			
cis-[Ar_2Pd]	147.2	125.9	122.8	121.6	139.8	72.2	49.0			
[$(ArPdOAc)_2$]	143.7	124.5	124.2	120.9	132.1	72.0	{52.3 [e], 51.0		180.5	24.3
[$(CN_2)PdOAc$]	144.9	119.9	124.6			73.8	52.1		177.2	23.1

[a] In $CDCl_3$; δ(^{13}C) in ppm relative to TMS; $J(^{203,205}Tl\text{—}^{13}C)$ and $J(^{199}Hg\text{—}^{13}C)$ between parentheses, respectively. [b] CN_2 = 2,6-$(Me_2NCH_2)_2C_6H_3$, Ar = 2-$Me_2NCH_2C_6H_4$, (*S*)-Ar = 2-$Me_2NCH(Me)C_6H_4$, OAc = O_2CMe. [c] NMe_2 methyl groups become diastereotopic at low temperature; 220 K: δ 44.4 ppm (32 Hz), δ 39.1 ppm (30 Hz); T_c = 250 K. [d] NMe_2 resonances are broad (T_c = 305 K) and become anisochronous at low temperature; 204 K: δ 44.2 ppm (96 Hz), δ 41.4 ppm (88 Hz). [e] Diastereotopic methyl groups.

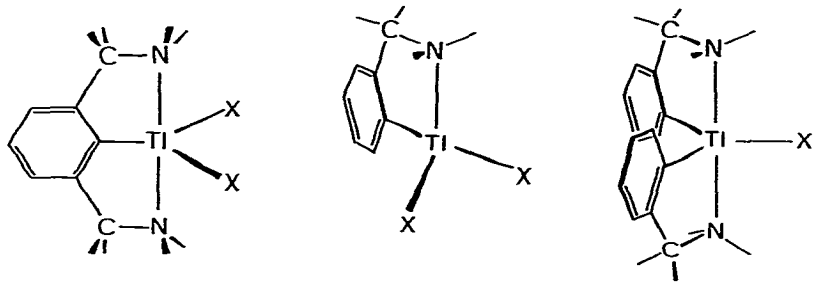


Fig. 1. Proposed structural geometries of the organothallium compounds [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlX_2$], [$\{2\text{-}Me_2NC(H)ZC_6H_4\}TlX_2$] and [$\{2\text{-}Me_2NCH(Z)C_6H_4\}_2TlX$] (X is either Cl, Br or O_2CR; Z is H or Me; for Z = Me the neighbouring carbon centre has *S*-chirality).

We thus propose the structures, having either four- or five-coordination, as shown in Fig. 1.

Stable four-coordination was previously established for a related indium compound, i.e. for [$\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}InMe_2$], by ^1H and ^{13}C NMR [13]. For the related five-coordinate indium compound [$(2\text{-}Me_2NCH_2C_6H_4)_2$-InCl] indium—nitrogen coordination was confirmed by an X-ray structure determination [12]. In solution at room temperature this coordination, which for [$\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2InCl$] is stable below 10°C, becomes labile but still contributes to the overall geometry at indium [13]. It is very likely that the coordination geometry of [$(2\text{-}Me_2NCH_2C_6H_4)_2TlCl$] parallels that of the indium compound. Furthermore, internal Tl—N coordination of both organo groups, which would result in five-coordination, may prevent replacement of the last chloride atom by a third organo group bearing a bulky *ortho* substituent.

It is noteworthy that [$\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2TlCl$], having a bipyramidal structure with five-coordinate Tl (see Fig. 1) can exist in two diastereo-isomeric forms. However, the low temperature ^{13}C NMR spectra indicate that only one of the two possible isomers is present in solution.

Reactions of cis-[(2-Me$_2$NCH$_2$C$_6$H$_4$)$_2$Pd] with Hg(O$_2$CR)$_2$ and Tl(O$_2$CR)$_3$

Reactions of *cis*-[$(2\text{-}Me_2NCH_2C_6H_4)_2Pd$] with mercury(II) and thallium(III) carboxylates in chloroform proceeded according to equation 5:

$$cis\text{-}[(2\text{-}Me_2NCH_2C_6H_4)_2Pd] + M(O_2CR)_x \rightarrow$$
$$\tfrac{1}{2}[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2] + [(2\text{-}Me_2NCH_2C_6H_4)M(O_2CR)_{x-1}] \quad (5)$$

(R = Me, Et, i-Pr; M = Hg, x = 2; M = Tl, x = 3).

The reactions are rapid, being complete within the time necessary for recording the ^1H NMR spectra. For $Hg(O_2CMe)_2$ a yellow crystalline compound was isolated by addition of THF to the reaction mixture. Elemental analytical data pointed to the stoichiometry of [$(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)$] (Table 1). This compound has been described by Thompson and Heck [16], and was also obtained by using a different route (vide infra). The ^1H and ^{13}C NMR data for the organopalladium carboxylates (R = Et, i-Pr) were almost identical to those of the acetato compound (see Tables 2 and 3) and the organomercury and organo-

thallium carboxylate data are similar to those obtained for [(2-$Me_2NCH_2C_6H_4$)-HgCl] and [{2,6-(Me_2NCH_2)$_2C_6H_3$}TlClBr], which were synthesized by independent procedures involving Li reagents (vide supra). The spectra of [(2-$Me_2NCH_2C_6H_4$)Hg(O_2CMe)] were identical to those previously reported [9].

Coordination of the organo ligand via carbon to thallium could be deduced unambiguously from the coupling constants between thallium and the various hydrogen and carbon nuclei in the aryl system. The presence of N—Tl coordination could not be deduced from the spectra (vide supra), but since inert N—Tl bonding was observed for [{(*S*)-2-$Me_2NCH(Me)C_6H_4$}$TlCl_2$] at low temperature, four-coordination in [(2-$Me_2NCH_2C_6H_4$)Tl(O_2CR)$_2$] can be assumed.

Reverse reactions: reactions of organomercury and organothallium compounds with Pd(O_2CR)$_2$

Reactions of the bis-organo-mercury(II) and -thallium(III) compounds [(2-$Me_2NCH_2C_6H_4$)$_2$Hg] and [(2-$Me_2NCH_2C_6H_4$)$_2$TlCl] with [Pd(O_2CR)$_2$]$_3$ (R = Me, Et, i-Pr) trimer [17] resulted in formation of mono-organometallic compounds according to equation 6:

$$Pd(O_2CR)_2 + [(2\text{-}Me_2NCH_2C_6H_4)_2MCl_x] \rightarrow$$
$$\tfrac{1}{2}[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2] + [(2\text{-}Me_2NCH_2C_6H_4)MO_2CR)Cl_x] \quad (6)$$

(M = Hg, $x = 0$; M = Tl, $x = 1$).

These reactions were complete in about 20 minutes and 5 minutes for the mercury and thallium systems, respectively. No NMR evidence was obtained for the formation of intermediates. The final spectra were identical to those of the products obtained in the previous section starting from *cis*-[(2-Me_2NCH_2-C_6H_4)$_2$Pd]. Formation of the mono-arylthallium compound is clearly indicated by a drastic increase of most of the coupling constants involving thallium relative to the bis-arylthallium starting compound (see Tables 2 and 3).

Addition of more than one equivalent of Pd(O_2CR)$_2$ to a solution of the bis-organo-mercury(II) or -thallium(III) compounds resulted in formation of the mono-organo-mercury or -thallium compounds whose CH_2 and NMe_2 nuclei resonances were broadened and shifted downfield relative to the pure mono-organometal complexes. The same behaviour was observed when Pd(O_2CMe)$_2$ was added to a solution of [(2-$Me_2NCH_2C_6H_4$)Hg(O_2CMe)]. These downfield shifts may be evidence for coordination of the NMe_2 moiety to palladium, but attempts to isolate a pure heterodinuclear complex with the aryl group bonded to Hg and the NMe_2 moiety bonded to palladium were unsuccessful.

Reaction of Pd(O_2CMe)$_2$ with the mono-organomercury compound [{2,6-(Me_2NCH_2)$_2C_6H_3$}HgCl] in $CHCl_3$ resulted in quantitative precipitation of Hg(O_2CMe)Cl within a few hours.

$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}HgCl] + Pd(O_2CMe)_2 \rightarrow$$
$$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe)] + Hg(O_2CMe)Cl \quad (7)$$

The complex [{2,6-(Me_2NCH_2)$_2C_6H_3$}Pd(O_2CMe)] was isolated from the solu-

tion. Transfer of the organo group from mercury to palladium is deduced from the observed change in chemical shifts for the CH_2NMe_2 nuclei (see Table 2).

Reaction of $Pd(O_2CMe)_2$ with $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr]$ resulted in the quantitative formation of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe) \cdot Tl(O_2CMe)\text{-}ClBr]$. Besides downfield shifts for the NMe_2 nuclei, similar to those noted above for Hg, the observed disappearance of the couplings between thallium and the various H and C atoms of the organic ligand is conclusive evidence for transfer of the aryl group from thallium to palladium. As a results a thallium salt is formed. Normally, pure acetato and chloride salts of thallium are insoluble in chloroform. Thus, the absence of a precipitate in the reaction with $Pd(O_2CMe)_2$ indicates that some kind of interaction between the organopalladium compound and the thallium salt must be present. In view of the NMR results, the presence of bridging carboxylato or halide groups between palladium and thallium is very likely (eq. 8).

$$Pd(O_2CR)_2 + [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}TlClBr] \rightarrow [\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Pd(O_2CMe) \cdot Tl(O_2CMe)ClBr] \quad (8)$$

Reactions of organotransition metal complexes with $Pd(O_2CR)_2$

The stoichiometric reaction of *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ with $Pd(O_2CR)_2$ (R = Me, Et, i-Pr) in $CHCl_3$ took about one day for completion and resulted in the quantitative formation of $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2]$, according to equation 9:

$$Pd(O_2CR)_2 + cis\text{-}[(2\text{-}Me_2NCH_2C_6H_4)_2Pd] \rightarrow [\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2] \quad (9)$$

The products were obtained pure from the solution. ^1H and ^{13}C NMR showed that only one isomer was present. Thompson and Heck [16] first reported the compound $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CMe)\}_2]$ and gave its ^1H NMR spectral data in C_6D_6. However, we have reassigned the pattern for the CH_2 ^1H atoms as an AB pattern ($\delta(H_a)$ 2.55 ppm; $\delta(H_b)$ 3.35; J(Ha—Hb) 13 Hz) (Table 2). On going from C_6D_6 to $CDCl_3$ as solvent, distinct chemical shift changes are observed for the NMe_2 ^1H resonances (Table 2), as a result of solvent—solute interactions, which is a normal feature for compounds with this type of ligand [18].

In $CDCl_3$ at room temperature, $Pd(O_2CMe)_2$ did not react with the corresponding platinum compound *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$. In contrast, reaction of $Pd(O_2CMe)_2$ with the *trans*-isomer, *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$, in $CDCl_3$, the starting compounds had disappeared within a few minutes. The ^1H NMR spectrum showed two resonances for both the CH_2 and NMe_2 hydrogen atoms each with platinum couplings ($\delta(CH_2)$: 4.21(34), 3.85(48); $\delta(NMe_2)$: 2.84(38), 2.70(38)). This latter observation indicates the presence of inert Pt—N coordination, as discussed for the structural elucidation of Pt-Hg carboxylato complexes in solution by NMR spectrometry [2]. The anisochronous resonances point to the presence of diastereotopic CH_2 ^1H atoms and NMe_2 methyl groups, and thus to the absence of a mirror plane through the respective C and N centres. A square pyramidal structure for the Pt-Pd complex with $Pd(O_2CMe)_2$ at the apical position would be in accord with these data (Fig. 2).

Further data in support of this suggestion could not be obtained because within about 10 minutes several new resonances for the CH_2, NMe_2 and acetato hydrogen atoms were observed, along with formation of a metal deposit. No attempts were made to isolate pure products.

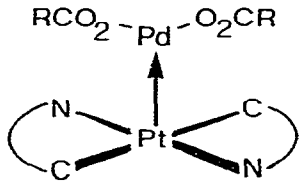


Fig. 2. Proposed structure for the intermediate in the reaction of *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ with $Pd(O_2CMe)_2$.

$Pd(O_2CMe)_2$ also reacted, but much faster, with the benzyl-platinum compound *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$, resulting in a metal deposit. The ^1H NMR spectrum of the resulting solution showed a slightly broadened resonance for the acetato groups at 2.05 ppm and various overlapping resonances around 3.2 ppm. Individual assignment and identification of the various products was not possible.

Isomerisation of $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$

Heating of solid *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ for 5 hours at 150°C under nitrogen resulted in 70% conversion of the *trans* isomer into the *cis* isomer, with decomposition to metallic platinum accounting for the remaining 30%. It is noteworthy that the *cis* isomer remained unchanged except for a small percentage of decomposition when treated similarly.

$$\textit{trans}\text{-}[(2\text{-}Me_2NCH_2C_6H_4)_2Pt] \xrightarrow{150°C} \textit{cis}\text{-}[(2\text{-}Me_2NCH_2C_6H_4)_2Pt] \quad (10)$$

Reactions of organomercury(II) compounds with zero-valent metal complexes

Reactions of $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ with the palladium(0) and platinum(0) compounds $[Pd_2(DBA)_3]$ (DBA = dibenzylideneacetone) and $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene) resulted in elimination of metallic mercury and formation of *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2M]$ (M = Pd, Pt) as the only transition metal products.

$$[(2\text{-}Me_2NCH_2C_6H_4)_2Hg^{II}] + M^0L_n \rightarrow \textit{cis}\text{-}[(2\text{-}Me_2NCH_2C_6H_4)_2M^{II}] + n\,L + Hg^0$$

$$M^0L_n = \tfrac{1}{2}\,[Pd_2(DBA)_3];\ [Pt(COD)_2] \quad (11)$$

The identity and the geometry of these organometallic compounds was deduced from their ^1H NMR spectra, which were identical to those of authentic samples [8]. In a similar experiment in toluene, $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ did not react either with the nickel(0) compound $[Ni(COD)_2]$ or with $[Pt(DBA)_2]$.

^{13}C NMR chemical shifts

The above reactions give information about the influence of internal coordination on transmetallation reactions. The identification of most of the products in the sometimes very complex reaction mixtures was carried out with the

help of ^1H and ^{13}C NMR. The inference of internal metal—N coordination for the organothallium, and previously for organomercury compounds [9], was performed by chiral labelling of the organo group (*S*)-2-$Me_2NCH(Me)C_6H_4$-. It was of interest to know whether internal metal—N coordination of organo groups could be deduced directly from ^{13}C NMR chemical shifts.

^{13}C NMR chemical shifts are rather sensitive to the metal to which the organic ligand is coordinated. They may also be sensitive to internal coordination of the organic ligand via built-in donor atoms. If so, such data could provide evidence for such an internal coordination. For other atoms in other compounds, e.g. for phosphorus, this has shown to be the case and characteristic downfield and upfield shifts are normally observed for ^{31}P nuclei participating in five and four (or six) membered chelate rings, respectively [19].

Since deduction of metal—nitrogen coordination is of importance for the interpretation of the present work, we have surveyed the ^{13}C NMR results for organometallic compounds with 2-$Me_2NCH_2C_6H_4$ as the ligand. The changes in the ^{13}C chemical shifts obtained for several of such compounds compared to those of free $Me_2NCH_2C_6H_5$ are given in Table 4. From these results it is obvious that the metal centre has a dominant influence on the chemical shifts: large downfield shifts for C(2) and C(6) occur in almost all cases, except for C(2) when M is Tl; C(3), C(4) and C(5) show only small downfield shifts for M = Tl or Hg, and rather large upfield shifts when M = Pd or Pt.

In principle, we have to consider two features i) chemical shifts due to coordination to and affected by the metal and the co-ligands and ii) chemical shifts due to internal coordination. For the *ortho*-carbons C(2) and C(6) in 2-$Me_2NCH_2C_6H_4$ these two features can be examined together in the same compound: C(2) can participate in a five-membered ring but C(6) cannot. $\Delta\delta(C(2))$ will be the result of both aspects, whereas $\Delta\delta(C(6))$ will only be affected by the first factor. Thus the difference $\Delta\delta(C(2)) - \Delta\delta(C(6))$ may give an idea of the effect of internal coordination.

TABLE 4

CHEMICAL SHIFT DIFFERENCES IN ^{13}C NMR

Compound [a]	$\Delta\delta$(C)					$\{\Delta\delta(C(2)) - \Delta\delta(C(6))\}$
	C(2)	C(3)	C(4)	C(5)	C(6)	
cis-[Ar_2Pt]	8.8	−3.2	−5.5	−5.4	11.1	−2.3
cis-[Ar_2Pd]	8.7	−2.5	−4.8	−4.8	12.2	−3.5
trans-[Ar_2Pt]	[c]	−5.0	−6.8	−7.0	5.7	[c]
trans-C-[$Ar_2Pt(OAc)_2$]	5.4	−2.8	−2.5	−3.9	4.3	1.1
trans-N-[$Ar_2Pt(OAc)_2$]	6.5	−2.0 [d]	0.6	5.7 [d]	5.9	0.6
[{ArPdOAc}$_2$]	5.2	−3.9	−3.4	−5.5	4.5	0.7
[ArHgOAc]	5.7	0.6	0.9	0.8	9.9	−4.2
[ArHgCl]	6.0	0.7	1.1	1.1	9.7	−3.7
[Ar_2Hg]	8.6	0	−1.0	−0.2	10.4	−1.8
[Ar_2TlCl]	0.2	2.9	0.7	1.2	6.1	−5.9
[$ArTl(OAc)_2$]	−0.5	2.2	2.4	1.3	7.3	−7.8

[a] Ar = 2-$Me_2NCH_2C_6H_4$; OAc = O_2CMe. [b] $\Delta\delta(C) = \delta(C)(complex) - \delta(C(Me_2NCH_2C_6H_5))$. [c] Not assigned. [d] Reversed assignment for C(3) and C(5) gives the values +3.3 and 0, respectively. ($\delta(^{13}C)$ values have been obtained from either this work or ref. 2 and 9.)

For the Pd and Pt compounds, for which internal coordination has been established, this difference can be seen to depend strongly on both the structure of the cyclometallated compound and the nature of the other ligands. This indicates that the metal and its coordination geometry are more important for the chemical shift than is internal coordination. Thus no conclusions concerning internal metal—N coordination in organometallic compounds can be drawn from the ^{13}C NMR data.

Discussion

In contrast to previously reported reactions between organoplatinum(II) compounds and mercury (or thallium) electrophiles, for which no transmetallation of the organo group was observed [1,10], the present work has shown that transmetallation of aryl groups containing internally coordinated *ortho*-Me_2NCH_2 substituents can occur between organometal compounds ML and electrophilic complexes M′X in which both M and M′ can be transition and post-transition metal atoms.

$$ML + M'X \rightarrow MX + M'L$$

$$M, M' = Pd, Hg, Tl;\ X = O_2CR;\ L = 2\text{-}Me_2NCH_2C_6H_4$$

The reaction routes and product formation are largely influenced by the ability of the nitrogen of the organo group to coordinate the various metal centres. This influence will be the result of a combination of factors: i) stabilization of metal—carbon bonds by the chelate effect, ii) effects of the electronic properties of the respective metal centres and iii) the strength of the metal—nitrogen interaction. Of course other factors, such as structure and type of ligand will also operate. These aspects are discussed in more detail below along with a consideration of the mechanism operating in transmetallation reactions involving the organopalladium compounds.

Electronic factors

Transition metal

Reaction between the organoplatinum compounds *cis*- and *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$, *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$, and the post-transition metal carboxylates $Hg(O_2CR)_2$ and $Tl(O_2CR)_3$ have previously been shown [1,2,10] to result in either stable Pt—Hg bonded complexes, oxidative elimination of $Tl(O_2CR)$ (or metallic mercury), or halide/carboxylato exchange. We have now shown that the reaction between *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ and $Hg(O_2CR)_2$ (or $Tl(O_2CR)_3$) results in transmetallation only. Furthermore, for the bis-cyclometallated phosphine complexes $[(2\text{-}R_2PCH_2C_6H_4)_2M]$ (M = Pt, R = Me; M = Pd, R = Ph) cleavage of both metal—carbon bonds by reaction with $HgCl_2$ has been reported [7], in that case no difference was recognized between the Pd and Pt complexes.

These facts show that internal coordination cannot prevent metal—carbon cleavage, but use of hard nitrogen donors can increase the electron donating ability of the metal centre by such an amount that oxidation of the organo

compound and reduction of the electrophile becomes an important alternative. However, for Pd as the metal centre this increase is not enough. In fact, Pd complexes containing the electron withdrawing carboxylato ligands can be used as electrophiles, as is shown by the transmetallation reactions between $Pd(O_2CR)_2$ and the organo compounds *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$, $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ and $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$, all of which give $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2]$ as one of the products. In a recent study, other transition metal complexes were used as electrophiles and exchange of alkyl and aryl groups between different phosphine-platinum complexes was reported [4,20].

Post-transition metals

Both reaction 5 of $[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ with $M(O_2CR)_x$ (M = Hg, $x = 2$; M = Tl, $x = 3$) and reaction 6 between $Pd(O_2CR)_2$ and $[(2\text{-}Me_2NCH_2C_6H_4)_2MCl_y]$ (M = Hg, $y = 0$; M = Tl, $y = 1$) resulted in formation of the same type of products, i.e. $[\{(2\text{-}Me_2NCH_2C_6H_4)Pd(O_2CR)\}_2]$ and $[(2\text{-}Me_2NCH_2C_6H_4)MX_n]$ (M = Hg, $n = 1$; M = Tl, $n = 2$; X = Cl, O_2CR). Both reactions involved transmetallation of only one cyclometallated ligand. Since the electrophilic character of the metal centre in the mono organo compounds will be greater than in the diorgano compounds, it is not surprising to find that they are not susceptible to attack by an excess of the carboxylates and thus they are kinetically stable.

Several of the above transmetallation reaction types have been reported before for mercury but not for thallium compounds, and not at all for *ortho*-CH_2NMe_2 substituted aryl ligands. The present results for reactions with mercury and thallium compounds are very similar when the transition metal is Pd, and no evidence for the formation of heterodinuclear metal—metal bonded species is obtained. With Pt as the transition metal the very different behaviour towards mercury and thallium complexes has already been noted [1,2].

Oxidation states

We noted above that transmetallation reactions occurred with maintenance of the oxidation states, II for Pd and Hg, III for Tl, and with transfer of only one organic ligand. However, when zerovalent metal complexes, $[Pt(COD)_2]$ and $[Pd_2(DBA)_3]$, were used as starting compounds, transfer of both organo groups from $[(2\text{-}Me_2NCH_2C_6H_4)_2Hg]$ to the transition metal occurred along with a redox reaction (reaction 11). A *cis*-geometry was deduced for the resulting bis-organo-transition metal complexes. This is consistent with results reported for reactions of organomercury compounds with bis-phosphineplatinum(0) complexes, which also give *cis* addition products [21]. In the light of these observations it is relevant to note that Sokolov et al. [22] suggested that $[\{2\text{-}(PhNN)C_6H_4\}_2Pd]$, prepared from $[Pd_2(DBA)_3]$ and $[\{2\text{-}(PhNN)C_6H_4\}_2Hg]$, had a *trans*-configuration.

Internal coordination

With regard to reaction 6 it is noteworthy that reactions of PdX_2 (X = Cl, O_2CR) with organomercury compounds which do not contain substituents capable of internal coordination resulted in C—C or C—X bond coupling products and decomposition into metallic palladium or mercury (reactions 10 and 11, [23]).

$$ArHgCl \xrightarrow{PdCl_2} Ar{-}Ar + HgCl_2 + Pd \quad (10)$$

$$R_2Hg + PdX_2 \xrightarrow[-HgX_2]{} [RPdX] \longrightarrow RX + Pd \quad (11)$$

The fact that this behaviour is not seen in reaction 6 in our work clearly demonstrates the importance of internal coordinating ligands.

The same effect of internal coordination is observed for reactions of organoplatinum compounds with mercury carboxylates. Whereas reaction of $[Me_2Pt(bipy)]$ (bipy = 2,2′-bipyridine) with excess $Hg(O_2CMe)_2$ has been reported to result in partial methyl for acetato exchange [24], no platinum—carbon bond cleavage nor transmetallation has been found for reactions of $Hg(O_2CR)_2$ with the cyclometallated platinum compounds *cis*- and *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$, *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$ and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ [1,2].

Furthermore, addition of $Pd(O_2CR)_2$ to solutions of the mono-organo compounds $[(2\text{-}Me_2NCH_2C_6H_4)MX_n]$ (MX_n = HgCl, $TlCl_2$) resulted in broadened and downfield shifted resonances for the CH_2NMe_2 nuclei in the ^1H and ^{13}C NMR spectra. This is interpreted in terms of a labile coordination of the N atom to Pd, thus reducing the ability of Pd to attack the final metal—carbon bond. In contrast, reaction of $Pd(O_2CMe)_2$ with the mono-organo compounds $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}MX_n]$ (MX_n = HgCl, TlClBr) resulted in transmetallation of the organo group. The driving force for this reaction might be the coordination of both nitrogen ligands to Pd, thus forcing the Pd atom into the neighbourhood of the carbon atom bonded to M (Hg, Tl). In this manner an intermediate with a 2*e*-3c phenyl bridge between Pd and Hg (or Tl) may be formed, thereby faciliting the transfer (see Fig. 3; vide infra).

Formation of this intermediate would imply a considerable distortion of the bond lengths and bond angles in the five-membered chelate rings. That the proposed structure for the intermediate is not unlikely, however, can be deduced from the structure of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3Me\}PtI](BF_4)$ in the solid and in solution, in which the platinum atom is coordinated by the two NMe_2 moieties and resides above the aryl ring [25].

Metal—nitrogen bond strength

The above data may be an indication that the metal—nitrogen bond is

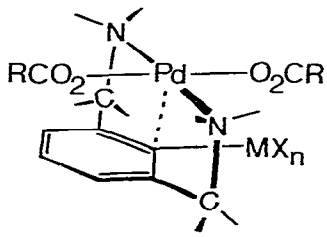


Fig. 3. Proposed structure for the intermediate in the reaction of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}MX_n]$ (MX_n = HgCl, TlClBr) with $Pd(O_2CMe)_2$.

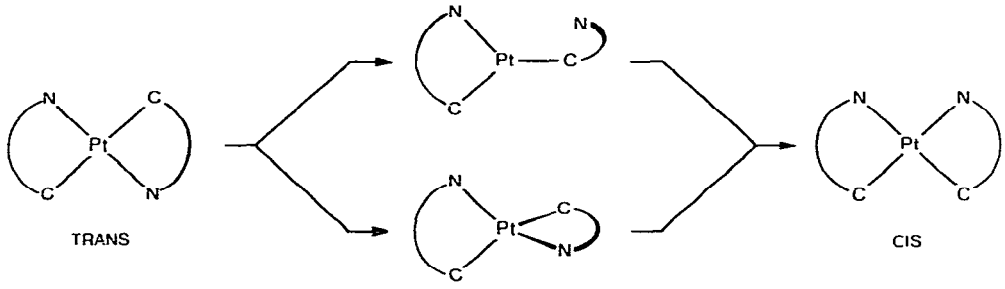
stronger in the palladium compound than in the post-transition metal compounds.

In contrast to *cis*-[(2-$Me_2NCH_2C_6H_4)_2Pt$], the *trans*-isomer reacts with Pd-($O_2CMe)_2$ ultimately resulting in decomposition. The fact that [{(2-Me_2NCH_2-$C_6H_4)Pd(O_2CMe)\}_2$] is not formed indicates that complete transfer of the cyclometallated ligand from Pt to Pd has not occurred. A reason for this might be that (initially) the N atom remains coordinated to Pt. The reaction pattern can thus be interpreted in terms of transfer of the carbon ligand from Pt to Pd followed by a coupling reaction and elimination of metallic palladium. The ^1H NMR observation of an intermediate compatible with a square pyramidal coordinated platinum compound (very similar data were obtained for the unstable Pt-Hg compound [*trans*-{(2-$Me_2NCH_2C_6H_4)_2Pt\}$ · $Hg(O_2CMe)_2$] [10]) might be an indication that some kind of Pt—Pd interaction precedes the transfer of the carbon ligands.

Structural geometry

The contrast between the reactivity of *trans*-[(2-$Me_2NCH_2C_6H_4)_2Pt$] towards $Pd(O_2CMe)_2$ and the inertness of the corresponding *cis*-isomer may be due to a greater thermodynamic stability of the latter compound, as demonstrated by conversion of the solid *trans* into the *cis* isomer on heating. Occurrence of this type of reaction in the solid state has previously been reported, but rearrangement of cyclometallated ligands on one metal centre in solution has been reported for the six-coordinate platinum(IV) compound *trans-C*-[(2-Me_2NCH_2-$C_6H_4)_2Pt(O_2CR)_2$]; a five-coordinate species was proposed as the intermediate.

It is very likely that the present reaction does not occur in the solid state but is a gas phase reaction, since it occurred at temperatures at which, according to DTA experiments, the compound starts to sublime. This sublimation and also the partial decomposition which occurred in the same temperature range inhibited accurate measurements of, for example, reaction enthalpies. If it takes place in the gas phase, the reaction is probably intramolecular, involving either a three- or four-coordinate intermediate (see Scheme 1). The present results are



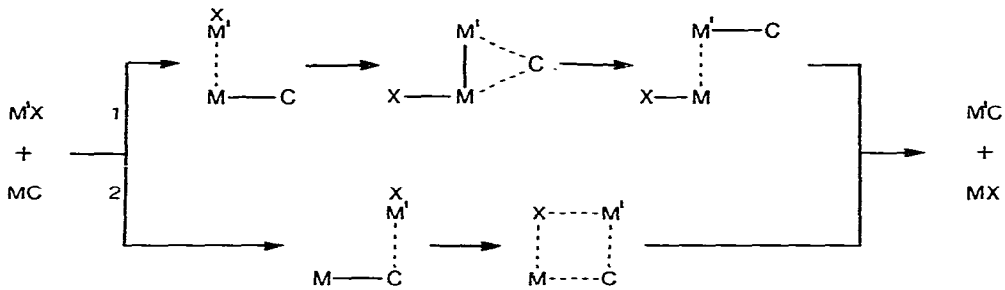
SCHEME 1

in line with others which also indicate greater stability of *cis* isomers over *trans* isomers for square planar complexes [8].

Reaction mechanism for cleavage of transition metal—carbon bonds

Cleavage of transition metal—alkyl and —aryl σ bonds by transition and post-transition metal electrophiles is of current interest, especially from a mecha-

nistic point of view [3,4]. Two mechanisms have been proposed for reactions involving mercury salts as the electrophile: 1) an oxidative addition/reductive elimination sequence and 2) direct electrophilic attack at carbon (see Scheme 2). In route 1 a metal—metal bond would be formed. Migration of the



SCHEME 2

aryl group then could occur along the metal—metal bond. Thus, in the intermediate state in both routes, the aryl group involved in the transmetallation bridges the two metal centres via a 2*e*-3c bonding (as illustrated in Scheme 1). Visser et al. have observed the transfer of methyl groups, which was postulated to occur via a 2*e*-3c interaction with a Me group bridging two metals (Pd, Pt) [20]. Such stable bonding interactions are quite common in, for example, organo-Li-Cu [26] and Al [27] chemistry.

Pt—Hg bonds bridged by a carboxylato group were found in the previously reported stable organoplatinum-mercury carboxylates, but no cleavage of a platinum—carbon bond was observed [1]. In contrast, in the present reactions involving cleavage of Pd—C bonds, no evidence for a Pd—Hg (or Pd—Tl) interaction was obtained. Thus we cannot say whether the electrophilic reagent attacks the metal—carbon bond at the metal site or at the carbon site.

For the reactions of diorganoplatinum phosphine complexes with mercury electrophiles the first mechanism has been shown to be appropriate for Pt—alkyl bonds and the second for Pt—aryl bonds [4]. On this basis, reaction of $Pd(O_2CMe)_2$ with the benzyl compound *cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$, which resulted in decomposition, makes an oxidative-addition/reductive-elimination mechanism seem likely. This may be supported by the observation in the reaction between *trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ and $Pd(O_2CMe)_2$ of an intermediate for which a structure with a Pt—Pd bond is proposed (see Fig. 2).

However, $Pd(O_2CR)_2$ did not react with the other isomer, *cis*-$[(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Pt]$. The inertness of this compound in contrast to the reactivity of the corresponding palladium compound argues against such a mechanism, since the oxidation potentials of platinum compounds are normally lower than those of corresponding palladium compounds [28]. A possible explanation is that electrophilic attack at the carbon centre is strongly favoured in organopalladium compounds.

Conclusions

It has been shown that internal coordination of the nitrogen atom of organic ligands to various metal centres has a large influence not only on the stability

of the starting compounds but also on the products of transmetallation reactions for the palladium compounds. This may be the result of the stabilization of the metal—carbon bond by the chelate effect, the electronic properties of the respective metal centres, and the strength of the metal—nitrogen bond. In this respect, we have seen that the electron donating ability of platinum is enhanced by the hard nitrogen ligands to such an extent that oxidation is preferred over M—C bond cleavage. With palladium as the metal centre, Pd—C bond cleavage was still the preferred reaction. The results furthermore indicate that the M—N bond strength follows the order Pt—N < Pd—N < Hg—N, Tl—N. For the platinum compounds it has been observed that reactivity is strongly influenced by their structure and ligands: *trans* < *cis;* methyl < aryl. The thallium and mercury complexes show similar behaviour in the transmetallation reactions.

The mechanism by which Pd—C bonds are cleaved by electrophiles probably involves direct attack at the carbon centre. For Pt—C bonds, an oxidative addition/reductive elimination sequence is more important.

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