

Synthesis of Novel Binuclear Palladium–Thallium Carboxylates of the Type $\text{PdTl}(\text{O}_2\text{CR})_5$ and their Structural Characterization Based on Observation of $J(^{203,205}\text{Tl}-^1\text{H})$ and $J(^{203,205}\text{Tl}-^{13}\text{C})$

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Reactions of palladium(II) carboxylates with thallium(III) carboxylates in toluene yield complexes of the type $\text{PdTl}(\text{O}_2\text{CR})_5$ (I), $R = \text{Me}, \text{Et}, i\text{-Pr}$, or $\text{PdTl}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ (II), $R = \text{Me}, \text{Et}, i\text{-Pr}, \text{Ph}$; $R' = \text{Me}, \text{Et}, i\text{-Pr}$. Substitution of the ligands in $\text{PdTl}(\text{O}_2\text{CMe})_5$ by free carboxylic acid has shown to be a second preparative route for compounds of type I. No reaction was observed for $\text{Pd}(\text{O}_2\text{CMe})_2$ with $\text{Hg}(\text{O}_2\text{CMe})_2$, $\text{PhHg}(\text{O}_2\text{CMe})$ or $\text{Ag}(\text{O}_2\text{CMe})$ nor was any reaction observed between $\{\text{Pd}(\text{O}_2\text{CMe})(\text{C}_6\text{H}_4\text{NNC}_6\text{H}_5)\}_2$ and $\text{Tl}(\text{O}_2\text{CMe})_3$. Reaction of $\text{Pd}(\text{O}_2\text{CMe})_2$ with $\text{Hg}(\text{O}_2\text{C}-i\text{Pr})_2$ yields $\text{Hg}(\text{O}_2\text{CMe})(\text{O}_2\text{C}-i\text{Pr})$.

The $\text{PdTl}(\text{O}_2\text{CR})_5$ complexes are the first examples of heterobinuclear palladium compounds lacking CO or phosphine ligands. Interaction of $\text{PdTl}(\text{O}_2\text{CR})_5$ with CO or phosphine leads to a breakdown of the binuclear unit. On the basis of ^1H and ^{13}C NMR spectra, which reveal coupling of the thallium nucleus with the respective carbon and hydrogen atoms, a structure is proposed which contains four carboxylato ligands bridging the PdTl unit and one apical ligand bonded to thallium. This structure does not involve a direct Pd-to-Tl bond. The dynamic ^1H and ^{13}C NMR spectra show in solution the occurrence of two distinct processes, i.e. dissociation of the apical ligand and exchange of bridging and apical ligands.

Introduction

During the last few years an increasing number of binuclear metal VIII B complexes has been reported [1]. In these studies special attention has been paid to the factors governing the formation of metal–metal bonds resulting in structures consisting either of one-dimensional linear metal stacks [2] or of binuclear units [3]. The greater part of the latter type of complexes contain bidentate ligands bridging two equal (e.g. $\{\text{Rh}_2(\text{O}_2\text{CMe})_4\}$ [4] and $\{\text{Pd}(\text{S}_2-$

$\text{CMe})_2\}_2$ [5]) or two different metal centers (e.g. $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrAg}(\text{O}_2\text{CCF}_3)_2$ [6], $(\text{Ph}_3\text{P})_2(\text{CO})(\text{MeCO}_2)_2\text{IrTl}(\text{O}_2\text{CMe})_2$ [7] and $(\text{Ph}_3\text{P})_2(\text{CO})(\text{MeCO}_2)\text{Cl-IrHg}(\text{O}_2\text{CMe})$ [8]). Heterobinuclear metal compounds containing a 2c–2e metal–metal bond have been synthesized via the insertion of a mono-nuclear metal VIII B complex in a Tl–X or Hg–X bond in which X can be a halogen or a bidentate anion [7, 8]. Complexes with a dative metal–metal bond stabilized by a bridging ligand have been obtained from the reaction of metal VIII B complexes with metal IB salts [6]. Interestingly, interaction of binuclear platinum complexes of the type $\{\text{Pt}(\text{II})\text{R}_2(\text{SR}'_2)\}_2$ with Tl(III), Hg(II) or Ag(I) acetate resulted in direct formation of complexes containing a Pt(III)–Pt(III) bond [9]. The electron transfer from Pt to the oxidizing metal acetate might proceed via formation of a direct Pt–metal interaction or via acetato groups bridging between the Pt and the other metal center.

In the present paper we report reactions of palladium carboxylates with thallium carboxylates, which do not comprise complete electron transfer reactions leading to a binuclear Pd–Pd compound, but instead give rise to a novel type of stable Pd–Tl carboxylato compounds $\text{PdTl}(\text{O}_2\text{CR})_5$. Observation of $J(^{203,205}\text{Tl}-^1\text{H})$ and $J(^{203,205}\text{Tl}-^{13}\text{C})$ in the ^1H and ^{13}C NMR spectra enabled elucidation of the structure and the dynamic behaviour of these compounds in solution. The occurrence of these exchange processes necessarily leads to the formation of mixed $\text{PdTl}(\text{O}_2\text{CR})_x(\text{O}_2\text{CR}')_{5-x}$ species when $R \neq R'$.

Experimental

Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere. Solvents were dried prior to use by standard methods. ^1H NMR spectra were recorded on a Varian T-60 and Varian XL-100, ^{13}C NMR spectra were recorded on a Bruker WP-80 and Varian XL-100 and ^{31}P NMR spectra were recorded on a Varian XL-100 spectro-

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meter. The IR spectra were recorded on a Perkin-Elmer 283 instrument. Molecular weights were determined with a Hewlett-Packard vapour-pressure osmometer, Model 320 B. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht. Analytical data and characteristic IR absorptions for the carboxylato groups are given in Table I while ^1H and ^{13}C NMR data are presented in Tables II and III, respectively.

$\text{Pd}(\text{O}_2\text{CR})_2$ [10], $\text{Tl}(\text{O}_2\text{CR})_3$ [7] and $\text{Pd}(\text{O}_2\text{CCH}_3)(\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4)_2$ [11] were prepared according to literature methods.

General Method for the Preparation of the Complexes $\text{PdTl}(\text{O}_2\text{CR})_5$ (I) ($R = \text{Me}, \text{Et}, i\text{-Pr}$) and $\text{PdTl}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ (II) ($R = \text{Me}, R' = \text{Et}, i\text{-Pr}$; $R' = \text{Me}, R = \text{Et}, i\text{-Pr}, \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{-}m\text{-OMe}$)

$\text{Pd}(\text{O}_2\text{CR})_2$ (0.5 mmol) was dissolved in toluene (15 ml). $\text{Tl}(\text{O}_2\text{CR}')_3$ (0.5 mmol) was added and the solution was stirred for 2 h at 80°C . The colour of the solution changed from brown-red to light yellow. Filtration and concentration of the solution to 2 to 3 ml followed by addition of hexane (15 ml) afforded a light yellow precipitate (yield 50–70%). A further fraction was obtained by concentration of the filtrate and washing of the resulting residue with a small portion of hexane.

Crystals of the non-mixed compounds (I) were obtained as follows: CH_2Cl_2 was added to a suspension of I in hot hexane until the complex just dissolved. Slow cooling and evaporation of the solvent in the open air afforded orange crystals up to 1 cm. The same procedure did not yield crystals for the mixed compounds II. However, in the case of $\text{PdTl}(\text{O}_2\text{CMe})_2(\text{O}_2\text{C-}i\text{-Pr})_3$ a small amount of pure $\text{PdTl}(\text{O}_2\text{C-}i\text{-Pr})_5$ could be obtained. For $\text{PdTl}(\text{O}_2\text{CMe})_2(\text{O}_2\text{CEt})_3$ slow crystallization yielded fractions with ligand ratios deviating from 2/3.

Alternative Method for the Preparation of the Complexes $\text{PdTl}(\text{O}_2\text{CR})_5$ (I), ($R = \text{Et}, i\text{-Pr}$)

$\text{PdTl}(\text{O}_2\text{CMe})_5$ (0.300 g, 0.5 mmol) was dissolved in toluene (15 ml) and propionic or isobutyric acid (0.8 ml, approx. 10 mmol) was added. The solution was stirred for 1.5 h at 80°C and then evaporated to dryness to remove the liberated acetic acid. This complete procedure was repeated. The oily residue was washed with hexane (15 ml) yielding a yellow precipitate which was filtered off and vacuum dried. Yield 0.3 g 90%.

Preparation of $\text{PdTl}(\text{O}_2\text{C-C}_6\text{H}_4\text{-}m\text{-Me})_5$

$\text{HO}_2\text{C-C}_6\text{H}_4\text{-}m\text{-Me}$ (0.340 g, 2.5 mmol) was added to a solution of $\text{PdTl}(\text{O}_2\text{CMe})_5$ (0.300 g, 0.5 mmol) in toluene (15 ml), stirred for 2 h at 80°C and evaporated to dryness in order to remove the liberated acetic acid. Toluene (15 ml) was added, the solution stirred for 2 h at 80°C and then evaporated

TABLE I. Analytical Data, Molecular Weights and Characteristic Infrared Absorptions for $\text{PdTl}(\text{O}_2\text{CR})_5$ (I) and $\text{PdTl}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ (II)^a.

Compound	Found (calcd) %			Moi. wt. ^b (calcd)	$\nu(\text{CO}_2)$ Region ^c (cm^{-1})		$\nu(\text{M-O})$ Region ^d (cm^{-1})
	C	H	O				
Ia $\text{PdTl}(\text{O}_2\text{CMe})_5$	20.27(19.80)	2.61(2.48)	26.29(26.41)	523(605)	1570; 1410; 1385; 1350	358; 303	
Ib $\text{PdTl}(\text{O}_2\text{CEt})_5$	26.03(26.64)	3.63(3.70)	22.84(23.68)	623(676)	1600; 1570; 1390; 1357	too weak	
Ic $\text{PdTl}(\text{O}_2\text{C-}i\text{-Pr})_5$	31.66(32.18)	4.68(4.69)	20.65(21.45)	704(746)	1576; 1400; 1361	364	
Id $\text{PdTl}(\text{O}_2\text{C-C}_6\text{H}_4\text{-}m\text{-Me})_5$	46.98(48.70)	3.50(3.55)	15.17(16.20)		1560; 1385; 1372	too weak	
IIa $\text{PdTl}(\text{O}_2\text{CMe})_3(\text{O}_2\text{CEt})_2$	22.22(22.72)	2.92(3.00)	24.92(25.24)	619(633)	1600; 1578; 1375	350	
IIb $\text{PdTl}(\text{O}_2\text{CMe})_2(\text{O}_2\text{CEt})_3$	23.25(24.08)	3.23(3.24)	24.83(24.70)	631(648)	1600; 1568; 1390	too weak	
IIc $\text{PdTl}(\text{O}_2\text{CMe})_3(\text{O}_2\text{C-}i\text{-Pr})_2$	24.20(25.39)	3.33(3.48)	23.91(24.18)	634(662)	1600; 1570; 1390; 1372	350(4b); 332	
IId $\text{PdTl}(\text{O}_2\text{CMe})_2(\text{O}_2\text{C-}i\text{-Pr})_3$	25.57(27.83)	3.69(3.91)	21.00(23.20)	757(690)	1600; 1570; 1400; 1375	353; 332	
IIe $\text{PdTl}(\text{O}_2\text{CMe})_3(\text{O}_2\text{C-C}_6\text{H}_5)_2$	36.42(37.88)	3.00(2.65)	19.76(20.20)	725(730)	1599; 1568; 1387	359; 338; 323	
IIf $\text{PdTl}(\text{O}_2\text{CMe})_3(\text{O}_2\text{C-C}_6\text{H}_4\text{-}m\text{-OMe})_2$	35.50(33.43)	3.17(2.91)	22.69(24.31)	753(790)	1571; 1380	355; 331	

^aAll compounds are pale yellow. ^bMeasured in CHCl_3 at 26°C . ^cAll absorptions are broad. ^dAll absorptions are weak.

TABLE II. ^1H NMR Data for $\text{PdTi}(\text{O}_2\text{CR})_5$ (I), $\text{PdTi}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ (II) and $\text{X}(\text{O}_2\text{CR})_y$ (X = H, Pd, Tl). ^{a,b}

Compound	O_2CCH_3		$\text{O}_2\text{CCH}_2\text{CH}_3$		$\text{O}_2\text{CH}(\text{CH}_3)_2$		Other Carboxylato Ligands							
	δHCH_3	apical bridge	δHCH_3	apical bridge	δHCH_3	apical bridge	δHCH_3	J _{H-H}						
I $\text{PdTi}(\text{O}_2\text{CR})_5$	2.30	2.06(5.2)	2.71	2.42(4.0)	1.35	1.06(14.5)	7.7	e	2.60 ^d	1.37	1.06(14.5)	6.7	8.0; 7.75; 7.20(aryl)	2.30(Me)
a, R = Me; b, R = Et;	2.30	2.06(5.0)	2.53	2.30(4.8)	1.30	1.03(15.5)	7.8							
c, R = Pr; d, R = $\text{C}_6\text{H}_4\text{-}m\text{-Me}$	2.29	2.05(5.0)	2.48	2.33(4.0)	1.29	1.03(14.5)	7.2							
II $\text{PdTi}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ ^{f,g}	2.33	2.05(5.0)								2.89	2.58 ^d	1.37	1.06(15.0)	7.0
R	2.30	2.05(4.5)								e	2.60 ^d	1.37	1.04(14.5)	6.7
a Et	2.35	2.00(5.2)												
b Me	2.35	2.05(5.1)												
c i-Pr														
d Me														
e C_6H_5														
f $\text{C}_6\text{H}_4\text{-}m\text{-OMe}$														
g Me														
HO ₂ CR	2.17		2.35		1.10		7.5	2.45						6.8
$\text{Pd}(\text{O}_2\text{CR})_2$	1.98		2.25		0.95		7.5	2.43						7.0
$\text{Tl}(\text{O}_2\text{CR})_3$	2.02(26) ^e		2.43		1.17		7.5	2.47						6.9

^a Chemical shifts (in ppm) downfield from TMS measured in CDCl_3 at ambient temperature. ^b Proton-thallium coupling constants (in Hz) between parentheses; the doublets due to ^{203}Tl (30%) and ^{205}Tl (70%) were not resolved. ^c From reference 16, measured in CD_3OD at -80°C . ^d Due to the complexity of this multiplet resonance the J(Tl-H) could not be assigned. ^e Obscured by neighbouring resonances. ^f Averaged values for shifts and coupling constants for the various isomers (see text).

TABLE III. ^{13}C NMR Data for $\text{PdTi}(\text{O}_2\text{CR})_5$ (I), $\text{PdTi}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ (II) and $\text{X}(\text{O}_2\text{CR})_y$ (X = H, Pd, Ti).^{a,b}

Compound	O_2CCH_3			$\text{O}_2\text{CCH}_2\text{CH}_3$			$\text{O}_2\text{CCH}(\text{CH}_3)_2$			Other Carboxylato Ligands			
	δCCO_2	δCCH_3	δCCO_2	δCCH_2	δCCH_2	δCCH_3	δCCO_2	δCCH	δCH_3	δCCO_2	$\delta\text{C}-\text{CO}_2$	Other Carbon Atoms	
I $\text{PdTi}(\text{O}_2\text{CR})_5$ ^c	180.9(228)	21.8(153)	183.6(241)	28.8(138)	10.0(8.8)	186.3(254)	35.6(123)	19.6(6.6)	174.5(235)	128.8(179)	130(m, aryl); 20.9(C _{Me})		
	181.2(605)	18.4(758)	183.6(605)	25.7(680)	10.0(50)	186.3(607)	32.5(613)	19.6(40)					
II $\text{PdTi}(\text{O}_2\text{CR})_2(\text{O}_2\text{CR}')_3$ ^d	R												
	a Et	Me	180.9(224)	21.6(145)	183.7(248)	28.8(145)	10.0(8.1)						
	b Me	Et	181.0(218)	21.8(146)	183.9(247)	28.8(139)	10.1(7.7)						
	c i-Pr	Me	180.7(225)	21.5(147)				186.3(269)	35.8(138)	19.8(5.3)			
	d Me	i-Pr	180.9(214)	21.6(141)				186.6(267)	35.8(132)	19.5(6.8)			
	e C ₆ H ₅	Me	180.9(229)	21.6(158)							174.2(216)	129.2(182)	128(m, aryl)
	f C ₆ H ₄ -m-OMe	Me	180.9(228)	21.6(152)							174.0(214)	131.2(178)	158.8(C _{OMe}); 123(m, aryl)
HO ₂ CR		177.7	20.7	181.2	27.7	8.9	184.0	34.2	18.8			55.2(C _{Me})	
Pd(O ₂ CR) ₂		188.8	23.1	191.3	29.8	10.1	194.4	36.1	19.4				
Ti(O ₂ CR) ₃		174.8 ^e	19.9 ^e	182.6	26.5	9.6	185.9	34.7	19.7				

^a Chemical shifts (in ppm) downfield from TMS measured in CDCl_3 at -60°C . ^b Carbon-thallium coupling constants (in Hz) between parentheses. The doublets due to ^{203}Tl (30%) and ^{205}Tl (70%) were not resolved. ^c Values for shifts and coupling constants as observed for the bridging and apical ligands are given in the upper and lower rows respectively. ^d The values given for the bridging ligands are averaged values for the various isomers (see text). Noteworthy is that the lowfield resonances of all the doublets were better resolved than the highfield part. Signals for the apical ligands were only observed under optimal conditions of the spectrometer and sample. The values obtained, but not given here, were similar to those observed for the apical ligands in $\text{Pd}(\text{O}_2\text{CR})_5$ (I). ^e From reference 16, measured in DMSO.

to dryness. The residue was recrystallized from toluene/hexane. Yield 0.44 g (90%).

Reaction of Pd(O₂CMe)₂ with Hg(O₂C-i-Pr)₂

Hg(O₂C-i-Pr)₂ (0.38 g, 1 mmol) was added to a solution of Pd(O₂CMe)₂ (0.21 g, 1 mmol) in CH₂Cl₂ (15 ml) and stirred for 4 h. The solution was concentrated up to 2 to 3 ml. Addition of ether (15 ml) afforded a white precipitate. Filtration yielded Hg(O₂CMe)(O₂C-i-Pr) (0.25 g, 70%) according to its ¹H NMR spectrum and elemental analysis: ¹H NMR (CDCl₃, internal Si(CH₃)₄) δ 1.20 (d, 6CH₃), 2.12 (s, 3CH₃), 2.66 (m, 1 CH). *Anal.* Calcd.: C, 20.77; H, 2.89; O, 18.47. Found C, 20.74; H, 2.98; O, 18.27. Evaporation of the filtrate yielded an oily mass, from which no pure product could be isolated. The ¹H NMR spectrum, measured in CDCl₃, revealed the presence of various non equivalent isobutyrate and acetato ligands, while resonances of the starting carboxylates were absent (δ 0.92, d; 1.95, s; 2.17, s; 2.60, m).

Attempted Reaction of Pd(O₂CMe)₂ with Hg(O₂CMe)₂

Hg(O₂CMe)₂ (0.32 g, 1 mmol) was added to a solution of Pd(O₂CMe)₂ (0.21 g, 1 mmol) in CH₂Cl₂ (15 ml) and stirred for 4 h. The starting compounds were recovered entirely unreacted.

Attempted Reaction of Pd(O₂CMe)₂ with PhHg(O₂CMe)

A solution of Pd(O₂CMe)₂ (0.070 g, 0.3 mmol) and PhHg(O₂CMe) (0.110 g, 0.3 mmol) in toluene (15 ml) was stirred for 4 h at 80 °C. The solvent was removed by evaporation at low pressure. The residue was dissolved in CDCl₃. The ¹H NMR spectrum showed peaks corresponding to the starting materials only (CDCl₃, internal Si(CH₃)₄): δ 1.99, s; 2.07, s; 7.30, s.

Attempted Reaction of Pd(O₂CMe)₂ with Ag(O₂CMe)

Ag(O₂CMe) (0.085 g, 0.5 mmol) was added to a solution of Pd(O₂CMe)₂ (0.107 g, 0.5 mmol) in toluene (10 ml) and stirred for 4 h at 80 °C. No reaction took place. Unreacted Ag(O₂CMe) could be recovered quantitatively by filtration, while Pd(O₂CMe)₂ was isolated by evaporation of the solvent from the filtrate.

Attempted Reaction of [Pd(O₂CMe)(C₆H₄N-NC₆H₅)₂] with Tl(O₂CMe)₃

Tl(O₂CMe)₃ (0.079 g, 0.2 mmol) was added to a solution of {Pd(O₂CMe)(C₆H₅NNC₆H₄)₂} in toluene (10 ml) and stirred for 4 h at 80 °C. Tl(O₂CCH)₃ was recovered quantitatively by filtration. The solvent was evaporated and the residue was dissolved in CDCl₃ (0.3 ml). The ¹H NMR spectrum showed only those peaks corresponding to the starting palladium complex.

Reaction of PdTi(O₂CMe)₅ with CO

Carbon monoxide was bubbled through a solution of PdTi(O₂CMe)₅ (0.060 g, 0.1 mmol) in 20 ml of toluene. After 1 h all the palladium was isolated as the metal. If acetic acid was used as a solvent the starting material was recovered unchanged.

Reaction of PdTi(O₂CMe)₅ with Tertiary Phosphines

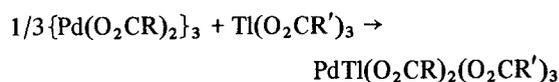
PPh₃ (0.40 g, 1.5 mmol) was added to a solution of PdTi(O₂CMe)₅ (0.30 g, 0.5 mmol) in toluene (15 ml). The solution became pale yellow in colour and somewhat turbid. Filtration gave a moisture sensitive precipitate. Addition of hexane to the filtrate gave a melon yellow precipitate which was filtered off and dried in vacuum. Yield 0.32 g (90%) of Pd(PPh₃)₂(O₂CMe)₂. *Anal.* Calcd. for C₄₀H₃₆O₄P₂Pd: C, 64.17; H, 4.81; O, 8.56; P, 8.29; mol. wt. 738. Found: C, 63.10; H, 5.00; O, 7.74; P, 7.72; mol. wt. (in CHCl₃, 26 °C) 754.

Other reactions of PdTi(O₂CMe)₅ with bis(diphenylphosphino)methane (DPPM) and bis(diphenylphosphino)ethane (DPPE) were carried out in CDCl₃. The ³¹P NMR spectroscopic results are discussed in the section Results and Discussion.

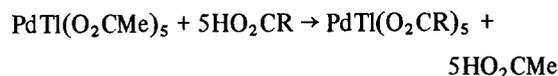
Results and Discussion

Reactions of Pd(O₂CR)₂

Reaction of the Pd(O₂CR)₂ trimer [10] (R = Me, Et, i-Pr, Ph) with Tl(O₂CR')₃ (R' = Me, Et, i-Pr) gave the novel palladium-thallium compounds of the formula PdTi(O₂CR)₂(O₂CR')₃ as evidenced by elemental analytical data and molecular weight measurements (Table I);



Complexes of formula PdTi(O₂CR)₅ (R = Et, i-Pr, *m*-tolyl) (I) could also be obtained by reaction of PdTi(O₂CMe)₅ with an excess of the corresponding carboxylic acid:



Where R = *m*-tolyl this is the only route for preparing the binuclear complex because Tl(O₂C-*m*-tolyl)₃ is unknown. Starting from Pd and Tl compounds having different carboxylato groups mixed binuclear compounds (II) were obtained. Although a variety of heterobinuclear compounds with ligands other than CO or phosphines have been reported for platinum, this is the first report of such compounds for palladium.

The synthesis of other binuclear palladium complexes failed: no reaction occurred between Pd(O₂-

CMe)₂ and Ag(O₂CMe), Hg(O₂CMe)₂ or PhHg(O₂CMe). However, reaction of Pd(O₂CMe)₂ with Hg(O₂C-i-Pr)₂ yielded the compound Hg(O₂CMe)(O₂C-i-Pr) indicating that exchange of carboxylato ligands between palladium and mercury occurs. Possibly, this exchange proceeds via a binuclear PdHg intermediate in which the transferred carboxylato bridge over both metal nuclei (*vide infra*).

No reaction was observed between the *ortho*-metallated compound [$\{\text{Pd}(\text{O}_2\text{CMe})(\text{C}_6\text{H}_4\text{NNC}_6\text{H}_5)\}_2$] and Tl(O₂CMe)₃. This result contrasts with the successful oxidation of [$\{\text{PtMe}_2(\text{SEt}_2)\}_2$] by Ag(I), Hg(II) or Tl(III) acetates yielding the compound [$\{\text{PtMe}_2(\text{O}_2\text{CMe})(\text{SEt}_2)\}_2$] containing a Pt(III)–Pt(III) bond [9]. These facts suggest that in the case of the palladium compounds the redox potential of the respective couples Ag(0)/Ag(I), Hg(0)/Hg(II) and Tl(I)/Tl(III) are too low to oxidize Pd(II) to Pd(III) or Pd(IV).

The binuclear palladium–thallium carboxylates I and II are unstable towards neutral donor molecules. The reactions of PdTl(O₂CMe)₅ with CO in toluene resulted in decomposition to metallic palladium, while in acetic acid no reaction occurred. The reaction of PdTl(O₂CMe)₅ with PPh₃ quantitatively yielded the complex Pd(O₂CMe)₂(PPh₃)₂ as evidenced by elemental analysis and molecular weight. Also the use of DPPM, which is known to be a powerful bridging ligand and thus might be expected to stabilize the Pd–Tl unit, results in breakdown of for example PdTl(O₂CMe)₅ into Pd(O₂CMe)₂(DPPM)*. Similarly, DPPE gave Pd(O₂CMe)₂(DPPE)*. Apparently, interaction with donor ligands promotes the dissociation of the binuclear unit into Tl(O₂CMe)₃ and stabilized Pd(O₂CMe)₂L_x complexes.

Structure of PdTl(O₂CR)₂(O₂CR')₃ in Solution

The compounds exist as monomers in CHCl₃ with the stoichiometry PdTl(O₂CR)₂(O₂CR')₃. The nature of the IR spectra which show broad absorptions arising from the CO₂ moiety did not allow detailed conclusions concerning the bonding mode of the carboxylato groups. In contrast detailed structural information could be obtained from the ¹H and ¹³C NMR data, which together with the data for the related compounds H(O₂CR), Pd(O₂CR)₂ and

*In separate experiments Pd(O₂CMe)₂ was reacted with DPPM and DPPE respectively. ³¹P NMR data for Pd(O₂CMe)₂(DPPM): δ P = –48.2 ppm (CDCl₃), and for Pd(O₂CMe)₂(DPPE) δ P = 59.3 ppm (CDCl₃). These values are comparable to those reported recently for the adducts of Pd(OC(S)Me)₂ and have been ascribed to the presence of 4 and 5 membered rings, respectively [12]. In the spectra of Pd(O₂CMe)₂ with DPPM additional resonances of minor intensity are observed at approx. –5 ppm, which might be assigned to binuclear compounds containing bridging DPPM ligands.

Tl(O₂CR)₃ (R = Me, Et, i-Pr), are summarized in Tables II and III. The assignments of chemical shifts and coupling constants are based on 60 and 100 MHz ¹H and 20.1 and 25.2 MHz ¹³C NMR experiments.

Comparison of the multiplet patterns in the 60 and 100 MHz ¹H NMR spectra of the non-mixed compounds PdTl(O₂CR)₅ (R = Me, Et, i-Pr), revealed that four of the carboxylato groups are isochronous and couple with thallium: ⁴J(^{203,205}Tl–¹H) = 5 Hz, R = Me; ⁵J(^{203,205}Tl–¹H) = 15 Hz, R = Et, i-Pr. The resonances belonging to the fifth carboxylato group appeared at lower field without thallium coupling. This is illustrated for R = Et in Fig. 1.

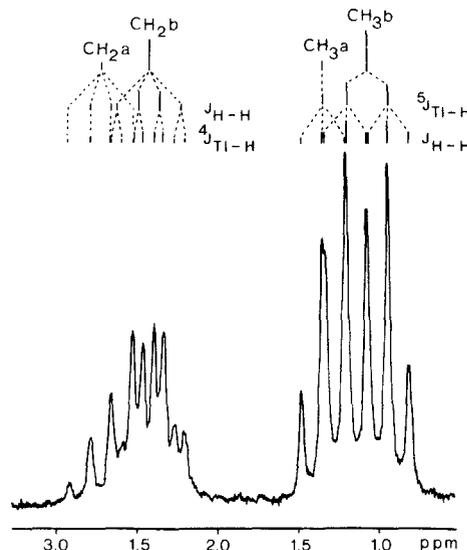


Fig. 1. 60 MHz ¹H NMR spectrum of PdTl(O₂CMe)₅ in CDCl₃ at 37 °C; a = apical; b = bridge.

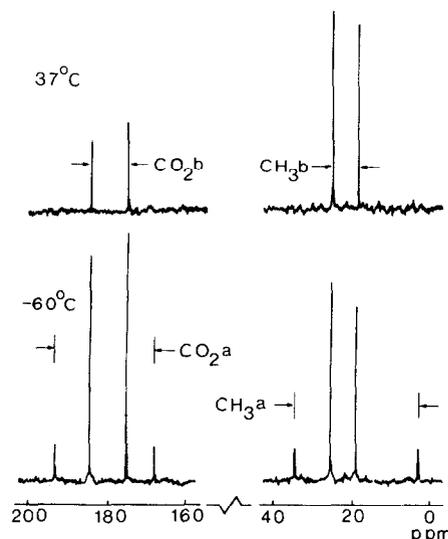


Fig. 2. 25.2 MHz ¹³C NMR spectra of PdTl(O₂CMe)₅ in CDCl₃ at –60 °C and 37 °C; a = apical; b = bridge.

The 20.1 and 25.2 MHz ^{13}C NMR spectra also show the presence of two different types of carboxylato groups in these compounds. This is illustrated for $\text{PdTl}(\text{O}_2\text{CMe})_5$ in Fig. 2. At low temperature both types of carbon resonances show coupling with thallium (*vide infra*).[†]

These observations can be explained by a structure containing four equivalent carboxylato groups bridging Pd and Tl. The fifth carboxylato group acts as an apical ligand either being bonded to Pd or to Tl. Figure 3 shows these two possibilities. Structure A

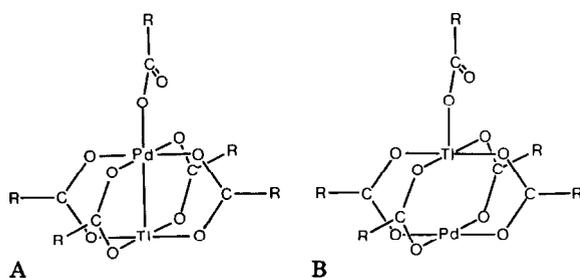


Fig. 3. Possible structures for $\text{PdTl}(\text{O}_2\text{CR})_5$.

implicates the presence of either a dative or a 2c-2e Pd-Tl bond, which would be in accord with the metal-metal interactions found in other heterobinuclear compounds [7]. However, the observation of a rather large $J(^{203,205}\text{Tl}-^{13}\text{C})$ for the apical carboxylato ligand makes structure A less likely, because in this case the coupling has to be transmitted via the Pd nucleus. For this reason we prefer structure B in which the geometry around the Tl center will be similar to that found previously in thallium(III) octaethylporphyrin acetate [14]. A large number of homobinuclear transition metal complexes have been reported which contain four bidentate bridging ligands as a common structural feature [15]. Coordination of Pd by four bridging ligands as is implied by structure B is also observed in $\text{Pd}(\text{S}_2\text{CMe})_2$ dimer [5]. The structure of the latter compound contains short Pd-Pd distances of 2.755 (2) Å within the dimer while the intermolecular Pd-Pd distances between the dimers which stack in columns is 3.398 (2) Å. The novel Pd-Tl complexes might have similar intermolecular structural features with the d_{z^2} orbital of the Pd atom lined up with the Pd-Tl axis. This

[†] Systematic trends are observed in the ^1H and ^{13}C chemical shifts and $J(^{203,205}\text{Tl}-^1\text{H})$ and $J(^{203,205}\text{Tl}-^{13}\text{C})$ coupling values as function of substituent R in $\text{PdTl}(\text{O}_2\text{CR})_5$ and as function of X in $[\text{X}(\text{O}_2\text{CR})_y]$ (X = H, y = 1; X = Pd, y = 2; X = Tl, y = 3; X = PdTl, y = 5) (see Tables II and III). These differences are only marginal compared with the differences between the values of the bridging and apical ligands. Interpretation of these results would be arguable (*cf.* discussions, concerning long range $J(^{203,205}\text{Tl}-^{13}\text{C})$ for aryl-thallium compounds [13]).

implies that in these compounds a dative PdTl interaction is possible.

On the basis of these structural considerations a structure for the mixed carboxylato compounds can also be proposed. The observation of chemical shifts and coupling constants in ^1H and ^{13}C NMR spectra (Tables II and III) which are comparable with those observed for the non-mixed compounds indicates that the mixed compounds can likewise be formulated as binuclear palladium-thallium species. In principle species which contain two types of ligands in the ratio of 2 to 3 can exist in three distinct isomeric forms as is shown in Fig. 4. However, it will be shown that as a result of ligand exchange between these isomers the actual situation is much more complex.

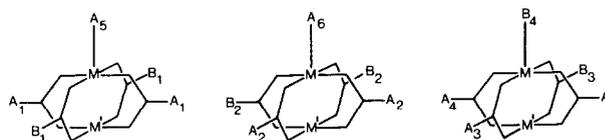
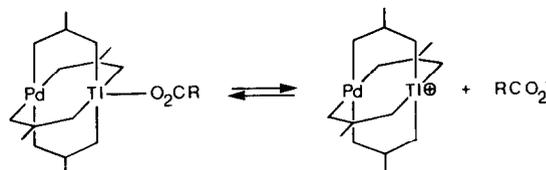


Fig. 4. Stereoisomers of compounds with stoichiometry $\text{PdTl}(\text{O}_2\text{CA})_3(\text{O}_2\text{CB})_2$.

Exchange Mechanism

The palladium-thallium carboxylates are unique in the sense that by observation of thallium coupling on the hydrogen and carbon atoms of the bridging and apical ligands[‡] information can be obtained about the dynamic behaviour of these compounds in solution. At least two processes can be distinguished: i) dissociation of the apical ligand with retention of the binuclear unit bridged by four ligands and ii) exchange of the bridging and apical ligands.



Scheme I

Dissociation of the apical ligand (scheme I) could be unambiguously deduced from the ^{13}C NMR spectra and is illustrated for $\text{PdTl}(\text{O}_2\text{CMe})_5$ in Fig. 2. At -60°C a $^2J(^{203,205}\text{Tl}-^{13}\text{C})$ of 605 Hz and a $^3J(^{203,205}\text{Tl}-^{13}\text{C})$ of 758 Hz has been observed for the apical ligand, which reveals that at this temperature the $\text{RCO}_2\text{-Tl}$ interaction is inert on the NMR time scale. At room temperature these resonances were completely absent. The occurrence of dissociation is

[‡] Coupling of thallium through the ester linkage is only observed previously for $\text{Tl}(\text{O}_2\text{CCH}_3)_3$ and $\text{Tl}(\text{O}_2\text{CCF}_3)_3$ at low temperature [16].

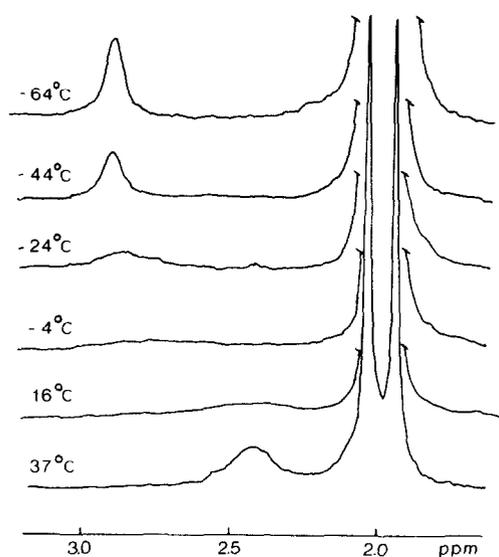


Fig. 5. Dynamic 100 MHz ^1H NMR spectra of $\text{PdTi}(\text{O}_2\text{CMe})_5$ in CD_2Cl_2 .

further supported by the dynamic ^1H NMR spectra of $\text{PdTi}(\text{O}_2\text{CMe})_5$ in CD_2Cl_2 (-85°C – $+35^\circ\text{C}$) (see Fig. 5). The bridging ligands do not take part in this process as evidenced by the unaffected doublet (4J –($^{203,205}\text{Tl}-^1\text{H}$) = 5 Hz) in the spectra. The methyl resonance at 2.87 ppm at -85°C corresponds with the coordinated apical ligand. Upon raising the temperature this signal broadens and finally gives rise to a new resonance at 2.42 ppm (35°C), which corresponds with the fast exchange situation. Intermolecular exchange of acetato anions between binuclear compounds and free acetic acid was separately studied by recording the ^1H NMR spectra of mixtures of $\text{PdTi}(\text{O}_2\text{CMe})_5$ and HO_2CMe . It appeared that indeed depending on the molar ratio $\text{PdTi}(\text{O}_2\text{CMe})_5/\text{HO}_2\text{CMe}$ both the coalescence temperature ($+5^\circ\text{C}$, pure $\text{PdTi}(\text{O}_2\text{CMe})_5$; -45°C , 1/1; -65°C , 1/4) and the chemical shift of the methyl signal at 37°C (2.42 ppm, pure $\text{PdTi}(\text{O}_2\text{CMe})_5$; 2.26 ppm, 1/1; 2.14 ppm, 1/4) changed.

The second process *i.e.* exchange of bridging and apical ligands, as was studied for $\text{PdTi}(\text{O}_2\text{CMe})_5$ in toluene- d_8 occurred at high temperatures. At 102°C , which is just below coalescence, one broadened signal was observed for the bridging and apical ligands (see Fig. 6). Addition of free acetic acid lowered the

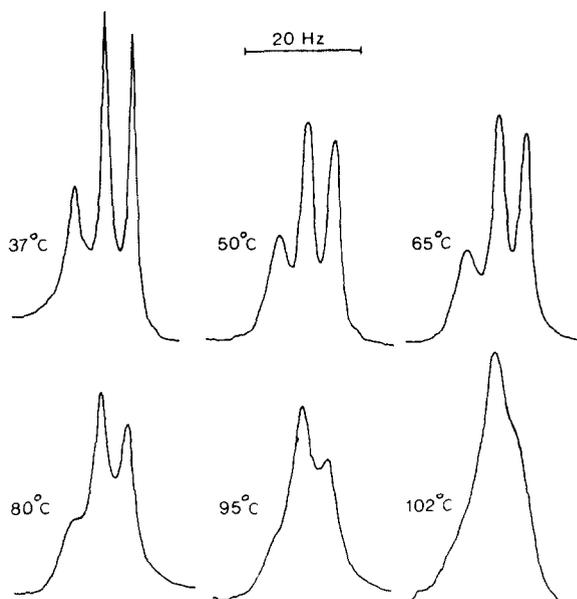
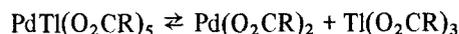


Fig. 6. Dynamic 100 MHz ^1H NMR spectra of $\text{PdTi}(\text{O}_2\text{CMe})_5$ in toluene- d_8 .

coalescence temperature (65°C , $\text{PdTi}(\text{O}_2\text{CMe})_5/\text{HO}_2\text{CMe} = 1/4$), leading to one sharp resonance (2.09 ppm) at 80°C . Intermolecular exchange of carboxylato ligands via the reaction:

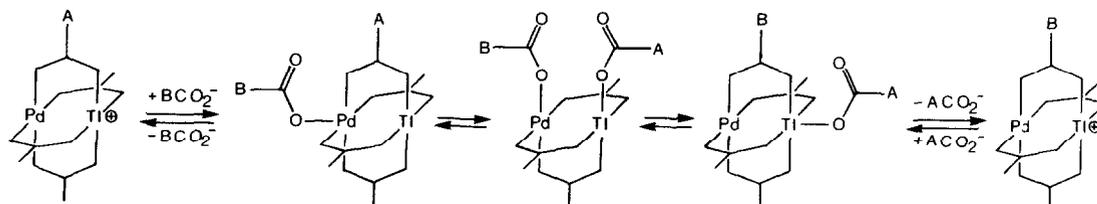


could be excluded, because addition of free $\text{Pd}(\text{O}_2\text{CMe})_2$ did not affect the ^1H NMR pattern.

On the basis of these qualitative measurements the pathway shown in Scheme II involving both inter- and intramolecular steps might be considered for the exchange of bridging and apical ligands.

A cationic $\text{PdTi}(\text{O}_2\text{CX})_4^+$ species might be attacked by a carboxylato anion either at the Pd or at the Ti site. In the resulting neutral species the bridging and apical ligands exchange via an intramolecular rearrangement. Attack of a second carboxylato anion at the Pd site in the neutral species $\text{PdTi}(\text{O}_2\text{CX})_5$ might be an alternative route.

The occurrence of these exchange processes necessarily leads to the formation of mixed $\text{PdTi}(\text{O}_2\text{CR})_x(\text{O}_2\text{CR}')_{5-x}$ species when $\text{R} \neq \text{R}'$. This is supported by the ^1H and ^{13}C NMR spectra of a 1 to 1 mixture of $\text{PdTi}(\text{O}_2\text{CMe})_5$ and $\text{PdTi}(\text{O}_2\text{C-}i\text{-Pr})_5$,



Scheme II

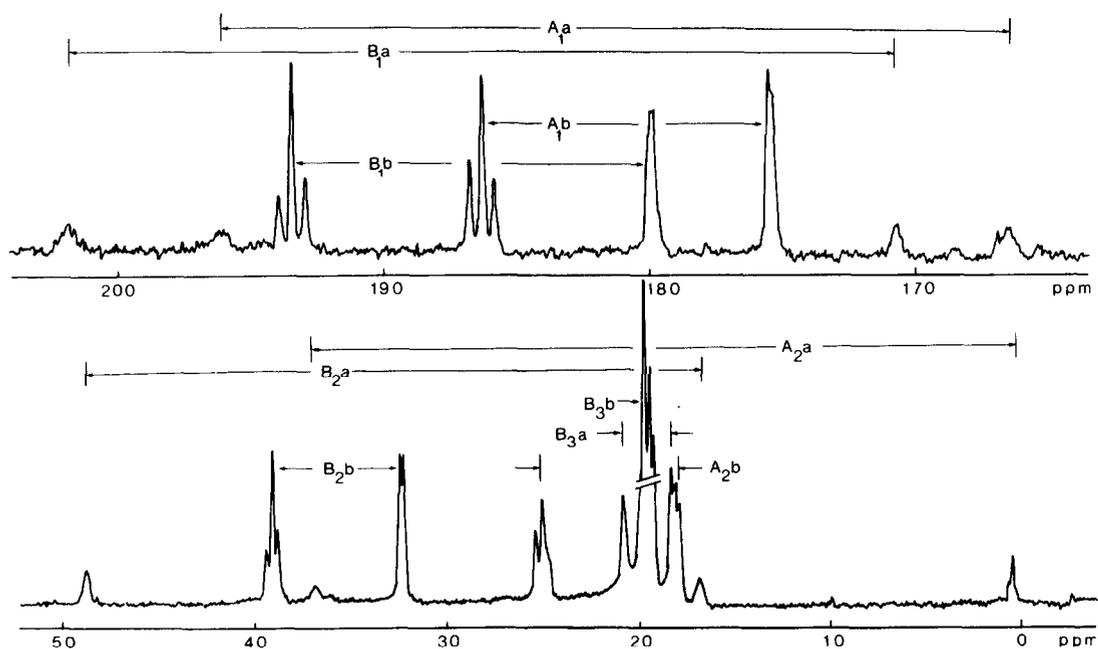


Fig. 7. 20.1 MHz ^{13}C NMR spectrum of a 1 to 1 mixture of $\text{PdTl}(\text{O}_2\text{C-i-Pr})_5$ and $\text{PdTl}(\text{O}_2\text{CMe})_5$ in CDCl_3 at -60°C . A = acetato ligand; B = isobutyrate ligand; a = apical; b = bridge; C_1 = carbonyl C-atom; C_2 = α -C-atom; C_3 = β -C-atom.

which reveals a random distribution of both carboxylato ligands in the palladium-thallium species. The equilibrium is reached after dissolution within the time necessary for recording the spectra. The ^{13}C NMR spectrum measured at -60°C (see Fig. 7) is almost equal to the superposition of the ^{13}C spectra of $\text{PdTl}(\text{O}_2\text{CMe})_x(\text{O}_2\text{C-i-Pr})_{5-x}$ ($x = 2, 3$) and clearly shows the presence of at least three inequivalent bridging acetato and isobutyrate ligands.

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