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(*N*,*N*-DIMETHYLBENZYLAMINE-2*C*,*N*)PALLADIUM(II) AND -PLATINIUM(II) β-DIKETONATES AND THIO-β-DIKETONATES

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Summary

(*N*,*N*-dimethylbenzylamine-2*C*,*N*)palladium(II) and -platinum(II) β-diketonates, DmbaML, have been synthesized by reaction of $[DmbaMCl]_2$ with the free ligand and KOH, or with the thallium(I) salt of the ligand. The various isomers formed have been investigated by ^1H and ^{19}F NMR spectroscopy. Infrared and mass spectroscopic studies have also been made on the compounds.

Introduction

We have previously reported a series of salicylaldimine Schiff-base complexes of the (*N*,*N*-dimethylbenzylamine-2*C*,*N*)palladium(II) and -platinum(II) systems, DmbaMSal=N—R [1], and report here a series of complexes of β-diketones with the same organometallic systems. In the cases with unsymmetrical β-diketones two isomers were obtained corresponding to the two orientations of the β-diketone relative to the *N*,*N*-dimethylbenzylamine unit in the square planar complex. Thin layer chromatography failed to separate these isomers. With the thio-β-diketones the palladium compound produced only one isomer, whereas the platinum complex gave a mixture. ^1H and ^{19}F NMR spectra have enabled assignment of the structures of the various complexes and isomers.

Results and discussion

Syntheses

Di-μ-chlorobis(*N*,*N*-dimethylbenzylamine-2*C*,*N*)dipalladium(II), $[DmbaPdCl]_2$, dissolves in a methanol solution of acacH* containing KOH to give the β-diketonate complex DmbaPdacac. Similar reactions occur with bzacH and tfacacH but hfacacH fails to give the expected complex. This derivative was obtained by reaction of $[DmbaPdCl]_2$ with hfacacTl in CH_2Cl_2, the product being isolated from the solution after filtering off the thallium(I) chloride. The reaction with the free β-diketone and KOH is also less successful for the platinum com-

* Abbreviations used in this paper: acac = $CH_3COCHCOCH_3$, bzac = $C_6H_5COCHCOCH_3$, tfacac = $CF_3COCHCOCH_3$, hfacac = $CF_3COCHCOCF_3$, Sacac = $CH_3CSCHCOCH_3$, tfSacac = $CH_3CSCHCOCF_3$.

TABLE 1

ANALYTICAL AND OTHER DATA ON DmbaM β-DIKETONATES AND THIO-β-DIKETONATES

Compound	Formula	Colour	Analysis, found (calcd.) (%)					m/e^a	S tl
			C	H	N	F	S		
DmbaPdL									
L = acac	$C_{14}H_{19}NO_2Pd$	Cream	49.74 (49.50)	5.48 (5.64)	4.08 (4.12)			339	*(i*
bzac	$C_{19}H_{21}NO_2Pd$	Cream	56.94 (56.80)	5.43 (5.27)	3.45 (3.49)			401	*(i)*
tfacac	$C_{14}H_{16}NO_2F_3Pd$	Pale yellow	42.93 (42.71)	4.07 (4.10)	3.85 (3.56)	14.4 (14.5)		393	*(i)*
hfacac	$C_{14}H_{13}NO_2F_6Pd$	Yellow	37.85 (37.56)	2.95 (2.93)	3.09 (3.13)	25.4 (25.5)		447	*(ii,*
Sacac	$C_{14}H_{19}NOSPd$	Yellow brown	47.03 (47.26)	5.45 (5.38)	4.05 (3.94)		8.8 (9.0)	355	*(ii)*
tfSacac	$C_{14}H_{16}NOSF_3Pd$	Deep yellow	41.15 (41.04)	3.78 (3.94)	3.33 (3.42)	13.8 (13.9)	8.1 (7.8)	409	*(ii)*
DmbaPtL									
L = acac	$C_{14}H_{19}NO_2Pt$	Cream	39.65 (39.25)	4.55 (4.47)	3.11 (3.27)			428	*(ii)*
tfacac	$C_{14}H_{16}NO_2F_3Pt$	Yellow	35.25 (34.86)	3.48 (3.34)	2.90 (2.90)	11.9 (11.8)		482	*(ii)*
hfacac	$C_{14}H_{13}NO_2F_6Pt$	Orange red	31.45 (31.35)	2.53 (2.44)	2.43 (2.61)	21.5 (21.3)		536	*(ii)*
Sacac	$C_{14}H_{19}NOSPt$	Orange	37.82 (37.83)	4.30 (4.31)	3.02 (3.15)		[c]	444	*(ii)*
tfSacac	$C_{14}H_{16}NOSF_3Pt$	Deep orange	33.77 (33.74)	3.26 (3.24)	2.71 (2.81)	11.3 (11.4)	[c]	498	*(ii)*

[a] Mass spectroscopic *m/e* values for ^{106}Pd and ^{195}Pt. These all correspond to the calculated values. [b] Method of synthesis as detailed in experimental section. [c] Satisfactory sulphur analyses could not be obtained in the presence of platinum, a feature commonly found for platinum sulphur compounds [2].

plexes, 62% of the starting material being recovered unchanged from the reaction of $[DmbaPtCl]_2$ with tfacacH after being allowed to continue overnight. The platinum complexes were therefore prepared from the thallium(I) salts, as were both the palladium and platinum complexes of the thio-β-diketones. The complexes prepared, with analytical figures and other data are shown in Table 1

The compounds are all soluble in organic solvents, though sparingly so in hexane, and insoluble in water. Attempts to obtain β-ketoamine complexes by reaction of DmbaPdacac with methylamine and aniline failed to produce any product, only starting materials being recovered.

Spectra and structure

The complexes presumably all have a square planar structure, as is usual for Pd^{II} and Pt^{II}. For the unsymmetrical β-diketones, two isomers are possible as in Fig. 1. In fact the ^1H NMR spectra of these complexes indicate the presence of two such isomers, and the ^{19}F NMR spectra of the tfacac derivatives show two peaks. Attempts to separate the isomers by thin layer chromatography proved unsuccessful, hence they were studied in the mixtures by NMR spectroscopy. As

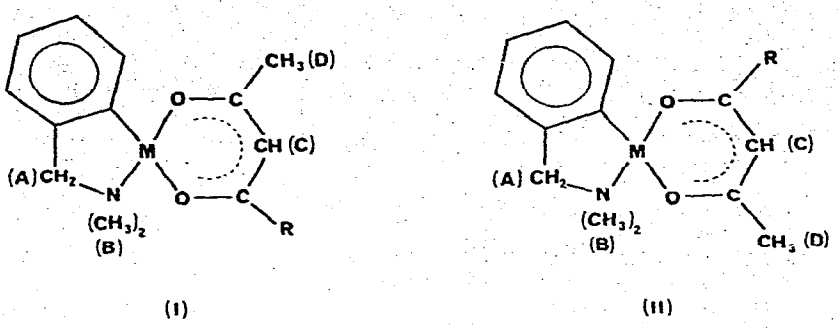

Fig. 1.

the isomers are not of exactly equal abundance it is possible to identify all the resonances due to each isomer, and to correlate the ^{19}F resonance with the appropriate isomer in the ^{1}H spectrum.

To assign the structures comparison was made with spectra of the Sacac and tfSacac complexes. In the case of palladium only one isomer was formed for each of these ligands, but with platinum two isomers occurred in each instance. The isomers possible in these compounds are as in Fig. 2. ^{1}H and ^{19}F NMR spectra are shown in Tables 2 and 3. Isomer (1) is in all cases that of greatest abundance.

The coupling constant of ^{195}Pt to another nucleus will be dependent on the covalency of bonding to the platinum [3] and it can be assumed that changes in $J(^{195}Pt—^{1}H_B)$ will be primarily caused by changes in the atom *trans* to nitrogen. Hence comparison of the ^{1}H spectra of DmbaPtacac and DmbaPtSacac suggests that isomer (1) for the latter has structure (IV) and isomer (2), which has a much smaller value of $J(Pt—H_B)$, structure (III). Comparison with DmbaPttfSacac indicates that in this compound isomer (1) corresponds to structure (III) and (2) to structure (IV). The ^{19}F spectrum therefore shows that the smaller value of $J(^{195}Pt—^{19}F)$ corresponds to structure (III), with the CF_3 group opposite the platinum—carbon bond, and hence for DmbaPttfacac isomer (1) is assigned the structure (I) and isomer (2) structure (II). This result is consistent with the reduced covalency of the bond *trans* to the platinum—carbon bond. Assignment of the isomers for the palladium compounds is more difficult as comparison of chemical shifts must be relied on. The ^{19}F chemical shift differences between isomers are larger and hence expected to be more reliable. Comparison of the ^{19}F spectra of DmbaPdtfacac and DmbaPttfacac indicates that isomers (1) and (2) of the palladium compound have structures (I) and (II) respectively, as in the

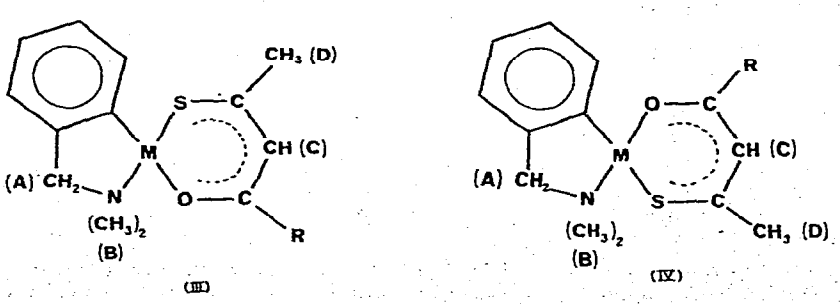

Fig. 2.

TABLE 2

^{1}H NMR SPECTRA[a]

Compound	Isomer	δ values (ppm)						$J(^{195}Pt—^1H)$ (		
		Aromatic	A	B	C	D	R	A	B	(
DmbaPdL										
L = acac		6.81 - 7.33	3.85	2.78	5.25	1.97	1.91			
bzac	(1)	6.82 - 7.94	3.90	2.87	5.94	2.13	Ar.			
	(2)	6.82 - 7.94	3.90	2.83	5.92	2.05	Ar.			
tfacac	(1)	6.82 - 7.28	3.87	2.79	5.64	2.12				
	(2)	6.82 - 7.28	3.86	2.81	5.67	2.05				
hfacac		6.87 - 7.21	3.91	2.84	6.03					
Sacac		6.83 - 7.33	3.91	2.77	6.37	2.35	2.05			
tfSacac		6.90 - 7.30	3.93	2.76	6.57	2.45				
DmbaPtL										
L = acac		6.85 - 7.33	3.86	2.92	5.33	1.86	1.84	49.5	40.8	7.
tfacac	(1)	6.84 - 7.20	3.85	2.89	5.71	1.92		51.8	42.9	6.
	(2)	6.84 - 7.20	3.85	2.91	5.75	1.92		51.8	42.9	6.
hfacac		6.85 - 7.09	3.85	2.90	6.11			55.3	45.7	5.
Sacac	(1)	6.81 - 7.46	3.96	2.99	6.33	2.10	1.89	49.4	45.3	
	(2)	6.81 - 7.46	3.96	2.89	6.33	2.06	1.82	36.5	29.1	
tfSacac	(1)	6.80 - 7.36	4.00	2.86	7.53			37.8	29.6	
	(2)	6.80 - 7.36	3.96	3.00	7.55			51.1	47.0	

[a]Measured at 100 MHz in $CDCl_3$ solutions using internal TMS as reference. Numbering of protons refe to Figs. 1 and 2.

case of platinum. As the chemical shifts of the protons D are probably the be indicators of stereochemistry, comparison of these in DmbaPdbzac with the tfacac derivative leads to the assignment of isomers (1) and (2) to structures (and (II) respectively.

For the thio-β-diketonates, comparison of the ^{19}F chemical shift in Dmb tfSacac with its platinum analogue suggests structure (III) for this compound, the same as the major isomer in the case of platinum. The protons B in this co

TABLE 3

^{19}F NMR SPECTRA[a]

Compound	Isomer	δ values (ppm)[b]		$J(^{195}Pt—^{19}F)$ (Hz)	
		R	E[c]	R	E[c]
DmbaPdL					
L = tfacac	(1)	−75.63			
	(2)	−74.61			
hfacac		−76.21	−75.20		
tfSacac		−75.12			
DmbaPtL					
L = tfacac	(1)	−75.54		5.4	
	(2)	−74.31		16.6	
hfacac		−76.08	−74.95	5.3	15.5
tfSacac	(1)	−74.95		6.3	
	(2)	−73.65		17.9	

[a]Measured at 56.45 MHz in $CHCl_3$ solutions using internal $CFCl_3$ as reference. [b]As we have used the same convention as for proton spectra, negative values of δ correspond to shifts upfield of $CFCl_3$. [c]Position E is that corresponding to methyl group D in structure (I).

pound, which are thus assigned *trans* to sulphur have resonances approximately 0.1 ppm to higher field than in the corresponding platinum isomer. Comparing the proton resonances of DmbaPdSacac and DmbaPtSacac therefore suggests that DmbaPdSacac corresponds to isomer (2) of the platinum complex, i.e. structure (III), which makes the lower abundance of the platinum isomer remarkable. This structure is the same as that of DmbaPdtfSacac, as would be expected if the sulphur is the primary influence in directing the stereochemistry.

The two CF_3 groups in the ^{19}F spectrum of DmbaPthfacac have been assigned on the basis of coupling with ^{195}Pt, the CF_3 group *trans* to carbon having a smaller coupling as in the tfacac derivative, and the palladium compound hence assigned by comparison of chemical shifts. The assignment of the CH_3 resonances in the acac complexes is more uncertain, but comparison with the ^1H spectrum of the previously assigned DmbaPdtfacac suggests that the protons with a higher δ value are those *trans* to nitrogen, as shown in the table [assuming structure (I)]. The CH_3 resonances of DmbaMSacac complexes have been assigned by comparison with DmbaMacac, the resonance at considerably lower field than in acac being assumed to be due to the methyl group adjacent to sulphur.

The coupling constants $J(^{195}Pt—^1H_B)$ in DmbaPtSacac and DmbaPttfSacac differ widely for the two isomers, the lower value when the nitrogen is *trans* to sulphur probably being due to the Pt—N bond being weakened by stronger bonding to sulphur than oxygen. The same effect has previously been observed for $J(Pt—CH_3)$ in $(CH_3)_3PtSacacL$ complexes (L = a monodentate ligand) [4]. As the values of $J(^{195}Pt—^1H_A)$ follow a similar trend it appears that the mechanism of this coupling is primarily also through the nitrogen. It may also be noted that in the DmbaPt β-diketonates the couplings $J(Pt—H_A)$ and $J(Pt—H_B)$ are quite markedly higher than the corresponding couplings in the Schiff-base complexes [1]. Presumably this is due to the stronger coordinating properties of the Schiff-base weakening bonding to the Dmba entity. The nitrogen donor of the Schiff-base, which has been found to be *trans** to the benzylamine nitrogen [1], is expected to be primarily responsible for this effect, and the fact that the effect in these complexes is also similar for protons A and B again indicates that coupling is mainly via the benzylamine nitrogen, as deduced above for the thio-β-diketones. These two couplings also increase with increasing fluorine substitution in the β-diketonates which parallels the expected reduction in donor power of the ligands.

The frequencies of ν(C—O), ν(C—C) and ν(C—S) in the infrared spectra of those compounds isolable as single isomers are shown in Table 4. These assignments are based on those now generally accepted for ν(C—O) and ν(C—C) in acac complexes [6—8] and ν(C—S) in Sacac compounds [9,10]. As has been found for simple complexes of Sacac [10] the ν(C—C) bond in DmbaPdSacac is shifted to much lower frequency than in DmbaPdacac. The frequency of ν(C—O) in the hfacac complexes is higher than in the acac analogues, an effect which has been interpreted as being due to greater ionic character in the bonding to the metal [11]. It is noteworthy that the opposite effect is observed in DmbaPdSacac and DmbaPdtfSacac.

* The crystal structure of DmbaPdSal=N—Ph has been determined [5], confirming the *trans* arrangement.

TABLE 4

INFRARED SPECTRA[a]

Compound	Frequencies (cm^{-1})		
	ν(CO)	ν(CC)	ν(CS)
DmbaPdL			
L = acac	1566	1518	
hfacac	1636	1551	
Sacac	1571	1478	721
tfSacac	1548	1513	717
DmbaPtL			
L = acac	1555	1497	
hfacac	1616	1550	

[a]KBr disc.

The mass spectra of all the compounds display the parent ion and the ions $[MC_6H_4CH_3]^+$, $[C_6H_4CH_2N(CH_3)_2]^+$ and $[C_7H_7]^+$. All except DmbaPdhfacac show $[CH_3C_6H_4ML]^+$ (L = β-diketonate or thio-β-diketonate) corresponding to loss of $CH_2{=}N{-}CH_3$ from the parent ion, this fragmentation being confirmed by the appropriate metastable peak in the case of DmbaPdtfacac. The ion $DmbaM^+$ is apparent for all but the thio-β-diketonates. The platinum thio-β-diketonates show an ion corresponding to loss of HS from the parent ion, metastable peaks confirming the fragmentation. All species except DmbaPdbzac and DmbaPdtfacac also give doubly charged parent ions. An interesting feature in the spectra of the palladium compounds is the appearance of an ion not containing palladium (apparent from lack of isotope pattern) with an *m/e* value corresponding to $[(Dmba)L{-}H]^+$ apparently formed by linking of the two ligands in the parent ion with the elimination of palladium and hydrogen.

Experimental

Instrumentation

^1H NMR spectra were measured on a Varian HA-100 spectrometer and the ^{19}F spectra on a Varian A56/60A instrument. Infrared spectra were recorded with a Perkin—Elmer 521 spectrophotometer. The mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6E instrument using an ion chamber temperature of 200° and an electron energy of 70 eV.

Starting materials

$[DmbaMCl]_2$ species were prepared as reported in the literature [12]. Thallium(I) β-diketonates were prepared by reaction of the ligand with thallium(I) ethoxide or carbonate. SacacH and tfSacacH were prepared by published methods [13,14] and converted to the thallium salts by reaction with thallium(I) ethoxide in ethanol.

Syntheses

The methods of synthesis indicated in Table 1 for the various compounds are detailed below.

(i). From the β-diketone and KOH. $[DmbaPdCl]_2$ (200 mg) suspended in methanol (20 ml) was treated with a slight excess of the β-diketone and the stoichiometric quantity of KOH as a 10% aqueous solution, and stirred for approx. 2 h by which time the starting material had dissolved. Addition of water and evaporation to smaller volume under reduced pressure gave the pure product which was filtered off, washed with water and dried in vacuo. Yields were generally over 90%. A similar reaction of $[DmbaPtCl]_2$ with tfacacH after stirring overnight led to recovery of 62% of the original platinum complex, and only a 26% yield of product.

(ii). From the thallium(I) β-diketonates and thio-β-diketonates. $[DmbaMCl]_2$ in dichloromethane was treated with the stoichiometric quantity of thallium(I) salt of the ligand, and the solution filtered after stirring overnight. The β-diketonates were obtained by evaporation of the solution and recrystallization from dichloromethane/hexane (DmbaPdacac and DmbaPdhfacac) or acetone/methanol/water. Yields ranged from 49% to 87%. Due to the low purity of the thallium thio-β-diketonates, the derivatives of these ligands were isolated by adding methanol to the dichloromethane solution, evaporating to smaller volume under reduced pressure to remove dichloromethane and then filtering off unreacted starting complex. The filtrate was treated with charcoal, refiltered, and after addition of water partly evaporated under reduced pressure to give the product. Yields were from 22% to 44%.

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