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N-SUBSTITUTED SALICYLALDIMINE COMPLEXES OF RHODIUM(III) AND RELATED RHODIUM(III) ORGANOMETALLIC DERIVATIVES

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Summary

A series of new Rh^{III} complexes with *N*-substituted salicylaldimines have been prepared of the form $[RhSBPy_2]PF_6$ where SB is a tetradentate *N,N'*-substituted bis(salicylaldimine) or represents two molecules of a corresponding bidentate derivative. Several of these complexes have been reduced with 0.5% sodium amalgam and the products reacted with CH_3I to yield the organometallic derivatives $CH_3RhSBPy$.

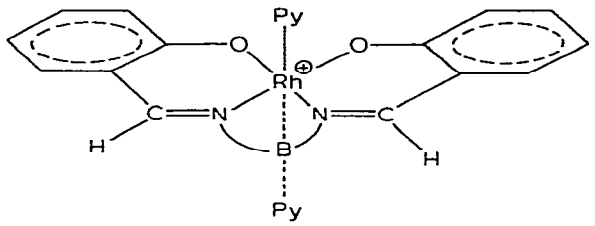
Introduction

A number of organorhodium(III) derivatives have been reported [1] in which the dianion of *N,N'*-ethylenebis(salicylaldimine) ($SalenH_2$) is also coordinated to the metal. These compounds were prepared by reducing PyRhSalenCl with sodium amalgam or $NaBH_4/Pd^{2+}$ and then reacting the product with an appropriate alkyl halide.

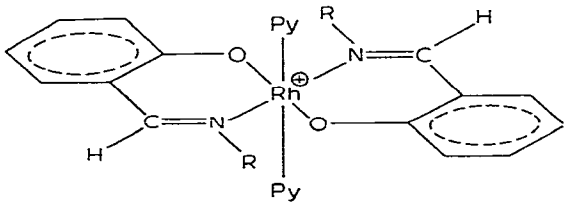
A further series of related rhodium(III) Schiff base complexes has been prepared containing both tetradentate and bidentate ligands derived from *N*-substituted salicylaldimines and a number of these complexes have been used to prepare further organorhodium(III) compounds.

Results and discussion

The reaction of *trans*-$[RhPy_4Cl_2]Cl$ [2] with various Schiff bases, e.g. *N,N'*-*o*-phenylenebis(salicylaldimine) (Salphen H_2) in boiling pyridine in the presence of zinc powder yields the cationic species $[RhSalphenPy_2]^+$ which can be isolated as the PF_6^- salt. A variety of other tetradentate and bidentate Schiff base ligands yield similar compounds (Fig. 1).



B* = 1,2-phenylene (Salphen)
4-methyl-1,2-phenylene (Sal-4-Me-phen)
4,5-dimethyl-1,2-phenylene (Sal-4,5-Me-phen)
ethylene (Salen)
1,3-propylene (Sal-1,3-pn)
1,4-butylene (Salbn)



R* = CH_3 (Sal-*N*-Me)
p-$CH_3C_6H_4$ (Sal-N-*p*-tol)

Fig. 1.

N,N'-ethylenebis(salicylaldimine) yields the bis-pyridine cation in this reaction together with the sparingly soluble substance [RhSalenPyCl] previously reported [1]. Complexes of empirical formula [RhSBPyCl] have also been isolated together with the appropriate bis-pyridine complexes $[RhSBPy_2]^+$ from reactions involving tetradentate ligands derived from alkyl diamines. Such complexes have not so far been prepared either with ligands containing a phenylenediimine bridge or with bidentate ligands, the bis-pyridine cationic species being the major products.

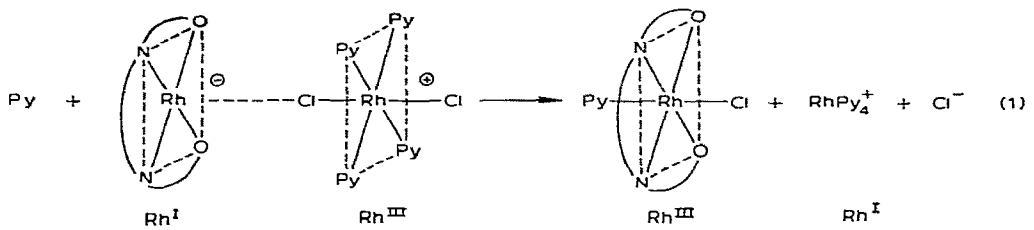
In the absence of zinc, *trans*-$[RhPy_4Cl_2]^+$ does not react with any of the ligands described even when the reagents are refluxed in pyridine for many hours. This is in line with the pronounced inertness to substitution of Rh^{III} complexes. The presence of two-electron reducing agents however is known to facilitate substitution through the production of Rh^{II} or Rh^{I} species [3] and subsequent catalysis. Zinc is believed to function in this way. A complete picture of the chemistry of the synthetic method has not so far emerged but the following observations are of note:

(a). In general, the yield of $[RhSBPy_2]^+$ compounds is highest when the amount of zinc added is equal to or greater than the equivalent amount of Rh. In the Salen reaction the yield of RhSalenPyCl is greater than that of $[RhSalenPy_2]^+$ when Zn < Rh but the yields are gradually reversed as the amount of Zn is increased above the equivalent amount of rhodium. When Salphen reacted using

* Protonated ligands will be referred to as $SalphenH_2$, etc., and the dianions as Salphen, etc.

an amount of Zn less than the equivalent amount of Rh the cation $[RhSalphen\text{-}Py_2]^+$ was obtained together with unreacted $[RhPy_4Cl_2]Cl$.

(b). The reactions using excess Zn proceed either in the presence of air or after degassing the solutions at the boiling point of pyridine with a stream of nitrogen. This suggests that if substitution is aided by an initial reaction with a Rh^I compound subsequent oxidation to Rh^{III} need not involve oxygen. One possible route may involve formation of the reactive and labile species $[RhPy_4]^+$ [3,4] by Zn reduction of $[RhPy_4Cl_2]^+$, which can react with SBH_2 to give $[RhSB]^-$. Such species could then be oxidised to the final products $[RhSBPy_2]^+$ or [RhSBPyCl]. A bridged-complex oxidative mechanism (eqn. 1) similar to that proposed for the Rh^I catalysed [5] substitution of $[Rh(H_2O)Cl_5]^{2-}$ by pyridine to give *trans*-$[RhPy_4Cl_2]^+$ could account for the formation of compounds such as RhSBPyCl since the inert character of the d^6 Rh^{III} ion would cause the retention of the bridging halide ion in the coordination sphere of the newly-formed Rh^{III} complex. Indeed, RhSalenPyCl does not exchange Cl for Py even on prolonged boiling in pyridine in the presence or absence of zinc, so that subsequent displacement of Cl by pyridine does not seem a feasible final step. Such bridged transition states are also believed to be of importance in Pt^{II} catalysis of substitution reactions with Pt^{IV} [6].



However an alternative oxidative mechanism must operate in order to form $[RhSBPy_2]^+$ species and to account for the fact that RhSBPyCl compounds are not produced in reactions involving Salphen and related ligands. Preliminary experiments suggest that Zn^{2+} ions could play a role in such oxidations when oxygen is absent.

Stereochemistry of the complexes

Six-coordinate complexes of the type $L_2M(SB)$, (SB = tetradentate ligand), may exist in three geometrical isomeric forms (Fig. 2). The *cis-α* isomer is unknown for tetradentate Schiff base complexes and it has been suggested [7] that such ligands cannot form stable compounds with this degree of distortion. The compounds Co^{III}Salen(Bzac) [7] and Co^{III}Salen(Acac) [8] have been shown to have the *cis-β* isomeric structure and other examples of related compounds have been reported [9,10]. There are however no cases so far established by X-ray structural determinations where complexes containing a tetradentate Schiff base ligand together with two monodentate ligands give the *cis-β* isomer. The most common arrangement has the tetradentate ligand occupying the equatcrial plane with two axial ligands in the *trans* position [11].

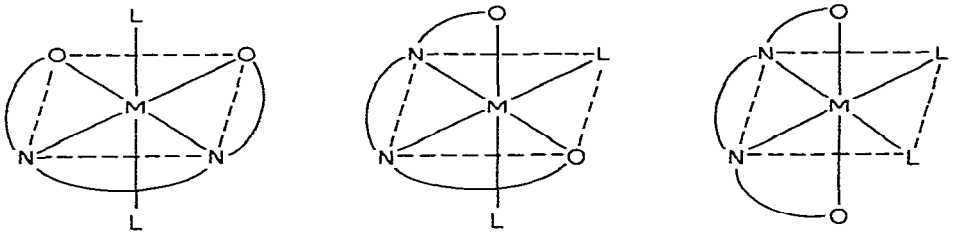


Fig. 2. Geometric isomers of complexes of the type $L_2M(SB)$.

A PMR study [10] of the complexes $L_2Co(SB)$, (SB = Salen or Acacen*, L_2 = a bidentate ligand or two monodentate ligands), has shown that the planar and *cis-β* arrangements are readily distinguished. The symmetry of the planar isomer causes the groups attached to the carbon atom of the azomethine links to be equivalent —RC=N—, R = H for Salen and CH_3 for Acacen. Thus a single resonance is observed for such protons when the Schiff base occupies the equatorial plane (the "*trans*" isomer) whilst the lower symmetry of the *cis-β* isomer results in two resonances being observed. The absorptions of the protons of the ethylenediamine residue in the ligand also become complex on the adoption of the *cis-β* configuration. Such criteria may need to be used with caution however since the proton spectrum [12] of $(CH_3)_2Sn$ Salen in solution is consistent with a *cis-β* configuration while in the solid state [13] the compound is reported to have *trans* methyl groups with the Schiff base occupying the equatorial plane. It remains to be determined whether the Sn compound isomerizes in solution.

The PMR spectra of the tetradentate complexes (Table 1) show only a single resonance, split by $^{103}Rh—^{1}H$ coupling, for the azomethine proton except for the complex derived from 3,4-diaminotoluene where two absorptions are observed due to the inherent asymmetry of the ligand. These observations indicate a planar arrangement of the ligand with *trans* pyridine ligands. The complexity of the methylene absorptions for the compounds derived from 1,3-diaminopropane and 1,4-diaminobutane is probably due to minor distortions of the carbon chain giving slightly non-equivalent protons and resulting in complex spin—spin interactions.

The situation is more complicated for the bidentate Schiff base complexes. There are now five possible isomers, three of them being optically active. In the PMR spectrum of the complex ion $[Py_2Rh(Sal\text{-}N\text{-}p\text{-}tol)_2]^+$, the observation of a single absorption for the methyl group of the *p*-tolyl moiety (δ 2.06 ppm) together with a single absorption split by $^{1}H—^{103}Rh$ coupling for the azomethine proton (δ 8.19 ppm, $J \simeq 2$ Hz), is consistent with the presence of a single isomer in which the two Schiff base ligands are equivalent. In contrast, there appear to be at least two isomers of $[Py_2Rh(Sal\text{-}N\text{-}Me)_2]^+$ produced. Two methyl resonances are observed (δ 3.44, 3.70 ppm) and the signals are in the ratio of 3/1. This indicates that the compound does not consist solely of a single isomer with non-equivalent methyl groups as would be expected for a 1/1 ratio. It must be concluded

* Acacen = *N,N'*-ethylenebis(acetylacetoneimine).

TABLE 1

PMR SPECTRA[a] OF THE COMPLEXES $[Py_2RhSB]PF_6$

Complex	H>C=N[b]	Assignment		Other
		Aromatic + Pyridine[c]		
B = CH_2CH_2	8.64 (2)	6.45-8.41	(18)	CH_2 4.35 (4)[d]
$\alpha\ \beta\ \alpha$ $CH_2CH_2CH_2$	8.23 (2)	6.33-8.61	(18)	$\alpha(CH_2)$ ca. 4.0 (4)[c] $\beta(CH_2)$ ca. 2.3 (2)[c]
$\alpha\ \beta\ \beta\ \alpha$ $CH_2CH_2CH_2CH_2$	Obscured	6.48-8.55	(20)[e]	$\alpha(CH_2)$ ca. 4.2 (4)[c] $\beta(CH_2)$ ca. 1.1 (4)[c]
	8.26[f]			
1,2-C_6H_4	9.35 (2)	6.49-8.58	(22)	
4-(CH_3)-1,2-C_6H_3	9.35 (1) 9.30 (1)	6.49-8.45	(21)	CH_3 2.51 (3)[d]
4,5-$(CH_3)_2$-1,2-C_6H_2	9.29 (2)	6.49-8.32	(20)	CH_3 2.44 (6)[d]
R = p-$CH_3C_6H_4$	Obscured	6.42-8.66	(14)[e]	CH_3 2.10 (3)[d]
	8.19[g]	6.36-8.43	(14)[e,g]	CH_3 2.06 (3)[d,g]
CH_3	8.14[c]	6.45-8.66	(20)[e]	CH_3 3.44[h] (ca. 4.5) 3.70[h] (ca. 1.5)

[a] Spectra recorded in acetone-d_6 unless otherwise specified. Chemical shifts expressed in ppm from TMS (δ 0 ppm) as internal reference. Integrated areas are given in parentheses. [b] Doublet, $J(^{103}Rh—^1H) \simeq 2$ Hz. [c] Complex pattern. [d] Singlet. [e] Includes azomethine proton(s). [f] In pyridine-d_5. [g] In DMSO-d_6. [h] Shows some fine structure.

that a mixture of isomers is present which also accounts for the observed complex azomethine proton spectrum at δ 8.14 ppm.

In both cases it is impossible, at this stage, to determine which of the possible isomers is present and further work to this end is currently in progress.

Organometallic derivatives

Organometallic derivatives of the type R—RhSalenPy (R = alkyl) have previously [1] been prepared by the reaction of an alkyl halide with reduced Rh species produced from RhSalenPyCl either by prolonged reduction with excess sodium amalgam in dry, degassed tetrahydrofuran (THF) or by reduction with $NaBH_4$ in the presence of $PdCl_2$ in degassed, strongly alkaline, aqueous methanol. The cationic compounds $[Py_2RhSB]PF_6$ (SB = Salen, Sal-1,3-pn, Salphen) have been found to undergo similar reactions.

Reduction of a solution of the cationic complexes in THF by 0.5% Na(Hg) with 2 moles of Na per Rh, rapidly gives brown (SB = Salen), red/brown (SB = Sal-1,3-pn) or green-blue (SB = Salphen) solutions, presumably containing species such as $Na[Rh^ISB]$. The addition of methyl iodide results in an immediate change to orange, yellow or red solutions (SB = Salen, Sal-1,3-pn, Salphen respectively) and the appropriate Rh—CH_3 derivatives can be isolated from the reaction mixture. Reduction of the Salen and Salphen complexes by $NaBH_4$ and Pd^{2+} followed by reaction with methyl iodide also gives the methyl derivatives. As with the previous report [1], the use of Na(Hg) is more convenient experimentally.

TABLE 2

PMR SPECTRA[a] OF THE ORGANOMETALLIC DERIVATIVES CH_3MSBPy

Compound		H>C=N	Assignment		M—CH_3	Other
M	SB		Aromatic + Pyridine[b]			
Rh	Salphen	9.12[c] (2)	6.40-8.34	(17)	0.65 (3)[c]	
	Salen	8.25[c] (2)	6.26-8.44	(13)	0.93[c] (3)	CH_2 3.68 (4)[d]
	Sal-1,3-pn	7.98[c]	6.25-8.54	(15)[e]	1.36[c] (3)	$\alpha(CH_2)$ 3.70 (4)[b]
						$\beta(CH_2)$ 1.80 (2)[b]
Co	Salphen	8.71 (2)[d]	6.33-9.10	(17)	2.18[d]	
	Salen[f]				2.22[d]	

[a] Spectra recorded in dimethylsulphoxide-d_6. Chemical shifts expressed in ppm from TMS (δ 0 ppm) as internal reference. Integrated areas are given in parentheses. [b] Complex pattern. [c] Doublet, $J(^{103}Rh—^1H) \simeq 2$ Hz. [d] Singlet. [e] Includes azomethine proton. [f] From ref. 14.

The ^1H NMR spectra of the methyl derivatives (Table 2) exhibit a characteristic splitting of the methyl resonance by $^{103}Rh—^1H$ coupling ($J \simeq 2$ Hz) thereby confirming the existence of a metal—carbon bond. The planar arrangement of the Schiff base ligand is also indicated by the presence of a single azomethine proton resonance, again split by coupling to the rhodium nucleus. The structure of the derivatives is, therefore, an octahedral monomeric unit with a square planar ligand and the methyl group *trans* to the pyridine ligand.

The doublet at δ 8.25 ppm ($J \simeq 2$ Hz) in the spectrum of CH_3 RhSalenPy is assigned as the azomethine proton absorption and differs from the previous assignment [1]. The doublet at δ 8.44 ppm, previously assigned as the azomethine proton*, is due to the α protons of the pyridine ligand, the value of the coupling constant ($J \simeq 5$ Hz), supporting this assignment. The basic doublet arises because of coupling between the α and β protons and there is fine structure also present resulting from further spin interactions with the proton in the γ position.

The magnitudes of chemical shifts (Table 2) of the methyl group attached to the metal ion in the complexes CH_3RhSBPy (SB = Salen, Salphen) are considerably smaller than for the analogous cobalt compounds [14] which is in contrast to the related derivatives $CH_3M(DMG)_2 \cdot H_2O$ (M = Co, Rh; DMG = anion of dimethylglyoxime) where the absorptions occur at the same value, viz: δ 0.64 ppm [15]. Modifications to the electronic environment of the metal ion and consequently of the methyl group by the equatorial ligand thus appear to be more important with salicylaldimine ligands than with dimethylglyoxime. However, in the absence of details of the shielding mechanism, it is not possible to determine which of a number of effects is responsible for the differences in chemical shift. It is also interesting to note that variation of the salicylaldimine ligand in the rhodium derivatives produces a larger variation in the methyl group

* It is necessary to reassign the absorptions previously reported [1] due to azomethine protons in the organorhodium derivatives R—RhSalenPy (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, σ-C_3H_5, $C_6H_5CH_2$, and CH_3CO) as resonances due to α-protons in pyridine. The correct values for azomethine proton absorptions are thus: CH_3, 8.25; C_2H_5, 8.22; n-C_3H_7, 8.24; i-C_3H_7, 8.23; n-C_4H_9, 8.23; σ-C_3H_5, 8.25; $C_6H_5CH_2$, 8.12; CH_3CO, 8.36. The coupling constants $J(^{103}Rh—^1H)$ are all of the order of 2 Hz.

onances than in the cobalt complexes. However, more examples need to be died in both series before this can be established as a general trend.

perimental

Nitrobenzene for conductivity measurements was of B.D.H. (A.R. grade). All er solvents were of reagent grade and, except for THF, were used without ther purification. THF was dried and stored as previously described [1] and illed, under N_2, directly into the reaction vessel as required.

Anhydrous rhodium trichloride was supplied by ROC/RIC Chemicals. ier chemicals were of reagent grade and were used without further purifica-1.

$[RhPy_4Cl_2]Cl \cdot 5H_2O$ was prepared by the published method [2] using an-lrous rhodium trichloride instead of the hydrated halide.

Analytical data and yields are listed in Table 3.

LE 3

LYTICAL DATA AND YIELDS

pound	Colour	Formula	Analysis found (calcd.) (%)					Yield (%)
			C	H	N	P	F	
$^{2}y_2RhSB]PF_6$								
3 Salphen	Orange	$RhC_{30}H_{24}N_4O_2PF_6$	50.03 (50.01)	3.36 (3.36)	8.03 (7.78)	3.9 (4.3)	16.0 (15.8)	70
Sal-4-Me-phen	Red	$RhC_{31}H_{26}N_4O_2PF_6$	50.64 (50.69)	3.46 (3.58)	7.75 (7.63)	4.1 (4.2)	15.0 (15.5)	75
Sal-4,5-Me-phen	Orange	$RhC_{32}H_{28}N_4O_2PF_6$	51.19 (51.34)	3.96 (3.78)	7.41 (7.49)	4.3 (4.1)	14.9 (15.2)	80
Salen	Yellow	$RhC_{26}H_{24}N_4O_2PF_6$	46.44 (46.44)	3.65 (3.60)	8.20 (8.33)	4.4 (4.6)	16.6 (16.9)	54
Sal-1,3-pn	Yellow	$RhC_{27}H_{26}N_4O_2PF_6$	47.39 (47.24)	4.18 (3.83)	7.93 (8.16)			35
Salbn	Yellow	$RhC_{28}H_{28}N_4O_2PF_6$	48.03 (48.00)	4.12 (4.04)	7.80 (8.00)			40
$y_2Rh(Sal{=}N{-}R)_2]PF_6$								
p-$CH_3C_6H_4$	Yellow	$RhC_{38}H_{34}N_4O_2PF_6$	54.96 (55.21)	4.13 (4.15)	6.63 (6.78)	3.7 (3.8)	13.4 (13.8)	68
CH_3	Yellow	$RhC_{26}H_{26}N_4O_2PF_6$	45.07 (46.30)	3.98 (3.89)	8.31 (8.04)			73
$RhSBCl$								
Salen[a]	Yellow							83
Sal-1,3-pn	Yellow	$RhC_{22}H_{21}N_3O_2Cl$	53.21 (53.07)	4.35 (4.26)	8.35 (8.44)	Cl = 7.1 (7.1)		25
Salbn	Yellow	$RhC_{23}H_{23}N_3O_2Cl$	53.67 (53.97)	4.42 (4.54)	8.16 (8.21)	Cl = 7.0 (6.9)		28
$_3RhSBPy$								
Salen[a]	Orange							65
Sal-1,3-pn	Yellow	$RhC_{23}H_{24}N_3O_2$	57.62 (57.86)	5.08 (5.08)	8.89 (8.80)			75
Salphen	Red	$RhC_{26}H_{22}N_3O_2$	60.86 (61.06)	4.56 (4.34)	7.81 (8.22)			85

ously reported, see ref. 1.

Synthesis of the complexes

Pyridine (25 ml) was heated to just below its boiling point and then SalphenH$_2$ (0.26 g, 0.83 mmole), Zn dust (ca. 0.1 g, 1.5 mmole) and RhPy$_4$Cl$_3$·5H$_2$O (0.50 g, 0.81 mmole) were added in succession. The mixture was boiled and stirred for a few minutes then allowed to cool. On addition of the rhodium compound, the yellow solution rapidly became red and darkened further on boiling. After cooling, the reaction mixture was filtered, evaporated to dryness and residue extracted with boiling water (2 × 75 ml portions) to give an orange solution from which [Py$_2$RhSalphen]PF$_6$ was precipitated by the addition of aqueous KPF$_6$. The precipitate was collected, washed with water, recrystallized by the slow concentration of an acetone/methanol/water solution and dried under vacuum over P$_2$O$_5$.

The other complexes were obtained similarly. Two moles of bidentate ligand per rhodium were used for these preparations.

The compounds are all soluble in acetone, dimethylsulphoxide and halocarbon solvents, less so in alcohols and, except for the Salphen derivatives, noticeably soluble in hot water. They are all insoluble in hydrocarbon solvents*.

The derivatives all have conductivities in nitrobenzene in the range expected for 1/1 electrolytes [16].

The complexes PyRhSBCl (SB = Salen, Sal-1,3-pn, Salbn) can be obtained by boiling the residue from the aqueous extraction with methanol (ca. 50 ml) and filtering the insoluble complex.

Synthesis of the organometallic derivatives

All operations until after the addition of methyl iodide were performed with the reaction mixture protected from the air by nitrogen.

(a). Na(Hg). A solution of [Py$_2$RhSB]PF$_6$ (SB = Salen, Sal-1,3-pn, Salphen) in dry degassed THF (ca. 50 ml) was mechanically shaken with 0.5% Na(Hg) (2 moles Na/Rh) for 4 h to give an extremely air sensitive solution. After about 30 min, no further colour change was observed. After the removal of the spent amalgam, methyl iodide and pyridine were added (in slight excess) to give a solution of the product CH$_3$—RhSBPy. The THF was removed and the residue crystallized from MeOH/H$_2$O and washed with water. The derivatives (CH$_3$)RhSBPy (SB = Sal-1,3-pn, Salphen) were recrystallized from CH$_2$Cl$_2$/pyridine/heptane, washed with hexane, and the micro crystalline material thus obtained dried in the air.

(b). NaBH$_4$. [Py$_2$RhSB]PF$_6$ (SB = Salen, Salphen) (100-150 mg) was dissolved in degassed methanol (ca. 50 ml) and a degassed 50% aqueous KOH solution (20 ml) added. On the addition of excess NaBH$_4$ (0.5 g) and 5% Na$_2$PdCl$_4$ solution (4 ml), the reaction mixture rapidly darkened to give an air sensitive solution which was stirred for 10 min. On the addition of CH$_3$I, the solution rapidly lightened. After filtration of the reaction mixture and precipitation of the methyl derivative by the addition of water to the filtrate, the derivatives were obtained as above. Yields varied (10-40%) and the Na/Hg method is the preferred synthetic procedure.

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* Attempts to crystallize the compounds from acetone/benzene lead to the occlusion of benzene.

The compounds are soluble in methanol, pyridine, dimethylsulphoxide and halocarbon solvents, less so in benzene and diethyl ether and insoluble in water and hexane.

Instrumentation

^{1}H NMR were recorded on a Varian HA 100 spectrometer. Conductivity measurements were made using a Wayne—Kerr bridge.

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