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SYNTHESIS OF A NEW CLASS OF ACYLPLATINUM COMPLEXES DERIVED FROM SALICYLALDEHYDE

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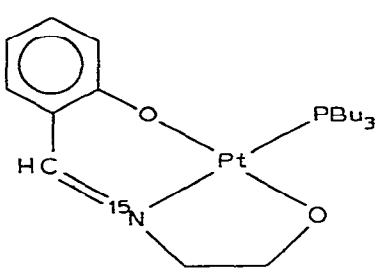
Summary

The synthesis of a new class of acylplatinum complexes of composition $[Pt(OC_6H_4CO)L_aL_b]$ $L_a = L_b = PR_3$, $P(OR)_3$, $Ph_2PCH_2CH_2PPh_2$, AsR_3; L_a = 2-picoline, 3-picoline, 4-picoline, $^{15}NH_2(CH_2)_5CH_3$, L_b = DMSO, is described. The complexes are synthesized from *o*-hydroxybenzaldehyde (salicylaldehyde) and K_2PtCl_4 and contain an organic chelating ligand bound to platinum via the phenolic oxygen and the aldehyde carbon. ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR data for the new complexes are reported.

Introduction

During the preparation of the complex $[Pt(OC_6H_4CH{=}^{15}NCH_2CH_2O)P(n\text{-}Bu)_3]$ (I) containing the dianic form of the ligand II, we observed the formation of a new acylplatinum complex which we were able to characterize as



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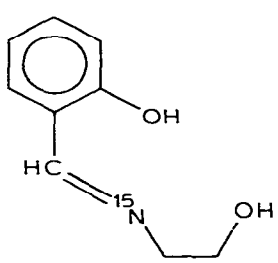

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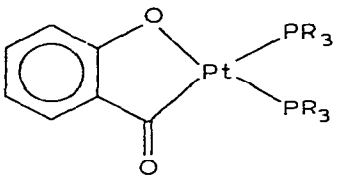
$[Pt(OC_6H_4CO)(P(n\text{-}Bu)_3)_2]$ (III) [1]. The complex III (R = n-Bu) arises from the reaction of unreacted salicylaldehyde (IV) with K_2PtCl_4 in dimethylsulfoxide, followed by further reaction with two equivalants of tertiary phos-



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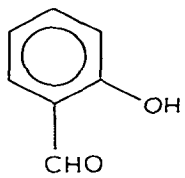
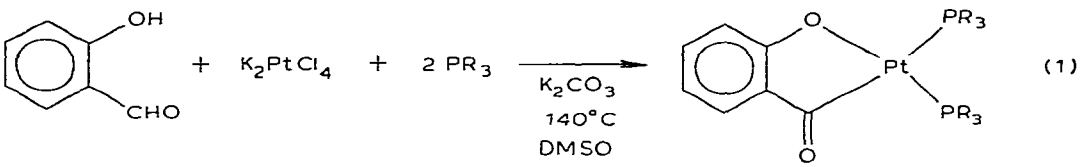


(IV)

phine. When the reaction is repeated using stoichiometric quantities of salicylaldehyde and K_2PtCl_4 (eq. 1), an excellent yield of the acyl-platinum complex III is obtained. Since the activation of an organic aldehyde by a transition



(1)

(III)

metal has relevance within the framework of the hydroformylation reaction [2], we have begun a study of this reaction in some detail and now present an extension of our preliminary report [1].

Experimental

NMR spectra were measured using a Bruker HX-90 spectrometer operating in Fourier transform mode. The data are given for $CDCl_3$ solutions. ^1H, ^{13}C, ^{31}P and ^{195} Pt NMR spectra were measured at 90.0, 22.6, 36.4 and 19.3 MHz, respectively. In one case a 360 MHz ^1H NMR spectrum was measured (see text). IR spectra were measured as CsCl pellets using a Beckman 4260 spectrometer. Microanalytical and molecular weight measurements were provided by the ETH analytical laboratory.

The complexes were all synthesized by the reaction of K_2PtCl_4 (Johnson-Matthey) with salicylaldehyde and two moles of added ligand in DMSO. The solvent functions as a ligand and this influences the work-up to some extent. A typical procedure for the synthesis of the complexes $[Pt(OC_6H_4CO)L_2]$, L = PR_3, $P(OR)_3$, AsR_3, is shown below and is followed by a typical preparation when L is a nitrogen ligand.

Preparation of $[Pt(OC_6H_4CO)(PPh_3)_2]$

Solid K_2CO_3 (420 mg, 3.0 mmol) was added to a solution of K_2PtCl_4 (415 mg, 1.00 mmol) in 5 ml DMSO at 100°C. To the resulting suspension was added a solution of salicylaldehyde (122 mg, 1.00 mmol Fluka puriss) in 5 ml DMSO, followed by heating to 140°C for 40 min. The suspension which remained was then cooled to 100°C and treated with solid PPh_3 (525 mg, 2.00 mmol) (liquid ligands were added via a syringe). Stirring at 100°C for ten min-

utes was follwed by cooling to 50° C and removal of the DMSO in vacuum (ca. 10^{-2} Torr). The residue was extracted with CH_2Cl_2 until the extract was colorless, and the solution treated with active charcoal. Filtration of the CH_2Cl_2 suspension through Celite was followed by concentration to afford crude product as an oil. This was then suspended in ether to afford a yellow powder which was filtered and dried under vacuum.

The following [$Pt(OC_6H_4CO)(L)_2$] complexes were prepared using this method (L, yield (%), form (recrystallization solvent): PPh_3, 86, yellow crystals (ether); P(*p*-$CH_3C_6H_4)_3$, 75, yellow crystals (acetone ether); P(n-Bu)$_3$, 90, yellow oil; PPh_2CH_2Ph, 84, Yellow powder; $Ph_2PCH_2CH_2PPh_2$, 95, yellow crystals (ether); P(OEt)$_3$, 87, yellow oil; P(On-Bu)$_3$, 82, yellow oil; P(Oi-Pr)$_3$, 84, yellow powder; $AsPh_3$, 66, yellow powder; $AsMePh_2$, 71, yellow powder.

Preparation of [Pt(OC$_6$H$_4$CO)(4-CH$_3$C$_5$H$_4$N) (DMSO)]

The procedure followed was identical to that described above until completion of the heating at 140° C for 40 minutes [K_2PtCl_4 (295 mg, 0.7 mmol) in 3.5 ml DMSO; K_2CO_3 (100 mg, 0.7 mmol); Salicylaldehyde (0.4 mg, 0.77 mmol) in 3.5 ml DMSO]. After this point the mixture was cooled to 50° C and the DMSO removed under vacuum. The residue was then treated dropwise with 15 ml CH_2Cl_2 containing 4-$CH_3C_5H_4N$ (143 mg, 1.54 mmol). Stirring for 30 min was followed by filtration. The resulting solution was treated with active charcoal and worked-up as described above.

The following [$Pt(OC_6H_4CO)(L)(DMSO)$] complexes were prepared using this method (L, yield (%)): 4-picoline, 53; 3-picoline, 66; 2-picoline, 66; $NH_2(CH_2)_5CH_3$, 73; $^{15}NH_2(CH_2)_5CH_3$, 67 (all as yellow powders).

The complex [$Pt(OC_6H_4CO)(NH_2CH_2CH_2NH_2)$] was prepared as described for the 4-picoline, DMSO complex, except that the work-up involved washing with water instead of extracting with CH_2Cl_2. The solid residue, which was then free of water-soluble salts, was washed with ether to afford the product as a yellow powder (57% yield). The product is not very soluble in CH_2Cl_2.

Preparation of K[Pt(OC$_6$H$_4$COCl(DMSO)]

This complex was prepared as described above (without PPh_3) as far as the addition of CH_2Cl_2. Since the anionic complex was not soluble in this chlorohydrocarbon, extraction was with acetone. The remainder of the work-up is as described above.

K_2PtCl_4 (415 mg, 1.00 mmol) and salicylaldehyde (122 mg, 1.00 mmol) afforded 375 mg of product (80%) as yellow-green crystals. The ^{1}H NMR spectrum showed ~0.75 equivalents of free DMSO.

Results and discussion

1. Characterization

Salicylaldehyde reacts with K_2PtCl_4 in DMSO at 140° C to form a complex which, in a second step, reacts with either an aliphatic or aromatic tertiary phosphine to afford the acyl complexes III as yellow air-stable solids *.

* In a few cases only oils could be isolated; see Experimental.

TABLE 1

ANALYTICAL DATA FOR THE ACYL COMPLEXES

[Pt(OC$_6$H$_4$CO)L$_a$L$_b$]		Analysis found (calcd.) (%)					
L_a	L_b	C	H	P	S	N	
P(n-Bu)$_3$	P(n-Bu)$_3$ — (CO) [b]	50.42 (51.73) (50.06)	7.93 (8.12)				703 (720)
P(*p*-CH$_3$C$_6$H$_4$)$_3$	P(*p*-CH$_3$C$_6$H$_4$)$_3$ — (CO) [b]	62.38 (63.70) (62.40)	5.19 (5.02)				893 (924)
PPh$_3$	PPh$_3$ — (CO) [b]	60.56 (61.50) (60.07)	4.18 (4.08)				805 (840)
Ph$_2$PCH$_2$Ch$_2$PPh$_2$		55.29 (55.24)	3.92 (3.96)				692 (714)
Cl	DMSO	25.68 (23.11)	2.75 (2.15)				
PPh$_2$CH$_2$Ph	PPh$_2$CH$_2$Ph	61.55 (62.28)	4.34 (4.41)	6.93 (7.14)			
P(Oi-Pr)$_3$	P(Oi-Pr)$_3$	40.91 (41.04)	6.35 6.35	8.65 (8.46)			
AsPh$_3$	AsPh$_3$	47.37 (49.33)	3.62 (3.76)				
3-picoline	DMSO	37.90 (37.04)	3.88 (3.52)	3.48 (2.88)	6.68 (6.59)		
2-picoline	DMSO	37.29 (37.04)	3.62 (3.52)		6.73 (6.59)	3.06 (2.88)	
3-picoline	3-picoline	46.00 (45.51)	3.61 (3.63)			5.68 (5.59)	
NH$_2$(CH$_2$)$_5$CH$_3$	DMSO	38.28 (36.43)	5.40 (5.10)		6.24 (6.48)	2.87 (2.83)	
NH$_2$CH$_2$CH$_2$NH$_2$		28.59 (28.80)	3.40 (3.22)			7.54 (7.46)	

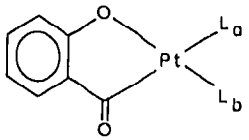
[a] In CH_2Cl_2. [b] There is a tendency towards evolution of carbon monoxide on heating.

Equally successful was the synthesis of III with the chelating disphosphine $Ph_2PCH_2CH_2PPh_2$. The microanalytical, NMR (^1H, ^{13}C, ^{31}P and ^{195}Pt) and IR data (Tables 1—4) are in agreement with the proposed structure, which contains two *cis* phosphine ligands and a chelating organic moiety bound to platinum via the phenolate oxygen and the aldehyde carbon.

The ^{31}P spectra are the most informative in that they immediately reveal the presence of two chemically different phosphine ligands whose ^{31}P spins couple to one another, $^2J(P, P) = 6—10$ Hz. (For P(OR)$_3$ complexes, $^2J(P, P) = 50—54$ Hz). The one-bond coupling constants between platinum-195 (natural abundance = 33.7%) and phosphorus-31 of <1,500 Hz and >4,000 Hz are typical for P *trans* to carbon and oxygen, respectively [3], suggesting very different ligands *trans* to the phosphines. For L = P(n-Bu)$_3$, the 360 MHz ^1H spectrum shows four aromatic protons with the expected [4] coupling patterns

TABLE 2

SPECTROSCOPIC PROPERTIES [a] FOR THE ACYL COMPLEXES CONTAINING PHOSPHORUS LIGANDS

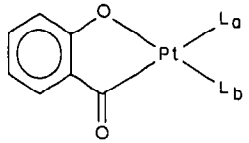


L_a	L_b	$^{31}P_1$	$^{31}P_2$	$^1J(Pt,P_1)$	$^1J(Pt,P_2)$	$^2J(P,P)$	^{195}Pt [b]	CO [c]
$P(n\text{-}Bu)_3$	$P(n\text{-}Bu)_3$	6.7	4.9	1461	4107	9.6	−4304	1615
$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}CH_3C_6H_4)_3$	23.3	18.7	1522	4520	7.4	−4316	1628
PPh_3	PPh_3	24.9	20.7	1491	4543	5.9		1640
PPh_2CH_2Ph	PPh_2CH_2Ph	20.1	13.9	1530	4471	8.8		1625
$Ph_2PCH_2CH_2PPh_2$		37.9	31.2	1490	4224	8.9	−4380	1605
$P(OEt)_3$	$P(OEt)_3$	134.0	83.2	2476	6536	54.0	−4390	
$P(Oi\text{-}Pr)_3$	$P(Oi\text{-}Pr)_3$	130.4	80.3	2529	6573	50.0		1628,1620
$P(On\text{-}Bu)_3$	$P(On\text{-}Bu)_3$	133.7	83.7	2489	6534	54.0		

[a] Chemical shifts are in ppm (H_3PO_4); coupling constants are in Hz. [b] In ppm relative to Na_2PtCl_6 (a low field reference). [c] In cm^{-1}. All band are very strong.

TABLE 3

SPECTROSCOPIC DATA [a] FOR THE DMSO COMPLEXES

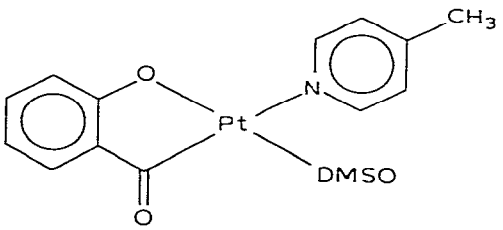


L_a	L_b	δ CH_3(DMSO)	$^3J(Pt,H)$	ν (S—O) [b]	ν (C=O) [b]
4-picoline [c]	DMSO	3.47	38.0	1140, 1130	1635
3-picoline [d]	DMSO	3.55	38.0	1135, 1130	1622
2-picoline [e]	DMSO	3.50	38.0	1140(sh), 1135	1634
$NH_2(CH_2)_5CH_3$	DMSO	3.42	40.0	1140(m), 1128	1630
3-picoline	3-picoline				1630
$H_2NCH_2CH_2NH_2$					1605
$K[Pt(OC_6H_4CO)Cl(DMSO)]$ [f]		3.40	31.5		1625 (1650sh)
$K[PtCl_3(DMSO)]$ [g]		3.60	23.8		
cis-$[PtCl_2(DMSO)P(n\text{-}Bu)_3]$ [h]		3.55	22.7		
trans-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)(DMSO)]$		3.36	19.7		
$[Pt(OC_6H_4CH{=}NCH_2CH_2O)(DMSO)]$ [h,i]		3.30	19.8		
trans-$[PtCl_2(DMSO)P(n\text{-}Bu)_3]$ [h]		3.14	12.4		

[a] Chemical shifts are in ppm (TMS); coupling constants are in Hz. [b] In cm^{-1}. Unless indicated, all bands are very strong. [c] Pyridine methyl at δ 2.34 ppm. [d] Pyridine methyl at δ 2.41 ppm. [e] Pyridine methyl at δ 2.98 ppm, $^4J(Pt,H)$ = 5.7 Hz. [f] In acetone-d_6. [g] In D_2O. [h] In $CDCl_3$. [i] The imine carbon and phenolate oxygen *ortho* to one another.

and no trace of an aldehyde proton. The ^{13}C spectrum of this same complex reveals a signal at δ 224.9 ppm, $^{1}J(^{195}Pt, ^{13}C)$ = 935 Hz. Both the low field position of this carbon resonance and the relatively large coupling to platinum-195 are in keeping with a σ-bonded acyl carbon ligand [5], and this is further supported by the large *trans* two-bond coupling $^{2}J(^{31}P, ^{13}C)$, of 173.7 Hz. There is a strong signal in the IR between 1600 and 1650 cm^{-1} which we assign to ν(C=O), in keeping with the work of Chatt and Booth [6].

The formulation of the complexes containing two arsine ligands, or one DMSO and one nitrogen ligand, is based primarily on the microanalytical, ^{1}H NMR and IR data. Thus, for the $AsMePh_2$ complex $[Pt(OC_6H_4CO)(AsMePh_2)_2]$ we find two CH_3 signals (—60° C, $CDCl_3$) at δ 1.32 and 2.04 ppm resulting from the two non equivalent arsine ligands *. The aromatic protons *ortho* and *para* to the phenolic oxygen always appear at about δ 6.80 and 6.49 ppm, respectively, and are typical for the coordinated OC_6H_4CO moiety and help in the characterization. The remaining aromatic protons are sometimes obscured by resonances from other ligands. The carbonyl stretch appears at 1622 cm^{-1}. For the 4-picoline complex [Pt(OC_6H_4CO)(4-picoline)(DMSO)] we find one CH_3 signal stemming from the substituted pyridine and one CH_3 resonance arising from the coordinated DMSO. This implies that only one of the two isomers V and VI is present in solution. The distinction between these can be made based on the value of $^{3}J(Pt—S—CH_3)$, which is known [7] to be depen-



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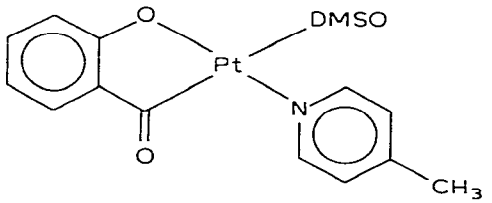


(VI)

dent upon the ligand *trans* to the coordinated sulfur **. The observed value of 38 Hz is relatively large (^{3}J(Pt, H) for *trans*-[$PtCl_2$(DMSO)(P(n-Bu)$_3$)] = 12.4 Hz) and strongly suggests that the DMSO is *trans* to the phenolic oxygen, and therefore that our complex has structure V. Proton NMR data for our DMSO-acyl complexes as well as values for some model DMSO complexes are shown in Table 3. The carbonyl stretch for this acyl complex appears at 1635 cm^{-1}.

2. Reaction intermediates

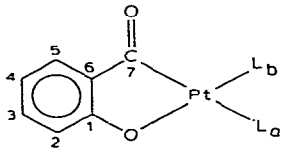
The appearance of coordinated DMSO as well as the sequence of addition of reagents (heating in DMSO, followed subsequently by addition of the ligand L) suggested that the solvent plays an important role in promoting the acylation reaction. In support of this proposition we find that no acyl complex is obtained when either DMF or $CHCl_3$ is used as solvent. To obtain further details

* No ^{195}Pt satellites were observed.

** The IR and NMR data are consistent only with sulfur coordination.

TABLE 4

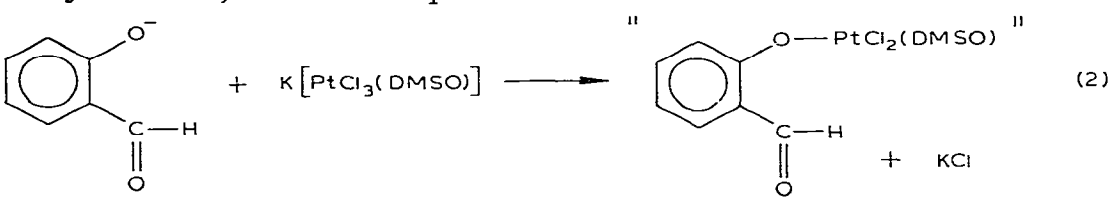
^{13}C DATA FOR SOME ACYL PLATINUM COMPLEXES [a]



L_a	L_b	δ C_1	δ C_2 $J(Pt,C_2)$	δ C_3 $J(Pt,C_3)$	δ C_4	δ C_5 $J(Pt,C_5)$	δ C_6 $J(Pt,C_6)$	δ C_7 $J(Pt,C_7)$
PBu_3	PBu_3 [b]	177.6	116.7 30.1	123.1 10.3	113.7	134.4 14.7	138.5 171.3	224.9 935
$P(OBu)_3$	$P(OBu)_3$ [c]	178.2	117.0 31.5	123.3 8.8	115.0	135.0 14.7	137.9	226.0
$^{15}NH_2R$	DMSO [d]	176.9	115.8 44.9	123.2 16.2	116.2	135.7 19.1	135.8	205.3
4-picoline	DMSO [e]	177.1	116.0 45.6	123.3 16.2	116.0	135.7 19.1	135.7	202.8
$NH_2CH_2CH_2NH_2$ [f]		180.1	114.9	121.4	112.8	132.7	138.0	207.2

[a] Chemical shifts are in ppm (TMS), coupling constants in Hz. The data are for $CDCl_3$ solutions at room temperature. [b] $^2J(P_a,C_7)$ = 173.7 Hz. [c] δ $P_a(OCH_2—)$ = 65.0, δ $P_b(OCH_2—)$ = 66.2 ppm. [d] δ CH_3-(DMSO) = 44.7 ppm, $^2J(Pt,C)$ = 78.0 Hz. [e] δ CH_3(DMSO) = 45.6 ppm, $^2J(Pt,C)$ = 76.5 Hz. [f] δ N_aCH_2 = 43.4 ppm, $^2J(Pt,C)$ = 13.2 Hz. δ N_bCH_2 = 46.5 ppm, $^2J(Pt,C)$ = 43.4 Hz.

on the possible intermediates which are present during the reaction we first studied the reaction of K_2PtCl_4 with DMSO using ^{195}Pt NMR. For our purposes, this method is superior to either ^1H or ^{13}C NMR in that the presence of excess solvent will not obscure smaller resonances derived from coordinated DMSO. The ^{195}Pt NMR spectrum of K_2PtCl_4 in DMSO at probe temperature shows signals at δ −2967 and −3460 ppm which may be assigned to the complexes $K[PtCl_3(DMSO)]$ and *cis*-$[PtCl_2(DMSO)_2]$ [8] with the former representing the major component (ratio: mono DMSO/bis DMSO ~3/1). Increasing the sample temperature to 60°C increases the amount of the anionic complex. At 100°C there is ~90% of the anion and 10% of the neutral compound. This suggested the possibility that $K[PtCl_3(DMSO)]$ might be the species which reacts with the salicylate anion, as shown in equation 2.

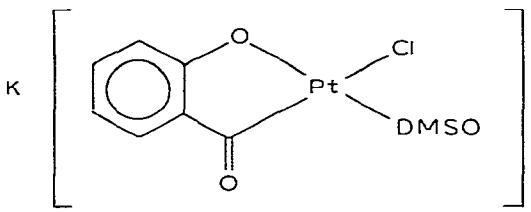


(2)

(VII)

The intermediate phenolate complex, VII, can now undergo a cyclometallation reaction [9,10], since the aldehyde function is held relatively close to the metal. We have been successful in isolating the complex VIII, identified primarily via its ^1H NMR spectrum (see Table 3 and the Experimental for details) which may represent one of the first stable derivatives immediately fol-

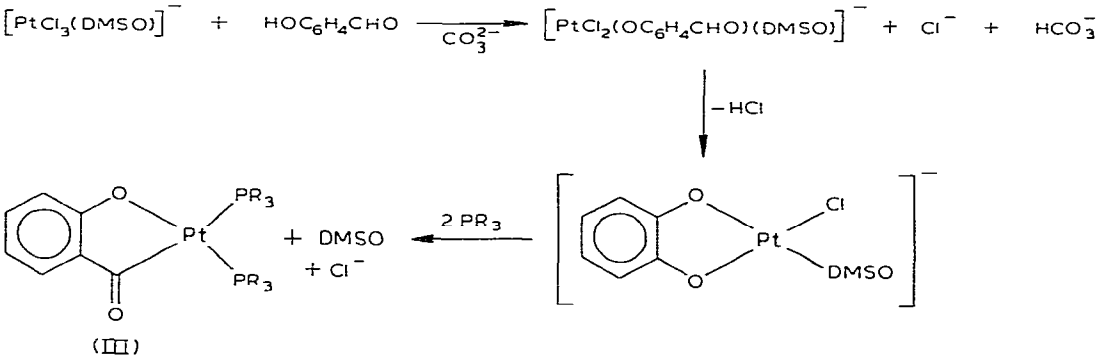
lowing the cyclometallation reaction. Complex VIII can react further with two equivalents of L to afford the complexes III with L = PR_3, $P(OR)_3$, AsR_3).



(VIII)

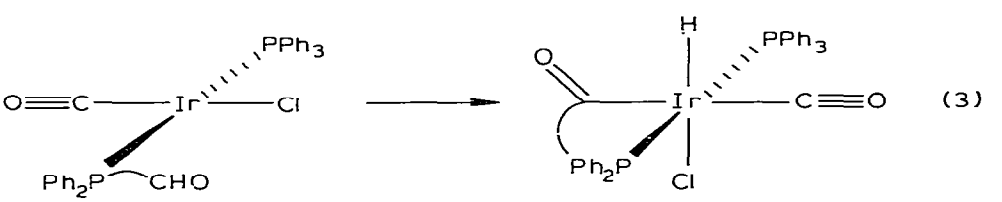
Addition of two equivalents of the methyl pyridine, on the other hand, results only in the displacement of chloride; however, the DMSO can be completely displaced when the complex VIII is treated with a large excess of 3-picoline. Using this approach we have also been able to prepare the bis chelate complex $[Pt(OC_6H_4CO)(NH_2CH_2CH_2NH_2)]$.

Putting our knowledge of these various intermediates together we envisage the following sequence:



(III)

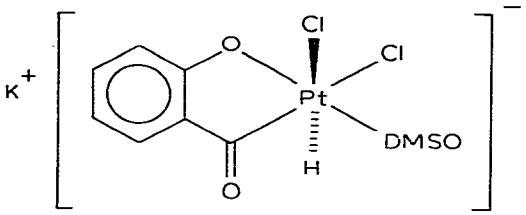
Obviously, we can not exclude the possibility that a bis DMSO complex such as $[PtCl_2(DMSO)_2]$ is actually the first active intermediate, nor do we have further information relevant to the mechanism of the cyclometallation reaction. We do note, however, that a recent study by Rauchfuss [11] has shown that *o*-diphenylphosphinobenzaldehyde oxidatively adds the elements of the aldehyde carbon to iridium(I) to afford an iridium(III) complex, according to equation 3. This suggests a possible intermediate such as IX for our reaction.



(3)

Ph_2P CHO = *o*-diphenylphosphinombenzaldehyde

(The relative orientation of the chloride and DMSO ligands is intuitive, and has



(IX)

no experimental basis.) The complex IX could then reductively eliminate HCl to afford the isolable complex VIII.

3. Further reactions

In view of the ease of preparation of the acyl-phosphine complexes we elected to attempt the conversion of III, L = $P(p\text{-}CH_3C_6H_4)_3$, into the analogue of the well known complexes *trans*-$[PtCl(RCO)(PPh_3)_2]$, recently described in detail by Heck and co-workers [12]. Reaction of $[Pt(OC_6H_4CO)(P(p\text{-}CH_3C_6H_4)_3)_2]$ with ethereal HCl results in protonation of the phenolic oxygen followed by ring opening and chloride ion coordination. The initially formed *cis*-$[PtCl(OHC_6H_4CO)(P(p\text{-}CH_3C_6H_4)_3)_2]$ isomerizes slowly on the NMR time scale to afford the corresponding *trans* isomer. The complex $[Pt(OC_6H_4CO)(Ph_2PCH_2CH_2PPh_2)]$, in which phosphine isomerization is hindered through chelation affords *cis*-$[PtCl(OHC_6H_4CO)(Ph_2PCH_2CH_2PPh_2)]$ under the same conditions. Obviously the presence of the *ortho* hydroxy group does not prevent the formation of arylplatinum complexes similar to those characterized for other tertiary aryl phosphines. We find that our acyl complexes can be made to react with CH_3I and $MeO_2CC{\equiv}CCO_2Me$, and will report these results more fully in the future.

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