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CHELATE ORGANOMETALLIC COMPOUNDS OF NICKEL(II), PALLADIUM(II) AND PLATINUM(II) DERIVED FROM *N*,*N*-DIALKYLBENZYLAMINES

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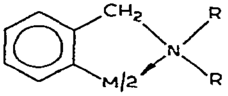
SUMMARY

The preparation of organometallic compounds of nickel(II), palladium(II) and platinum(II) containing two chelate five-membered rings of type (A) (M = Ni,



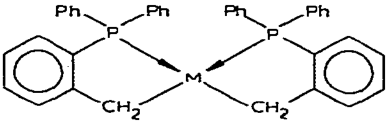
(A)

R = Me; M = Pd, R = Me, Et; M = Pt, R = Me, Et) are described. The platinum(II) derivatives are monomeric, and the corresponding *cis* and *trans* isomers have been characterized. The palladium(II) derivatives are also monomeric, but only the *cis* derivatives have been isolated.

There is a sharp change of reactivity in going from the nickel to the platinum derivatives, as well as of solubility in going from the *N*,*N*-dimethyl to *N*,*N*-diethyl derivatives. The reactions with carbon monoxide have been studied in detail, and several different types of acyl complexes of platinum(II) have been isolated.

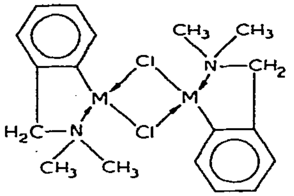
INTRODUCTION

Recently[1] we described the synthesis of chelate organometallic compounds of nickel(II), palladium(II) and platinum(II) of type (I).



(I)

The high stability of these compounds shows that the phosphorus chelation is able to change the unstable benzylic metal–carbon bond present in the non-chelate organometallic compounds of type $[(PR_3)_2MR_2]$ [2-4] into a very stable one. In order to obtain more information on this chelating effect, we have studied the related nitrogen compounds, particularly the metal *ortho*-substituted *N,N*-dialkylbenzylamine derivatives, whose stability was discovered by Bahr in 1963[5]. Monosubstituted compounds of palladium(II) and platinum(II) of the type (II) were prepared by Cope[6] via intramolecular aromatic substitution, involving reaction of alkali tetrachloropalladates and platinates with *N,N*-dimethylbenzylamine.



(II)

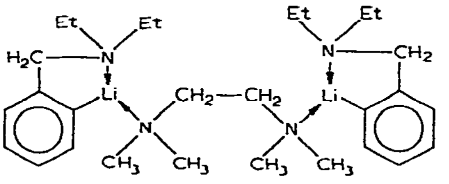
Among related disubstituted organometallic compounds, however, only a tetrahedral palladium disubstituted derivative has so far been reported[7]. In this paper we describe the synthesis and characterization of such compounds.

RESULTS AND DISCUSSION

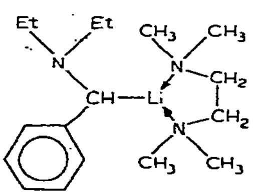
Synthesis of the compounds

Metalation of *N,N*-dimethylbenzylamine (DMBA) in the *ortho* position with n-butyllithium, in diethyl ether at room temperature[8] or in boiling hexane[9] is well known, but under the same conditions there is no metalation of the homologous *N,N*-diethylbenzylamine (DEBA). Such different behaviour reflects the critical importance of the steric requirements in the aggregate-formation step which precedes or is simultaneous with the exchange step.

DEBA can be metalated in the presence of *N,N,N′,N′*,-tetramethylethylenediamine or of sodium or potassium tert-butoxide, but in these cases, owing to the increased ionicity of the metalating agent, the *ortho* directing effect is lost and substitution of the more acidic benzylic protons is preferred. After decomposition with D_2O, NMR analysis of the recovered DEBA shows that in the first case a mixture of the pale yellow *ortho*-derivative, (III), and the dark red benzyl derivative (IV), is formed, while in the presence of sodium or potassium tert-butoxide only benzyl metalation occurs. The required *ortho*-metalated DEBA was prepared by metal–halogen exchange by treatment of *o*-bromo-*N,N*-diethylbenzylamine with either n-butyllithium[10] or with magnesium metal.



(III)



(IV)

TABLE 1

No.	*Compounds*	*Synthesis method*	*Colour*	*M.p.*[a] (°C)	*Mol. wt.*[b] *found* (*calcd.*)	$\mu(D)$
(V)	*trans*-Bis{2-[(dimethylamino)methyl]phenyl}nickel(II)	(a+d)	Lemon yellow crystals			
(VI)	*cis*-Bis{2-[(dimethylamino)methyl]phenyl}-palladium(II)	(a+e)	White needles	180–210	300[c] (374.8)	
(VII)	*cis*-Bis{2-[(diethylamino)-methyl]phenyl}palladium(II)	(b+e)	Colourless prisms	141	442 (430.9)	6.8
(VIII)	*cis*-Bis{2-[(dimethylamino)-methyl]phenyl}platinum(II)	(a+e)	White needles	240–270	405[c] (463.5)	
(IX)	*trans*-Bis{2-[(dimethylamino)-methyl]phenyl}platinum(II)	(a+e)	Colourless rhombic prisms	190–220	470 (463.5)	
(X)	*cis*-Bis{2-[(diethylamino)-methyl]phenyl}platinum(II)	(b+e)	Colourless prisms	176	528 (519.6)	7.1
(XI)	*trans*-Bis{2-[(diethylamino)-methyl]phenyl}platinum(II)	(c+e)	Colourless rhombic prisms	158	514 (519.6)	~0

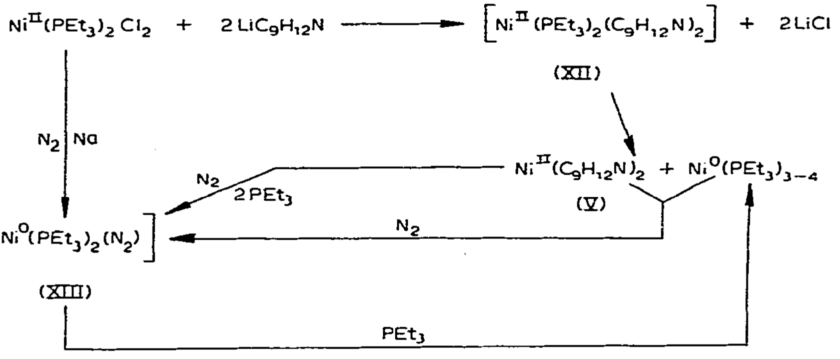
[a] With decomposition. [b] In benzene. [c] In chloroform.

The syntheses of the transition metal derivatives were carried out by treating 2-[(dimethylamino)methyl]phenyllithium (*o*-lithio-DMBA) (a), 2-[(diethylamino)-methyl]phenyllithium (*o*-lithio-DEBA) (b), or 2-[(diethylamino)methyl]phenylmagnesium bromide, (c), with the triethylphosphine (d) or diethylsulfide (e) complexes of the transition metal halides. The reagent used in each case is indicated in Table 1.

The use of complexed halides containing a ligand, which was chosen on the basis of its unreactivity with the starting organo-alkali reagent and its volatility, is necessary in order to produce a homogeneous reaction system.

For the synthesis of bis{2-[(dimethylamino)methyl]phenyl}nickel(II), (V), the reaction conditions are rather critical. The compound (V) is obtained in about 60% yield by treating *trans* $(PEt_3)_2NiCl_2$ with *o*-lithio-DMBA at −80° in tetrahydrofuran under argon, and only in 15–20% yield if the reaction is carried out at 25° in benzene or hexane under argon. Under the latter conditions, use of nitrogen in place of argon gives a red solution from which (V) cannot be isolated. Concentration and cooling of this red solution gives an unstable red solid, and both the solution and the solid product show a strong infrared absorption at 2075 cm^{-1}. On bubbling argon or hydrogen through the red solution, the colour becomes orange and the 2075 absorption band diminishes. This process can be reversed, but addition of triethylphosphine brings about an irreversible disappearance of the nitrogen stretching band. The same band at 2075 cm^{-1} is observed by simple reduction of *trans* $(PEt_3)_2$-$NiCl_2$ with sodium metal under nitrogen, or when pure (V) is treated with two moles of triethylphosphine in the presence of nitrogen gas. All these facts are consistent with the formation of a nickel–triethylphospine–nitrogen complex, tentatively formulated as complex (XIII), shown in Scheme 1, by analogy with the recently reported $Ni[P(c\text{-}C_6H_{11})_3]_2N_2$[11].

SCHEME 1



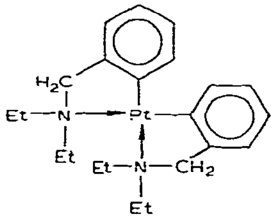
We showed by IR spectroscopy that a pure sample of (V) reacts with two moles of triethylphosphine to give (XIII). Although we have no direct experimental evidence for (XII), this complex is postulated by analogy with the corresponding platinum compound (XIV) (*vide infra*). It is noteworthy that the nitrogen stretching frequency found for the compound (XIII) is similar to that reported for a compound formulated as $[Ni(PEt_3)_2(N_2)H]$ (2075 cm^{-1})[12], although in our case a Ni–H stretching absorption was not be observed.

Treatment of *o*-lithio-DMBA with *trans*-$[(SEt_2)_2PdCl_2]$ gives a brown suspension, from which, after separation of some palladium metal and crystallization, bis{2-[(dimethylamino)methyl]phenyl}palladium(II), (VI), is obtained as long white needles. The low solubility of this compound makes its physico-chemical characterization difficult. However, it differs considerably from the yellow soluble tetrahedral isomer isolated[7] from the reaction between *o*-lithio-DMBA and bis(benzonitrile)-palladium dichloride (*vide infra*). Hoping to obtain a greater solubility by increasing the alkyl groups bonded to the nitrogen atoms, we similarly prepared the bis{2-[(diethylamino)methyl]phenyl}palladium(II), (VII), as colourless prisms, which were, indeed, quite soluble in organic solvents. Similar reaction of *o*-lithio-DMBA with $[(SEt_2)_2PtCl_2]$ gives bis{2-[(dimethylamino)methyl]phenyl}platinum(II) as two distinct isomers, (VIII) and (IX), which could be separated owing to their differing solubilities in benzene. Surprisingly, the corresponding reaction with *o*-lithio-DEBA gives only one isomeric form of bis{2-[(diethylamino)methyl]phenyl}platinum(II), (X). The other isomer, (XI), has been obtained from 2-[(diethylamino)methyl]-phenylmagnesium bromide. Apparently the two syntheses are stereospecific, each giving only one isomeric form.

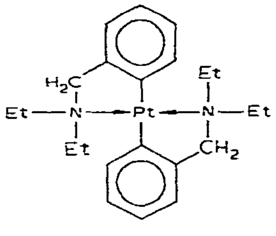
Structural characterization

Owing to the low stability of compound (V) and to the low solubility of compound (VI), we have not been able to characterize the DMBA derivatives, although the featureless NMR spectrum of compound (VI) suggests that it has a square-planar configuration. The DEBA derivative (VII), on the other hand, is very soluble, and complete physico-chemical characterization is possible. Molecular weight measurements of this palladium derivative show it to be monomeric in benzene. The NMR spectrum (in which both the methylenic and the methylic protons are equivalent) and dipole moment measurements (μ 6.8 D) are consistent with a *cis* square-planar structure. This fact, together with the similarity in IR spectra and physico-chemical properties between (VI) and (VIII), suggest that (VI) is also the *cis* isomer. This result is in contrast with the isolation of an isomer formulated as tetrahedral[7] on the basis of its NMR spectrum, which shows that the *N*-methyl protons in the *N,N*-dimethylamine group are non-equivalent and appear as two singlets, at τ 7.52 and 6.56. Moreover, the two protons of each methylenic groups are also non-equivalent and appear as an AB system (τ 7.04 and 6.20, J 10 Hz). We have tried to prepare this isomer by treating *o*-lithio-DMBA with bis(benzonitrile) palladium dichloride, as described in the literature[7], but, surprisingly, the primary product was again the *cis* isomer (VI). We have also isolated a yellow-orange compound as a by-product, and this gives an NMR spectrum very similar to that reported for the tetrahedral isomer. However, both conventional and NMR analyses of this compound agree with the presence of combined benzonitrile in the ligand, and its IR spectrum shows bands at 1605, 701 and 300 cm^{-1}, which are usually absent in the true disubstituted derivatives. Unfortunately, its low yield prevents a better characterization.

The platinum compounds (X) and (XI) are also monomeric, and dipole moment measurements show (X) to be the *cis* square-planar isomer (μ 7.1 D) and (XI) to be the *trans* isomer ($\mu \sim 0$ D)



(X)



(XI)

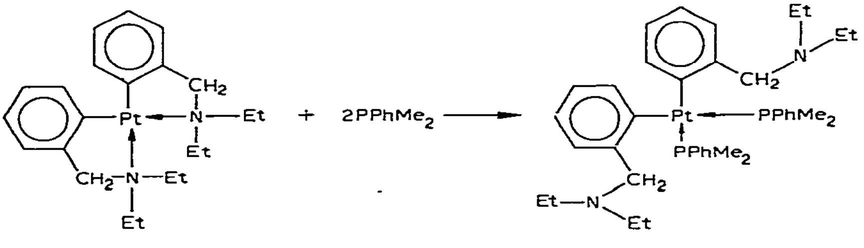
The NMR spectra are consistent with this conclusion. The benzyl protons of the *cis* isomer (X) show a coupling constant $|^3J(\text{Pt–H})|$ of 18.5 Hz, while in the *trans* isomer (XI) this constant is 44.0 Hz. The strength of the Pt–N bond is dependent on the *trans*-substituent and is expected to be stronger in (XI), giving rise to a higher $|^3J(\text{Pt–H})|$. Unfortunately, the methylenic and methyl signals of the ethyl groups are not well resolved and the corresponding coupling constants could not be measured.

These NMR observations can be extended to the less soluble platinum(II) derivatives of DMBA, (VIII) and (IX). In these cases it was possible to measure not only the benzyl protons coupling constants, but also those of the methyl protons. Compound (VIII) shows a $|^3J(\text{Pt–H})|$ of 19 and 14.6 Hz respectively, while in compound (IX) the values are 42 and 45 Hz. This implies the *cis* structure for (VIII) and the *trans* structure for (IX). Scale models of the *cis* isomers indicate some slight distortion of the molecules owing to steric hindrance between the alkyl groups bonded to nitrogen atoms and the aromatic protons *ortho* to the metal.

The IR spectra of compounds (V) to (XI) are consistent with their general formulation, but do not give much further information. The absence of an absorption at about 700 cm^{-1} and the presence of strong absorptions at about 850 and 750 cm^{-1} indicate a disubstituted phenyl ring. Moreover, the presence of an absorption at about 1580 cm^{-1}, which is much stronger than in the free ligand, suggests that there is a direct bond between the phenyl ring and the metal[13]. These structural assignments have been confirmed by studying the differing reactivities of the isomers.

Chemical characterization

All the compounds (V) to (XI) are stable in the solid state at room temperature in an inert atmosphere, although compounds (VI) and (VII) turn black over a period of several months. In solution, (V) decomposes easily on heating. The reactivity of the nickel derivative is shown also by its high sensitivity both to air and protonic solvents as ethanol and water; even the neutral ligand triethylphosphine brings about cleavage of the nickel–carbon bonds, as already discussed. In contrast, the palladium and the platinum derivatives are air stable and do not react with protonic solvents. The NMR spectra of the platinum derivatives (X) and (XI) and of the palladium derivative (VI) are identical in $CDCl_3$ and in perdeuteropyridine, showing that this nitrogen ligand is not able to open the chelate ring. The ring can be opened, however, by addition of the softer ligand dimethylphenylphosphine to (X), complex (XIV) being formed:



(X) (XIV)

That the *cis* structure is preserved in (XIV) is shown by the NMR spectrum, in which the methyl groups of the phosphine appear as a doublet split by ^{195}Pt[14]. It is noteworthy that the benzyl protons appear in the NMR spectrum not as a singlet, but as a complicated multiplet. This could be due to the hindered rotation around the Pt–C bond and perhaps to the interaction of the benzyl protons with the metal. Compound (XIV) can readily be isolated in the crystalline state, and in its stability to air and protonic solvents closely resembles the $(PR_3)_2PtR_2$ compounds discovered by Chatt and Shaw[3]. In solution or in suspension in tetrahydrofuran all the compounds (V) to (XI) react with hydrogen at room temperature and atmospheric pressure. Free metal is formed, and *N,N*-dialkylbenzylamine can be identified by gas-chromatography. Under the same conditions reaction also occurs with carbon monoxide, and the nickel derivative (V) is rapidly converted into $Ni(CO)_4$, which is easily identified by means of the characteristic strong infrared absorption at 2055 cm^{-1}. On the other hand, the palladium derivatives (VI) and (VII) are converted into palladium metal, in agreement with the well known instability of palladium carbonyls.

The *trans* derivatives of platinum (IX), (XI) react with CO in a rather complex way. First one mole of carbon monoxide is absorbed and an infrared band at about 2060 cm^{-1} is observed. Then, in a slower reaction, a second mole of carbon monoxide is absorbed and another new infrared absorption at about 1640 cm^{-1} appears. The

TABLE 2

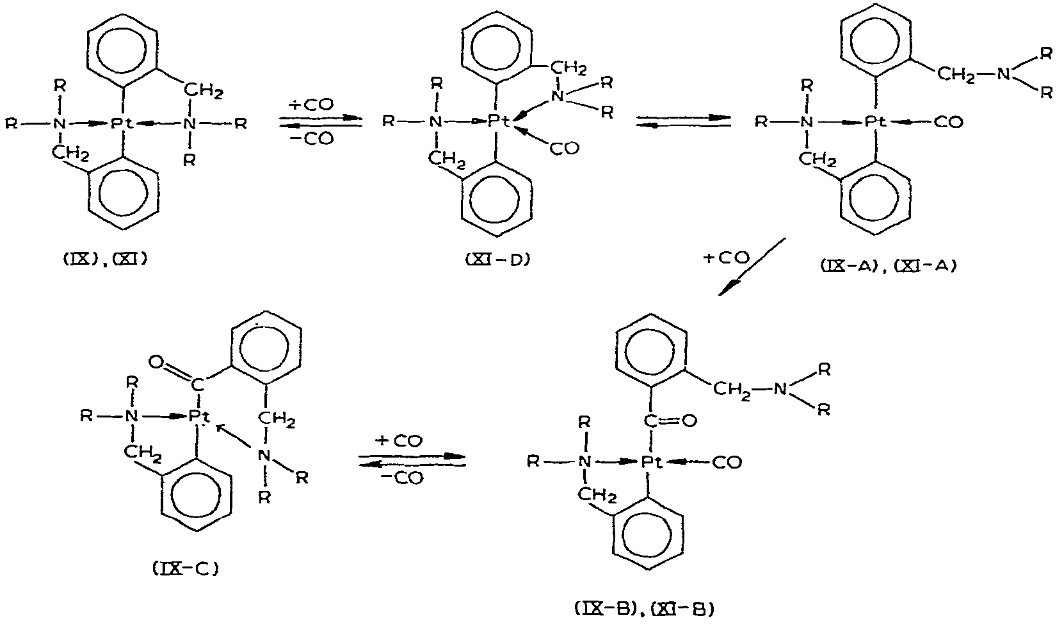
INFRARED STRETCHING FREQUENCIES (cm^{-1}) OF THE CARBONYL AND ACYL DERIVATIVES

Compound	*THF*	*Nujol*
(VIII-A)	2060	
(IX-A)	2065	
(IX-B)	2065–1640	2065–1632
(IX-C)		1606
(X-B)	2050	2050[a]
(XI-A)	2055	2055[a]
(XI-B)	2055–1635	2055–1630[a]

[a] Oil.

SCHEME 2

REACTION OF *trans* DERIVATIVES OF PLATINUM WITH CARBON MONOXIDE



final carbonyl–acyl compound could be isolated in the crystalline state starting from DMBA derivative (IX). It has an infrared spectrum (see Table 2) and analysis in complete agreement with formula (IX-B) of Scheme 2. Furthermore, the NMR spectrum shows that both the methyl and benzyl protons of one nitrogen ligand are still coupled with the platinum atom [$|^3J(\text{Pt–H})|$ of 14.6 and 18.5 Hz], while the protons of the second non-chelate ligand show a chemical shift similar to that of the free ligand, and are not coupled with the platinum atom (Table 3).

TABLE 3

NMR SPECTRAL DATA[a]

Compound	*Solvent*	$(Ph)CH_2-N<$	$>N-CH_3$	$>N-CH_2-C\leqq$	$>N-\overset{\mid}{\underset{\mid}{C}}-CH_3$
Dimethyl-benzylamine	$CDCl_3$	6.64 (s)	7.8 (s)		
Diethyl-benzylamine	CD_3COCD_3	6.52 (s)		7.56 (q)	9.04 (t)
	C_6D_6	6.56 (s)		7.58 (q)	9.05 (t)
(VI)	$CDCl_3$	6.2 (s)	7.42 (s)		
(VII)	$CDCl_3$	6.12 (s)		7.14 (q)	8.82 (t)
(VIII)	$CDCl_3$	6.1 (s, 19)[d]	7.2 (s, 14.6)[d]		
(VIII-A)	$CDCl_3$	6.13 (s, 18.5)[d]	7.22 (s, 14.6)[d]		
(IX)	$CDCl_3$	6.01 (s, 42)[d]	6.94 (s, 45)[d]		
(IX-A)	$CDCl_3$	6.01 (s, 14.6)[d] 6.28 (s)	7.08 (s, 18.5)[d] 7.8 (s)		
(IX-B)	$CDCl_3$	6.02 (s, 14.5)[d] 6.28 (s)	7.05 (s, 18.5)[d] 7.8 (s)		
(X)	CD_3COCD_3	5.98 (s, 18.5)[d]		6.85 (q)[b]	8.73 (t)[b]
(X–B)	CD_3COCD_3	5.85 (s, 19)[d] 6.23 (m)		6.67–6.72 (q)[b] 7.45 (q)	8.5–8.55 (t)[b] 9.0 (t)
(XI)	CD_3COCD_3	6.0 (s, 44.0)[d]		6.93 (m)[b]	8.73 (m)[b]
(XI-B)	CD_3COCD_3	5.89 (s, 16.2)[d] 6.1 (s)		6.8 (q)[b] 7.48 (q)	8.58 (t)[b] 9.0 (t)
(XIV)[c]	C_6D_6	5.8 (m)		7.25 (q)	8.85 (t)

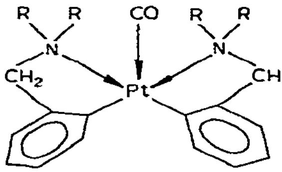
[a] The NMR spectra was recorded at room temperature with TMS as internal standard. The bands are given as τ values. The multiplicity and coupling constants (Hz) are reported in parenthesis. The bands of aromatic protons are omitted. [b] $|^3J(Pt-H)|$ or $|^4J(Pt-H)|$ is very small or complicated. [c] Doublet for the methyl protons of the dimethylphenylphosphine at 9.11 with $J(P-H)$ of ~7.8 Hz split by ^{195}Pt with $|J(Pt-H)|$ of ~18.6 Hz. [d] Singlet with side bands due to the ^{195}Pt.

If at the end of the reaction carbon monoxide is swept out with nitrogen or hydrogen, a different white insoluble compound, which contains only an acyl group, is obtained. Its analysis and IR spectrum are consistent with formula (IX-C) of Scheme 2, although its low solubility prevents a better characterization by NMR spectroscopy.

Further evidence for the reaction scheme has been obtained by studying the NMR spectra during the reaction. Although compound (IX-A) could not be isolated in a pure state, it is of particular significance that the NMR spectrum at this stage, in which only the infrared absorption at 2065 cm^{-1} is present, shows the same pattern as compound (IX-B); this is strong evidence that at this stage only one ligand is chelated to the platinum atom.

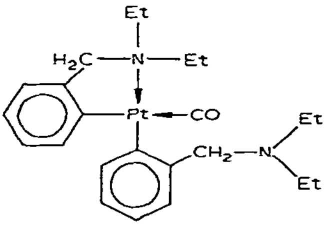
The same course of reaction has been found also for (XI), but the NMR spectrum of (XI-A) is very complex, probably owing to an equilibrium which involves also the intermediate (XI-D). In this case the final product is the carbonyl–acyl compound (XI-B) which was obtained only as an oil; its IR and NMR spectra agree with this formulation.

Reaction of *cis* derivatives (VIII) and (X) with carbon monoxide occurs with absorption of one mole of gas and predominant formation of the adduct (VIII-A) and (X-A), which show strong infrared stretching bands at about 2060 cm^{-1}.



(VIII-A) R=Me
(X-A) R=Et

This square pyramidal structure is in agreement with the NMR spectrum, which indicates that all the *N*-alkyl and benzyl protons are still coupled with the platinum atom, with a $|^3J(\text{Pt–H})|$ similar to that of the starting materials. Neither of the compounds (VIII-A) and (X-A) could be isolated pure. Compound (VIII-A) easily decomposes to the starting material, while compound (X-A) is slowly transformed to compound (X-B):



(X-B)

Scale models provide a reasonable explanation for this last transformation, showing that in (X-A) there is considerable steric hindrance between the ethyl groups. Compound (X-B) was obtained only as an oil, which could not be purified. Its NMR spectrum is quite complex, but agrees with formula (X-B) in that both ethyl and benzyl protons of one nitrogen ligand are still coupled with the platinum atom, while the protons of the second non-chelate ligand show a chemical shift similar to that of the free ligand, and are not coupled with the platinum atom. Moreover, both the methylenic and the methylic protons of the ethyl groups on the nitrogen chelate ligand are split, into two quartets and two triplets respectively, probably as a result of long range shielding by carbon monoxide. In this case, as in (XIV), the benzyl protons of the non-chelate amine appear not as a singlet but a multiplet.

During the reaction with carbon monoxide both *cis* and *trans* isomers give some colloidal platinum carbonyl[15]. This becomes the primary product upon increasing the temperature and pressure of the reaction. Finally reaction of (VIII) with sulfur dioxide gives a red crystalline solid of composition $Pt(C_9H_{12}N)_2 \cdot SO_2$, whose complete characterization was not possible owing to its complete insolubility. The infrared spectrum which shows new absorption bands at 1230, 1185 and 1075 cm^{-1}, indicates that it is a simple SO_2 addition product, similar to (VIII-A).

Conclusions

The stability of the nitrogen chelate organometallic compounds reported in Table 1 recalls the behaviour of the chelate 2,2'-bipyridine alkyl derivatives of palladium[4] and nickel[16,17]. This increased stability parallels that found for phosphorus chelate[1] compared with non chelate[2-4] benzyl derivatives of the same metals. Chatt and Shaw originally proposed that electronic factors are responsible for the stability of the metal–carbon bonds in the planar organometallic complexes, and have stressed the importance of a high ligand field which increases the separation between filled and unfilled molecular orbitals and decreases the ease of promotion of metal–carbon bond electrons to higher energy vacant orbitals. The present results confirm the previously scant evidence[18] that kinetic lability of the ligands is also of great importance. In fact dissociation to an intermediate coordinatively unsaturated species would lead to formation of new unfilled low-energy molecular orbitals which would be easily accessible to the metal–carbon bond electrons.

EXPERIMENTAL SECTION

All reactions of organometallic compounds were carried out under nitrogen or argon in carefully dried and distilled solvents. Diethylsulphide complexes of palladium and platinum dichlorides and the triethylphosphine complex of nickel dichloride were prepared according to literature[20-22] methods.

2-[(Dimethylamino)methyl]phenyllithium was prepared by treatment of *N*,*N*-dimethylbenzylamine with n-butyllithium in refluxing hexane as described by Cope[9]; 2-[(diethylamino)methyl]phenyllithium was obtained (yield 80%) by halogen–metal interchange of *o*-bromo-*N*,*N*-diethylbenzylamine with n-butyllithium, as previously reported for *o*-bromo-*N*,*N*-dimethylbenzylamine by Jones and Hauser[10].

Measurements

Infrared spectra, in the range 4000–250 cm^{-1}, were recorded on a Perkin–Elmer 457 double beam grating spectrophotometer calibrated with polystyrene films. Proton magnetic resonance spectra were recorded at room temperature on 60 MHz Perkin–Elmer R 10 and Jeol C 60 HL instruments, with TMS as internal standard. Molecular weights were determined at 25° in AnalaR solvents, using a Mechrolab vapor pressure osmometer (Model 301 A). Melting points (uncorrected) were measured on samples sealed in evacuated capillaries on a hot stage apparatus. Dipole moments were evaluated by the method of Halverstadt and Kumler[23]; dielectric constants were determined with a W.T.W. Dipolmeter (Model DM 01); the refractive indices with an Abbe refractometer and specific volumes with the usual U-shaped pyknometer.

trans-Bis{2-[(dimethylamino)methyl]phenyl}nickel(II), (V)

A solution of *trans*-$[(PEt_3)_2NiCl_2]$ (2.3 g) in THF (10 ml) was added dropwise at −80° to a stirred suspension of 2-[(dimethylamino)methyl]phenyllithium (1.8 g) in THF (20 ml) under argon. After 1 h of stirring, the yellow suspension was warmed to −20° and evaporated to dryness. The residue was suspended in hexane (10 ml) (red tinge developed), rapidly filtered, and washed repeatedly with 5 ml of hexane until the filtrate was colourless. The yellow product was extracted twice with benzene, and recrystallized from THF to give 1.25 g of bis{2-[(dimethylamino)methyl]phenyl}-nickel(II), (V), as lemon-yellow crystals.

cis-Bis{*2-[(dimethylamino)methyl]phenyl*}*palladium(II)*, (*VI*)

A solution of *trans*-$[(SEt_2)_2PdCl_2]$ (1.7 g) in benzene (10 ml) was added dropwise to a stirred suspension of 2-[(dimethylamino)methyl]phenyllithium (1.5 g) in benzene (20 ml). After 1 h of stirring, the dark suspension was filtered and evaporated to dryness. The crude product was dissolved in THF, filtered from finely divided metallic palladium, and recrystallized by cooling to give 0.9 g of *cis*-bis{2-[(dimethylamino)-methyl]phenyl}palladium(II), (VI), as white needles. (Found: C, 58.02; H, 6.7; N, 7.48. (VI) calcd.: C, 57.7; H, 6.41; N, 7.47%.) M.p.: 180–210° dec.

Attempts to synthesize tetrahedral bis{*2-[(dimethylamino)methyl]phenyl*}*palladium(II)*

A mixture of *N,N*-dimethylbenzylamine (2.70 g; 0.02 mol), n-butyllithium in hexane (0.027 mol contained in 10 ml) and diethyl ether (80 ml) was stirred under nitrogen atmosphere for 24 h[7]. The resulting suspension of *o*-lithio-DMBA was cooled to −20° and treated with bis(benzonitrile)palladium dichloride (3.89 g; 0.01 mol). After stirring for 6 h at room temperature, the dark suspension was treated with 50 ml of water and extracted with methylene chloride. The extract was washed with water, dried over anhydrous magnesium sulphate and concentrated. The resulting brown oil was treated with 50 ml of hexane and filtered. From this solid, after crystallization in THF, 0.4 g of (VI) were obtained as white needles. The hexane solution was evaporated, and the yellow solid was recrystallized from benzene to give 0.2 g of yellow-orange crystals. (Found: C, 48.58; H, 3.94; N, 7.20. Calcd.: C, 57.7; H, 6.41; N, 7.47%.) Infrared spectrum (nujol): 3060, 3020, 1605, 1570, 980, 850, 790, 752, 730, 701, 545 and 300 cm^{-1}. NMR spectrum (τ in $CDCl_3$): 7.66 (s); 7.02 (d, *J* 11 Hz); 6.62 (s); 6.18 (d, *J* 11 Hz) and 2.75–2.25 (m).

cis-Bis{*2-[(diethylamino)methyl]phenyl*}*palladium(II)*, (*VII*)

A solution of *trans*-$[(SEt_2)_2PdCl_2]$ (2.9 g) in benzene (10 ml) was added dropwise to a stirred suspension of 2-[(diethylamino)methyl]phenyllithium (2.7 g) in benzene (20 ml). After 45 min stirring at room temperature, the dark suspension was filtered and evaporated to dryness. The crude product, after two crystallizations in THF/hexane, gave 2.1 g of *cis*-bis{2-[(diethylamino)methyl]phenyl}palladium(II), (VII), as colourless prisms. (Found: C, 61.1; H, 7.51; N, 6.43, (VII) calcd.: C, 61.33; H, 7.43; N, 6.50%.) M.p.: 141° dec.

cis-Bis{*2-[(dimethylamino)methyl]phenyl*}*platinum(II)*, (*VIII*)

A solution of *trans*-$[(SEt_2)_2PtCl_2]$ (4.46 g) in benzene (20 ml) was added dropwise to a stirred suspension of 2-[(dimethylamino)methyl]phenyllithium (2.8 g) in benzene (10 ml). After 30 min stirring, the clear suspension was filtered. The dried residue was washed with water and crystallized from boiling THF to give 2.3 g of *cis*-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (VIII), as white needles. (Found: C, 47.0; H, 5.4; N, 6.11. (VIII) calcd.: C, 46.6; H, 5.18; N, 6.04%.) M.p.: 240–270° dec.

trans-Bis{*2-[(dimethylamino)methyl]phenyl*}*platinum(II)*, (*IX*)

A solution of *trans*-$[(SEt_2)_2PtCl_2]$ (4.46 g) in benzene (20 ml) was added dropwise to a stirred suspension of 2-[(dimethylamino)methyl]phenyllithium (2.8 g) in benzene (10 ml). After 30 min stirring, the clear suspension was filtered. The pale yellow filtrate was evaporated to dryness, and the residue, on crystallization from THF, gave 0.9 g of *trans*-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (IX), as colourless rhombic prisms. (Found: C, 46.6; H, 5.10; N, 6.05. (IX) calcd.: C, 46.6; H, 5.18; N, 6.04%.) M.p.: 190–200° dec.

cis-Bis{2-[(diethylamino)methyl]phenyl}platinum(II), (X)

A solution of *trans*-$[(SEt_2)_2PtCl_2]$ (3.2 g) in benzene (20 ml) was added dropwise to a stirred suspension of 2-[(diethylamino)methyl]phenyllithium (2.4 g) in benzene (10 ml). After 1 h of stirring, the clear suspension was filtered and evaporated to dryness. Crystallization of the residue from THF gave *cis*-bis{2-[(diethylamino)-methyl]phenyl}platinum(II), (X), (2.8 g) as colourless prisms. (Found: C,51.00; H, 6.21; N, 5.21; (X) calcd.: C, 50.86; H, 6.16; N, 5.39%.) M.p.: 176°.

trans-Bis{2-[(diethylamino)methyl]phenyl}platinum(II), (XI)

2-[(Diethylamino)methyl]phenylmagnesium bromide was prepared by first activating magnesium (0.5 g) in THF (10 ml) with iodine and then adding a solution of *o*-bromo-*N*,*N*-diethylbenzylamine (2.4 g) in THF (20 ml). After the initial exothermic reaction had subsided, the mixture was stirred for 1 h at 25°, filtered, and titrated. *trans*-$[(SEt_2)_2PtCl_2]$ (4 g) in THF (20 ml) was added dropwise with stirring. After completion of the reaction, the main part of THF was removed under vacuum, and 40 ml of benzene were added. The resulting precipitate was filtered off and discarded. The filtrate was evaporated to dryness, and the residue was crystallized from THF to yield 2.8 g of *trans*-bis{2-[(diethylamino)methyl]phenyl}platinum(II), (XI), as colourless rhombic prisms. (Found: C, 50.79; H, 6.23; N, 5.30. (XI) calcd.: C, 50.86; H, 6.16; N, 5.39%.) M.p.: 158° dec.

cis-Bis(dimethylphenylphosphine)bis{2-[(diethylamino)methyl]phenyl}platinum(II), (XIV)

Dimethylphenylphosphine (0.548 g) was added to a stirred solution of *cis*-bis{2-[(diethylamino)methyl]phenyl}platinum(II), (X), (1 g) in THF (10 ml). After 2 h of stirring, the solvent was removed under vacuum and the residue crystallized from methanol/water mixture. (XIV) was isolated as white needles (1.3 g). (Found: C, 57.0; H, 6.51; N, 3.46. (XIV) calcd.: C, 57.35; H, 6.79; N, 3.52%.) M.p.: 118° without decomposition (Mol. wt. found: 820. (XIV) calcd.: 795.5).

Adduct of cis-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (VIII), with SO_2

Bubbling SO_2 into a stirred suspension of *cis*-bis{2-[(dimethylamino)methyl]-phenyl}platinum(II), (VIII), (0.5 g) in THF (5 ml) gave an orange-red solution which on standing afforded 0.4 g of the adduct with SO_2 as orange-red needles. (Found: C, 40.58; H, 4.34; N, 5.29. $Pt(C_9H_{12}N)_2 \cdot SO_2$ calcd.: C, 40.98; H, 4.54; N, 5.31%.) M.p.: at ~160° turned white, at ~210° dec.

Carbon monoxide adsorption measurements

Carbon monoxide absorption measurements were carried out at atmospheric pressure in a standard apparatus thermostatted at ~25°. The gas measuring apparatus was charged with THF (20 ml) and carbon monoxide. Solid *cis*-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (VIII), (0.5514 g) was added and the solution was stirred until the gas absorption ceased (~2 h). [25 ml at 24.5°/760 mm; 0.88

moles/mole of *cis*-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (VIII).]

At 25.2°/757 mm, *trans*-bis{2-[(dimethylamino)methyl]phenyl}platinum(II), (IX), (0.2684 g) absorbed 25 ml of carbon monoxide [1.97 moles/mole of (IX)]. Evaporation then yielded 0.15 g of (IX-B) as white crystals. (Found: C,46.6; H, 4.58; N, 5.31. (IX-B) calcd.: C, 46.2; H, 4.62; N, 5.4%.)

A solution of (IX-B) in THF, on standing in nitrogen atmosphere, gave (IX-C) as white crystals. (Found: C, 46.6; H, 4.84; N, 5.63. (IX-C) calcd.: C, 46.43; H, 4.88; N, 5.7%.)

At 25.2°/763.9 mm, *cis*-{bis[2-(diethylamino)methyl]phenyl}platinum(II), (X), (0.9839 g) absorbed 46 ml of carbon monoxide [1 mole/mole of (X)].

At 24.5°/758 mm, *trans*-bis{2-[(diethylamino)methyl]phenyl}platinum(II), (XI), (0.3210 g) absorbed 30 ml of carbon monoxide [1.97 moles/mole of (XI)]. In this case, on evaporation, no crystalline derivatives were isolated.

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