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INSERTION REACTIONS OF ISOCYANIDES WITH PLATINUM—CARBON σ-BONDED COMPLEXES

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Summary

[Pt($C_{10}H_{12}OCH_3$)(PPh_3)Cl] reacts readily with isocyanides by displacement of the coordinated olefinic end of the organic moiety followed by insertion of the isocyanide into the metal—carbon σ-bond The reaction between the methoxydienyl complex [Pt($C_{10}H_{12}OCH_3$)Cl]$_2$ and cyclohexyl isocyanide involves chloride bridge-splitting to give [Pt($C_{10}H_{12}OCH_3$)(C_6H_{11}NC)Cl], followed by olefin displacement and finally isocyanide insertion The imino derivative produced in this latter reaction has a *trans*-isocyanide configuration

The chemical properties of these new isocyanide complexes are discussed in terms of relative *trans* influences, coordinating abilities, and electrophilic characters in comparison with the CO analogues

Introduction

There have been several studies* of the insertions of unsaturated molecules such as CO, CNR, SO_2, olefins, and acetylenes into platinum—carbon and platinum—hydrogen bonds. Carbon monoxide inserts into the M—C σ-bond of platinum(II) [2] and palladium(II) methoxydicyclopentadienyl complexes [3,4] When an excess of CO is used with complexes of the type [M($C_{10}H_{12}$-OCH_3)(PPh_3)Cl] displacement of the olefinic end by CO is also observed [2,3]. These carbon monoxide insertions and olefin displacements, are not, however, a general feature of the chemical behaviour of methoxydienylplatinum and -palladium complexes Thus, treatment of [Pt(DieneOCH_3)Cl]$_2$ (Diene = 1,5-cyclooctadiene, 1,5-hexadiene, and dicyclopentadiene) with CO in chloroform at 0° does not lead to CO insertion into the Pt—C σ bond. Instead, in the case of the 1,5-cyclooctadiene complex, the methoxyl group migrates to the CO ligand which has become coordinated to the metal through a halide bridge-splitting reaction, to give the methoxycarbonyl derivative, [Pt(C_8H_{12})-($COOCH_3$)Cl] [5].

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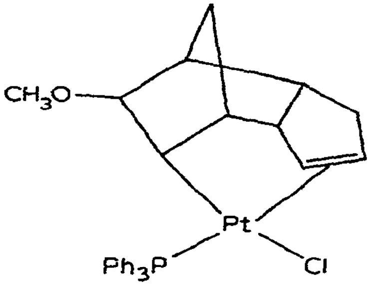
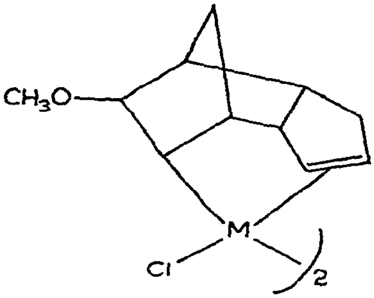
*For a survey see ref 1

In continuation of our studies on insertions of unsaturated molecules into metal—carbon σ bonds, we have examined some reactions of complexes of types (I) and (II) with isocyanides, which are isoelectronic with carbon monoxide.



(I)



(II)

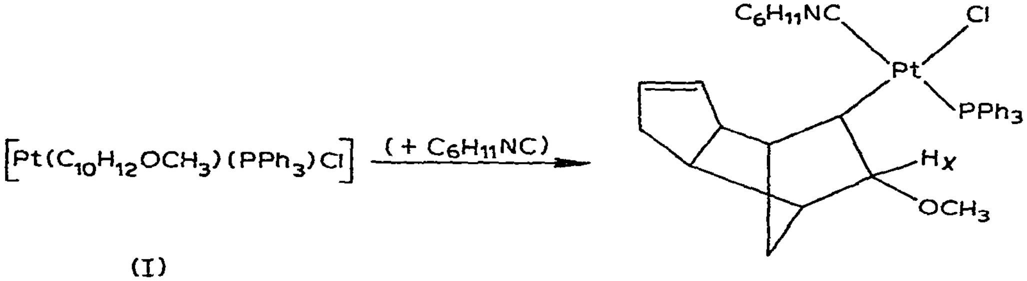
(M = Pt, Pd)

Results and discussion

Reactions of $[Pt(C_{10}H_{12}OCH_3)(PPh_3)Cl]$ with RNC ($RNC = C_6H_{11}NC$, p-$CH_3C_6H_4NC$)

Reactions of complexes of the type $[Pt(C_{10}H_{12}OCH_3)(PPh_3)Cl]$ with cyclohexyl and p-tolyl isocyanide in benzene or dichloromethane at room temperature involved complex/RNC molar ratios ranging from 1 to 0 5.

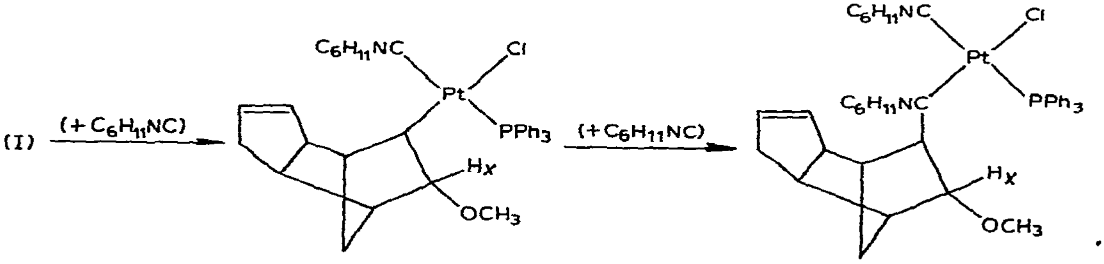
The reaction of $[Pt(C_{10}H_{12}OCH_3)(PPh_3)Cl]$ with cyclohexyl isocyanide with a complex/RNC ratio of 1.0 proceed according to the reaction.



(I)

(III)

When the complex/RNC ratio is 0 5, insertion of one molecule of isocyanide into the Pt—C σ bond of complex (III) takes place (eqn. 1) The initial conversion of (I) into (III) may be a consequence of the overall energy change, since



(III)

(IV)

(1)

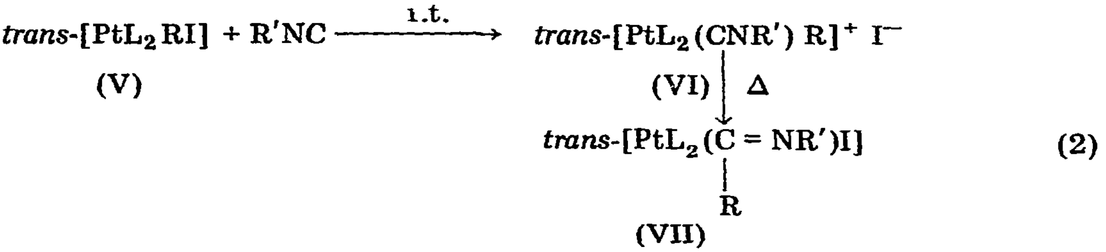
the cyclohexyl isocyanide is expected to displace Cl (*trans* to a Pt—C σ bond) rather than C=C (*trans* to phosphine) judging from relative *trans* influences. However the product is stable, and apparently does not undergo insertion until further reaction occurs. This latter reaction, which take place at a molar ratio of complex/isocyanide = 0.5, presumably involves displacement of Cl followed by rapid insertion. In the absence of kinetic data one cannot rule out the possibility that reaction (1) is made up of two consecutive steps of very different rates.

Complex (III) was characterized by elemental analysis (Table 1), IR, and ^{1}H NMR spectra (Table 2). Its IR spectrum shows the stretching absorption at 2190 cm^{-1} {cf. ν(N≡C) 2188 cm^{-1} for *trans*-$[\mathrm{Pt(PPh_3)_2(C_6H_{11}NC)(CH_3)]I}$} [6]. This frequency is some 60 cm^{-1} higher than the corresponding frequency for uncoordinated isocyanide [7]. The ^{1}H NMR spectrum shows uncoordinated olefin protons at τ 4.20 and 4.40 ppm.

Complex (IV), a white solid, was similarly characterized. Its IR spectrum shows a band at 1606 cm^{-1}, characteristic of an N=C double bond {ν(N=C) 1604 cm^{-1} in *trans*-$[\mathrm{Pt(PPh_3)_2(CH_3CNC_6H_{11})I}]$} [6], and a strong absorption at 2205 cm^{-1} assigned to ν(C≡N). Its ^{1}H NMR spectrum shows the absorptions of uncoordinated olefin protons at τ 4.20 and 4.40 ppm, whereas the other main features in the spectrum of the rest of the organic moiety are unchanged relative to those of the starting complex $[\mathrm{Pt(C_{10}H_{12}OCH_3)(PPh_3)Cl}]$ [4,8].

The course of reaction (1) was monitored by recording the change of the IR spectrum of the reaction mixture in $\mathrm{CH_2Cl_2}$ with time, at complex/RNC molar ratios varying over the range 0.5 - 2. When the ratio is greater than unity, one single band at 2190 cm^{-1} appears, which increases in intensity with time and corresponds to the terminal isocyanide ν(C≡N) [complex (III)]. For complex/RNC < 1, a new band at 1606 cm^{-1} appears along with the 2190 cm^{-1} band, which is diagnostic of the imino group arising from insertion of isocyanide into the Pt—C σ bond.

Both (III) and (IV) are non-conductors in $\mathrm{CH_2Cl_2}$. The possibility of cationic intermediates being produced during the reaction cannot be ruled out. Cationic complexes such as (VI) were isolated as intermediates in the isocyanide insertion reactions (eqn. 2) [6,9,10]. An analogous cationic mechanism was proposed as a general feature of insertion reactions of Pt$^{\mathrm{II}}$ hydrides or



$$\begin{array}{ccc} trans\text{-}[\mathrm{PtL_2RI}] + \mathrm{R'NC} & \xrightarrow{\text{r.t.}} & trans\text{-}[\mathrm{PtL_2(CNR')\,R}]^+\ \mathrm{I}^- \\ \text{(V)} & & \text{(VI)}\ \Big\downarrow\ \Delta \\ & & trans\text{-}[\mathrm{PtL_2(\underset{\substack{|\\ R}}{C}=NR')I}] \\ & & \text{(VII)} \end{array} \qquad (2)$$

$(\mathrm{L = PMe_2Ph,\ PPh_3,\ R = CH_3,\ C_6H_5;\ R' = CH_3,\ C_6H_{11},\ CMe_3})$

organo-derivatives [11,12]. This involves attack of the reagent (olefin, acetylene, CO, isocyanide) on a reactive cationic species (possibly R—Pt$^+$—solv) to occupy a position *trans* to the Pt—H or Pt—C bond in a square-planar environment.

(Continued p 422)

TABLE 1

PRODUCTS OF REACTIONS OF ISOCYANIDES WITH METHOXYDIENYLPLATINUM (II) AND -PALLADIUM (II) COMPLEXES

Compound		M p (°C) [a]	Analyses found (calcd) (%)				Mol. wt. found [b]
			C	H	N	Cl	(calcd)
(III)	$[Pt(C_{10}H_{12}OCH_3)(C_6H_{11}NC)$- $(PPh_3)Cl]$	63—65	56.50 (56.48)	5.47 (5.40)	1.81 (1.83)	4.70) (4.63)	730 (765)
(IV)	$[Pt(C_{10}H_{12}OCH_3C_6H_{11}NC)$ $(C_6H_{11}NC)(PPh_3)Cl]$ $\frac{1}{2}CH_2Cl_2$	80–85	56.89 (57.10)	5.85 (5.78)	3.04 (3.06)	7.59 (7.73)	
(IVa)	$[Pt(C_{10}H_{12}OCH_3pCH_3C_6H_4NC)$- $(p\ CH_3C_6H_4NC)(PPh_3)Cl]$	72	60.63 (60.70)	5.01 (4.98)	3.20 (3.14)	3.83 (3.87)	
(VIII)	$[Pt(C_{10}H_{12}OCH_3)(C_6H_{11}NC)$ $Cl]$	155—160	43.03 (42.98)	5.23 (5.21)	2.97 (2.98)	7.07 (7.05)	
(IX)	$[Pt(C_{10}H_{12}OCH_3C_6H_{11}NC)$- $(C_6H_{11}NC)_2Cl]$	95	53.25 (53.30)	6.68 (6.72)	5.76 (5.82)	4.90 (4.92)	705 (721)
(VIIIa)	$[Pd(C_{10}H_{12}OCH_3)(C_6H_{11}NC)$- $Cl]$	135	52.26 (52.19)	6.30 (6.33)	3.40 (3.38)	8.64 (8.56)	
(XIV)	*cis* $[Pt(C_6H_{11}NC)(PPh_3)Cl_2]$	> 300	47.20 (47.10)	4.10 (4.08)	2.20 (2.20)	11.30 (11.25)	

[a] All compounds melted with decomposition [b] In benzene

TABLE 2

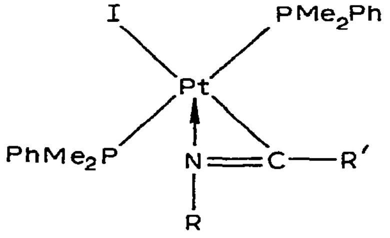
SELECTED IR AND ^{1}H NMR SPECTRA OF COMPLEXES

Compound	ν(C≡N) (cm^{-1})	ν(C=N) (cm^{-1})	ν(M—Cl) (cm^{-1})	τ (OCH$_3$)	$\tau\ (\underset{H}{C}=\underset{H}{C})$	τ (Hx)
[Pt($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)(PPh_3)Cl]	2188 vs		276 w	6 72	4 20 4.40	6.38
[Pt($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)($PPh_3$)Cl] $\frac{1}{2}$ CH_2Cl_2	2205 vs	1606 m	275 w	6 75	4 20 4 40	6.38
[Pt($C_{10}H_{12}OCH_3$ p $CH_3C_6H_4NC$)(p $CH_3C_6H_4NC$)-(PPh_3)Cl]	2190 vs	1602 m	276 w	6 74 [a]	4 15 4 32	6 50 [b]
[Pt ($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)Cl]	2213 vs		267 ms	6 75	3 42 3 70	6 40
[Pt ($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)$_2$Cl]	2214 vs	1603 m	265 (br)	6 76 [a]	4 18 4 35	6 50
[Pd ($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)Cl]	2204 vs		262 ms	6 72	3 20 [c]	6 40
cis-[Pt ($C_6H_{11}NC$)(PPh_3)Cl_2]	2217 vs		344 s, 297 s			

[a] This absorption, when the spectrum is recorded at high resolution with a *Bruker* 90 MHz spectrometer, appears as two peaks of different intensity, with a separation of 0.03 ppm. This unexpected feature is being investigated further [b] Tentatively assigned [c] Unresolved multiplet

Reaction (1) also applies when *para*-tolyl isocyanide is used as the reactant.

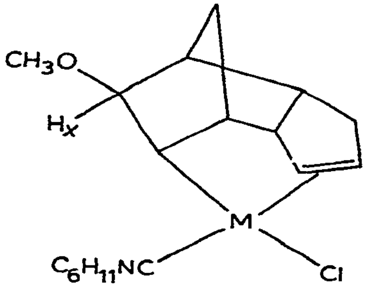
One cannot discount the possibility of a coordinative interaction of the imino nitrogen with the central metal in (IV), as was found for complex (VII). In this latter case the ^{1}H NMR absorption pattern of the phosphine methyl groups is indicative of five-coordination for platinum [6]. However, a similar diagnostic feature is not available in the case of the triphenylphosphine complexes (IV)



(VII)

Reactions of $[M(C_{10}H_{12}\cdot OCH_3)Cl]_2$ *with* $C_6H_{11}NC$

These chloride-bridged dimeric complexes react with cyclohexyl isocyanide in CH_2Cl_2 to give bridge-splitting products of type (VIII).



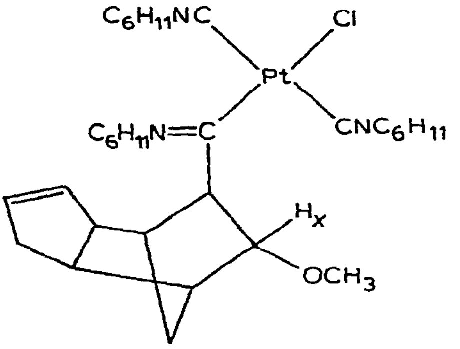
(VIII)

[M = Pt, Pd, $\nu(C{\equiv}N)$ 2213 and 2204 cm^{-1} for the Pt and Pd complex, respectively.]

The platinum product could be recovered unchanged after several hours heating at reflux in chloroform in the dark. This indicates that migration of the methoxide group to the coordinate isocyanide did not take place, in contrast to the behaviour of the carbonyl complex [5].

The platinum complex (VIII) reacts with cyclohexyl isocyanide in CH_2Cl_2 to give the imino derivative (IX). The IR spectrum of this product shows one single absorption in the terminal isocyanide region, indicating a *trans*-isocyanide configuration.

The *trans*-chloride configuration relative to the metal—carbon σ bond in complexes (III), (IV), (VIII) and (IX) was based on the presence of an infrared band in the 280 - 260 cm^{-1} region, characteristic of ν(M—Cl) for Cl *trans* to an M—C σ bond in this type of complex [13,14]. Thus, insertion of isocyanide into the metal—chloride bond [15] is ruled out.



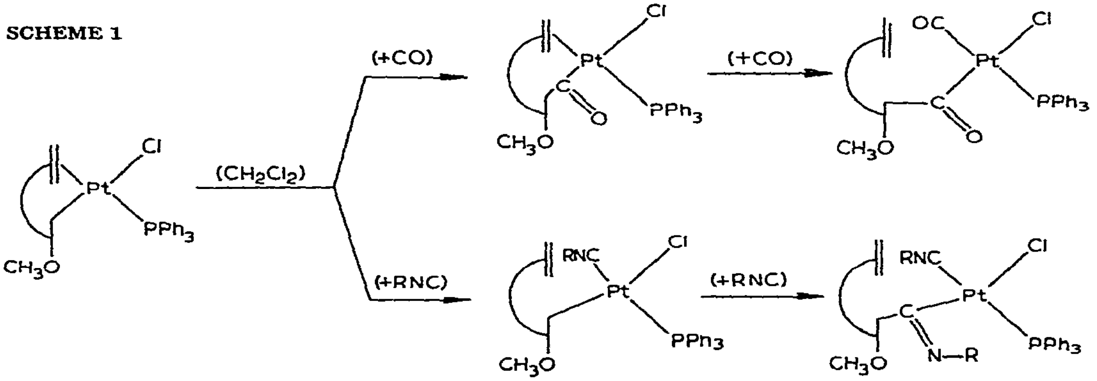
(IX)

Carbon monoxide compared with isocyanide insertion into metal—carbon σ bonds

Insertion reactions of carbon monoxide and isocyanide into metal—carbon σ bonds in complexes of the type $[Pt(C_{10}H_{12}OCH_3)(PPh_3)Cl]$ and $[Pt(C_{10}H_{12}OCH_3)Cl]_2$ display the following features.

(i) Unlike the carbonylation reaction, the isonitrile insertion permits isolation of the platinum—isocyanide bonded complex arising from displacement of the olefinic end by the entering isocyanide (Scheme 1)

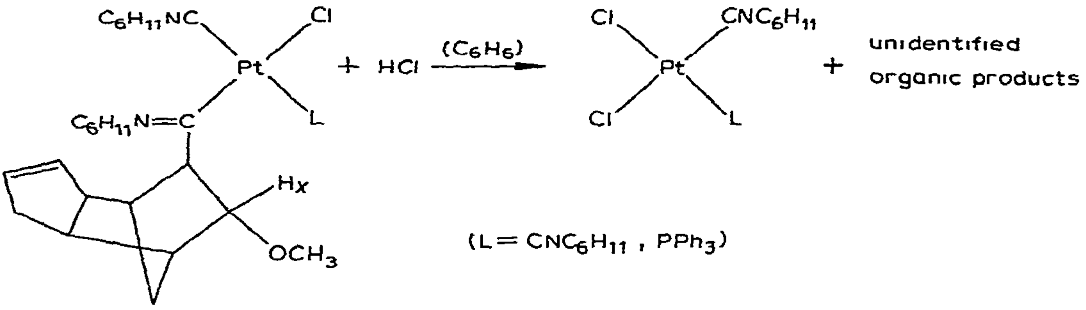
SCHEME 1



(ii). Comparison of the complexes $[Pt(C_{10}H_{12}OCH_3)(CO)Cl]$ (X) and $[Pt(C_{10}H_{12}OCH_3)(CNR)Cl]$ (XI) shows that in the carbonyl complex carbon monoxide does not displace the olefinic end of the dienyl moiety, whereas an excess of RNC does react with the isocyanide complex to displace the olefin. These findings point to both a greater *trans* labilizing influence and a greater coordinating ability toward platinum(II) of RNC than of CO.

In order to shed some light on these matters in which bonding and reactivity factors of these unsaturated groups are involved, we are carrying out reactions of (X) with RNC and of (XI) with CO Isocyanide insertions in the dimeric complexes $[M(DieneOCH_3)X]_2$ with various dienes are also being studied.

SCHEME 2



Reactions of [Pt($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)(L)Cl] (L = $C_6H_{11}NC$, PPh_3) with hydrogen chloride

The reaction of these complexes with hydrogen chloride proceeds according to Scheme 2.

The *cis* structure for this compound is based on the appearence of two strong bands in the ν(Pt—Cl) region of the IR spectrum, attributed to *cis* chlorides. The *cis* configuration is the most stable for complexes of this type [16].

Experimental

The compounds [M($C_{10}H_{12}OCH_3$)Cl]$_2$ and [Pt($C_{10}H_{12}OCH_3$)(PPh_3)Cl] were prepared according to literature methods [14,17,18]. All other chemicals were reagent grade materials

Infrared spectra were recorded in the region 4000 - 250 cm^{-1} with a Perkin—Elmer 457 spectrophotometer, and in the region 450 - 80 cm^{-1} with a Beckman IR 11. The ^{1}H NMR spectra were recorded on Perkin—Elmer R20A and Bruker 90 MHz instruments, with $CDCl_3$ solutions at room temperature. Molecular weights were determined with a HP 302B vapor pressure osmometer.

Reactions of [Pt($C_{10}H_{12}OCH_3$)(PPh_3)Cl] with isocyanides

(a). Cyclohexyl isocyanide (109 mg, 1 mmol) in benzene (10 ml) was added dropwise to a benzene solution of the complex (655 mg, 1 mmol, molar ratio Pt/CNR = 1) at room temperature with vigorous stirring under nitrogen. The mixture was stirred for 5 hours. It was then concentrated to low volume under reduced pressure, and ether and pentane were added to give an oily product The supernatant liquid was separated by decantation, and the oil was dried, leaving an off-white solid which was washed with ether This was recrystallized to give [Pt($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)(PPh_3)Cl].

(b) Similarly, but in CH_2Cl_2 with a molar ratio Pt/CNR = 0.5, the white compound [Pt($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)($PPh_3$)Cl] · ½$CH_2Cl_2$ was prepared. The yellow compound [Pt($C_{10}H_{12}OCH_3$-*p*-$CH_3C_6H_4NC$)(*p*-CH_3-C_6H_4NC)(PPh_3)Cl] was prepared similarly.

Reactions of [M($C_{10}H_{12}OCH_3$)Cl]$_2$ with cyclohexyl isocyanide

(a). Cyclohexyl isocyanide (109 mg, 1 mmol) in CH_2Cl_2 was added dropwise to a dichloromethane solution of the complex [Pt($C_{10}H_{12}OCH_3$)-

Cl]$_2$ (394 mg, 0.5 mmol; molar ratio Pt/CNR = 1) at room temperature with stirring under nitrogen. After 1 hour the solution was evaporated, leaving a white solid. This was washed with ether and recrystallized to give the off-white complex [Pt($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)Cl]. [Pd($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)Cl] was prepared similarly

(b) Under similar experimental conditions, using a molar ratio M/CNR $\leqslant$ 1/3 the off-white complex [Pt($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)$_2$Cl] was obtained.

Reactions of [Pt($C_{10}H_{12}OCH_3$)($C_6H_{11}NC$)(PPh_3)Cl] or [Pt($C_{10}H_{12}OCH_3$-$C_6H_{11}NC$)($C_6H_{11}NC$)(PPh_3)Cl] with hydrogen chloride

A solution of the complex in benzene was saturated with anhydrous hydrogen chloride at room temperature The concentrated solution was treated with ether to give a white product identified as [Pt($C_6H_{11}NC$)(PPh_3)Cl_2]. In a similar way, from [Pt($C_{10}H_{12}OCH_3C_6H_{11}NC$)($C_6H_{11}NC$)$_2$Cl] the compound *cis*-[Pt($C_6H_{11}NC$)$_2Cl_2$] was obtained, and was identified by comparison of its IR spectrum with that of an authentic sample

Acknowledgements

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