The Physico–chemical Behaviour of Tetraazadiene Complexes

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The ^1H nmr spectra at variable temperature for the series of tetraazadiene complexes $M(NO)(PPh_3)_n$ (N_4R_2) $(M = Rh, Ir; n = 1,2)$, $Pt(L)(PPh_3)(N_4R_2)$ $(L = CO, PPh_3; R = p\text{-}CH_3C_6H_4SO_2)$ have been studied. From the simulated ^1H nmr spectra of the iridium complex $(n = 1)$ the activation parameters for an iso-merization process which takes place in solution have been calculated. Studies on the chemical reactivity of the tetraazadiene ligand bound to a transition metal have shown that the organic moiety is susceptible to attack only by mineral acids.
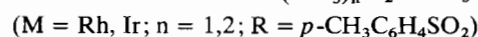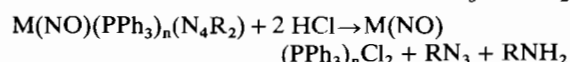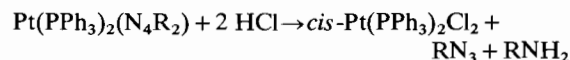
Introduction

Previous studies have shown that the reactions of organic azides with low oxidation state transition metal complexes can lead to the formation of tetraazadiene derivatives[1,2,3,4]. This type of compound has also been obtained by coupling of two diazonium cations on a transition metal complex[5], and the similarity between the tetraazadiene, R–N=N–N=N–R, und buta-diene ligands has been pointed out[1,4]. The chemical reactivity towards hydrochloric acid of these complexes suggested that in solution the chelate tetraazadiene ring might be open, with formation of nitrenes species having the organic azide bound to the metal[1]. Prelim-inary ^1H nmr studies seemed to support this suggestion. We have thus undertaken a study of the chemical and physico–chemical behaviour of a series of tetraazadiene complexes, in order to gain a better understanding of the properties of the tetraazadiene molecule, a ligand which is stabilized only by coordination on a transition metal.

Results

Reactivity of Tetraazadiene Complexes

We have previously shown that in the reactions of tetraazadiene complexes such as $Pt(PPh_3)_2(N_4R_2)$ and $M(NO)(PPh_3)_n(N_4R_2)$ $(M = Rh, Ir; n = 1,2; R = p\text{-}CH_3C_6H_4SO_2)$ with hydrochloric acid, the organic moiety is displaced with formation of the correspond-ing azide and amide[1]:

$$Pt(PPh_3)_2(N_4R_2) + 2\ HCl \rightarrow cis\text{-}Pt(PPh_3)_2Cl_2 + RN_3 + RNH_2$$

$$M(NO)(PPh_3)_n(N_4R_2) + 2\ HCl \rightarrow M(NO)(PPh_3)_nCl_2 + RN_3 + RNH_2$$

$$(M = Rh, Ir; n = 1,2; R = p\text{-}CH_3C_6H_4SO_2)$$

When this reaction was carried out on $Pt(PPh_3)_2(N_4R_2)$ with an acid having a poor nucleophilic char-acter such as HBF_4, we have again observed the for-mation of the azide and the amide. In this latter case the complex isolated from the reaction was $[Pt(PPh_3)_2(OH)]_2^{2+}(BF_4^-)_2$, a hydroxo-platinum derivative which may contain bridging OH groups[6].

On the other hand, the tetraazadiene–platinum complex did not show any reaction with methyl iodide in different experimental conditions. This seems to suggest that the attack by the proton in the reactions with acids proceeds directly on the nitrogen of the ligand, without the assistance of the metal.

With carbon monoxide, $Pt(PPh_3)_2(N_4R_2)$ ex-changes one phosphine with CO giving $Pt(CO)(PPh_3)(N_4R_2)$, and no insertion of carbon monoxide into the tetraazadiene ring was observed. The last insertion reaction was in principle, quite probable, since the reactions of carbonyl–phosphine platinum(0) and palladium(0) complexes with toluene-p-sulphonyl azide proceed *via* a cycloaddition reaction of the azide to the coordinated carbon monoxide[7].

On the other hand the coordinatively unsaturated rhodium and iridium–tetraazadiene complexes, $M(NO)(PPh_3)(N_4R_2)$, simply add one molecule of carbon monoxide and again no insertion reaction takes place[1].

In $Pt(CO)(PPh_3)(N_4R_2)$, ν_{CO} was observed at 2110 cm^{-1}, while the other bands due to the organic ligand did not differ significantly from those of the starting complex[8]. This carbonyl stretching frequency is typical of platinum(II) carbonyl complexes, suggest-ing that of the two limiting forms which can represent the bonding of the ligand to the metal, the one (a) having two σ metal–nitrogen bonds makes a major contribution:[5]
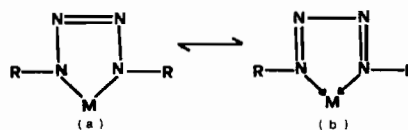
We have also studied the reactions of Ir(NO)(PPh$_3$)(N$_4$R$_2$) and Pt(PPh$_3$)$_2$(N$_4$R$_2$) with cyclohexene morpholine, since it is known that enamines readily react with sulphonyl azides at room temperature to give amidines[9]. However we did not observe any reaction with the platinum complex even in refluxing chloroform, while the iridium complex was partially decomposed during the reaction in warm benzene, but we did not find evidence for the formation of the amidine.

TABLE I. Methyl ^{1}H Nmr Resonances of the Tolyl Residue in Tetraazadiene Complexes at Room Temperature[a].

Compound[b]		τCH$_3$
(I)	Rh(NO)(PPh$_3$)(N$_4$R$_2$)	7.68
(II)	Ir(NO)(PPh$_3$)(N$_4$R$_2$)	7.67
(III)	Pt(PPh$_3$)$_2$(N$_4$R$_2$)	7.71
(IV)	Rh(NO)(PPh$_3$)$_2$(N$_4$R$_2$)	7.76
(V)	Ir(NO)(PPh$_3$)$_2$(N$_4$R$_2$)	7.78
(VI)	Pt(CO)(PPh$_3$)(N$_4$R$_2$)	7.59–7.72
(VII)	Rh(NO)(CO)(PPh$_3$)(N$_4$R$_2$)	7.65–7.70
(VIII)	Ir(NO)(CO)(PPh$_3$)(N$_4$R$_2$)	7.64–7.70
(IX)	Ir(NO)(PPh$_3$)(N$_4$R$_2$)[c]	7.54–7.71

[a] CDCl$_3$ as solvent. [b] R = p-CH$_3$C$_6$H$_4$SO$_2$. [c] at –50° C.
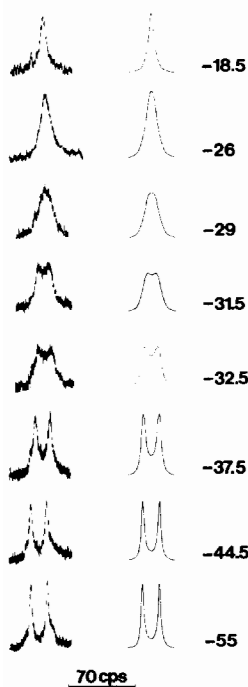
Figure 1. ^{1}H nmr spectra at various temperatures of Ir(NO)(PPh$_3$)(N$_4$R$_2$) (R = p-CH$_3$C$_6$H$_4$SO$_2$) in CDCl$_3$ and computer simulated spectra.

Spectroscopic Properties of Tetraazadiene Complexes

The i.r. spectra in chloroform of the two formally isoelectronic complexes, Ir(NO)(PPh$_3$)(N$_4$R$_2$) and Pt(CO)(PPh$_3$)(N$_4$R$_2$) have been measured from room temperature down to –70° C. No appreciable variations have been observed on ν_{NO}[1] and ν_{CO} respectively with respect to solid state spectra and no new bands were observed to be formed in the region 2300–1600 cm^{-1}.

In the ^{1}H nmr spectra, the methyl resonances at room temperature of the tolyl residue for a series of tetraazadiene complexes are reported on Table I. Two distinct signals have been observed only for the asymmetric compounds (VI), (VII), and (VIII), for which the molecular structure induces different environments around the two methyl groups. In the other cases, only one signal was detected. This implies for compounds (I) and (II) a pseudo-tetrahedral structure and not a square planar one. On lowering the temperature, the signal for compound (II) splits into two distinct peaks in a one to one ratio (Figure 1), with a coalescence temperature of –29° C.

For compound (I) only a slight broadening was observed down to –50° C; in the other cases no significant variations were observed. A line shape analysis had shown that the rates satisfy the Arrhenius equation[10] (Figure 2):
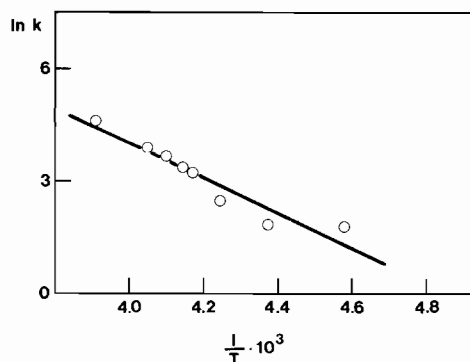

Figure 2. Arrhenius plot of the exchange rates for Ir(NO)(PPh$_3$)(N$_4$R$_2$) (R = p-CH$_3$C$_6$H$_4$SO$_2$) as a function of temperature.

From the linear plot, the thermodynamic activation parameters, log A = 9.92 ± 0.80 and E$_a$ = 9.33 ± 0.87, have been calculated. According to the Eyring equation ΔH‡ = 8.74 ± 0.87 (kcal/mol), ΔS‡ = –19.73 ± 9.53 e.u. and ΔG$^{\ddagger}_{298}$ = 14.62 ± 1.97.

Conclusions

The i.r. spectra at variable temperature of the Ir(NO)(PPh$_3$)(N$_4$R$_2$) and Pt(CO)(PPh$_3$)(N$_4$R$_2$) complexes have shown that no substantial changes for the

structure of these compounds in solution have to be considered. This, together with the chemical inertness of the tetraazadiene ligand, is in contrast with the previous suggestion that in solution there might be a nitrene species, having the organic azide bound to the metal[1].

It seems now more likely that the observed splitting at low temperature of the methyl resonance of the tolyl residue in $Ir(NO)(PPh_3)(N_4R_2)$, should be attributed to a conformational effect.

The activation parameters that we have calculated are comparable with those observed for the interconversion of the boat and chair conformations of the cyclohexane ring[11]. However the X-ray structure of $[Ir(CO)(PPh_3)_2(N_4R_2)]^+(BF_4^-)$ (R = p-FC$_6$H$_4$), has shown that the IrN_4 ring is essentially planar[5]. It is thus probable that the conformer that we observe at low temperature corresponds to that having the R substituents one above the IrN_4 ring (toward the NO ligand) and the other below (toward the PPh_3 ligand). At room temperature, the rotation about the –N–S– bond averages the resonances of the two methyl groups.This implies a certain degree of –N–S– double bond in the R substituents and this effect compares for
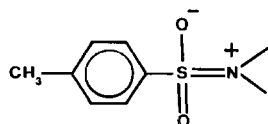
example with the hindered internal rotation of amides[10].

Experimental

The known compounds were prepared according to our previous reports[1,8]. We only observed that the synthesis of $Pt(PPh_3)_2(N_4R_2)$ (R = p-CH$_3$C$_6$H$_4$SO$_2$) is more readily achieved starting from $Pt(PPh_3)_3$ instead of $Pt(PPh_3)_4$; in this way the amount of the RN=PPh$_3$ adduct, formed in the reaction is reduced and the complex is more easily purified.

^{1}H nmr spectra were recorded on a Varian NV-14 instrument operating at 60 MHz and on a Varian HA 100 (100 MHz) instrument equipped with a variable temperature accessory. The probe temperature has been determined with methanol standard. Line shape analysis of the spectra was carried out using the method suggested by Gutowsky and Holm[10].

The experimental line shapes have been reproduced by least squares refinement of the τ factor for each of the eight temperatures:

T(°C)	−55.0	−44.5	−37.5	−32.5
τ	0.0816	0.0766	0.0423	0.0206
	−31.5	−29.0	−26.0	−18.5
	0.0156	0.0119	0.0094	0.0048

The i.r. spectra at variable temperature were taken on a Perkin Elmer 621 (grating) spectrometer, with a variable temperature unit VLT-2 and with a heating Jacket WJ2 (Riik), in a 0.1 mm cell with NaCl windows.

$Pt(CO)(PPh_3)(N_4R_2)$ (R = p-CH$_3$C$_6$H$_4$SO$_2$)

To a suspension of $Pt(PPh_3)_2(N_4R_2)$ (0.3 g) in benzene (20 ml), CH_2Cl_2 was added until a clear solution was obtained. Carbon monoxide was bubbled through the solution for 24 hr. The resulting solution was evaporated under vacuum to a small volume and ethyl ether was added. The white precipitate was filtered off, washed with ethyl ether and dried *in vacuo*. The compound melts at 218°C (found: C, 45.9; H, 3.6; N, 5.7; m.w., 760. $C_{33}H_{29}N_4O_5PPtS_2$ requires: C, 46.5; H, 3.4; N, 6.5; m.w. 851).

Reaction of $Pt(PPh_3)_2(N_4R_2)$ (R = p-CH$_3$C$_6$H$_4$SO$_2$) with HBF_4

To $Pt(PPh_3)_2(N_4R_2)$ suspended in ethyl ether, few drops of aqueous HBF_4 were added under an atmosphere of nitrogen. After 12 hr the white precipitate was filtered off, washed with ethyl ether and dried *in vacuo*. It was shown to be $[Pt(PPh_3)_2(OH)]_2^{2+}$ $(BF_4^-)_2$[6] by its i.r. spectrum, molar conductivity and elemental analysis. In the liquor mother the presence of RNH_2 and RN_3 was determined as already described[1]

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