Tuning the reactivity of metals held in a rigid ligand environment

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Abstract – Research on the chemistry of monoanionic aryl ligands having ortho- or bis-orthodimethylaminomethyl substituents, *i.e.*, $C_6H_4(CH_2NMe_2)$-2, **A**, $C_{10}H_6NMe_2$-8, **B** and $C_6H_3(CH_2NMe_2)_2$-2,6, **C**, that form organometallic compounds with a direct $M-C_{aryl}$ σ-bond, will be discussed. Through coordination of the N-donor site(s) of the ortho CH_2NMe_2 arm(s) five-membered M-C-C-C-N chelate ring formation occurs. In particular, the rigid bis-ortho chelation of the terdentate ligand **C** provides the complexed metal centre with a set of unusual properties. Firstly, this ligand restricts the number of coordination sites that are available for incoming reagents and other ligands. This is a situation that can frustrate the normal course of, for example, an oxidative reaction at the bound d^8 metal centre and lead to "trapped intermediates" with a considerable stability. Secondly, the hard C and N donor atoms make these ligands extremely electron-rich and consequently they afford complexed (d^8) metal centres with an enhanced nucleophilicity. Together, these features provide their complexes with unexpected and novel properties; e.g. η^1-coordination of I_2 to Pt^{II}, stable Ni^{III}-carbon bonds, and intramolecular rearrangements involving C-H bond activation. Here, the first experiments aimed at modelling the available space for incoming reagents by a variation of the alkyl substituents at the nitrogen donor atoms will be described.

INTRODUCTION

The search for (in)organic and organometallic systems that have their metal centre(s) encapsulated in a specifically modelled organic environment is the focus of many research groups. Metal-containing systems in nature, *e.g.*, metal porphyrins, have proved to be a source of inspiration for extensive studies in this area.

Over the last decade, we have directed our attention to the chemistry of monoanionic aryl ligands with functionalized heteroatom containing substituents; some representative examples of which are shown in Fig. 1. In general, aryl ligands with chelating properties are extensively used in organometallic synthesis to obtain compounds which, compared to those having an equivalent number of monodentate ligands, have an improved kinetic stability (ref. 1).

R=H, Me or CH₂NMe₂

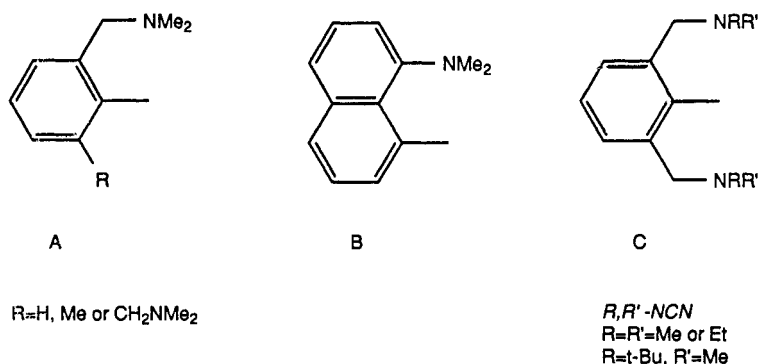R,R'-NCN
R=R'=Me or Et
R=t-Bu, R'=Me

Fig. 1. Bi- and terdentate monoanionic aryl ligands with C- and N-ligating sites.

However, in our study these chelating organic systems have been selected for a different reason. Specific bis- and terdentate monoanionic aryl ligands, which can in principle bind to the metal centre via a direct $M-C_{aryl}$ σ-bond, were chosen for their ability to tune the reactivity of the complexed metal centre without taking part in processes occurring at the metal centre.

Before explaining the surprises we encountered during our research based on this simple approach, it is interesting to summarize in retrospect the lessons we learned concerning the role of these ligands in tuning the metal reactivity.

The effects that ligands **A**, **B**, and **C** can exert on the complexed metal are twofold. The first has to do with the electronic properties of the set of donor atoms and the second effect, a more important one, is due to the spatial arrangement of the chelating donor atoms and the stereochemical configuration and rigidity of the carbon chain connecting these donor atoms.

The electronic influence on the metal properties is directly related to the choice of hard C and N donor atoms as ligating sites; a choice which at first seemed somewhat unusual when the extensive use of phosphine ligands in organometallic chemistry was taken into account (ref. 1). However, it now appears that the presence of hard donor atoms makes, for example, the terdentate-"pincer" ligand C an extremely electron-rich system, which consequently enhances the nucleophilicity of a complexed metal centre to a large extent (ref. 2).

Although **A**, **B**, and **C** have N- and C-ligating sites in common, it is the stereochemistry of these three ligands that is entirely different and needs further comment. In metal complexes the stereochemical effect of the aryl (**A** and **C**) or naphthyl ring (**B**) severely limits the degree of spatial freedom the (di)amine donor has for its coordination. In fact, the chelating amine substituents are forced to lie more or less coplanar to the C-bonded aryl (naphthyl) moiety. This implies, for example, that in octahedral complexes **C** can only act as a terdentate ligand when it coordinates in a meridional manner. Moreover, in **C**, the N-atoms will always be in *trans*-positions, thus restricting the geometry of the σ-C-bonded metal centre to either square-planar (Fig. 2a), square-pyramidal, trigonal-bipyramidal (tbp), or octahedral. Other configurations for the metal centre can only occur when one or both N donor atoms are not coordinated or when a different type of M-C interaction is realized (*e.g.*, by three centre-two electron C–M bonding as in the aryl-lithium (ref. 3) and -copper (ref. 4) compounds in Fig. 2b).
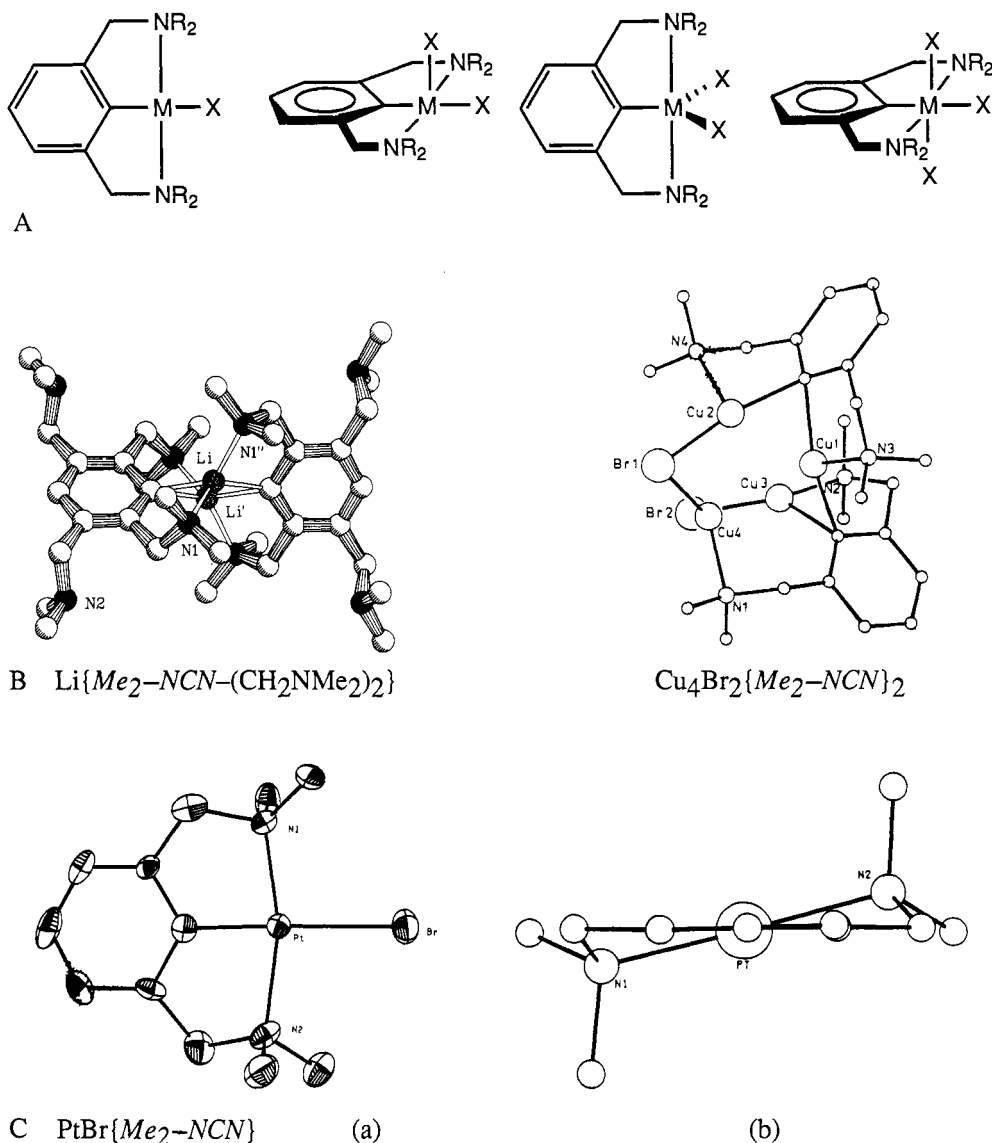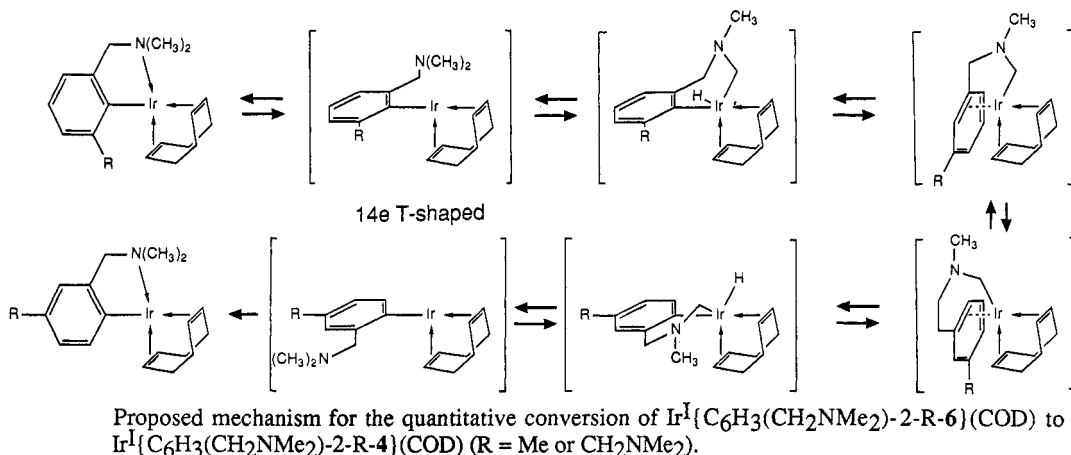

A

B   Li{*Me₂-NCN*-(CH₂NMe₂)₂}   Cu₄Br₂{*Me₂-NCN*}₂

C   PtBr{*Me₂-NCN*}   (a)   (b)

Fig. 2.(a). Possible coordination geometries for a metal centre bound to the terdentate "pincer" ligand **C**.(**b**). Binding of **C** to metals with preference for trigonal or tetrahedral coordination geometries. In both compounds C$_{ipso}$ is three centre two electron bridge bonded to two lithium or two copper(I) atoms. (**c**). Structure of PtBr{*Me₂-NCN*} (Pt-C 1.90(1), -N 2.07(1) and 2.09(1) Å; N-Pt-N 164.4(4)° with (**b**) showing the projection along the Pt–C$_{ipso}$ axis.

In the case of terdentate bonding of **C**, the substituents R and R' (for the abbreviations used see Fig. 1) at the coordinated N atoms are also held in a fixed position that is determined by the puckering in the two "fused", five-membered chelate rings (see Fig. 2A) that have a common M-C bond. With the correct combination of R and R' substituents one can create certain channels of access so that incoming ligands are guided to the positions either *trans* or *cis* to the σ-C ligand; this is a further line of thinking we are following in some of our present research (ref. 5). For example, in the case where R = Me and R' = *t*-Bu (*t-Bu,Me-NCN*) the N donor atoms are slightly better Lewis bases than in the parent ligand with R = R' = Me (*Me₂-NCN*). However, the princial factor for the difference in reactivity between analogous metal complexes containing *t-Bu,Me-NCN* and *Me₂-NCN*, as we will see later on, is found in the different space-filling characteristics of these terdentate ligands.

The above discussion applies particularly to the use of terdentate **C** as a passive matrix for tuning the reactivity of the complexed metal. However, another lesson we learned during our studies is that metal reactivity is not solely directed by heteroatom sites of a multidentate ligand. This can be illustrated by the chemistry of bidentate, monoanionic **A**, where R, for example, is CH_3 (or a likewise uncoordinated CH_2NMe_2 group). When the N atom coordinates to a metal M, that has a square planar coordination geometry, then this CH_3 group will be held in a position near the region, *trans* to the coordinated-N, where a new ligand is supposed to enter the coordination sphere and bind to the metal centre. Steric interference between this CH_3 group and the incoming ligand may then be the reason for destabilization of M-N coordination. With disruption of the M-N bond the σ-C monodentate bonded ligand can now rotate around the M-C bond resulting in a complex conformation in which the aryl and metal-coordination planes are perpendicular. In this conformation there is less steric interference while the original M-N site has become another free ligand site for incoming substrates. In this process the primary role of the ligand is restricted to covering and uncovering reactive sites at the metal centre ,*cf.* the first step in Scheme 1 which involves an equilibrium between three en four coordinate iridium(I) species (refs. 6, 7).

It must be noted, that the uncoordinated *ortho*-amino substituent represents a considerable steric bulk that can subsequently trigger further reactions in which our modelling ligand, **A**, **B** or **C**, may become involved. An excellent example of this is the intramolecular rearrangement of $Ir\{C_6H_3(CH_2NMe_2)-2-R-6\}(COD)$ (R = Me, or CH_2NMe_2) to $Ir\{C_6H_3(CH_2NMe_2)-2-R-4\}(COD)$ (ref. 8), that we recently found (Scheme I; ref. 7). This quantitative reaction, which we investigated

Scheme 1

14e T-shaped

Proposed mechanism for the quantitative conversion of $Ir^I\{C_6H_3(CH_2NMe_2)-2-R-6\}(COD)$ to $Ir^I\{C_6H_3(CH_2NMe_2)-2-R-4\}(COD)$ (R = Me or CH_2NMe_2).

using deuterium labelling, starts with the formation of a 14e, T-shaped Ir-intermediate which undergoes intramolecular C-H oxidative addition with one of the N-CH_3 groups and is succeeded by a unique sequence of highly regiospecific C–Ir and C–H bond-breaking and -making processes. The irreversibility of this rearrangement results from on the one hand the presence of severe steric interference between R' and the olefinic part of the coordinated COD ligand in $Ir\{C_6H_3(CH_2NMe_2)-2-R-6\}(COD)$ and on the other hand the absence of such interference in $Ir\{C_6H_3(CH_2NMe_2)-2-R-4\}(COD)$.

That reactions at a σ-C bonded metal centre can be initiated by a fixed stereochemistry of ligating atoms, is further illustrated by the process shown in Fig. 3.

In the tetraorganotin compound $SnPh_3\{C_{10}H_6NMe_2-8\}$ the Lewis basicity of the tin centre is too low to result in coordination of the NMe_2 group. However, since for steric reasons the N donor centre in the naphthyl ligand **B** is held in a fixed spatial orientation with its lone pair of electrons oriented towards the Sn atom, the metal centre will adopt a tbp-like geometry with an N---Sn-Ph^a alignment of 168.5 (1)° (Sn---N 2.884 (3) Å) (ref. 9, 10). As such, $SnPh_3\{C_{10}H_6NMe_2-8\}$ can be envisaged as a model for the early stages in S_N2 type processes where NMe_2 and Ph^a represent the entering and leaving groups, respectively. The reality of this view is suggested by the facile transfer of the Me group from Sn to Pt (Fig. 3) resulting in the formation of $SnClMe_2\{C_{10}H_6NMe_2-8\}$ (ref. 10). In this reaction anchimeric assistance for the Me transfer process is provided by the N donor atom. The X-ray structure of the corresponding triorganotin halide $SnBrMe_2\{C_{10}H_6NMe_2-8\}$ showed that these compounds are a true five-coordinate species with an N-Sn-Br angle of 171.5 (1)° and a much shorter N-Sn distance (2.496 (6) Å) than in $SnPh_3\{C_{10}H_6NMe_2-8\}$ (ref. 9). It is likely that reactions of this type, in which a process at a reacting metal centre is assisted by a donor atom that is not coordinated but held in a fixed spatial position in the coordination sphere, have great potential for the development of novel organometallic compounds or intermediates which exhibit new reactivity.
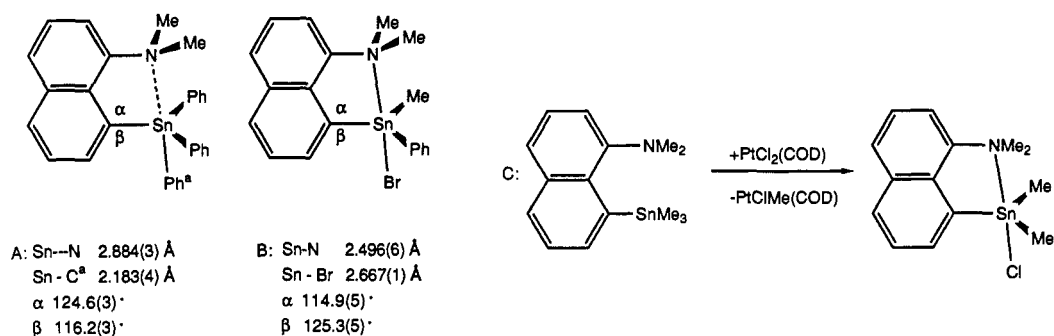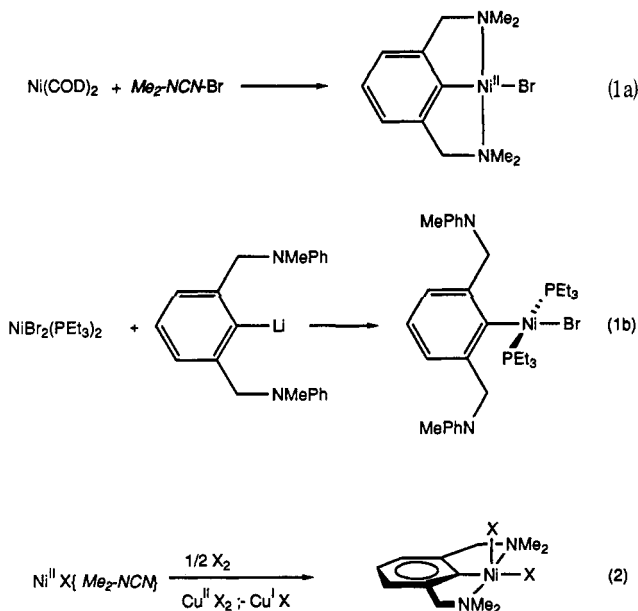
A: Sn---N 2.884(3) Å
   Sn - Cᵃ 2.183(4) Å
   α 124.6(3)°
   β 116.2(3)°

B: Sn-N 2.496(6) Å
   Sn - Br 2.667(1) Å
   α 114.9(5)°
   β 125.3(5)°

Fig. 3.(a). Schematic structure of a tetraorganotin compound with a trigonal bipyramidal-like geometry at the Sn [IV] centre caused by the fixed spatial orientation of the N lone pair of electrons. (b). Schematic structure of the corresponding triorganotin bromide in which the NMe_2 group coordinates to the Sn[IV] centre. (c). Methyl transfer reaction with anchimeric assistance by the N donor atom.

Here, our attention will be mainly directed to research in the area of oxidative addition reactions in which we employ metal d^8 centres that are bonded to C. By making use of the electron richness of these "pincer"-ligands, their stereochemical rigidity, and the restricted number of available coordination sites for the substrate, we study whether oxidative addition processes at the metal centre can be controlled.The results that have been obtained with two electrophilic substrates, *i.e.*, halogens and alkyl halides, clearly illustrate the points mentioned above and many aspects of this chemistry are unique.

A discussion of recently reported research done by others using terdentate ligand systems is beyond the scope of this paper (ref. 11). However, the many interesting features of this research will be incorporated in a forthcoming review on the synthesis and reactivity of terdentate monoanionic systems (ref. 12).

HALOGENS AS ELECTROPHILIC REAGENTS

The starting materials MX{R,R'-NCN }(M = Pd , Pt) were obtained by metathesis of the appropriate metal salt MX_2L_2 (L = a weakly coordinating ligand) and Li{R,R'-NCN}. (The structural features of {Li{$C_6H(CH_2NMe_2)_4$-2,3,5,6}]$_2$, an example of a dimeric aryllithium compound (ref. 3), are shown in Fig 2b). From the structure of PtBr{Me_2-NCN} (see Fig. 2C), one can see the flat appearance of these metal d^8 complexes and the puckering of the chelate rings in which the methyl groups occupy equatorial and axial positions (ref. 13). For a square-planar complex of *t-Bu,Me-NCN* there are in principle two diastereomers possible, *i.e.*, the *meso* and (*SS,RR*) enantiomeric pair which are separable by crystallization. In complex PtBr{Me_2-NCN} the characteristic $^1J^{195}Pt,^1H$ values for NCH_3 (38 Hz) and for NCH_2 (46 Hz) show that the N-Pt[II] interaction is considerable (ref. 13). The synthesis of analogous Ni[II] complexes is extremely interesting and two routes are available; *i.e.*, the oxidative addition reaction of the aryl bromides to Ni(COD)$_2$ (ref. 14; eqn.1a), or the reaction of an aryllithium with an appropriate Ni[II] salt (refs. 5,16 ; eqn 1b).

Ni(COD)$_2$ + *Me₂-NCN*-Br ⟶ (1a)

NiBr$_2$(PEt$_3$)$_2$ + ⟶ (1b)

Ni[II] X{ *Me₂-NCN*} $\xrightarrow[\text{Cu}^{II} X_2 : \text{Cu}^I X]{1/2 X_2}$ (2)

The route using bis(trialkylphosphine)nickel bromides with Li{*R,R'-NCN*} affords NiBr(*RR'-NCN*)(PR₃)₂ complexes in which the N donor atoms are not coordinated; P-Ni coordination of the monodentate PR₃ ligands being clearly more effective than intramolecular N-Ni bonding. The structure of the *Ph,Me-NCN* compound, as determined by X-ray crystallography, is shown in Fig.4 (ref. 5).
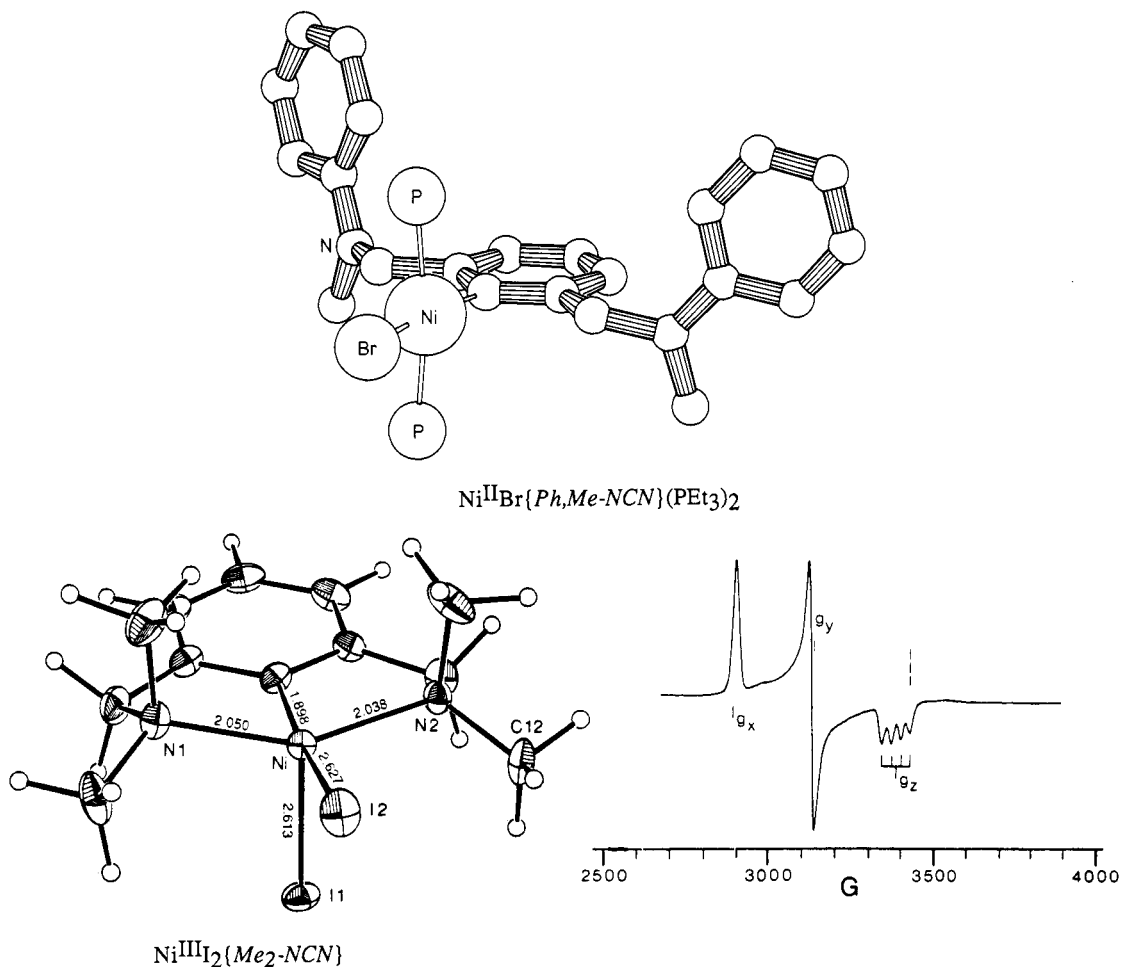

$Ni^{II}Br\{Ph,Me\text{-}NCN\}(PEt_3)_2$

$Ni^{III}I_2\{Me_2\text{-}NCN\}$

Fig. 4. Top: Structure of NiBr{*Ph,Me-NCN*}(PEt₃)₂ with free *ortho*-amino substituents (the ethyl groups of PEt₃ are omitted for clarity). Bottom: Structure of $Ni^{III}I_2\{Me_2\text{-}NCN\}$ (Ni-C 1.898, -I(2) 2.627, -I(1) 2.613, -N(1) 2.050 and -N(2) 2.038 Å) with next to it the 9.50 GHz X band ESR spectrum of $Ni^{III}Cl_2\{Me_2\text{-}NCN\}$ (A_z 28G) establishing the d^7 electronic configuration of the Ni centre.

In this compound the N atoms are probably not coordinated because of the favourable resonance stabilization of the N-lone pair with the Ph substituent which gives rise to the trigonal N atoms seen in the structure. The reaction of BrC₆H₃(CH₂NMe₂)₂-2,6 and Ni(COD)₂ that is the preferred route for the synthesis of $Ni^{II}Br\{Me_2\text{-}NCN\}$, affords a small amount of $Ni^{III}Br_2\{Me_2\text{-}NCN\}$, vide infra (ref. 14).

Halogen and copper(II) halide reactions of Ni(II)
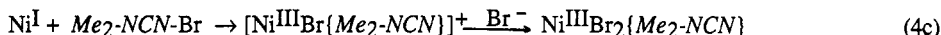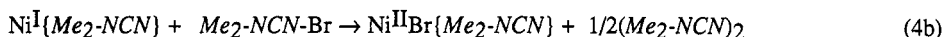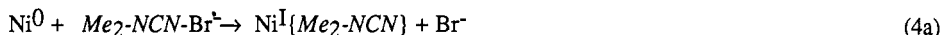
$Ni^{III}Br_2\{Me_2\text{-}NCN\}$, which is the first example of a true organometallic Ni^{III} complex, could be obtained via an independent route in a good yield involving oxidation of square-planar NiBr{*Me₂-NCN*} with Br₂ in benzene at room temperature, see eqn 2 (refs. 14, 16).
This is an example of an overall one-electron transfer reaction. Surprisingly, with another electrophilic reagent, $Cu^{II}X_2$ (X = Cl, Br), instead of the initially expected C-Ni bond cleavage, a similar one-electron transfer reaction with $Ni^{II}Br\{Me_2\text{-}NCN\}$ occurs. An X-ray structure of the corresponding iodo-complex $Ni^{III}I_2\{Me_2\text{-}NCN\}$ (see Fig.4B) shows a square-pyramidal nickel coordination sphere where the N,C,N-ligating atoms and one iodine atom define the basal plane and the second iodine atom is the apex. The ESR spectral data of this air-stable species and those of the bromo and chloro-analogues are consistent with a d^7 electronic configuration in which the metal-centred, unpaired electron is primarily in the d_{z^2}-orbital, see Fig. 4C for the ESR spectrum of $Ni^{III}Cl_2\{Me_2\text{-}NCN\}$ (ref. 16). The kinetically stable (aryl)C-Ni bond in these complexes supports the postulate that species with Ni^{III}-C σ-bonds are possible intermediates in the oxidative addition of aryl or alkyl halides to Ni^0-substrates (ref. 17). The reaction of BrC₆H₃(CH₂NMe₂)₂-2,6 (*Me₂-NCN*-Br) with Ni^0(COD)₂ is thus likely to have an

electron transfer mechanism in which the following pathway dominates:

$$Ni^0 + \ Me_2\text{-}NCN\text{-}Br \rightarrow [Ni^{I+} \{Me_2\text{-}NCN\text{-}Br\}^{\bullet-}] \rightarrow Ni^{II}Br\{Me_2\text{-}NCN\} \tag{3}$$
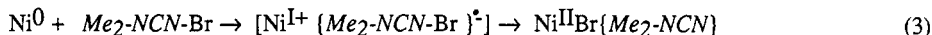
Side reactions that then can generate both Ni^{II} and Ni^{III} products can be envisaged

$$Ni^0 + \ Me_2\text{-}NCN\text{-}Br^{\bullet-} \rightarrow Ni^I\{Me_2\text{-}NCN\} + Br^- \tag{4a}$$

$$Ni^I\{Me_2\text{-}NCN\} + \ Me_2\text{-}NCN\text{-}Br \rightarrow Ni^{II}Br\{Me_2\text{-}NCN\} + 1/2(Me_2\text{-}NCN)_2 \tag{4b}$$

$$Ni^I + \ Me_2\text{-}NCN\text{-}Br \rightarrow [Ni^{III}Br\{Me_2\text{-}NCN\}]^+ \xrightarrow{\ Br^-\ } Ni^{III}Br_2\{Me_2\text{-}NCN\} \tag{4c}$$

Here, due to the special electronic properties of the NCN ligand, the Ni^{III} species (otherwise transient intermediates in reactions of $Ni^0(COD)_2$ with aryl halides) become trapped and thus isolable (ref. 14).

Striking is the ease with which the Ni^{II} centre of $NiX\{Me_2\text{-}NCN\}$ can be oxidized to Ni^{III} with retention of the σ-C-Ni bond. In water, independent of X, the oxidation of $Ni^{II}X\{Me_2\text{-}NCN\}$ and the reduction of $Ni^{III}X_2\{Me_2\text{-}NCN\}$ both occur at the same potential (E $= + 0.14$ V (vs. SCE) (ref. 14)). This independence suggests that in water the Ni^{II}/Ni^{III}-system constitutes a quasi-reversible redox couple:

$$[Ni^{II}\{Me_2\text{-}NCN\}(H_2O)] + \xrightarrow{\ e^-\ } [Ni^{III}\{Me_2\text{-}NCN\}(H_2O)_n]^{2+} \tag{5}$$
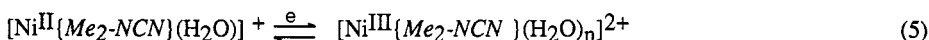
Preliminary experiments have indicated that by changing the amino substituents in $Ni\{R,R'\text{-}NCN\}$ complexes the $E_{1/2}$ values can be nicely tuned (refs. 5, 16). It is interesting to note that the low Ni(II)/Ni(III) redox couple for aqueous $Ni^{II}Cl\{Me_2\text{-}NCN\}$ is comparable to the Cu(I)/Cu(II) couple of -0.08 V of the inorganic copper catalyst applied for the Karasch addition reaction of polyhalogenoalkanes to an alkene double bond. This observation has led to the discovery that $Ni^{II}Cl\{Me_2\text{-}NCN\}$ is also, and an even more efficient homogeneous catalyst for this type of reaction, see the example shown in eqn.6 (ref. 18);


$$(6)$$
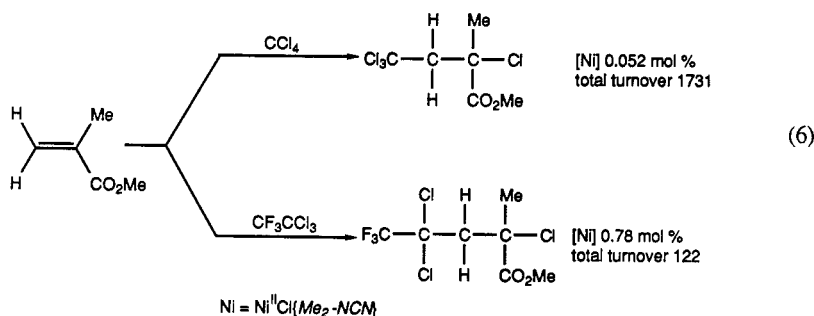
Preliminary studies have pointed to the absence of free radicals in solution (e.g., there is no telomer formation), but the involvement of carbon-centered radicals is almost certain. It is remarkable, therefore, that $Ni^{II}Cl\{Me_2\text{-}NCN\}$ can promote this reaction and at the same time retain the potentially reactive Ni^{II}-C σ-bond.

Halogen and copper(II) halide reactions of Pd(II) and Pt(II)

Oxidative addition of an electrophile (such as halogen or alkyl halides) to a Pt^{II} complex usually leads to a stable octahedral Pt^{IV} configuration (refs. 5, 19). This was found to be true for reactions of $PtX\{Me_2\text{-}NCN\}$ with Cl_2, Br_2 and $Cu^{II}X_2$ (X = Cl or Br) that quantitatively afforded octahedral $PtX_3\{Me_2\text{-}NCN\}$ complexes. In these latter species, the axial halogen atoms are both positioned close to an amino methyl group as a result of ring puckering (see Scheme 2 for the structure of a representative compound, X = Cl) (ref.19).

Scheme 2
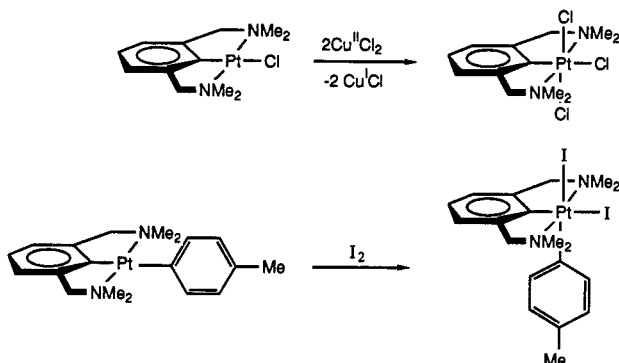
Reactions of electrophiles with $PtX\{Me_2\text{-}NCN\}$ (X = Cl or p-tolyl) to the corresponding octahedral platinum(IV) compounds of which the structures are schematically shown.

Moreover, in the related reaction of Pt(p-tolyl){Me₂-NCN} with I₂ the corresponding Pt^{IV}product was obtained in a high yield (refs. 5, 20); complexes derived from a possible cleavage of the Pt-C(tolyl) bond were not found. In this Pt^{IV} product the p-tolyl group is held between the axially positioned amino-methyl groups and, as a consequence, it cannot rotate around the Pt^{IV}-C(tolyl)-bond. This result suggests that (in the coordination sphere of the complexed metal centre) even the sterically smallest organic substituent on the N donor atom can significantly effect the amount of space that is available for other groups.

A real surprise was the outcome of the reaction of PtI{Me₂-NCN} with I₂. This reaction quantitatively affords a dark-purple, diamagnetic complex (possessing a PtI₃{Me₂-NCN} stoichiometry) whose spectroscopic features are not consistent with a Pt^{IV}configuration and, furthermore, are totally unlike those of the Pt^{II} starting material. The X-ray structure, see Fig. 5a,
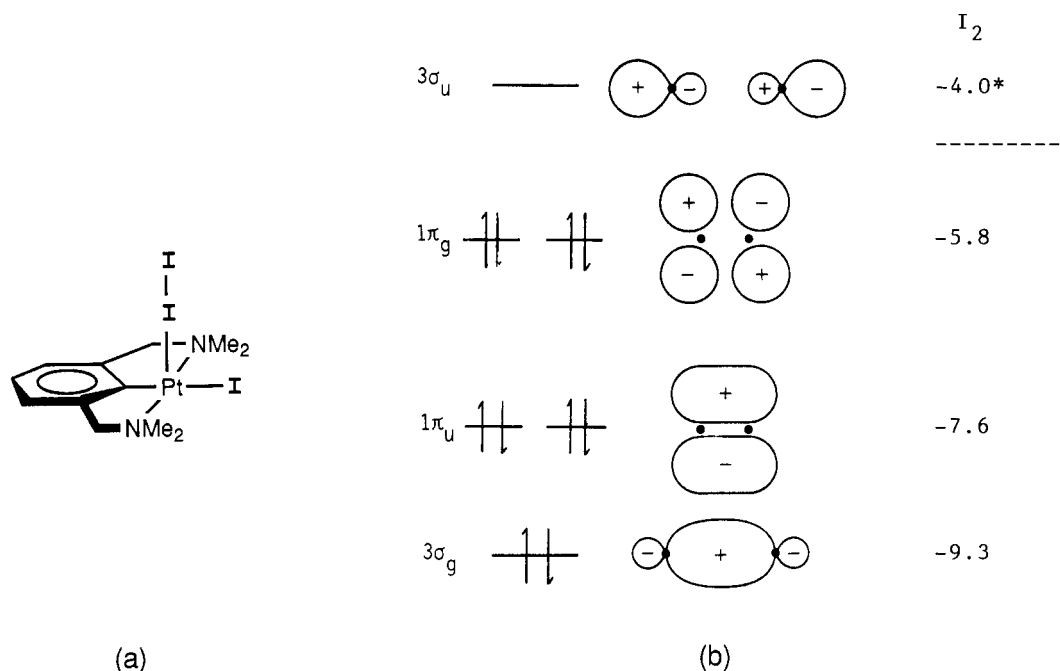
Fig. 5.(a). A schematic structure of PtI{Me₂-NCN}(η'-I₂) (Pt-C 1.937(9), -N 2.116(7), -I 2.727, -I (η'-I₂) 2.895 and I-I 2.822(1) Å) (b). The calculated MO data for I₂ showing the LUMO (3σ$_u$) of I₂ that interacts with the filled d$_z$2 orbital a platinum(II) leading to the η'-I₂ complex

shows that the PtI{Me₂-NCN} starting material is caught in what can be considered as the intimate first step of its interaction with an intact I₂ molecule (ref. 20). The halogen molecule approaches the Pt^{II} centre end-on along the z-axis (perpendicular to the coordination plane), and as a result a complex with a square pyramidal geometry is formed. (Note that chelate ring puckering is now such that the two axially positioned methyl groups are on the same side of the Pt-aryl ring plane). This platinum species is a true "trapped" intermediate. In this complex, that has a linear Pt-I-I allignment ($\angle$ = 179.43(4)°), a strong interaction exists between the filled d$_z$2 orbital on Pt and an σ*-orbital on I₂ (Fig. 5b) (ref. 21); this is reflected by the increase of the I-I bond length from 2.78 Å in free I₂ to 2.822(1) Å. Here, even though the halogen is activated, the electron transfer oxidative addition pathway, which led to formation of Ni^{III} (see eqn. 2), is obviously blocked. After the discovery of this first transition metal coordinated halogen molecule, we directed our efforts to obtaining insights into the factors that can influence this halogen coordination and subsequent oxidative addition reactions. Besides further synthetic work, resonance-Raman, NMR, and IR spectroscopic and electrochemical studies (ref. 22) were carried out to examine the role of the amino substituents and the nature of the metal centre. Although some aspects of this chemistry are not yet fully understood, the three structures in Figs. 5 and 6 form a sound basis for further discussion.

The complexes, PtI{Me₂-NCN}, PtI{Et₂-NCN} and PtI{t-Bu,Me-NCN} all react with iodine and form species in which the halogen molecule is tightly bonded (ref. 5). PdI{Me₂-NCN} binds I₂ only in the crystalline form and, in contrast to the above three complexes, readily looses I₂ on dissolution in hexane. The X-ray structure of PdI{Me₂-NCN}.2I₂ (Fig. 6a) shows two I₂ molecules in the crystal lattice. Neither of these interact with the Pd centre since chelate ring puckering is fully comparable to that found in the related compound PtI{Me₂-NCN}.

The I₂ complexes of PtI{Me₂-NCN} and PtI{Et₂-NCN} (see above) could be crystallized and were found by elemental analysis and X-ray crystallography to be the 1:1 adducts, PtI{R₂-NCN}(η'-I₂) (Fig. 5b). In solution the I₂ of the Pt^{II}-I₂ complexes react with a large excess of NEt₃ to give known Et₃N(η'-I₂) (ref. 23) and Pt^{II} starting material. The ¹H NMR spectrum of PtI{Me₂-NCN}(η'-I₂) reveals that the NCH₂ protons and NMe groups are not diastereotopic; this is not what we would expect for a molecule having a square-pyramidal structure
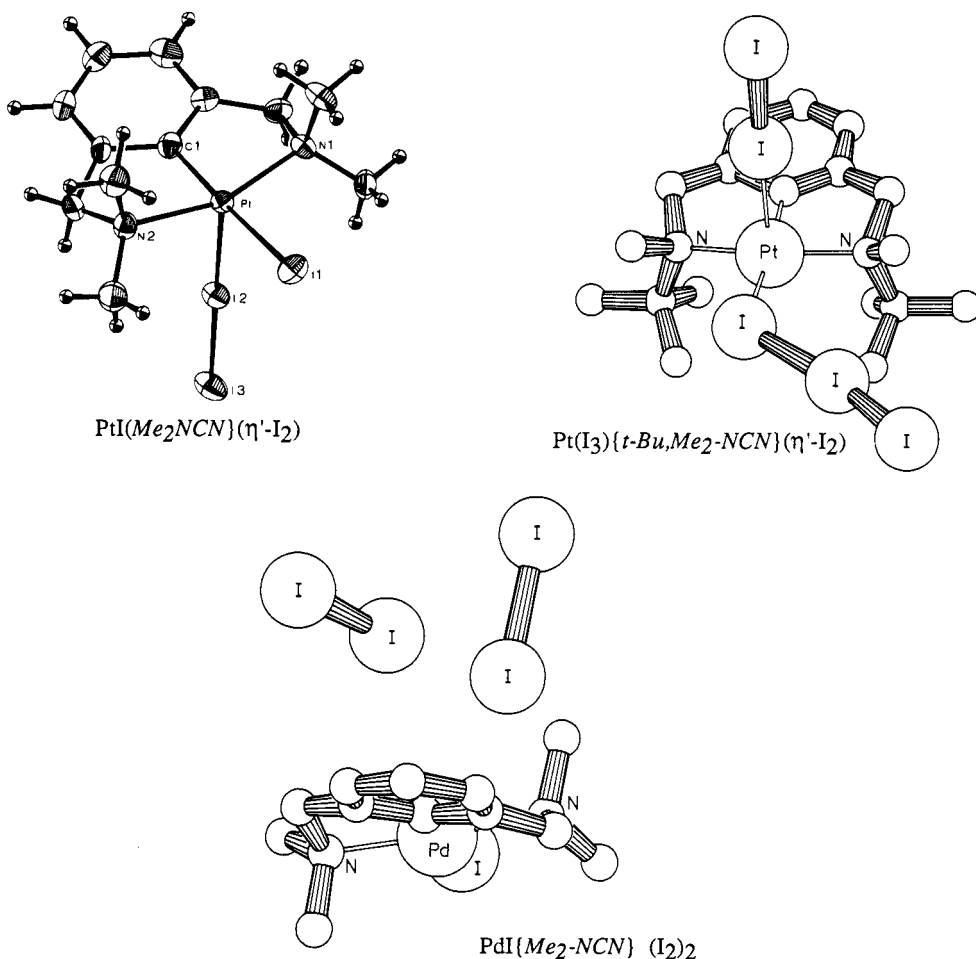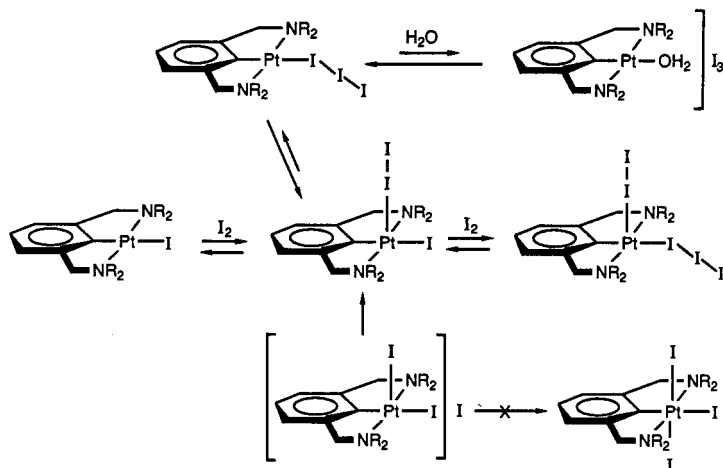
PtI{*Me₂NCN*}(η'-I₂)

Pt(I₃){*t-Bu,Me₂-NCN*}(η'-I₂)

PdI{*Me₂-NCN*} (I₂)₂

Fig. 6.X-ray structures of two η'-I₂ complexes (top) and of a Pd-complex with 2 molecules of I₂ included in the crystal lattice. Some data for PtI{*Me₂-NCN*}(η'-I₂) are in Fig. 5; Pt(I₃){*t-Bu,Me-NCN*}(η'-I₂): Pt-I(I₃) 2.773(2), Pt-I(η'-I₂) 2.908(2), I-I (of I₂) 2.793(3), I-I (of I₃⁻) are 3.072(4) and 2.768(4) Å (terminal). PdI{*Me₂-NCN*}: note that the shortest I(-Pd)...I (of I₂) distance is 3.591(3) and Pd...I (of I₂) is 3.992(3) Å.

like that established for PtI{*Me₂-NCN*}(η'-I₂). A possible explanation for this phenomenon is the process shown in Scheme 3.

Scheme 3

Proposed intermediates and equilibria for the reaction of PtI{*Me₂-NCN*} with I₂.

In resonance-Raman spectra of the I_2 complexes of PtI{Me_2-NCN} and PtI{Et_2-NCN } certain signals could indicate the presence of free I_2 and I_3^-. For this reason the formation of PtI$_3$\{t-Bu,Me-NCN\}(η'-I_2) from the reaction of PtI\{t-Bu,Me-NCN\} with I_2 was a real surprise. Its structure suggests that one I_2 molecule (some data are in Fig. 6b) has coordinated to Pt^{II} and a second one has coordinated to I. The two t-Bu groups are situated on one side of the basal plane of the square-pyramidel Pt^{II}-array. Obviously intermediate A (Scheme 3) is caught *flagrante delicto* with a second molecule. It must be noted that, <u>a</u> no oxidative addition has occurred; this supports the postulate that there is insufficient room to house three iodine atoms around a Pt^{II} centre held in the NCN terdentate matrix and, <u>b</u> the presence of two t-Bu groups, instead of two Me groups, as found in intermediate A (Scheme 3), enhances the nucleophilicity (Lewis basicity) of the Pt^{II}-centre and enables stabilization of the I_3-anion.

Mechanistic consequences

The structural features and reactivity of the PtI{R_2-NCN}-I_2 complexes provide a better insight into the possible mechanism by which metal-d^8 NCN complexes are oxidized with electrophilic reagents, *e.g.*, halogens and $Cu^{II}X_2$.

The synthesis of $Ni^{III}I_2${Me_2-NCN} and cis-PtI$_2${Me_2-NCN}(p-tolyl) from the reaction of I_2 with their corresponding Ni^{II} and Pt^{II} precursors probably involves an initial formation of a donor M^{II}-to-I_2 complex that is analogous to the molecular iodine complex PtI{Me_2-NCN}(η'-I_2). In a donor complex of this type, oxidative addition occurs by electron-transfer from the metal centre to the iodine molecule. In the case of the Pt^{II}-(p-tolyl) species, this step leads to a cationic Pt^{IV} intermediate and a free $I^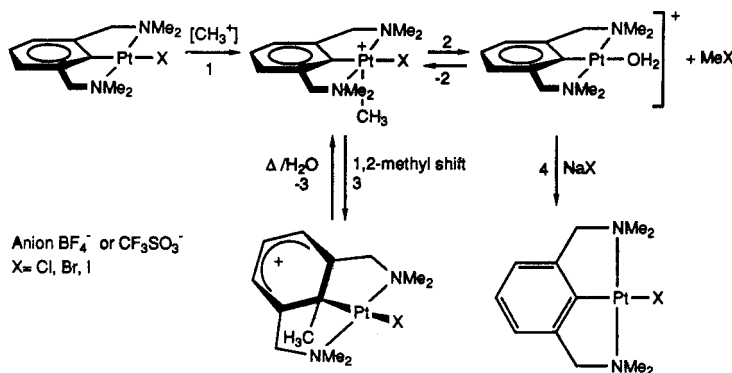-$ anion which, in the next step, recoordinates. In the case of Ni^{II} the formation of a Ni^{III} product suggests that one-electron transfer has occurred. In this reaction it is not clear whether a Ni^{IV}-intermediate is involved (that in a subsequent reaction with a Ni^{II} substrate could form $Ni^{III}I_2${Me_2-NCN}) or whether an $I^\bullet$ radical is involved (which could combine with Ni^{II} to form Ni^{III}).

Similarly, the oxidation reaction of $Cu^{II}X$ with MX{R,R'-NCN}, which forms the corresponding Ni^{III} and Pt^{IV} complexes, is likely to involve an initial interaction of the filled d_z2 orbital of the d^8 metal ion with the copper(II) salt. A subsequent inner-sphere electron ligand transfer oxidation reaction then affords the oxidized products and $Cu^{I}X$ (ref. 2). In this type of reaction the hard C and N donor atoms, which make the R,R'-NCN ligand extremely electron rich, are important for the determination of metal centre reactivity; corresponding oxidations of $Ni^{II}X${$C_6H_3(CH_2PPh_2)_2$-2,6} complexes (refs. 11, 24) (which have C and P donors) with either halogen or copper(II) salts to Ni^{III} analogues are not successful (ref. 24). Moreover, whereas the Ni^{III}- and Pt^{II}-{Me_2-NCN} complexes are oxidized by copper(II) salts the corresponding Pd^{II}-complex is not. This observation seems to corroborate with the fact that the UV-PE spectra of the Ni and Pt complexes show a lower first ionization energy (IE) than the corresponding Pd^{II} complex. This rather low IE is attributed to the presence of a π-type orbital delocalized over a large part of the molecule with antibonding M–C character (ref. 25).

ALKYL IODIDES AS ELECTROPHILIC REAGENTS

Other aspects of the mechanism of oxidative addition are highlighted when MeY reagents instead of halogens are used with MX{R,R'-NCN } substrates. For example the reaction of MeOTf (OTf is trifluoromethanesulphonate) with PtX{Me_2-NCN} (X = Cl, Br, I) affords the unusual cationic arenonium species [PtX{Me_2-NCN-Me}]OTf, and the corresponding reaction of MeI with Pt{Me_2-NCN}(o-tolyl) affords related [Pt{Me_2-NCN-Me}(o-tolyl)]I, (see Scheme 4 and Fig. 7; ref. 26).
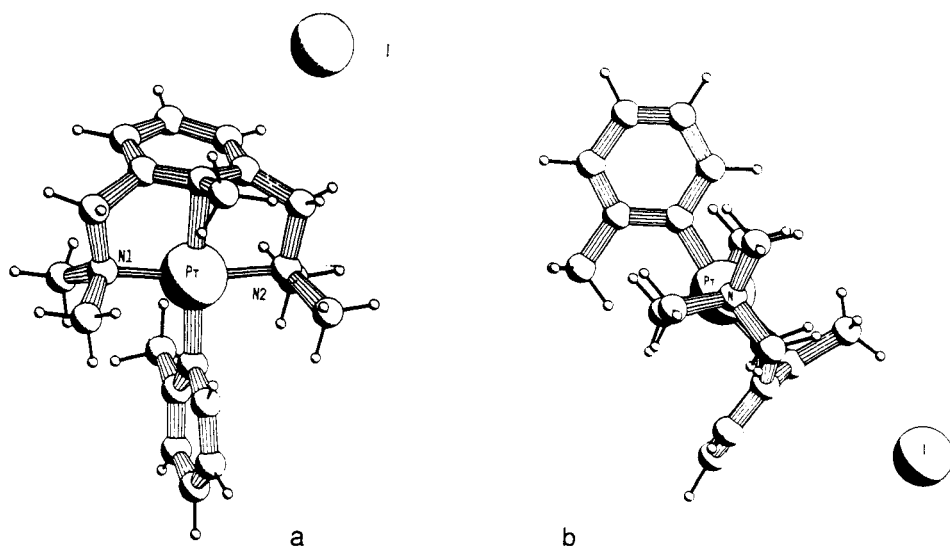
Scheme 4

Reaction pathways of neutral $Pt^{II}X${Me_2-NCN} and cationic [Pt{Me_2-NCN}(H$_2$O)]$^+$ with MeOTf, MeI or CD$_3$I explaining the observed C-C bond making and breaking processes.

a   b

Fig. 7. Structure of [Pt(*p*-tolyl){*Me2-NCN*-Me}]I which is formed quantitatively in the reaction of Pt(*p*-tolyl) {*Me2NCN*} with methyl iodide.; b shows the view along the N-Pt-N axis.

In both cases a methyl group, formally a Me^+, becomes bonded to the aryl C_{ipso} atom of the *Me2-NCN* ligand and the aryl ring acquires a positive charge; the product can consequently be considered to be a metal substituted Wheland intermediate (ref. 27). One can envisage, based on results obtained with I_2, that in these reactions of a Pt{*Me2-NCN*}-containing substrate, the d_z2 orbital interacts as a nucleophile with the carbon atom in the MeY reagents. It is postulated that an S_N2 reaction affording the five-coordinate cationic platinum intermediate [Pt{*Me2*-*NCN*}- (Me)(aryl)]Y occurs. This species is not stable and the Me group transfers, by a 1,2-shift (refs. 26, 28) to the metal bonded C_{ipso} atom of the *Me2-NCN* ligand in what can be interpreted as an abortive attempt at reductive elimination of 1,3-(Me_2NCH_2)$_2$-2-MeC_6H_3. However, this organic moiety remains firmly held to the metal centre by the two strongly bonded CH_2NMe_2 arms and the compound [Pt{*Me2-NCN*-Me}(aryl)]Y that results is another novel trapped "intermediate". Note that a species of this type could be regarded as an intermediate in the oxidative addition of a C-C bond of a Me substituted aromatic compound (*e.g.*, toluene) to a [PtL$_2$(aryl)]Y complex. However, the reaction of MeI with PtBr{*Me2-NCN*} does not give an arenonium product, but affords an equilibrium mixture of the starting materials, PtI{*Me2-NCN*} and MeBr. Although no intermediate(s) could be identified in this system, the involvement of five coordinate Pt^{IV} cationic species is, based on the aforementioned reactions, highly likely.

An interesting outcome of further studies on oxidative additions of [Pt{*Me2-NCN*}- (H_2O)]OTf with other alkyl halides (to prepare analogues of [PtX{*Me2-NCN*-Me}]OTf) was the finding that there is another reaction pathway which can predominate over the one described above for MeY. When an excess of EtI or i-PrI is added to [Pt{*Me2-NCN*}(H_2O)]OTf in acetone at room temperature a slow reaction (ca. 10 days) takes place and this affords the remarkable dimeric complex [Pt{$C_6H_3(CH_2NHMe_2)_2$-2,6}I_2]$_2$(OTf)$_2$ (structure shown in Fig. 8) together with 2 equivalents of ROH for each equivalent of Pt^{II} starting material, see Scheme 5 (ref.29).

Moreover, preliminary experiments indicate that benzyl iodide and allyl iodide react even faster than ethyl and i-propyl iodide and also result in formation of the same [Pt{$C_6H_3(CH_2NHMe_2)_2$-2,6}I_2]$_2$(OTf)$_2$. The structure of the dimeric unit of this novel platinum(II) compound contains two bridging iodo atoms that link two square planar Pt^{II} centres; each Pt^{II} coordination sphere is completed by a terminal iodine atom and the C_{ipso} atom of a NCN system that has two protonated, uncoordinated CH_2NMe_2 arms. Since the dinuclear dication carries four $[CH_2NHMe_2]^+$ units the central [aryl$_2$Pt$_2$I$_4$]-system will then carry a double negative charge; the implication is that this organometallic species is Zwitterionic. It appears that coordination of three iodine atoms to a single Pt^{II} centre is only feasible when the arms of *Me2-NCN* are not coordinated. This idea is supported by the proton abstraction reaction of [Pt{$C_6H_3(CH_2NHMe_2)_2$-2,6}I_2]$_2$(OTf)$_2$ with EtNi-Pr$_2$ that results both in reformation of the Pt-N coordination and in loss of two Pt-I interactions at each metal centre.

Scheme 5
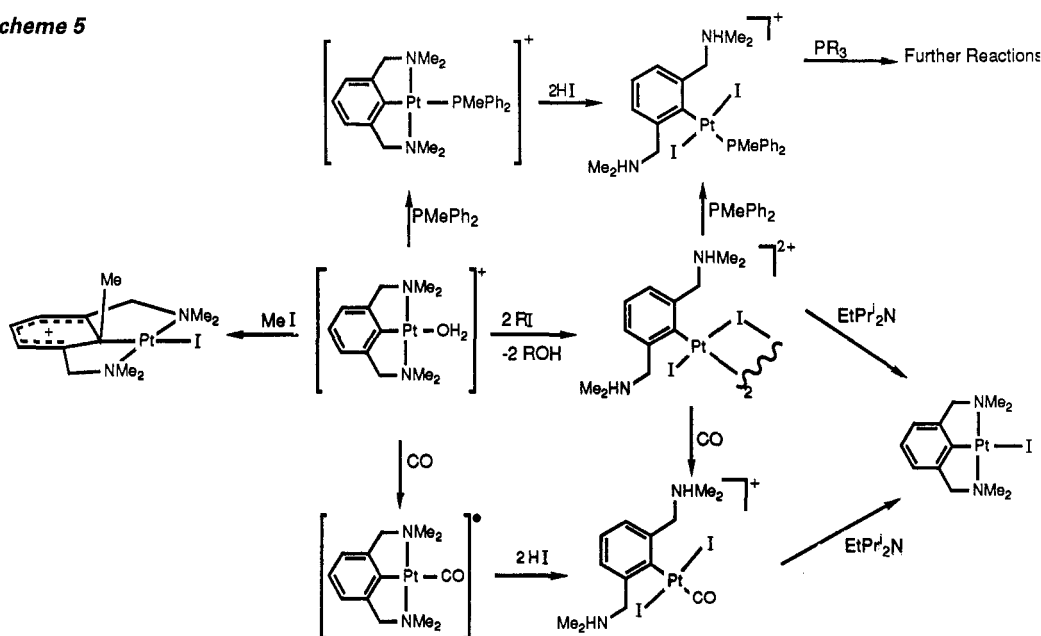
Observed reaction of [Pt{*Me₂-NCN*}(H₂O)]-cation. Note that the reaction with HI does not yield [Pt{C₆H₃(CH₂NHMe₂)₂-2,6}I₂]₂²⁺ but instead neutral PtI{*Me₂-NCN*} and the iodine complex PtI{*Me₂-NCN*}(η'-I₂).
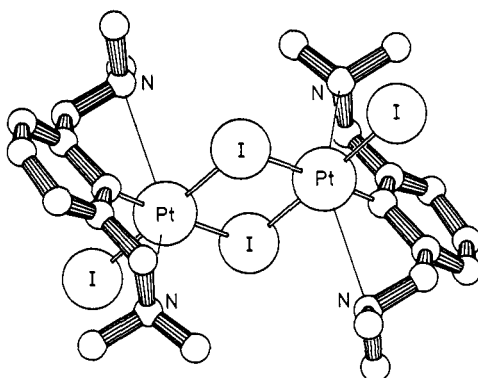
Fig. 8. X-ray structure of Zwitterionic [Pt{C₆H₃(CH₂NHMe₂)₂-2,6}I₂]₂(OTf)₂: only the dication is shown. Pt-C 1.98, -N 3.25 (mean), -I (terminal) 2.58, -I (bridge) 2.69 (*trans* to C_{ipso}) and 2.59 (*cis* to C_{ipso}).

An other reaction with an unexpected result is that of the cationic carbon monoxide complex [Pt{*Me₂-NCN*}(CO)] with HI, see Scheme 5. This reaction afforded [Pt{C₆H₃(CH₂- NHMe₂)₂-2,6}I₂(CO)](OTf) in which the CO molecule is still coordinated and the Pt^{II} coordination sphere is completed by two terminal iodide ions and the C_{ipso} atom of a NCN system that has two protonated, uncoordinated CH₂NHMe₂⁺ arms. It is interesting that different types of product are formed in reactions of [Pt{*Me₂-NCN*}(H₂O)]⁺ with MeI and with other alkyl iodides. A possible explanation for this difference is that the MeI reaction follows an S_N2 type of process whereas this route is blocked (or too slow) for the other alkyl iodides. There are several alternative routes available. Firstly, these iodides could react via a mechanism that involves the pre-equilibrium (eq.7) in which the formation of HI is the slow step.

$$RI + H_2O \rightleftharpoons ROH + HI \tag{7}$$

$$[Pt\{Me_2\text{-}NCN\}(H_2O)]^+ \rightarrow [Pt\{Me_2\text{-}NCN\}(OH)] + H^+ \tag{8}$$
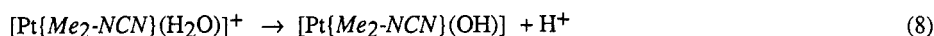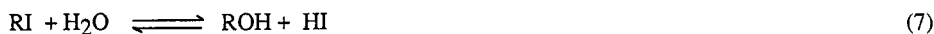
Any HI thus formed could then react with the [Pt{*Me₂-NCN*}(H₂O)]⁺ species (*cf.* the reaction of HI with cationic [Pt{*Me₂-NCN*}(CO)]⁺). However, the direct reaction of Pt{*Me₂-NCN*}(H₂O)]⁺ with HI affords neutral PtI{*Me₂-NCN*} as well as the iodine complex PtI{*Me₂-NCN*}(η'-I₂). This result seems to exclude a mechanisme with pre-equilibrium 7 as a key-step.

Secondly, the mechanism could involve preformation of a neutral $Pt^{II}OH$ product (eqn. 8) that subsequently reacts with RI. This reaction with RI would again be of an S_N2 type and its occurrence is less likely (slower) with the higher alkyl iodides. Finally, a mechanism could be considered whose initial step is the coordination of the alkyl

iodide via the iodine donor (*cf.*, ref. 30) to the Pt cationic centre; a process that would be expected to weaken Pt-N coordination.

Scheme 6
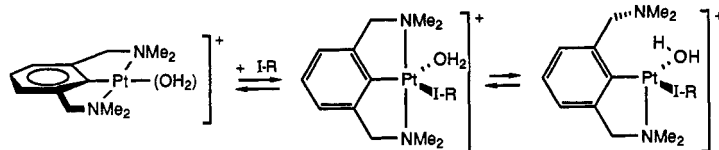
Proposed first step in the reaction of [Pt{*Me$_2$-NCN*}(H$_2$O)]$^+$ with RI.

We can now consider the latter mechanism in detail. In an <u>intramolecular</u> sequence of reactions (one possibility for the first step is suggested in Scheme 6) one could imagine the formation of ROH, the generation of a Pt-I interaction, and the protonation of a dissociated N donor atom. The fact that protonation requires prior dissociation of the rather strong Pt–N bond may explain the low reaction rate. As is shown in Scheme 5 each [Pt{*Me$_2$-NCN*}(H$_2$O)]$^+$ cation produces two ROH molecules. On steric grounds it is likely that the mono-protonated intermediate, that is formed after the first RI → ROH cycle, will be more reactive than the starting platinum cation with the stable situation of bis *ortho* chelation. In the mono-protonated intermediate the presence of one uncoordinated, bulky *ortho* substituent (*i.e.*, CH$_2$NHMe$_2$$^+$) makes Pt-N dissociation of the second CH$_2$NMe$_2$ group irreversible, *cf.*, the discussion above of the steric interference exerted by an uncoordinated CH$_2$NMe$_2$ group on the process shown in Scheme 1. If this mechanism is operative it would be a nice (and to our knowledge first) example in organometallic chemistry of a reaction that occurs on a metal centre and is assisted by a nearby, intramolecularly placed Lewis base that is held in a fixed spacial orientation to this reactive metal centre.

At this moment, the role played by the CH$_2$NMe$_2$ groups in reactions of metal-NCN complexes with alkyl iodides and HI is incompletely understood. If the N donor atom of this group is coordinated it cannot react with electrophilic substrates whereas the free CH$_2$NMe$_2$ arm can rapidly react with alkyl iodides or HI and provide the quaternary ammonium group [CH$_2$NRMe$_2$]$^+$ (R is alkyl or H).

In the reaction of [Pt{*Me$_2$-NCN*}(H$_2$O)]$^+$ with alkyl iodides we assumed that at a certain point in the reaction the Pt-N bond has to dissociate to give the ammonium group, however, in Au(I) and Rh(I) compounds shown in Fig. 9 a free CH$_2$NMe$_2$ substituent is already present.
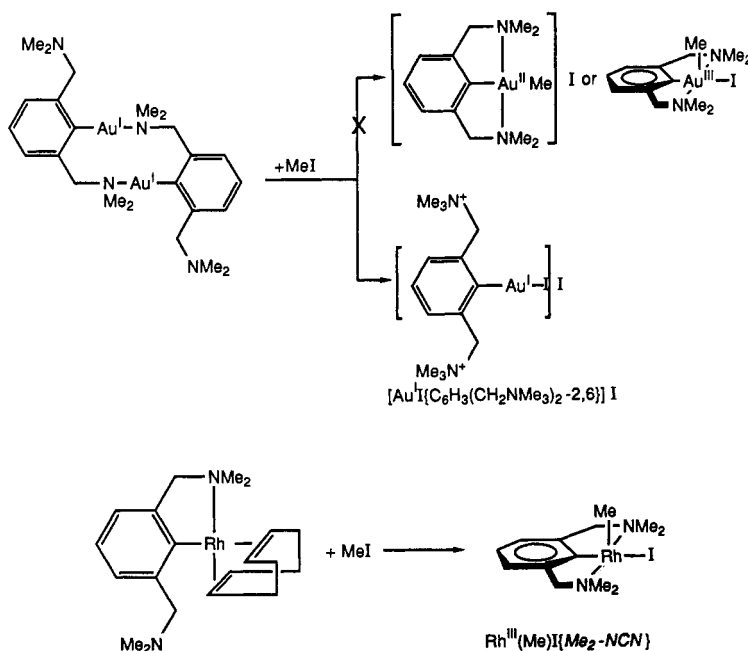

Fig. 9. Reactions of methyl iodide with metal-*Me$_2$NCN* complexes which already contain one non-coordinated *ortho*-CH$_2$NMe$_2$ arm.

Both compounds react quantitatively with methyl iodide, however, with a completely different outcome. In the case of the gold(I) dimer we had expected the formation of the corresponding cationic or neutral gold(III) product, [Au(Me){*Me$_2$-NCN*}]I or Au(Me)I{*Me$_2$-NCN*}, respectively (ref. 31). Instead this reaction afforded an other interesting example of a Zwitterionic organometallic compound, [AuI{C$_6$H$_3$(CH$_2$NMe$_3$)$_2$-2,6}]I which moreover seems to be the first example of a heteroaurate(I) compound. Whether this reaction involves a direct nucleophilic attack of the free amine function of [Au{*Me$_2$-NCN*}]$_2$ to MeI to form the Zwitterionic product with the [CH$_2$NMe$_3$]$^+$ substituent or proceeds via a prior oxidative addition reaction to give a transient Au(III) species is currently studied. In the case of the reaction of Rh^I{*Me$_2$-NCN*}(COD) the oxidative addition product Rh^{III}(Me)I{*Me$_2$-NCN*} is formed (refs. 6, 32). If this reaction proceeds via an S$_N$2 type of mechanism the exclusive formation of five coordinate Rh^{III}(Me)I{*Me$_2$-NCN*} indicates that the Rh^I centre in Rh^I{*Me$_2$-NCN*}(COD) is a better Lewis base that the N donor atom in the uncoordinated CH$_2$NMe$_2$ arm.

CONCLUSIONS

The use of heteroatom containing substituents in the organo group of organometallic species provides an interesting means of steering the reactivity of a complexed metal centre. This particularly applies when the donor atoms are held in a fixed spatial orientation to the metal centre (metal-donor atom coordination vs. metal-substituent steric interference).

The present results indicate that it is important to pay more attention to organometallic species in which one or various N-donor ligands (instead of P-donor ligands) bind to the metal centre because this particular binding could lead to: **1.** new stability patterns, *cf.* η'-I$_2$ complexation, formation of complexes with stable Ni^{III}-C bonding *vide infra.* and **2.** new reaction patterns in homogeneous catalysis. Moreover, when the N-donor atom is connected to the organo group but not coordinated to the metal centre, this N-donor atom can participate (assist) in reactions which take place at the metal centre (*cf.* reaction of alkyl iodides with a Pt{*Me$_2$-NCN*}(H$_2$O)-cation).

Acknowledgement

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