

## SYNTHESIS OF METAL-TETRAAZADIENE COMPLEXES VIA $\text{Ar}_2\text{N}_4$ LIGAND TRANSFER. EVIDENCE FOR A STABLE TETRAAZADIENE-BRIDGED INTERMEDIATE

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### Summary

Tetraazadiene ligands ( $\text{Ar}_2\text{N}_4$ ,  $\text{Ar} = 4\text{-MeC}_6\text{H}_4$  or  $3,5\text{-Me}_2\text{C}_6\text{H}_3$ ) have been transferred under mild conditions from  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  to another nickel or platinum centre to yield  $[\text{M}(\text{Ar}_2\text{N}_4)(\text{t-BuNC})_2]$  complexes. No transfer was observed to a palladium centre, and neither was it observed to Ni or Pt in the presence of coligands other than t-BuNC. The reactions proceed via dinuclear intermediates of the type  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$ . These complexes have also been isolated in cases when further transfer reactions did not take place (i.e.  $\text{M} = \text{palladium}$  or  $\text{L} = \text{PEt}_3$ ). One of the  $\text{Ar}_2\text{N}_4$  ligands in these dinuclear complexes is assumed to be bridging between nickel and M in a mode analogous to the  $\sigma\text{-N}, \sigma\text{-N}'$  bridge bonding mode found in platinum and palladium complexes of the 1,4-diaza-1,3-butadiene ligand.

### Introduction

To date, two preparative routes to the formation of tetraazadiene-metal complexes are known, comprising the reaction of a metal centre with an aryl azide [1] or a diazonium salt [2]. Both routes lead to formation of mono-(tetraazadiene)metal complexes  $[\text{M}(\text{R}_2\text{N}_4)(\text{L})_n]$ .

In the course of our studies of tetraazadiene-metal chemistry we have prepared a series of mono(tetraazadiene)metal complexes, including  $[\text{Ni}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$  [3] and  $[\text{Pt}(\text{Ar}_2\text{N}_4)(\text{COD})]$  [4], as well as the first examples of bis-(tetraazadiene)metal complexes;  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  [3a,5].

All reported tetraazadiene-metal complexes are monomeric, with the  $\text{R}_2\text{N}_4$  ligand bonded to the metal via the two  $\text{N}^\alpha$  atoms, a coordination mode

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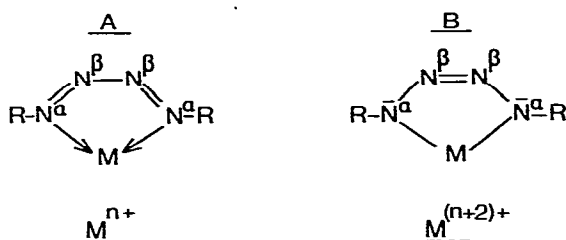


Fig. 1. Two canonical forms for the formal valence structure of the coordinated tetraazadiene ligand.

established in crystal structure determinations of these complexes [2,3,4b,5,6]. In principle two bonding modes for these complexes can be expected (see Fig. 1). Type A represents the ligand bonded in its neutral heterodiene form and is the main canonical form encountered in  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ , containing almost equal  $\text{N}^{\alpha}-\text{N}^{\beta}$  and  $\text{N}^{\beta}-\text{N}^{\alpha}$  bond lengths [3a,5]. By contrast, accommodation of charge from the metal in the LUMO of the  $\text{R}_2\text{N}_4$  ligand leads to a bonding mode according to B, representing the ligand bonded in dianionic form. Prevalence of the latter bonding mode is found in complexes with coligands, which are less strongly  $\pi$  accepting than the tetraazadiene ligand. Examples are  $[\text{Ni}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$  [3],  $[\text{Co}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$  [6b] and  $[\text{Pt}(\text{Ar}_2\text{N}_4)(\text{COD})]$  [4].

The difference in the two  $\text{MN}_4$  bonding modes is reflected in the reactivity of the  $\text{R}_2\text{N}_4$  ligands in these complexes. Whereas one tetraazadiene ligand in  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  can be replaced by tert-butyl isocyanides, leading to formation of  $[\text{Ni}(\text{Ar}_2\text{N}_4)(\text{t-BuNC})_2]$  [3a,5], attempts to replace an  $\text{R}_2\text{N}_4$  ligand by neutral ligands in mono(tetraazadiene)metal complexes failed [1].

We report now an alternative route for the preparation of  $[\text{M}(\text{Ar}_2\text{N}_4)(\text{t-BuNC})_2]$  complexes, using the reactions of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  with  $[\text{Ni}(\text{COD})_2]$  or  $[\text{Pt}(\text{COD})_2]$  in the presence of excess t-BuNC under mild conditions. These reactions involve transfer of the  $\text{Ar}_2\text{N}_4$  ligand from  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  to another nickel or platinum centre. FD-mass, infrared and analytical evidence is presented for the formation of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  complexes. The presence of dinuclear species in tetraazadiene transfer reactions is evidenced by the isolation of a stable intermediate of that type from such a reaction. Those dinuclear complexes  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  in which M was palladium ( $\text{L} = \text{PEt}_3$ , t-BuNC) or L was  $\text{PEt}_3$  (M = platinum and palladium) did not react further. Part of this work has been reported in a preliminary communication [4a].

## Experimental

All preparations were carried out under deoxygenated  $\text{N}_2$ . Solvents were dried and distilled before use.  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  complexes [3a,5], tert-butyl isocyanide [7], bis(1,5-cyclooctadiene)nickel,  $[\text{Ni}(\text{COD})_2]$ , [8], bis(1,5-cyclooctadiene)platinum,  $[\text{Pt}(\text{COD})_2]$ , [9], tris(norbornene)palladium,  $[\text{Pd}(\text{Nor})_3]$ , [9],  $[\text{Pt}_3(\text{t-BuNC})_6]$  [10] and  $[\text{Ni}_4(\text{t-BuNC})_7]$  [11] were prepared according to literature methods.

The IR spectra of the compounds as KBr disks or Nujol mulls were recorded

on a Perkin-Elmer 283 spectrophotometer.

Field Desorption mass spectra were obtained with a Varian MAT 711 spectrometer. The samples were placed on the emitter by the dipping technique.

*Preparation of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2\text{M}(\text{L})_2]$  complexes*

$\text{M} = \text{Pt}$  and  $\text{L} = t\text{-BuNC}$  (I). I was prepared by the addition of  $t\text{-BuNC}$  (0.2 ml, 2 mmol) to a mixture of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  (270 mg, 0.5 mmol) and  $[\text{Pt}(\text{COD})_2]$  (205 mg, 0.5 mmol) in toluene (7 ml) at  $25^\circ\text{C}$ . In 2 minutes the colour of the mixture changed from deep red-purple to red and a red oil was deposited on the wall of the reaction vessel. The solution was decanted off and the remaining oil was washed with toluene until the washings were only slightly red ( $3 \times 5$  ml). The product was then taken up in THF (5 ml), the solution filtered through Celite and the product precipitated with hexane (15 ml). The oily precipitate was washed with hexane ( $3 \times 10$  ml) and vigorously stirred with hexane (10 ml) for one hour at  $0^\circ\text{C}$  to yield 300 mg (67%) of I as a dark red powder.

$\text{M} = \text{Pt}$  and  $\text{L} = \text{PEt}_3$  (II),  $\text{M} = \text{Pd}$  and  $\text{L} = t\text{-BuNC}$  (III) or  $\text{PEt}_3$  (IV). The complexes II–IV were prepared as described above for I. The yields were about 70%. Complexes III and IV were prepared using  $[\text{Pd}(\text{Nor})_3]$  as starting material, and the reaction mixtures were kept at  $0^\circ\text{C}$  until the addition of  $t\text{-BuNC}$  or  $\text{PEt}_3$  was completed. Complex III was prepared more easily by addition of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  to  $[\{\text{Pd}(t\text{-BuNC})_2\}_n]$ .

$[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  was recovered from products I to IV in almost quantitative yield by passing their THF solutions down a silica column.

Analyses for products I–IV: Anal. Calcd. for I ( $\text{C}_{38}\text{H}_{46}\text{N}_{10}\text{NiPt}$ ): C, 50.90; H, 5.17; N, 15.63. Found: C, 50.3; H, 5.8; N, 14.5%. Calcd. for II ( $\text{C}_{40}\text{H}_{58}\text{N}_8\text{P}_2\text{NiPt}$ ): C, 49.69; H, 6.05; N, 11.59; P, 6.41. Found: C, 53.5; H, 6.8; N, 11.7; P, 6.0%. Calcd. for III ( $\text{C}_{38}\text{H}_{46}\text{N}_{10}\text{NiPd}$ ): C, 56.49; H, 5.74; N, 17.34. Found: C, 55.7; H, 6.4; N, 16.2%. Calcd. for IV ( $\text{C}_{40}\text{H}_{58}\text{N}_8\text{P}_2\text{NiPd}$ ): C, 54.71; H, 6.66; N, 12.76; P, 7.06. Found: C, 53.7; H, 6.7; N, 12.0; P, 7.5%.

*Ligand transfer reactions*

*Preparation of  $[\text{Pt}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}(t\text{-BuNC})_2]$  (V).* (i) *Starting from I.* A solution of I (200 mg, 0.22 mmol) in THF (5 ml) was kept for 8 h at  $60^\circ\text{C}$ . The solution was filtered and pentane was added (15 ml). The resulting precipitate was washed with pentane ( $3 \times 5$  ml) and crystallized from a THF/pentane mixture to yield 60 mg (45%) of known V [4]. When I was heated in the presence of an excess of  $t\text{-BuNC}$ , a mixture of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}(t\text{-BuNC})_2]$  (VI) [3] and V was obtained, as evidenced by comparison of IR data and FD mass spectra with those of authentic samples of V and VI.

(ii) *Starting from  $[\text{Pt}_3(t\text{-BuNC})_6]$ .* A mixture of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  (200 mg, 0.37 mmol) and  $[\text{Pt}_3(t\text{-BuNC})_6]$  (135 mg, 0.12 mmol) in THF (4 ml) was heated for 8 h at  $60^\circ\text{C}$ . Work-up of the mixture was as described above. The yield was 65 mg (30%).

*Preparation of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}(t\text{-BuNC})_2]$  (VI).* (i) *From  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$ ,  $[\text{Ni}(\text{COD})_2]$  and  $t\text{-BuNC}$ .*  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  (270 mg, 0.5 mmol) was added to a suspension of  $[\text{Ni}(\text{COD})_2]$  (140 mg, 0.5 mmol)

in toluene (10 ml). The colour of the mixture immediately turned brown, and on adding *t*-BuNC (0.2 ml, 2 mmol) changed to dark red purple. After heating the mixture for 8 h at 60°C the colour was green. After cooling to room temperature pentane was added (20 ml). The resulting precipitate was filtered off, washed with pentane (3 × 5 ml) and recrystallized from a THF/pentane mixture to yield 90 mg (40%) of known VI [3].

(ii) From  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  and  $[\text{Ni}_4(\text{t-BuNC})_7]$ .  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  (270 mg, 0.5 mmol) was added to a solution of  $[\text{Ni}_4(\text{t-BuNC})_7]$  (100 mg, 0.12 mmol) in toluene (10 ml). The colour of the mixture changed from red to dark red-brown. *t*-BuNC (0.2 ml, 2 mmol) was added and the colour turned to dark red-purple. Heating and subsequent work-up of the mixture was carried out as described above. The yield was the same.

The preparation of  $[\text{Ni}\{1,4-(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4\}(\text{t-BuNC})_2]$  (VII) proceeded along the same lines as the preparation of VI, but the dark red-purple colour, indicative of the presence of free  $[\text{Ni}\{1,4-(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4\}_2]$ , did not appear upon addition of an excess of *t*-BuNC. The yield of known VII [3] was 80%. The yields for the preparations of VI and VII are calculated for the total amount of nickel present.

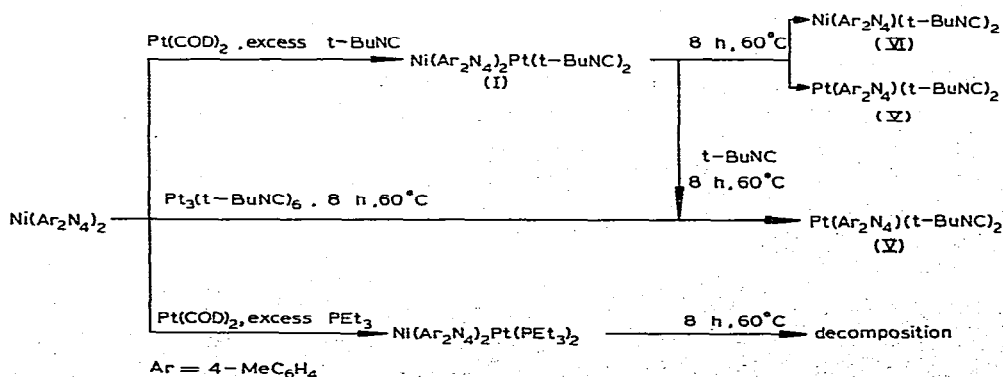
## Results

$[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  reacted with  $[\text{Pt}(\text{COD})_2]$  or  $[\text{Pd}(\text{Nor})_3]$  upon addition of excess *t*-BuNC or  $\text{PEt}_3$  to give the complexes  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  (I, M = Pt and L = *t*-BuNC; II, M = Pt and L =  $\text{PEt}_3$ ; III, M = Pd and L = *t*-BuNC; IV, M = Pd and L =  $\text{PEt}_3$ ). These compounds are red to red-brown, only sparingly soluble in toluene but soluble in THF.  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{Pd}(\text{t-BuNC})_2]$  (III) could also be prepared by reaction of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  with  $[\{\text{Pd}(\text{t-BuNC})_2\}_n]$  (see Schemes 1 and 2).

THF solutions of the complexes I to IV decomposed upon filtering through a silica column to give back the  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  starting material. Although the complexes seemed to remain intact after filtering through Celite, this method did not yield samples of very high analytical purity. However, FD-mass spectra, indicat-

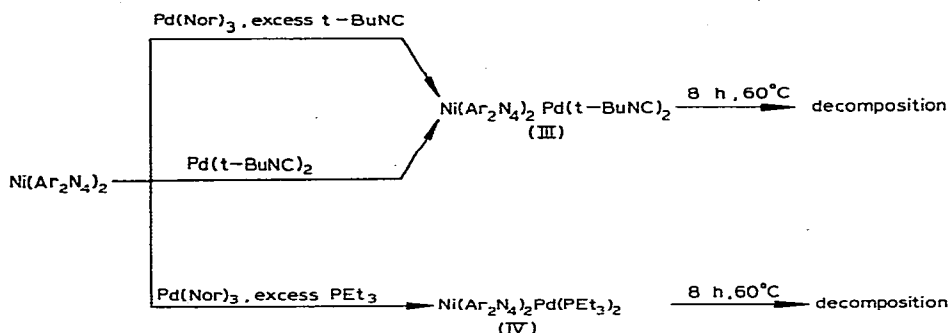
### SCHEME 1

REACTIONS LEADING TO DINUCLEAR,  $\text{Ar}_2\text{N}_4$ -BRIDGED SPECIES AND TETRAAZADIENE TRANSFER



## SCHEME 2

REACTIONS LEADING TO DINUCLEAR TETRAAZADIENE-METAL SPECIES CONTAINING A BRIDGED  $\text{Ar}_2\text{N}_4$  LIGAND



ing the presence of the parent ions, confirmed the stoichiometry of the complexes I, II and IV. (See Fig. 2 for the calculated and observed FD-mass spectrum of IV.)

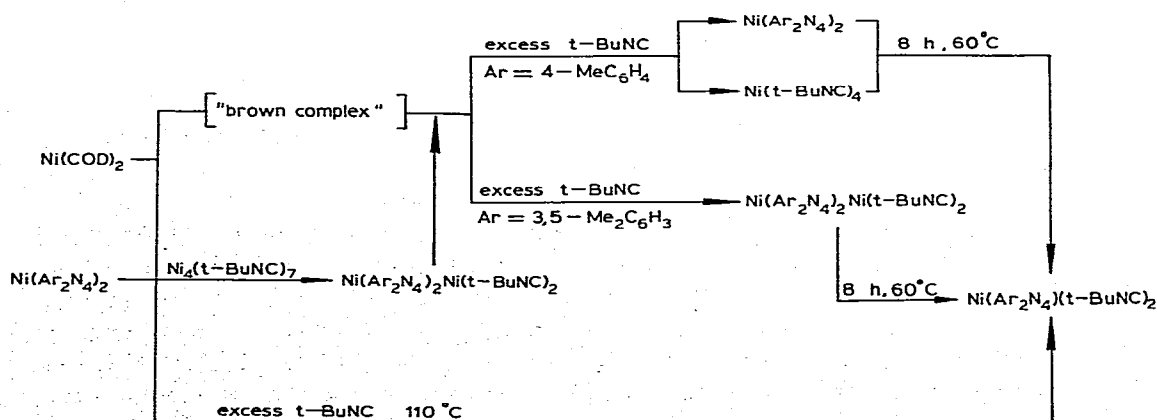
Due to solubility problems and the marginal purity of the compounds, no reliable NMR spectra could be recorded.

Infrared spectra of the complexes I and III showed very strong bands at 2192/2163 and 2177  $\text{cm}^{-1}$ , respectively, pointing to symmetrically bonded terminal isocyanide ligands.

$[\text{Ni}\{1,4\text{-(4-MeC}_6\text{H}_4)_2\text{N}_4\}_2\text{Pt(t-BuNC)}_2]$  (I) yielded, upon heating, 40% of known  $[\text{Pt}\{1,4\text{-(4-MeC}_6\text{H}_4)_2\text{N}_4\}(\text{t-BuNC})_2]$  (V) [9], which could also be prepared, albeit in lower yield and purity, by the reaction of  $[\text{Ni(Ar}_2\text{N}_4)_2]$  with  $[\text{Pt}_3(\text{t-BuNC})_6]$ . In the presence of an excess of  $t\text{-BuNC}$  the reactions also yielded the known  $[\text{Ni}\{1,4\text{-(4-MeC}_6\text{H}_4)_2\text{N}_4\}(\text{t-BuNC})_2]$  (VI) [3]. The complexes V and VI were identified by comparing their IR and FD-mass spectra with those of authentic samples. Heating of the complexes II, III and IV did not lead to other identifiable products (see Schemes 1, 2 and 3).

## SCHEME 3

REACTIONS INVOLVING DINUCLEAR  $\text{Ar}_2\text{N}_4$ -BRIDGED SPECIES AND TETRAAZADIENE TRANSFER



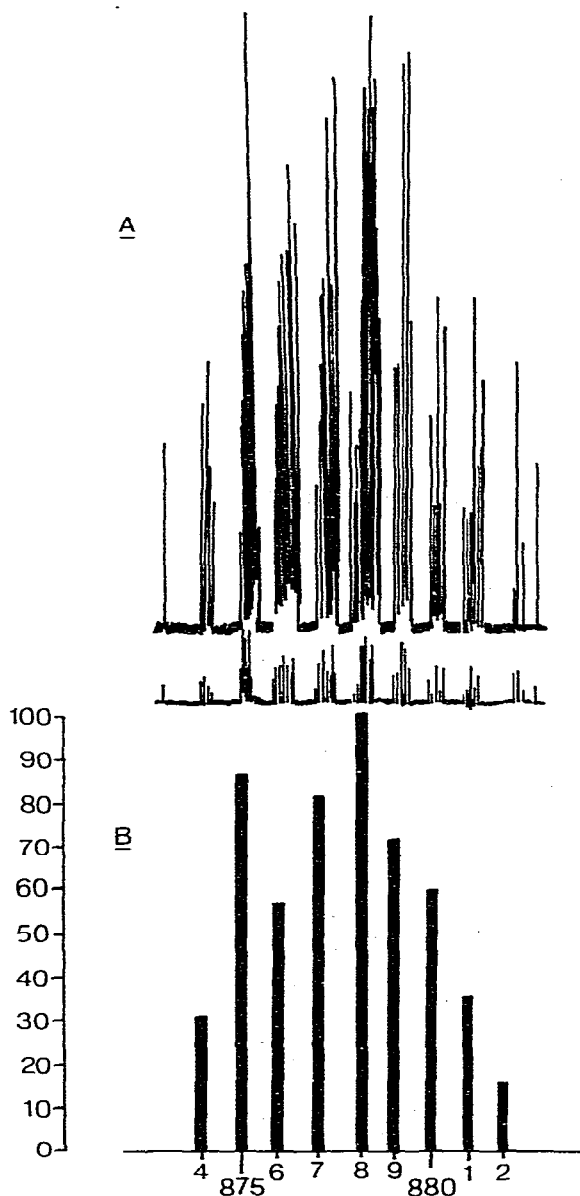


Fig. 2. Field Desorption mass spectrum of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2\text{Pd}(\text{PEt}_3)_2]$  (IV). Trace A: Found; Trace B: Calculated.

$[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  reacted with  $[\text{Ni}(\text{COD})_2]$  to form an extremely unstable brown complex which was insoluble in toluene and THF. The nature of this brown product was not further investigated. Upon addition of an excess of *t*-BuNC to a suspension of this product in toluene the colour changed to red-purple, indicative of the presence of free  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$ . This clear solution after heating and work-up yielded 40% of VI (the same product and yield were obtained by treating  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  with  $[\text{Ni}(\text{t-BuNC})_4]$

for 8 h at 60°C).  $[\text{Ni}\{1,4-(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4\}_2]$  reacted likewise with  $[\text{Ni}(\text{COD})_2]$ , but upon addition of *t*-BuNC the red-purple  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  colour did not return and instead, the mixture turned red-brown. Heating this mixture yielded 80% of  $[\text{Ni}\{1,4-(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4\}(\text{t-BuNC})_2]$  (VII). Reactions of  $[\text{Ni}\{1,4-(4\text{-MeC}_6\text{H}_4)_2\text{N}_4\}_2]$  or  $[\text{Ni}\{1,4-(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4\}_2]$  with  $[\text{Ni}_4(\text{t-BuNC})_7]$  led to unstable red-brown coloured oily products. Addition of an excess of *t*-BuNC led, in the case of  $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ , to the reappearance of the deep-purple colour indicative of dissociation of the product and formation of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  and  $[\text{Ni}(\text{t-BuNC})_4]$ . In the case of  $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$  the red-brown product did not react at room temperature (see Scheme 3).

## Discussion

The present results show that the transfer of a complete tetraazadiene ligand from  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  to another metal centre provides a new route for the preparation of mono(tetraazadiene)metal complexes. Although in only one case was the two-step character of this reaction confirmed by isolating a stable  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  intermediate, there are several reasons to believe that intermediates of this type also play a part in the other tetraazadiene transfer reactions observed. Firstly, the tetraazadiene ligand is unknown as a free species [1]. It has to be generated at a metal centre and subsequently stabilized by coordination. Hence it is to be expected that an intermediate in which the tetraazadiene ligand bridges between two metals is a prerequisite for transferring the ligand intact. Secondly, the reactions in which dinuclear intermediates were most easily formed provided the highest yields of the transferred products  $[\text{M}(\text{Ar}_2\text{N}_4)(\text{t-BuNC})_2]$ . The yield of transferred product V was higher in the reaction of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  with  $[\text{Pt}(\text{COD})_2]$  followed by addition of *t*-BuNC, (which at room temperature already led to formation of the intermediate I) than in the reaction between  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  and  $[\text{Pt}_3(\text{t-BuNC})_6]$ , which proceeds only at elevated temperatures. The same situation is encountered in the reactions of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{Ni}(\text{t-BuNC})_2]$ . Upon addition of an excess of *t*-BuNC at room temperature this intermediate dissociates for  $\text{Ar} = 4\text{-MeC}_6\text{H}_4$  but not for  $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ . The yield from the subsequent transfer reaction is 40% in the former case and 80% in the latter case (see Scheme 3).

As  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  complexes have been isolated for  $\text{M} = \text{Pt}$  or  $\text{Pd}$  and  $\text{L} = \text{t-BuNC}$  or  $\text{PEt}_3$ , it is surprising to find that in only one case was tetraazadiene transfer observed, namely for  $\text{M} = \text{Pt}$  and  $\text{L} = \text{t-BuNC}$ . Heating of the complexes II, III or IV does not lead to identifiable products. Although the palladium-containing complexes III and IV are readily formed, this metal, unlike nickel and platinum, seems very reluctant to form a mononuclear  $\sigma, \sigma, N^\alpha, N^\alpha'$  coordinated tetraazadiene complex [12].

### Bonding in the $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$ complexes

FD mass spectra (see Fig. 2) confirmed the stoichiometry of  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  complexes. The IR spectrum of I shows sharp bands at 2192 and 2163  $\text{cm}^{-1}$  characteristic of equivalently bonded terminal isocyanide ligands. In III, which shows a slightly broader band at 2177  $\text{cm}^{-1}$ , the bonding is expected to be similar. The  $\nu(\text{NC})$  values of I lie halfway between those found for the

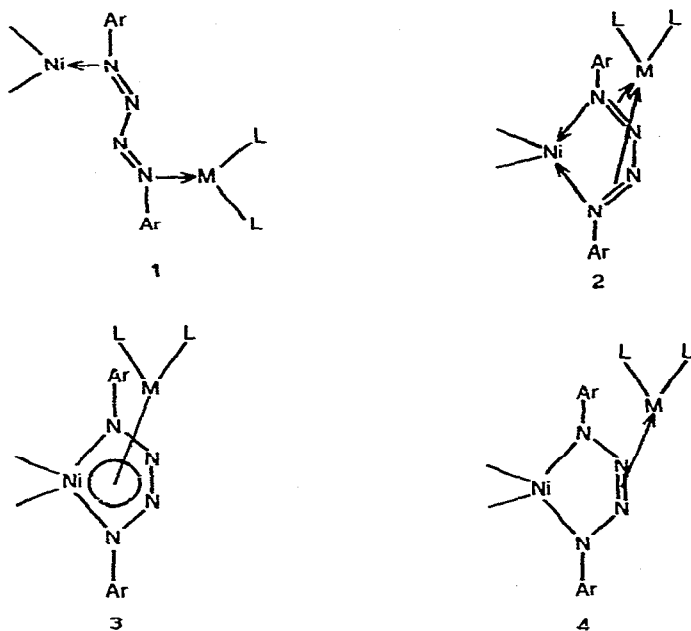


Fig. 3. Some possibilities for the bonding mode in  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  complexes I–IV. The second  $\text{Ar}_2\text{N}_4$  ligand on nickel has been omitted.

nickel and platinum mononuclear  $[\text{M}(\text{Ar}_2\text{N}_4)(\text{t-BuNC})_2]$  complexes (Ni: 2168/2146; Pt: 2214/2186  $\text{cm}^{-1}$ ) [4b] indicating that I is a specific complex rather than a mixture. Although it is not clear from these results to which metal centre the isocyanide ligands are bonded, the observation that  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$  can be reisolated from I–IV in essentially quantitative yield suggests that they are bonded to M. Furthermore, the finding that one complete  $\text{Ar}_2\text{N}_4$  ligand can be transferred from nickel to M implies that this tetraazadiene moiety bridges between  $\text{Ni}(\text{Ar}_2\text{N}_4)$  and  $\text{ML}_2$  and is present intact in these dinuclear complexes. So far, no bonding modes for tetraazadiene ligands other than  $\sigma, \sigma\text{-N}^\alpha, \text{N}^{\alpha'}$  (chelate) have been reported. However, the very versatile coordination chemistry of the isoelectronic 1,4-diaza-1,3-butadiene ligand ( $\text{RN}=\text{CHCH}=\text{NR}$ ) [13] may be used to provide some reasonable possibilities for the bridge bonding mode of the  $[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{M}(\text{L})_2]$  complexes. A few examples, adapted to the  $\text{Ar}_2\text{N}_4$  ligand, are shown in Fig. 3. Bonding modes 1 and 2 make use of the neutral valence structure of the coordinated tetraazadiene ligand according to canonical form A (see Fig. 1). Bonding mode 3 depicts the  $\text{N}_4\text{Ni}$  unit as a  $6\pi$  electron 5-membered ring system, a view which has been advocated before in the case of  $[\text{Co}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$  [6b]. Mode 4 relies on a formal bonding of the  $\text{Ar}_2\text{N}_4$  ligand according to the dianionic form B.

The observed equivalence of the ligands L in complex I can be accounted for in bonding modes 1, 3 and 4 since the  $\text{ML}_2$  unit can rotate, and excludes the  $\eta^2\text{-}\eta^2$  bonding mode 2 where such rotation is not to be expected. However, we have not observed formation of tetraazadiene-bridged species in reactions of



[Pt(Ar<sub>2</sub>N<sub>4</sub>)(COD)], [Ni(Ar<sub>2</sub>N<sub>4</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] or [Co(Ar<sub>2</sub>N<sub>4</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] [14], in which canonical form B dominates the bonding. Modes 3 and 4 are therefore unlikely, since they derive directly from the dianionic form B of bonded tetraazadiene. This leaves only mode 1\*, which is analogous to the bridging mode found for R-DAB ligands in the complexes [ {Pd(dmf)<sub>2</sub> }<sub>2</sub>(t-BuDAB)]\*\* [15a] and [ {PtCl<sub>2</sub>(PBU<sub>3</sub>) }<sub>2</sub>(t-BuDAB)] [15b]. An X-ray crystal structure determination of the latter compound revealed a perfect planarity of the PtNCCNPt system, resulting in a conjugated heterodiene type orbital system. In this respect it is interesting that the tetraazadiene seems to be activated towards a bridging mode only when the neutral heterodiene form A is the main contributor to the bonding in the original mononuclear complex.

If the bridging mode is actually of type 1 then this is not surprising, since the ability of the tetraazadiene ligand to change its coordination mode from  $\sigma, \sigma$ -N <sup>$\alpha$</sup> , N <sup>$\alpha'$</sup>  (chelate) to  $\sigma$ -N <sup>$\alpha$</sup> ,  $\sigma$ -N <sup>$\alpha'$</sup>  (bridging) depends on the possibility of rotation around the N <sup>$\beta$</sup> -N <sup>$\beta$</sup>  bond. Any contribution of form B to the bonding will increase the activation barrier to rotation around the N <sup>$\beta$</sup> -N <sup>$\beta$</sup>  bond and limit the ability to change to the bridging mode.

## Conclusions

Tetraazadiene ligands can be transferred intact under mild conditions from [Ni(Ar<sub>2</sub>N<sub>4</sub>)<sub>2</sub>] to another nickel or platinum centre. In our experiments no transfer was observed from [Ni(Ar<sub>2</sub>N<sub>4</sub>)<sub>2</sub>] to a palladium centre nor in the presence of other coligands than t-BuNC. The reactions are believed to proceed via dinuclear intermediates of the type [Ni(Ar<sub>2</sub>N<sub>4</sub>)<sub>2</sub>M(L)<sub>2</sub>] and from one such reaction a species of this type was isolated. These complexes have also been isolated in cases when further (transfer) reactions do not take place. One of the Ar<sub>2</sub>N<sub>4</sub> ligands in these complexes is proposed to be bridging between nickel and M in a mode analogous to the  $\sigma$ -N,  $\sigma$ -N' bridge bonding mode found in platinum and palladium complexes of the 1,4-diaza-1,3-butadiene ligand\*.

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## References and Notes

- 1 For a review see: S. Cenini and G. La Monica, *Inorg. Chim. Acta, Rev.*, 18 (1976) 279.
- 2 F.W.B. Einstein and D. Sutton, *Inorg. Chem.*, 11 (1972) 2827.
- 3 a) P. Overbosch, G. van Koten and O. Overbeek, *J. Amer. Chem. Soc.*, 102 (1980) 2091.  
b) P. Overbosch, G. van Koten, A.L. Spek, G. Roelofsen and A.J.M. Duisenberg, *Inorg. Chem.*, 21 (1982) in press.
- 4 a) P. Overbosch, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, 208 (1981) C21.

\* See Note added in proof, p. 202.

\*\* dmf = dimethyl fumarate.

- b) P. Overbosch, G. van Koten, A.L. Spek, D.M. Grove and A.J.M. Duisenberg, *Inorg. Chem.*, 21 (1982) in press.
- 5 P. Overbosch, G. van Koten and O. Overbeek, *Inorg. Chem.*, 21 (1982) in press.
- 6 a) R.J. Doedens, *J. Chem. Soc. Chem. Commun.*, (1968) 1271.  
 b) M.E. Gross, W.C. Trogler and J.A. Ibers, *J. Amer. Chem. Soc.*, 103 (1981) 192; for the preparation of the reported complex see ref. 14.
- 7 I. Ugi and R. Meyr, *Chem. Ber.*, 93 (1960) 239.
- 8 R.A. Schunn, *Inorg. Synth.*, XV (1974) 5.
- 9 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Dalton*, (1977) 271.
- 10 M. Green, J.A.K. Howard, M. Murray, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Dalton*, (1977) 1509.
- 11 M.G. Thomas, W.R. Pretzer, B.F. Beier, F.J. Hirsekorn and E.L. Muetterties, *J. Amer. Chem. Soc.*, 99 (1977) 743.
- 12 So far, reactions aimed at producing palladium-tetraazadiene complexes by reactions of zerovalent metal complexes with organic azides have failed, see also: W. Beck, M. Bauder, G. La Monica, S. Cenini and R. Ugo, *J. Chem. Soc. A*, (1971) 113.
- 13 G. van Koten and K. Vrieze, *Recl. Trav. Chim. Pays-Bas*, 100 (1981) 4.
- 14 S. Otsuka and A. Nakamura, *Inorg. Chem.*, 7 (1968) 2542.
- 15 a) K.J. Cavell, D.J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, 47 (1980) 67.  
 b) H. v.d. Poel, G. van Koten, K. Vrieze, M. Kokkes and C.H. Stam, *Inorg. Chim. Acta*, 39 (1980) 197.
- 16 C. Chang, C.E. Johnson, T.G. Richmond, Y. Chen, W.C. Trogler and F. Basolo, *Inorg. Chem.*, 20 (1981) 3167.

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\* *Note added in proof:* A possibility which is not depicted in Fig. 3 involves coordination of the  $ML_2$  species to one of the  $N^\beta$  atoms of the chelate bonded  $Ar_2N_4$  ligand in  $[Ni(Ar_2N_4)_2]$ . This bonding mode makes use of the lone pair on the  $N^\beta$  atom. Accordingly, the  $N^\beta-M$  bond is in the  $NiN(Ar)NNN(Ar)$  chelate plane and therefore can also account (like structure 1) for the observed equivalence of the ligands L. Recently this type of bonding of the  $R_2N_4$  ligand in  $[Fe(CO)_3(R_2N_4)]$  with  $BF_3$  was used to explain the enhanced rates of substitution of CO ligands [16].