

Preliminary communication

SYNTHESIS OF METAL—TETRAAZADIENE COMPLEXES VIA LIGAND TRANSFER; TWO ROUTES TO NICKEL— OR PLATINUM—TETRAAZADIENE COMPLEXES $[M(Ar_2N_4)(L)_2]$

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Summary

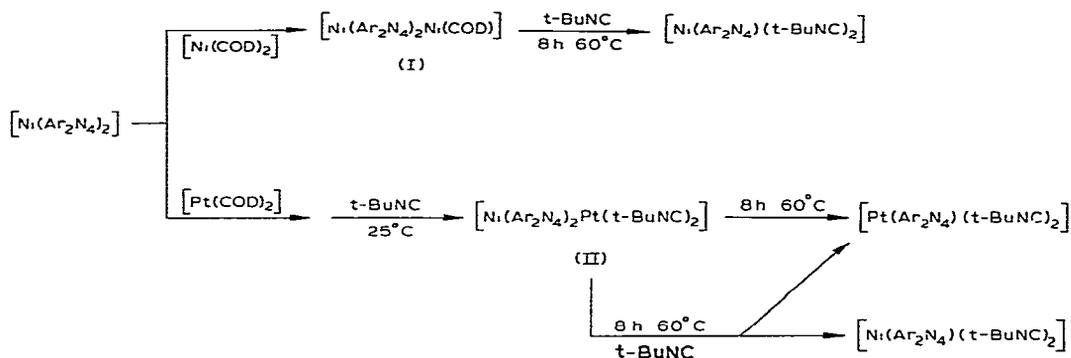
A novel route for the synthesis of metal—tetraazadiene complexes is reported involving the direct transfer of a Ar_2N_4 ligand from $[Ni(Ar_2N_4)_2]$ to Ni^0 and Pt^0 centres in the presence of *t*-butylisocyanide, resulting in $[M(Ar_2N_4)(t-BuNC)_2]$ species. For $M = Pt$ the latter complexes can also be prepared by reaction of the zerovalent isocyanide complex with the appropriate azide or by addition of *t*-BuNC to $[Pt(Ar_2N_4)(COD)]$.

Although the tetraazadiene species RN_4R is unknown as a free compound, tetraazadiene complexes can be generated by reaction of a metal centre with an azide or diazonium salt [1]. The transfer of a complete Ar_2N_4 ligand from the bis-tetraazadiene complex $[Ni(Ar_2N_4)_2]$ [2] to another Ni- or Pt-centre, described below, represents the first application of a new method of preparation of tetraazadiene complexes.

$[Ni(COD)_2]$ reacts with $[Ni(Ar_2N_4)_2]$ (1/1) to form a brown complex (I) which is insoluble in toluene. Reaction of this complex with excess *t*-BuNC (8 h at 60°C, see Scheme 1) results in the formation of the known $[Ni(Ar_2N_4)(t-BuNC)_2]$ [2]. The yields, calculated on the basis of the total amount of Ni present, for $Ar = 4-MeC_6H_4$ and 3,5- $Me_2C_6H_3$, are 40 and 80%, respectively. The latter yield also represents recovery of 80% of the Ar_2N_4 ligand in a single mono-nuclear complex, which is conclusive evidence that Ar_2N_4 transfer has occurred.

A toluene solution of $[Ni(Ar_2N_4)_2]$ and $[Pt(COD)_2]$ (1/1) yields upon addition of *t*-BuNC a red compound which is only sparingly soluble in toluene, but very soluble in THF. Elemental analyses indicate a complex with stoichiometry

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(Ar = 4-MeC₆H₄ or 3,5-Me₂C₆H₃ all reactions in toluene)

SCHEME 1

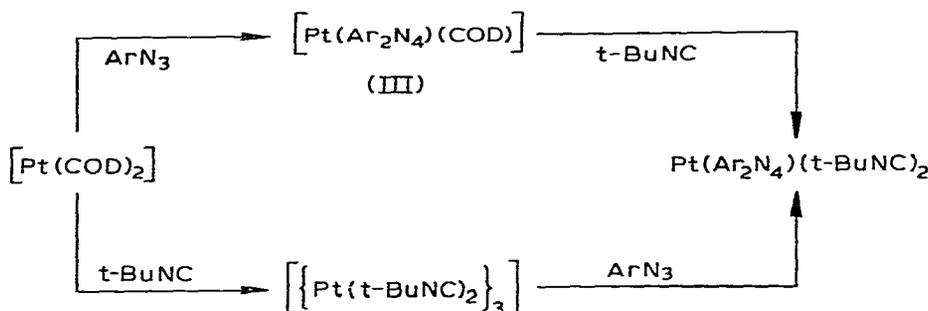
$[\text{Ni}(\text{Ar}_2\text{N}_4)_2\text{Pt}(t\text{-BuNC})_2]$ (II), while the IR spectra show only terminal bonded *t*-BuNC ($\nu(\text{NC})$ 2190 cm⁻¹ (br)). The deep purple $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ may be recovered from the intermediate II by passing the red THF solution through a silica column. This suggests that in II both Ar₂N₄ ligands may still be bonded to Ni, with the Pt(*t*-BuNC)₂ fragment probably coordinated to one Ar₂N₄ unit. After heating II for 8 h at 60°C in toluene, $[\text{Pt}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ can be isolated in approximately 25% yield (see Scheme 1). If I is heated in the presence of excess *t*-BuNC, a mixture of $[\text{Ni}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ and $[\text{Pt}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ is obtained*. The formation of $[\text{Ni}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ in this mixture can be explained by coordination of two *t*-BuNC units to the Ni centre following the transfer of one of the Ar₂N₄ ligands to the Pt centre.

Interestingly the Ar₂N₄ ligand transfer is also observed in the direct reaction of $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ with the metal isocyanide complexes $[\text{Ni}(t\text{-BuNC})_4]$ and $[\{\text{Pt}(t\text{-BuNC})_2\}_3]$ [3], which afford $[\text{Ni}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$ and $[\text{Pt}(\text{Ar}_2\text{N}_4)(t\text{-BuNC})_2]$, respectively.

Tetraazadiene ligand transfer from $[\text{Ni}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ [2] and $[\text{Co}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ [4] to other metal centres has not so far been observed, which may be due to the different type of bonding in these $[\text{M}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ species. A recent X-ray structure determination of $[\text{Ni}(\text{Ar}_2\text{N}_4)(\eta^5\text{-C}_5\text{H}_5)]$ (Ar = 4-MeC₆H₄) [5] has shown significant differences from $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$ (Ar = 3,5-MeC₆H₃); a shorter central N—N bond distance of 1.278(3) Å was found with two longer adjacent N—N bonds of 1.344(2) and 1.346(2) Å (cf. the equal N—N bond lengths of 1.319(4) and 1.325(3) Å, respectively, in $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$), while the aryl groups are twisted 45° out of the NiN₄ plane (cf. the coplanarity of aryl rings and NiN₄ plane in $[\text{Ni}(\text{Ar}_2\text{N}_4)_2]$).

An alternative route to the platinum—tetraazadiene complexes [2], namely the reaction of $[\text{Pt}(\text{COD})_2]$ with the corresponding azide (see Scheme 2), yielded $[\text{Pt}(\text{Ar}_2\text{N}_4)(\text{COD})]$ (III, Ar = 4-MeC₆H₄, 4-ClC₆H₄, 4-NO₂C₆H₄) in approximately 30% yield. The reactions were carried out at room temperature and proceed more rapidly with increasing electronegativity of the substituent on the aryl groups. Comparison of the ¹³C NMR shift data of the olefinic COD carbon

*The mixture was identified by FD mass spectroscopy and comparison of the IR spectra with those of the pure compounds.



(Ar = 4-MeC₆H₄, 4-ClC₆H₄ or 4-NO₂C₆H₄; all reactions in toluene)

SCHEME 2

atoms of III (Ar = 4-ClC₆H₄, δ 86.5 ppm, $J(\text{Pt}-\text{C})$ 168 Hz; Ar = 4-NO₂C₆H₄, δ 89.0 ppm, $J(\text{Pt}-\text{C})$ 168 Hz) with those of [Pt(COD)(DAB)] [2] * [DAB = ArN=CHCH=NAr, Ar = 4-ClC₆H₄: δ 80.6 ppm, $J(\text{Pt}-\text{C})$ 174 Hz] and those of other known platinum cyclooctadiene complexes [6] indicates that complexes of type III contain zerovalent platinum. Reactions of III with t-BuNC yield [Pt(Ar₂N₄)(t-BuNC)₂] complexes, which can also be prepared by treatment of [Pt(t-BuNC)₂]₃ with the appropriate azide (see Scheme 2).

It is noteworthy that the [Pt(Ar₂N₄)(COD)] complexes show unusual reactions. Reactions of complexes III with DAB and RNSNR resulted in recovery of the starting materials as did attempted reactions with MeI and Hg(CH₃COO)₂. The fact that complexes III were not oxidized points to an interesting difference compared with the [Pt(COD)(DAB)] complexes, which are extremely sensitive towards oxidation.

Reaction of III (Ar = 4-MeC₆H₄, 4-ClC₆H₄) with PEt₃ gave [Pt(Ar₂N₄)(PEt₃)₂] (IV) (³¹P NMR; Ar = 4-MeC₆H₄, δ -7.1 ppm, $J(\text{Pt}-\text{P})$ 3338 Hz; Ar = 4-ClC₆H₄, δ -6.5 ppm, $J(\text{Pt}-\text{P})$ 3330 Hz)**.

So far complete transfer of Ar₂N₄ from Ni to Pd has not been accomplished. The reaction of [Ni(Ar₂N₄)₂] with [Pd(t-BuNC)₂]_n [8] yielded an isolable complex, which, by analogy to the above-mentioned Ni-Pt intermediate II, can be formulated as [Ni(Ar₂N₄)₂Pd(t-BuNC)₂] (V).

The [Ni(Ar₂N₄)₂ML₂] intermediates I, II and V might contain the Ar₂N₄ unit as a metal-metal bridging ligand using either the lone pairs on the N atoms, or the π -electrons in addition to these lone pairs. This is not unlikely in view of the recent characterization of 2e + 2e, 6e and 8e donating 1,4-diaza-1,3-

*[Pt(COD)(DAB)] complexes will be the subject of a forthcoming paper.

** For Ar is 4-NO₂C₆H₄, the reaction with PEt₃ gave an intensely blue-coloured compound [7], in sharp contrast to the pale yellow and orange colours of complexes III and derivatives. A recent X-ray structure determination of this blue compound revealed that the structure must be formulated as [{4-NO₂C₆H₄ }₂N₄ } (PEt₃)₂PtCHC(PEt₃)H(CH₂)₂CH=CHCH₂CH₂] [5]. The 1,5-cyclooctadiene ligand is η^2 -bonded via one C=C unit to Pt, the second C=C unit has undergone nucleophile attack by PEt₃ resulting in a C-Pt σ -bond.

The reported complexes were identified by a combination of techniques, including ¹H and ¹³C NMR, FD mass spectroscopy [9], elemental analysis and IR.

butadiene (DAB) units [10], a ligand which is isostructural with Ar_2N_4 . Whether these intermediates react further to give the exchanged products seems to depend on the nature of the aryl substituent, the co-ligand L and the metal. Further research is being directed towards elucidation of the structure of the $[\text{Ni}(\text{Ar}_2\text{N}_4)\text{ML}_2]$ intermediates in order to obtain insight into the mechanism of these Ar_2N_4 ligand transfer reactions.

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