*Journal of Organometallic Chemistry*, 208 (1981) C21—C24
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**Preliminary communication**

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

PETER OVERBOSCH, GERARD VAN KOTEN* and KEES VRIEZE

*Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

(Received December 5th, 1980)

## Summary

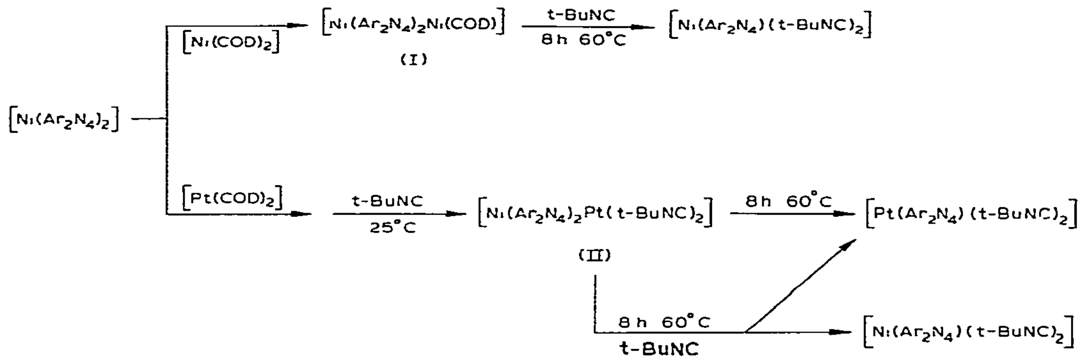
A novel route for the synthesis of metal—tetraazadiene complexes is reported involving the direct transfer of a $Ar_2N_4$ ligand from $[Ni(Ar_2N_4)_2]$ to $Ni^0$ and $Pt^0$ centres in the presence of t-butylisocyanide, resulting in $[M(Ar_2N_4)(t\text{-}BuNC)_2]$ species. For M = Pt the latter complexes 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 $[Ni(Ar_2N_4)(t\text{-}BuNC)_2]$ [2]. The yields, calculated on the basis of the total amount of Ni present, for Ar = $4\text{-}MeC_6H_4$ and $3,5\text{-}Me_2C_6H_3$, are 40 and 80%, respectively. The latter yield also represents recovery of 80% of the $Ar_2N_4$ ligand in a single mononuclear 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

*Author to whom correspondence should be addressed.




(Ar = 4-MeC$_6$H$_4$ or 3 5-Me$_2$C$_6$H$_3$ all reactions in toluene)

SCHEME 1

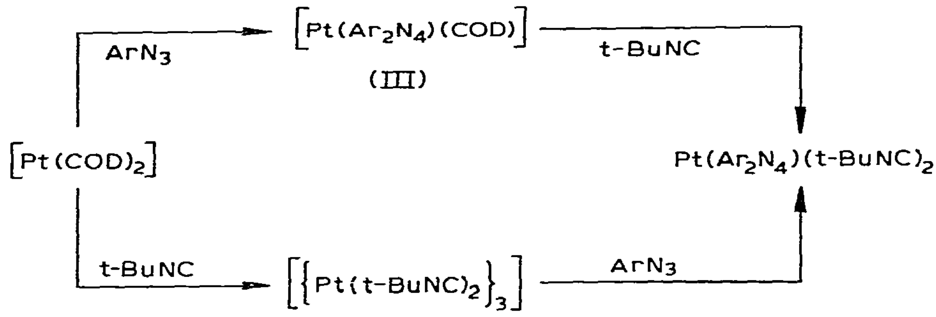
[Ni(Ar$_2$N$_4$)$_2$Pt(t-BuNC)$_2$] (II), while the IR spectra show only terminal bonded t-BuNC ($\nu$(NC) 2190 cm$^{-1}$(br)). The deep purple [Ni(Ar$_2$N$_4$)$_2$] may be recovered from the intermediate II by passing the red THF solution through a silica column. This suggests that in II both Ar$_2$N$_4$ ligands may still be bonded to Ni, with the Pt(t-BuNC)$_2$ fragment probably coordinated to one Ar$_2$N$_4$ unit. After heating II for 8 h at 60°C in toluene, [Pt(Ar$_2$N$_4$)(t-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 [Ni(Ar$_2$N$_4$)(t-BuNC)$_2$] and [Pt(Ar$_2$N$_4$)(t-BuNC)$_2$] is obtained*. The formation of [Ni(Ar$_2$N$_4$)(t-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 Ar$_2$N$_4$ ligands to the Pt centre.

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

Tetraazadiene ligand transfer from [Ni(Ar$_2$N$_4$)($\eta^5$-C$_5$H$_5$)] [2] and [Co(Ar$_2$N$_4$)($\eta^5$-C$_5$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 [M(Ar$_2$N$_4$)($\eta^5$-C$_5$H$_5$)] species. A recent X-ray structure determination of [Ni(Ar$_2$N$_4$)($\eta^5$-C$_5$H$_5$)] (Ar = 4-MeC$_6$H$_4$ [5] has shown significant differences from [Ni(Ar$_2$N$_4$)$_2$] (Ar = 3,5-MeC$_6$H$_3$); 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 [Ni(Ar$_2$N$_4$)$_2$]), while the aryl groups are twisted 45° out of the NiN$_4$ plane (cf. the coplanarity of aryl rings and NiN$_4$ plane in [Ni(Ar$_2$N$_4$)$_2$]).

An alternative route to the platinum—tetraazadiene complexes [2], namely the reaction of [Pt(COD)$_2$] with the corresponding azide (see Scheme 2), yielded [Pt(Ar$_2$N$_4$)(COD)] (III, Ar = 4-MeC$_6$H$_4$, 4-ClC$_5$H$_4$, 4-NO$_2$C$_6$H$_4$) 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 $^{13}$C 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-$MeC_6H_4$ , 4-$ClC_6H_4$ or 4-$NO_2C_6H_4$ ; all reactions in toluene)

SCHEME 2

atoms of III (Ar = 4-$ClC_6H_4$, $\delta$ 86.5 ppm, $J$(Pt—C) 168 Hz; Ar = 4-$NO_2C_6H_4$, $\delta$ 89.0 ppm, $J$(Pt—C) 168 Hz) with those of [Pt(COD)(DAB)] [2]* [DAB = ArN=CHCH=NAr, Ar = 4-$ClC_6H_4$: $\delta$ 80.6 ppm, $J$(Pt—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($Ar_2N_4$)(t-BuNC)$_2$] complexes, which can also be prepared by treatment ot [{Pt(t-BuNC)$_2$}$_3$] with the appropriate azide (see Scheme 2).

It is noteworthy that the [Pt($Ar_2N_4$)(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($CH_3COO$)$_2$. 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-$MeC_6H_4$, 4-$ClC_6H_4$) with $PEt_3$ gave [Pt($Ar_2N_4$)($PEt_3$)$_2$] (IV) ($^{31}$P NMR; Ar = 4-$MeC_6H_4$, $\delta$ −7.1 ppm, $J$(Pt—P) 3338 Hz; Ar = 4-$ClC_6H_4$, $\delta$ −6.5 ppm, $J$(Pt—P) 3330 Hz)**.

So far complete transfer of $Ar_2N_4$ from Ni to Pd has not been accomplished. The reaction of [Ni($Ar_2N_4$)$_2$] 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($Ar_2N_4$)$_2$Pd(t-BuNC)$_2$] (V).

The [Ni($Ar_2N_4$)$_2ML_2$] intermediates I, II and V might contain the $Ar_2N_4$ unit as a metal—metal bridging ligand using either the lone pairs on the N atoms, or the $\pi$-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-$NO_2C_6H_4$ the reaction with $PEt_3$ 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-$NO_2C_6H_4$)$_2N_4$}($PEt_3$)PtCHC($PEt_3$)H($CH_2$)$_2$CH=CHCH$_2$CH$_2$] [5]. The 1,5-cyclooctadiene ligand is $\eta^2$-bonded via one C=C unit to Pt, the second C=C unit has undergone nucleophile attack by $PEt_3$ resulting in a C—Pt $\sigma$-bond.

The reported complexes were identified by a combination of techniques, including $^1$H and $^{13}$C 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 $[Ni(Ar_2N_4)ML_2]$ intermediates in order to obtain insight into the mechanism of these $Ar_2N_4$ ligand transfer reactions.

We thank Mr. R.H. Fokkens for recording the F.D. mass spectra, Mr. J. Ernsting for recording the $^{31}P$ NMR spectra, and Dr. D.M. Grove for many helpful discussions.

## References

1 See S. Cenini and G. la Monica, Inorg. Chim. Acta Rev., 18 (1976) 279.
2 P. Overbosch, G. van Koten and O. Overbeek, J. Amer. Chem. Soc., 102 (1980) 2091.
3 M. Green, J.A.K. Howard, M. Murray, J.L. Spencer, and F.G.A. Stone, J. Chem. Soc. Dalton, (1977) 1509.
4 S. Otsuka and A. Nakamura, Inorg. Chem., 7 (1968) 2542; M.E. Gross, W.C. Trogler, and J.A. Ibers, to be published.
5 A.L. Spek, G. Roelofsen and A.J. Duisenberg, to be published.
6 M.T. Chicote, M. Green, J.L. Spencer, F.G.A. Stone, and J. Vicente, J. Chem. Soc. Dalton, (1979) 536; D.M. Grove, Ph.D. thesis, Bristol, 1977.
7 Cf.: C.M. Flynn, Jr, T.S. Viswanathan and R.B. Martin, Inorg. Nucl. Chem., 39 (1979) 437, and ref. cited therein.
8 E.O. Fischer and H. Werner, Chem. Ber., 95 (1962) 703; S. Otsuka, A. Nakamura, and Y. Tatsuno, J. Amer. Chem. Soc., 91 (1969) 6994.
9 L.H. Staal, G. van Koten, R.H. Fokkens, and N.M.M. Nibbering, Inorg. Chim. Acta, in press; C.N. McEwe and S.D. Ittel, Org. Mass. Spectrom., 15 (1980) 35.
10a H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C.H. Stam, Inorg. Chim. Acta, 39 (1980) 197.
10b H.W. Frühauf, A. Landers, R. Goddard and C. Krieger, Angew. Chem., 90 (1978) 56; L.H. Staal, L.H. Polm, R.W. Balk, G. van Koten, K. Vrieze and A.M.F. Brouwers, Inorg. Chem., 19 (1980) 3343.
10c L.H. Staal, L.H. Polm, K. Vrieze, F. Ploeger and C.H. Stam, J. Organometal. Chem., 199 (1980) C13.